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Julien Paquier. Relativistic range-separated density functional theory. Theoretical and/or physical chemistry. Sorbonne Université, 2020. English. NNT : 2020SORUS059 . tel-03182509

HAL Id: tel-03182509

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SORBONNE UNIVERSITÉ

École Doctorale 388

Laboratoire de Chimie Théorique

Théorie de la fonctionnelle de la densité relativiste à séparation de portée
Relativistic range-separated density functional theory

par Julien PAQUIER

Thèse de doctorat de Chimie Théorique

Dirigée par Julien TOULOUSE

Présentée et soutenue publiquement le 08 juillet 2020

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Remerciements

Je remercie Olivier Parisel et Jean-Philip Piquemal, qui furent successivement directeurs du Laboratoire de Chimie Théorique de Sorbonne Université, pour un accueil très chaleureux et bienveillant ainsi que pour m'avoir permis de participer à de multiples école d'été et congrès : *Modern Wavefunction Methods in Electronic Structure Theory* à Gelsenkirchen, *Strong correlation in electronic structure theory* à Strasbourg, Première réunion générale du GDR NBODY : "Problème Quantique à N corps en Chimie et Physique" à Lille, ...

Je remercie grandement Julien Toulouse, mon directeur de thèse, pour m'avoir enseigné durant plus de trois années, pour son soutien sans faille et sa présence toujours bienveillante.

Je remercie les membres du jury, Emmanuel Fromager, Aurélien de la Lande, Christian Brouder, Marcella Grasso et Maria Hellgren, pour avoir accepté de juger ce travail. Je remercie en particulier Christian Brouder, pour des présentations claires et passionnantes sur l'électrodynamique quantique.

Je remercie Emmanuel Giner, pour de passionnantes discussions et d'incalculables conseils concernant le travail d'implémentation.

I am thankful to Stefan knecht, for a very pleasant and profitable stay in Zurich.

Je remercie l'ensemble des membres du Laboratoire de Chimie Théorique, pour avoir partagé ensemble cette vie de scientifiques.

Pour finir, je remercie Frédéric Célerse, pour plus de cafés que je ne saurais en compter et un soutien réciproque à travers les heures les plus sombres et les réussites les plus douteuses.

Théorie de la fonctionnelle de la densité relativiste à séparation de portée

Résumé

Cette thèse de doctorat constitue une contribution à l'extension relativiste de la théorie de la fonctionnelle de la densité à séparation de portée, en combinant un calcul de fonction d'onde relativiste à quatre composantes pour la contribution de longue portée avec une fonctionnelle de la densité relativiste à courte portée complémentaire, basée sur l'Hamiltonien Dirac-Coulomb ou Dirac-Coulomb-Breit sans paire.

Nous avons étudié les propriétés du gaz d'électrons homogène relativiste dans l'approximation sans paire pour développer des fonctionnelles de la densité d'échange-corrélation relativistes à courte portée dans l'approximation de la densité locale (LDA). Nous avons implémenté un code de fonctionnelle de la densité relativiste à séparation de portée en tant que module dans le logiciel QUANTUM PACKAGE 2.0 pour tester ces fonctionnelles. Nous avons étendu la fonctionnelle d'échange relativiste à courte portée au niveau de l'approximation du gradient généralisée (GGA). Enfin, nous avons relevé le rôle important de la densité de paire d'échange à coalescence dans l'évaluation correcte de l'énergie d'échange à très courte portée.

Mots-clés

relativité restreinte; chimie quantique relativiste; approximation sans paire; théorie de la fonctionnelle de la densité; décomposition longue portée/courte portée; échange électronique; corrélation électronique; approximation de la densité locale; approximation du gradient généralisée; gaz d'électrons homogène relativiste; atomes.

Relativistic range-separated density functional theory

Abstract

This PhD thesis constitutes a contribution to the relativistic extension of the range-separated density functional theory scheme, by combining a relativistic four-component wave function calculation for the long-range contribution with a complementary relativistic short-range exchange-correlation density functional based on the no-pair Dirac-Coulomb or Dirac-Coulomb-Breit Hamiltonian.

We have studied properties of the relativistic homogeneous electron gas in the no-pair approximation to develop relativistic short-range exchange-correlation density functionals at the local density approximation (LDA) level. We have implemented a four-component range-separated density functional code as a plugin in the software QUANTUM PACKAGE 2.0 to test these functionals. We have extended the relativistic short-range exchange density functional to the generalized-gradient approximation (GGA) level. Finally, we have pointed out the important role of the on-top exchange pair density in the correct evaluation of the exchange energy at very short-range.

Keywords

special relativity; relativistic quantum chemistry; no-pair approximation; density functional theory; long-range/short-range decomposition; electronic exchange; electronic correlation; local density approximation; generalized-gradient approximation; relativistic homogeneous electron gas; atoms.

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General introduction

Quantum relativistic equations stem from the will to extend the quantum mechanical equation of a particle developed first in 1925 and published in 1926 [1] by E. Schrödinger, into the relativistic framework of special relativity developed first in 1905 [2] by A. Einstein. The equation which forms the basis for modern relativistic quantum chemistry is the Dirac equation, developed in 1928 [3,4] by P. A. M. Dirac. As such, the fundamental equations describing the behaviour of particles of chemical interest date back from the 1920s both in non-relativistic and relativistic framework.

However, due to the greater complexity, both mathematical and in term of computational cost, of working within a relativistic framework and the fact that relativistic effects in chemical systems are usually neglected for light atoms (with the notable exceptions of spin and spin-orbit coupling, which must be added in an *ad hoc* fashion when one starts from the Schrödinger equation), *ab initio* relativistic quantum chemistry methods are not widely used. Indeed, relativistic effects in quantum chemistry are mostly related to high electronic densities, corresponding in practice to core electrons, and these electrons do not play an essential role in most chemical reactions and spectroscopic methods. This line of thought is the reason why relativistic effects are usually thought as non-important in quantum chemistry.

Nevertheless, this statement is at best correct only for light atoms and some very usual chemical systems are on the contrary constituted of heavy atoms and show properties which cannot be predicted without taking in account relativistic effects properly. The most common examples are the color of gold and the liquid state of mercury at room temperature [5, 6], but the lead-acid battery electro-chemical potential [7] is also one of these everyday and experimentally known results which non-relativistic quantum chemistry cannot reproduce. Most chemically relevant system requiring to work within a relativistic framework are lanthanides or heavier elements [8, 9] and as the atomic number increases so does the number of electrons to treat if one works with a full-electron method, making relativistic calculations necessarily costly in computational time if they are to be meaningful. Working within either a four-component framework or a two-component framework further increases the computational cost as it increases the number of matrix elements to calculate at all steps of a calculation, leading to a multiplicative prefactor in the computational time [9], but not to a change of scaling with respect to the number of basis functions.

In addition, working in a relativistic framework does imply many difficulties, such as non-bounded Dirac Hamiltonians with a continuum of negative-energy solutions and either the absence of a true minimization principle or the use of renormalization through a normal ordering of the Hamiltonian in second quantization [10], leading to effects of vacuum polarization and electron-positron pair creation and destruction [11]. Although these effects are correct and do lead to a very detailed and precise description of the atomic or molecular electronic structure, thus bringing new information and understanding, it is not strictly necessary to use all this apparatus to make meaningful relativistic quantum chemistry calculations if one is willing to sacrifice some precision.

The most common approximation to take care of negative-energy solutions and remove any need for renormalization is the so-called no-pair approximation [12], which consists in projecting out negative-energy eigenfunctions and considering only positive-energy electronic solutions to describe electrons. Such approximation conserves the correct non-relativistic limit, such that it has close to no effect in regions with low electronic densities such as valence regions of light atoms. Even within the no-pair

approximation, wave function relativistic calculations are very computationally costly, and appear to have quite slow convergence rates [11] with respect to the number of basis functions.

Even though density functional theory [13] is nowadays the most usual method to reduce computational costs for calculations in a non-relativistic framework, it suffers from many conceptual difficulties in a relativistic framework [14, 15] and relativistic density functional theory has not reached yet the level of efficiency of its non-relativistic counterpart. Another approach to reduce computational costs is to improve the convergence with the number of basis functions of wave function methods through range-separated density functional theory [16, 17], which corresponds to a splitting of the electron-electron interaction into a long-range interaction which is no longer divergent at coalescence and is to be treated with a wave function method, and a complementary short-range interaction which decreases to zero very quickly and is to be treated with a complementary density functional. The removal of the divergence in the long-range interaction removes the electron-electron correlation cusp, making for an easier description with Gaussian basis sets and thus a faster convergence with respect to the basis set [18], while the short-range interaction makes the local density approximation and all subsequent improvements less of an approximation, the short-range local density approximation becoming even exact in the very short-range limit. Furthermore, range-separated density functional theory has been shown to improve description of strong-correlation effects [19, 20] and weak intermolecular interactions [21–23] with respect to standard density functional theory.

As such, range-separated density functional theory has been extended to also take in account relativistic effects, first through the use of a standard scalar-relativistic effective-core potentials [24,25] in order to account for the relativistic effects of core electrons, and then with the combination of a four-component relativistic long-range second-order Møller-Plesset (MP2) perturbation theory [26] or coupled-cluster theory [27] with a complementary non-relativistic short-range semi-local exchange-correlation density functional approximation.

This PhD thesis proposes to extend the latter four-component relativistic range-separated density functional theory and make it possibly more rigorous with the construction of adapted relativistic short-range exchange-correlation density functional approximations, constructed such as to complement four-component wave functions methods and based on the no-pair Dirac-Coulomb or Dirac-Coulomb-Breit Hamiltonians. Such relativistic short-range exchange-correlation density functional approximations differ from previous relativistic density functional approximations which had been mostly derived in the more complete quantum electrodynamics formalism [15, 28, 29], as there is the need for consistency in the level of description of electron-electron interactions between the long-range wave function methods and the complementary short-range density functional. As such, we started studying the properties of the relativistic homogeneous electron gas in the no-pair approximation, first using plane wave 4-spinors solutions of the non-interacting Dirac Hamiltonian to construct short-range exchange density functionals at the local density approximation level for the Coulomb and Coulomb-Breit interaction and then using non-interacting Green's functions to construct a short-range correlation density functional at the local density approximation level for the Coulomb interaction. The Dirac-Coulomb Hamiltonian containing only charge-charge instantaneous interactions between particles, it uses the same two-electron integrals as the usual non-relativistic Coulomb interaction and we readily implemented a four-component range-separated density functional code based on the Dirac-Coulomb Hamiltonian as a plugin in the software QUANTUM PACKAGE 2.0 [30] to test the short-range Coulomb exchange-correlation density functional approximations.

The manuscript is divided in 5 chapters.

Chapter 1 corresponds to the basics of special relativity, with equations of motion and electrodynamics being worked out in a relativistic framework up to the non-quantized Lagrangian formalism that is one step remote from quantum electrodynamics.

Chapter 2 corresponds to the basics of relativistic quantum chemistry, from the one-electron Dirac equation and its free-particle solutions to the many-electron Hamiltonians in first quantization and second quantization, within both configuration and Fock space. We also write the basic equations of relativistic density functional theory and give some informations as to practical calculations and implementations of a four-component relativistic quantum chemistry method.

Chapter 3 corresponds to the construction of a relativistic short-range exchange density functional at the local density approximation level, for the Coulomb and Coulomb-Breit interactions. We develop these functionals first with the use of the exchange hole and then with two different kinds of expansions, Padé approximants in powers of c/k_F making no approximation on the dependence on the scaled range-separation parameter μ/k_F , and small and large- μ expansions making no approximations on the dependence on c/k_F .

Chapter 4 corresponds to tests and improvements of the previously defined short-range Coulomb exchange density functional. We start with tests on isoelectronic systems ranging from light atoms to heavy ions, before making a first extension of the local density approximation using the on-top exchange pair density, and finishing with a semi-local extension at the generalized-gradient approximation level. In particular, we make use of a parameterized relativistic exchange gradient correction factor.

Chapter 5 corresponds to the construction of a relativistic short-range correlation density functional at the local density approximation level, for the Coulomb interaction only. In particular, we make use of a relativistic correlation correction factor to introduce relativistic effects locally while making use of previous non-relativistic short-range correlation density functionals.

After the general conclusion are appendices, containing explicit derivations of many formulas used in the main chapters.

Atomic units (a.u.) are implicitly used throughout this manuscript when they are not explicitly written.

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Chapter 1

Special relativity and electrodynamics

This chapter corresponds to an introduction to special relativity, going from the very general principles of relativity to the non-quantized Lagrangian formalism of electrodynamics. In particular, the behaviour of electromagnetic fields, massive particles and their interactions in a relativistic framework are worked out in some details.

1.1 General principles of special relativity

Classical mechanics traces back to Sir Isaac Newton with his work *Philosophiae Naturalis Principia Mathematica* [1], which was published in 1687. He presented three laws of motion which are nowadays written as

- Law I: *There exists **inertial frames**, in which the motion of a particle remains constant unless acted upon by an external force.*
- Law II: *The motion of a particle of constant mass m acted upon by an external force \mathbf{F} in an inertial frame obeys the **equation of motion***

$$\mathbf{F} = \frac{d\mathbf{p}}{dt} = m \frac{d\mathbf{v}}{dt} = m \frac{d^2\mathbf{r}}{dt^2}. \quad (1.1)$$

- Law III: *For any force \mathbf{F}_{12} exerted from particle 1 onto particle 2 there is a force $\mathbf{F}_{21} = -\mathbf{F}_{12}$ exerted from particle 2 onto particle 1, which is the **principle of action-reaction**.*

These laws thus define classical mechanics for any and all inertial frames, relying on the Galilean principle of relativity

All inertial frames are equivalent.

Newton's laws of motion have the same form in all inertial frames.

Considering two inertial frames \mathbf{J}' and \mathbf{J} with the same direction axes and where \mathbf{J}' moves relatively to \mathbf{J} with a uniform velocity \mathbf{v} , the Galilean transformation of position and time is

$$\begin{aligned} \mathbf{r}' &= \mathbf{r} - \mathbf{v}t \\ t' &= t \end{aligned} \quad (1.2)$$

and states the existence of an absolute time, which does not match experimental results for high velocity particles [2, 3] and thus cannot be a fundamental law of nature. This relativity principle must be abandoned to the profit of Einstein's special principle of relativity [4]

All inertial frames are equivalent.

The laws of physics have the same form in all inertial frames.

The speed of light c is a constant, independent of the relative motion of the source.

The latter postulate is a conclusion of numerous interferometer experiments which started with the Michelson-Morley experiment [5].

1.1.1 Four-dimensional space-time

Considering two events $E_1(t_1, \mathbf{r}_1)$ and $E_2(t_2, \mathbf{r}_2)$ connected by a light signal, the measure of the speed of light c within the inertial frames \mathbf{J}' and \mathbf{J} leads to the relation

$$\frac{|\mathbf{r}'_2 - \mathbf{r}'_1|}{t'_2 - t'_1} = c = \frac{|\mathbf{r}_2 - \mathbf{r}_1|}{t_2 - t_1}, \quad (1.3)$$

such that the squared space-time interval s_{12}^2 between the two events

$$s_{12}^2 = c^2(t'_2 - t'_1)^2 - (\mathbf{r}'_2 - \mathbf{r}'_1)^2 = c^2(t_2 - t_1)^2 - (\mathbf{r}_2 - \mathbf{r}_1)^2, \quad (1.4)$$

is invariant and equal to zero in both inertial frames. If we assume homogeneity of space and time as well as isotropy of space we have conservation of the space-time interval between any two events, as shown for example in the book of Reihner and Wolf [6], such that

$$s_{12}'^2 = s_{12}^2, \quad (1.5)$$

where positive values of s_{12}^2 corresponds to time-like distances, negative values to space-like distances and vanishing values to light-like distances. To reflect the space-time structure of the four-dimensional distance s_{12} we introduce the four-dimensional vector (4-vector) position

$$x = (x^\mu) = \begin{pmatrix} ct \\ x^i \end{pmatrix} = \begin{pmatrix} ct \\ \mathbf{r} \end{pmatrix}, \quad (1.6)$$

where μ runs from 0 to 3 and i runs from 1 to 3, as well as the metric tensor

$$g = (g_{\mu\nu}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \quad (1.7)$$

to construct a flat four-dimensional space denoted as the Minkowski space. We name 4-vectors with superscript indices as contravariants and those with subscript indices as covariants. The metric tensor g can raise or lower indices as

$$x_\mu = \sum_{\nu} g_{\mu\nu} x^\nu \iff x^\nu = \sum_{\mu} g^{\nu\mu} x_\mu, \quad (1.8)$$

with $(g_{\mu\nu}) = (g^{\mu\nu})$, such that

$$(x_\mu) = \begin{pmatrix} ct \\ x_i \end{pmatrix} = \begin{pmatrix} ct \\ -\mathbf{r} \end{pmatrix}. \quad (1.9)$$

Four-dimensional scalar product

This definition of covariants and contravariants 4-vectors enables us to define a scalar product between two 4-vectors a and b

$$\begin{aligned} a \cdot b &= \sum_{\mu=0}^3 a^{\mu} b_{\mu} \\ &= a^0 b^0 - \sum_{i=1}^3 a^i b^i \\ &= a^{\mu} b_{\mu}, \end{aligned} \tag{1.10}$$

where the last line corresponds to Einstein's summation convention, meaning that any Greek indices occurring twice (once as a subscript and once as a superscript) are summed from 0 to 3, and any Latin indices occurring twice are summed from 1 to 3. This convention will be adopted in the rest of the manuscript, for the sake of brevity. Using this scalar products we can re-express the squared space-time interval s_{12}^2 between two events x_1 and x_2 as

$$s_{12}^2 = (x_2 - x_1) \cdot (x_2 - x_1), \tag{1.11}$$

and the squared space-time interval ds^2 between two infinitesimally close events x_1 and $x_2 = x_1 + dx$ as

$$ds^2 = dx \cdot dx. \tag{1.12}$$

1.1.2 Lorentz transformations

A coordinate transformation between two inertial frames within the four-dimensional space-time leaving ds^2 invariant is called a Lorentz transformation (written as a matrix Λ). The homogeneity of space and time enforcing linearity between the two sets of coordinates, we have for two inertial frames \mathbf{J}' and \mathbf{J}

$$x' = \Lambda x + a, \tag{1.13}$$

where Λ is a real-valued 4×4 matrix

$$\Lambda = \left(\Lambda_{\nu}^{\mu} \right) = \begin{pmatrix} \Lambda_0^0 & \Lambda_1^0 & \Lambda_2^0 & \Lambda_3^0 \\ \Lambda_0^1 & \Lambda_1^1 & \Lambda_2^1 & \Lambda_3^1 \\ \Lambda_0^2 & \Lambda_1^2 & \Lambda_2^2 & \Lambda_3^2 \\ \Lambda_0^3 & \Lambda_1^3 & \Lambda_2^3 & \Lambda_3^3 \end{pmatrix}, \tag{1.14}$$

and a is a trivial temporal or spatial shift of the origin of \mathbf{J}' with respect to \mathbf{J} , such that the space-time coordinate differential is

$$dx' = \Lambda dx \iff dx'^{\mu} = \Lambda_{\nu}^{\mu} dx^{\nu}. \tag{1.15}$$

As such, the components of the transformation matrix Λ can be expressed as the derivative of the new coordinates with respect to the old ones

$$\Lambda_{\nu}^{\mu} = \frac{\partial x'^{\mu}}{\partial x^{\nu}} = \partial_{\nu} x'^{\mu}, \tag{1.16}$$

where the last expression makes use of the 4-gradient

$$\partial = (\partial_{\mu}) = \left(\frac{\partial}{\partial x^{\mu}} \right) = \begin{pmatrix} 1 & \frac{\partial}{\partial t} \\ c & \nabla \end{pmatrix}, \tag{1.17}$$

which we define using the usual gradient operator ∇ (Nabla).

Lorentz transformations of position and time

Considering our two inertial frames \mathbf{J}' and \mathbf{J} , coinciding at $t = t' = 0$ and where \mathbf{J}' moves relatively to \mathbf{J} with a uniform velocity \mathbf{v} , the Lorentz transformation of position and time [see Appendix A.1] is

$$\begin{pmatrix} ct' \\ \mathbf{r}' \end{pmatrix} = \Lambda(\mathbf{v}) \begin{pmatrix} ct \\ \mathbf{r} \end{pmatrix} = \begin{pmatrix} \gamma \left(ct - \frac{\mathbf{v} \cdot \mathbf{r}}{c} \right) \\ \mathbf{r} + (\gamma - 1) \frac{(\mathbf{r} \cdot \mathbf{v})\mathbf{v}}{v^2} - \gamma \mathbf{v}t \end{pmatrix}, \quad (1.18)$$

with the Lorentz factor $\gamma = 1/\sqrt{1 - \frac{v^2}{c^2}}$. It correctly reduces to the Galilei transformation when $c \rightarrow \infty$, which is called the non-relativistic limit.

1.1.3 Dynamical properties

Having worked out the proper Lorentz transformation of position and time, we make an extension of dynamical quantities, that is velocity and momentum, in a covariant formalism. Such an extension requires the construction of proper time τ such that an infinitesimal space-time interval ds can be written as $c d\tau$, which leads to

$$ds = \sqrt{c^2 dt^2 - d\mathbf{r}^2} = c \sqrt{1 - \frac{v^2}{c^2}} dt = c \frac{dt}{\gamma}, \quad (1.19)$$

yielding

$$d\tau = \frac{dt}{\gamma}. \quad (1.20)$$

In particular, we have $d\tau = dt$ in the non-relativistic limit as well as within the rest frame of any moving particle as $\gamma \rightarrow 1$ when either $c \rightarrow \infty$ or $v \rightarrow 0$. We now extend the notion of three-dimensional velocity \mathbf{v} to the 4-velocity (u^μ) by differentiating the 4-position with respect to proper time, leading to

$$(u^\mu) = \frac{d}{d\tau}(x^\mu) = \gamma \begin{pmatrix} c \\ \mathbf{v} \end{pmatrix}. \quad (1.21)$$

In the same way, we extend the three-dimensional momentum \mathbf{p} to the 4-momentum (p^μ) for massive particles using the rest mass m such that

$$(p^\mu) = m(u^\mu) = m\gamma \begin{pmatrix} c \\ \mathbf{v} \end{pmatrix} = \begin{pmatrix} E/c \\ \mathbf{p} \end{pmatrix}, \quad (1.22)$$

highlighting the fact that the relativistic momentum $\mathbf{p} = \gamma m \mathbf{v}$ and energy $E = \gamma m c^2$ cannot be considered separately.

Energy-momentum dispersion relation

From the previous equations, we can derive the squared 4-momentum in two ways:

$$p \cdot p = m^2 u^\mu u_\mu = m^2 c^2 \quad \text{and} \quad p \cdot p = E^2/c^2 - \mathbf{p}^2, \quad (1.23)$$

yielding

$$E^2 = \mathbf{p}^2 c^2 + m^2 c^4, \quad (1.24)$$

the energy-momentum dispersion relation. It features two roots for the energy, positive energy solutions which are usually related to massive particles, and negative energy solution which are usually related to massive anti-particles.

Expansions at low momentum / velocity

One can always expand the energy in powers of the momentum, such that when $|\mathbf{p}| \ll mc$

$$E = mc^2 + \frac{\mathbf{p}^2}{2m} - \frac{1}{8} \frac{\mathbf{p}^4}{m^3 c^2} + \dots \quad (1.25)$$

with mc^2 the rest mass energy, and where care has to be taken to remember that $\mathbf{p}^2/2m$ is not the non-relativistic kinetic energy expressed in momentum formalism as the relativistic momentum contains the Lorentz factor γ . One has to expand the relativistic energy in powers of the velocity to recover clearly the non-relativistic kinetic energy, such that when $|\mathbf{v}| \ll c$

$$E = mc^2 + \frac{1}{2} m \mathbf{v}^2 + \frac{3}{8} \frac{m \mathbf{v}^4}{c^2} + \dots \quad (1.26)$$

with mc^2 the rest mass energy, $\frac{1}{2} m \mathbf{v}^2$ the correct non-relativistic kinetic energy and the following terms the relativistic corrections to the energy.

1.2 Covariant electrodynamics

Quantum chemistry being a science focused on the interactions between charged particles, we need to account for such interactions in a relativistic formalism to tread the road to relativistic quantum chemistry. We start by rewriting the equations of electrodynamics in a covariant form, where the charge-current density must now be expressed as the 4-current j such that

$$j(x) = (j^\mu(x)) = \begin{pmatrix} c\rho(x) \\ \mathbf{j}(x) \end{pmatrix} = \begin{pmatrix} c\rho(t, \mathbf{r}) \\ \mathbf{j}(t, \mathbf{r}) \end{pmatrix}, \quad (1.27)$$

containing the charge density, defined for a system of N point-charge particles of electric charges q_i at positions \mathbf{r}_i as

$$\rho(t, \mathbf{r}) = \sum_{i=1}^N q_i \delta^{(3)}(\mathbf{r} - \mathbf{r}_i(t)), \quad (1.28)$$

such that the total charge of a system within a region of space Ω is obtained through spatial integration of the charge density

$$Q_\Omega(t) = \int_\Omega \rho(t, \mathbf{r}) \, d\mathbf{r} = \frac{1}{c} \int_\Omega j^0(x) \, d\mathbf{r}, \quad (1.29)$$

and the current density, defined for a system of N moving point charges of electric charges q_i at positions \mathbf{r}_i with velocities \mathbf{v}_i as

$$\mathbf{j}(t, \mathbf{r}) = \sum_{i=1}^N q_i \mathbf{v}_i(t) \delta^{(3)}(\mathbf{r} - \mathbf{r}_i(t)). \quad (1.30)$$

1.2.1 Electromagnetic field and gauge potential

The interactions between charges and currents are usually expressed using respectively electric (denoted as \mathbf{E}) and magnetic (denoted as \mathbf{B}) fields, which are observable-s but do not represent independent variables, nor do they transform properly under Lorentz transformations. Their six components are uniquely determined by the gauge field 4-vector A

$$A(x) = (A^\mu(x)) = \begin{pmatrix} \phi(x) \\ \mathbf{A}(x) \end{pmatrix} = \begin{pmatrix} \phi(t, \mathbf{r}) \\ \mathbf{A}(t, \mathbf{r}) \end{pmatrix}, \quad (1.31)$$

containing respectively the scalar (ϕ) and vector (\mathbf{A}) potentials, such that

$$\mathbf{E} = -\nabla\phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \quad \text{and} \quad \mathbf{B} = \nabla \times \mathbf{A}. \quad (1.32)$$

Maxwell's equations

The electromagnetic field respects, by construction, Gauss's law of magnetism as well as Maxwell-Faraday equation, respectively

$$\nabla \cdot \mathbf{B} = 0, \quad (1.33)$$

and

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \quad (1.34)$$

the relations between charges, currents and the electromagnetic field being denoted as Gauss's law and Ampère's circuital law, respectively

$$\nabla \cdot \mathbf{E} = 4\pi\rho, \quad (1.35)$$

and

$$\nabla \times \mathbf{B} - \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} = \frac{4\pi}{c} \mathbf{j}, \quad (1.36)$$

where Eq. (1.33) to (1.36) are also known as Maxwell's equations [7].

Continuity equation

The continuity equation ensuring the local conservation of the 4-current j is obtained, in a covariant form, by taking the 4-gradient of the 4-current such that

$$\partial_\mu j^\mu = \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0, \quad (1.37)$$

according to Gauss's law [Eq. (1.35)] and Ampère's circuital law [Eq. (1.36)].

1.2.2 Gauge invariance and field strength tensor

A very important characteristic of the electric and magnetic fields is that they are invariant under gauge transformations [see Appendix B]

$$A^\mu \rightarrow A'^\mu = A^\mu - \partial^\mu g, \quad (1.38)$$

where $g = g(x)$ is any sufficiently smooth gauge function. In order to have both a covariant and gauge invariant quantity containing the observable \mathbf{E} and \mathbf{B} we use the field strength tensor

$$F = (F^{\mu\nu}) = (\partial^\mu A^\nu - \partial^\nu A^\mu) = \begin{pmatrix} 0 & -E_x & -E_y & -E_z \\ E_x & 0 & -B_z & B_y \\ E_y & B_z & 0 & -B_x \\ E_z & -B_y & B_x & 0 \end{pmatrix}, \quad (1.39)$$

which is an antisymmetric Lorentz tensor, and thus both gauge invariant and covariant by construction. We can use this tensor to express Gauss's law as well as Ampère's circuital law, respectively

$$\nabla \cdot \mathbf{E} = 4\pi\rho \iff \partial_\mu F^{\mu 0} = \frac{4\pi}{c} j^0, \quad (1.40)$$

and

$$\nabla \times \mathbf{B} - \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} = \frac{4\pi}{c} \mathbf{j} \iff (\partial_\mu F^{\mu i})_{i=1,3} = \left(\frac{4\pi}{c} j^i \right)_{i=1,3}, \quad (1.41)$$

in the very compact form

$$\partial_\mu F^{\mu\nu} = \frac{4\pi}{c} j^\nu. \quad (1.42)$$

Lorentz transformations of electromagnetic field

Considering once more our two inertial frames \mathbf{J}' and \mathbf{J} , coinciding at $t = t' = 0$ and where \mathbf{J}' moves relatively to \mathbf{J} with a uniform velocity \mathbf{v} , the transformation of electric and magnetic fields with a general Lorentz boost derives from the Lorentz transformation of the field strength tensor [see Appendix A.2] as

$$\begin{aligned} \mathbf{E}'_{\parallel} &= \mathbf{E}_{\parallel} \quad \text{and} \quad \mathbf{E}'_{\perp} = \gamma(\mathbf{E}_{\perp} + \frac{1}{c}\mathbf{v} \times \mathbf{B}), \\ \mathbf{B}'_{\parallel} &= \mathbf{B}_{\parallel} \quad \text{and} \quad \mathbf{B}'_{\perp} = \gamma(\mathbf{B}_{\perp} - \frac{1}{c}\mathbf{v} \times \mathbf{E}), \end{aligned} \quad (1.43)$$

where fields with the \parallel subscripts are parallel to the velocity \mathbf{v} , and fields with the \perp subscripts are their orthogonal counterparts. As such, it means that a particle moving through an electric field experiences a magnetic field in its own rest frame, which is the origin of the spin-orbit effect [8].

1.3 Covariant equation of motion

With a correct understanding of the transformation of time, position and the electromagnetic fields between inertial frames, we can now derive equations of motion and the forces related to electromagnetic interaction between particles. We consider a particle of constant mass m moving at velocity $\mathbf{v}(t)$ within the inertial frame \mathbf{J} , and choose \mathbf{J}' to be the instantaneous rest frame of the particle at a given time t , such that $\mathbf{v}'(t) = 0$. Assuming that the acceleration of the particle is finite, and for an infinitesimal time variation dt , the norm of the particle velocity at a time $t + dt$ in \mathbf{J}' should be small with respect to c , such that we can assume Newton's equation of motion [see Eq. (1.1)] to hold exactly in \mathbf{J}' at this given time t . As this reasoning does not impose any condition on the time t , we have at each time

$$\mathbf{F} = \frac{d\mathbf{p}'_{\text{NR}}}{dt'} = m \frac{d\mathbf{v}'}{dt'} = m \frac{d^2\mathbf{r}'}{dt'^2}, \quad (1.44)$$

where $\mathbf{p}'_{\text{NR}} = m\mathbf{v}'$ is the usual non-relativistic momentum vector (and not the relativistic momentum $\mathbf{p}' = m\gamma\mathbf{v}'$ defined in Eq. (1.22)). This equation of motion holds in \mathbf{J}' , and only in \mathbf{J}' . To build an equation of motion which holds in all inertial frames we extend it using only covariant quantities, yielding

$$f^{\mu} = \frac{dp^{\mu}}{d\tau} = m \frac{du^{\mu}}{d\tau} = m \frac{d^2x^{\mu}}{d\tau^2}, \quad (1.45)$$

where the three-dimensional force \mathbf{F} has been extended to the 4-force f^{μ} , known as the Minkowski force.

1.3.1 Minkowski force

We first check if the Minkowski force correctly reduces to the three-dimensional forces F within the rest frame \mathbf{J}' of the particle. We have in all generality

$$m \frac{du^{\mu}}{d\tau} = m\gamma \frac{d}{dt} \left[\gamma \begin{pmatrix} c \\ \mathbf{v} \end{pmatrix} \right] = m\gamma^4 \frac{1}{c^2} \frac{d\mathbf{v}}{dt} \cdot \mathbf{v} \begin{pmatrix} c \\ \mathbf{v} \end{pmatrix} + m\gamma^2 \begin{pmatrix} 0 \\ \frac{d\mathbf{v}}{dt} \end{pmatrix}, \quad (1.46)$$

such that in \mathbf{J}' , where $\mathbf{v}' = 0$ and $\gamma(\mathbf{v}') = 1$,

$$f' = (f'^{\mu}) = m \begin{pmatrix} 0 \\ \frac{d\mathbf{v}'}{dt} \end{pmatrix} = \begin{pmatrix} 0 \\ \mathbf{F} \end{pmatrix}, \quad (1.47)$$

and we thus recover the correct three-dimensional force from the spatial components of the Minkowski force. The general expression of the Minkowski force can be derived from its expression in the rest frame

of the particle through a Lorentz transformation (in the same way as the 4-position [see Eq. (1.18)], but with a $-\mathbf{v}$ Lorentz boost)

$$f = \Lambda(-\mathbf{v})f', \quad (1.48)$$

such that

$$f = \begin{pmatrix} \gamma \frac{\mathbf{v} \cdot \mathbf{F}}{c} \\ \mathbf{F} + (\gamma - 1) \frac{(\mathbf{F} \cdot \mathbf{v}) \mathbf{v}}{v^2} \end{pmatrix}. \quad (1.49)$$

A special case of Minkowski force: the Lorentz force

From this expression, we derive the 4-component Lorentz force between a charged particle and an external electromagnetic field as a special case of Minkowski force. In the rest frame of the particle, we have the three-dimensional Lorentz force $\mathbf{F}^{\text{Lorentz}}$ written as

$$\begin{aligned} \mathbf{F}^{\text{Lorentz}} = q \mathbf{E}' &= q (\mathbf{E}'_{\parallel} + \mathbf{E}'_{\perp}) = q \left(\mathbf{E}_{\parallel} + \gamma (\mathbf{E}_{\perp} + \frac{1}{c} \mathbf{v} \times \mathbf{B}) \right) \\ &= q \left(\mathbf{E} + (\gamma - 1) \mathbf{E}_{\perp} + \gamma \frac{1}{c} \mathbf{v} \times \mathbf{B} \right), \end{aligned} \quad (1.50)$$

where we explicitly split the electric field \mathbf{E}' (in the rest frame \mathbf{J}') into its longitudinal and orthogonal components, and expressed each component as a function of the electromagnetic field \mathbf{E} and \mathbf{B} (in \mathbf{J}) such that

$$\begin{aligned} f^{\text{Lorentz}} &= q \begin{pmatrix} \gamma \frac{\mathbf{v} \cdot \mathbf{E}'}{c} \\ \mathbf{E}' + (\gamma - 1) \frac{[\mathbf{E}' \cdot \mathbf{v}] \mathbf{v}}{v^2} \end{pmatrix} \\ &= q \begin{pmatrix} \gamma \frac{\mathbf{v} \cdot \mathbf{E}}{c} \\ \left(\mathbf{E} + (\gamma - 1) \mathbf{E}_{\perp} + \gamma \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) + (\gamma - 1) \mathbf{E}_{\parallel} \end{pmatrix} \\ &= \gamma q \begin{pmatrix} \frac{\mathbf{v} \cdot \mathbf{E}}{c} \\ \mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \end{pmatrix}. \end{aligned} \quad (1.51)$$

1.4 Covariant Lagrangian formulation

Having determined the covariant equation of motion of a massive charged particle within an external electromagnetic field, we want to derive the covariant Lagrangian $L(x, u)$ describing such a particle. The Hamiltonian principle states that the trajectory of a system corresponds to a stationary point of the action S in configuration space

$$\delta S = \delta \int_{\tau_0}^{\tau_1} L(x, u) \, d\tau = 0, \quad (1.52)$$

for any variation of the four-dimensional path δx^{μ} with vanishing variations at the extremities of the path. The Euler-Lagrange equations are derived from a Taylor expansion of the Lagrangian, starting from the

Hamiltonian principle such that

$$\begin{aligned}
\delta S = S[x + \delta x] - S[x] &= \int_{\tau_0}^{\tau_1} \left(\frac{\partial L}{\partial x^\mu} \delta x^\mu + \frac{\partial L}{\partial u^\mu} \delta u^\mu \right) d\tau \\
&= \int_{\tau_0}^{\tau_1} \left(\frac{\partial L}{\partial x^\mu} - \frac{d}{d\tau} \frac{\partial L}{\partial u^\mu} \right) \delta x^\mu d\tau + \frac{\partial L}{\partial u^\mu} \delta x^\mu \Big|_{\tau_0}^{\tau_1} \\
&= \int_{\tau_0}^{\tau_1} \left(\frac{\partial L}{\partial x^\mu} - \frac{d}{d\tau} \frac{\partial L}{\partial u^\mu} \right) \delta x^\mu d\tau \\
&= 0,
\end{aligned} \tag{1.53}$$

where the second line is obtained after integration by parts, and vanishing variations at the boundaries ensure that the surface term is 0. Since this equation has to be valid for any infinitesimal variation δx^μ , the Hamiltonian principle is satisfied for any and all variations if and only if the integrand vanishes. From this statement we extract the covariant Euler-Lagrange equations

$$\left(\frac{\partial L}{\partial x^\mu} - \frac{d}{d\tau} \frac{\partial L}{\partial u^\mu} \right)_{\mu=0,3} = 0. \tag{1.54}$$

1.4.1 Lagrangian of a relativistic particle

The covariant Lagrangian of a massive charged particle can be split into two parts. The first part corresponds to the covariant Lagrangian of a free particle of mass m [see Appendix C.1], which is written as

$$L_{\text{free}}(u) = -mc\sqrt{u^\mu u_\mu}, \tag{1.55}$$

where the prefactor is chosen arbitrarily to have the correct non-relativistic limit. The second part corresponds to the covariant interaction Lagrangian for a particle of charge q within an external electromagnetic field determined by the gauge field A [see Appendix C.2], which is written as

$$L_{\text{int}}(x, u) = -\frac{q}{c} A_\mu(x) u^\mu, \tag{1.56}$$

such that the covariant Lagrangian of a particle of mass m and charge q is

$$\begin{aligned}
L(x, u) &= L_{\text{free}}(u) + L_{\text{int}}(x, u) \\
&= -mc\sqrt{u^\mu u_\mu} - \frac{q}{c} A_\mu(x) u^\mu.
\end{aligned} \tag{1.57}$$

1.4.2 Minimal coupling of the gauge field to matter

In order to gain some insight we re-express the covariant Lagrangian of a massive charged particle as a function of the time t , the three-dimensional position \mathbf{r} and the three-dimensional velocity \mathbf{v} such that $L(t, \mathbf{r}, \mathbf{v})$ describes the same trajectory as before, and must therefore have the same action. We have thus

$$L(t, \mathbf{r}, \mathbf{v}) = -mc^2 \sqrt{1 - \frac{\mathbf{v}(t)^2}{c^2}} - q\phi(t, \mathbf{r}) + \frac{q}{c} \mathbf{v}(t) \cdot \mathbf{A}(t, \mathbf{r}) \tag{1.58}$$

such that the generalized momentum for a charged particle is

$$\mathbf{p} = \left(\frac{\partial L}{\partial v_i} \right)_{i=1,2,3} = \gamma m \mathbf{v} + \frac{q}{c} \mathbf{A}, \tag{1.59}$$

and depends on the vector potential \mathbf{A} , a dependency that is denoted as the minimal coupling.

1.5 Toward Quantum electrodynamics

Quantum electrodynamics (QED) is hailed as the most accurate physical theory, describing electrons and photons on equal footing in a fully covariant and quantized form [6, 9] with an extreme precision, reaching up to twelve digits of concordance with experiments designed to test it [10]. The first building blocks of this theory are usually expressed in a non-quantized covariant Lagrangian formulation, which must be quantized later on to account for quantum mechanical properties of matter and electromagnetic fields. It is therefore constituted of an electromagnetic Lagrangian part, describing the electromagnetic field and its interaction with charged particles in a covariant formalism, and a matter Lagrangian part, describing relativistic particles.

1.5.1 Electromagnetic Lagrangian

In order to build the electromagnetic Lagrangian, we need to step up from a Lagrangian describing particles within an external electromagnetic field to a Lagrangian describing both electromagnetic field, charges and currents on an even footing in covariant form. The gauge field A must now be treated as the dynamical variable and no longer as an external potential, i.e. $L = L(A, \partial A) = L(A, \partial A, x, u)$ with the 4-position x and 4-velocity u being treated as non-dynamical variables for the working of the equation of motion of the electrodynamic field. Considering that the gauge field is a continuous real-valued function of the 4-position as $A^\mu = A^\mu(x)$, we need to construct an electromagnetic Lagrangian density \mathcal{L}_{em} such that its spatial integration over the available space Ω yields the electromagnetic Lagrangian L_{em} through

$$L_{\text{em}} = \int_{\Omega} \mathcal{L}_{\text{em}} \, d\mathbf{r}, \quad (1.60)$$

and such that an integration over time and the available space Ω yields the electromagnetic action S_{em} through

$$\begin{aligned} S_{\text{em}} &= \int_{t_1}^{t_2} \left[\int_{\Omega} \mathcal{L}_{\text{em}} \, d\mathbf{r} \right] dt \\ &= \frac{1}{c} \int_{ct_1/c}^{ct_2/c} \int_{\Omega} \mathcal{L}_{\text{em}} \, d\mathbf{r} \, d(ct) \\ &= \frac{1}{c} \int \mathcal{L}_{\text{em}} \, dx. \end{aligned} \quad (1.61)$$

We derive the Euler-Lagrange equations for the electromagnetic Lagrangian density in the same spirit as Eq. (1.53), such that

$$\begin{aligned} \delta S[A] = S[A + \delta A] - S[A] &= \frac{1}{c} \int dx \left(\frac{\partial \mathcal{L}_{\text{em}}}{\partial A^\mu} \delta A^\mu + \frac{\partial \mathcal{L}_{\text{em}}}{\partial (\partial^\nu A^\mu)} \delta (\partial^\nu A^\mu) \right) \\ &= \frac{1}{c} \int dx \left(\frac{\partial \mathcal{L}_{\text{em}}}{\partial A^\mu} - \partial^\nu \frac{\partial \mathcal{L}_{\text{em}}}{\partial (\partial^\nu A^\mu)} \right) \delta A^\mu + 0 \\ &= 0, \end{aligned} \quad (1.62)$$

where the second line is obtained after integration by parts, with the surface term just written as 0 due to its vanishing variations at the boundaries of the space-time integration domain. Since this equation has to be valid for any infinitesimal variation δA^μ , the Euler-Lagrange equations for the electromagnetic Lagrangian density are

$$\left(\frac{\partial \mathcal{L}_{\text{em}}}{\partial A^\mu} - \partial^\nu \frac{\partial \mathcal{L}_{\text{em}}}{\partial (\partial^\nu A^\mu)} \right)_{\mu=0,3} = 0. \quad (1.63)$$

The covariant electromagnetic Lagrangian density can be split into two parts. The first part corresponds to the interaction Lagrangian density, which can be seen as a generalization of the interaction Lagrangian

for a particle of charge q within an external electromagnetic field [see Eq. (1.56)] to an interaction Lagrangian density for the dynamical gauge field A with its sources, the charged particles described by the 4-current j [see Appendix C.3], and is written as

$$\mathcal{L}_{\text{int}}(A, x, u) = -\frac{1}{c} A_\mu(x) j^\mu(x), \quad (1.64)$$

such that this interaction Lagrangian density is Lorentz invariant by construction, and gauge invariant due to the continuity equation of the four-current. The second part corresponds to the radiation Lagrangian density, which describes the electromagnetic field itself [see Appendix C.4], and is written as

$$\mathcal{L}_{\text{rad}}(\partial A, x) = -\frac{1}{16\pi} F^{\mu\nu} F_{\mu\nu}, \quad (1.65)$$

such that this radiation Lagrangian density is Lorentz invariant and gauge invariant by construction, as it only depends of the field strength tensor [see Eq. (1.39)]. The covariant electromagnetic Lagrangian density is therefore written as

$$\begin{aligned} \mathcal{L}_{\text{em}}(A, \partial A, x, u) &= \mathcal{L}_{\text{rad}}(\partial A, x) + \mathcal{L}_{\text{int}}(A, x, u) \\ &= -\frac{1}{16\pi} F^{\mu\nu} F_{\mu\nu} - \frac{1}{c} A_\mu(x) j^\mu(x), \end{aligned} \quad (1.66)$$

such that we have worked out a covariant Lagrangian taking in account electromagnetic fields and their interactions with charged particles.

1.5.2 Matter Lagrangian

The only building bloc missing is now the matter Lagrangian describing charged particles, and we make use of the Dirac equation with some advance here. While the Dirac equation is usually seen as an equation describing quantum particles in covariant formalism, we regard here the Dirac wave function ψ as a classical Dirac field [11], such that the matter Lagrangian is supposed to yield the Dirac equation as an equation of motion for this classical Dirac field, which has to be quantized later on.

The matter Lagrangian is usually written $L_{\text{mat}}(\psi, \partial\psi, \bar{\psi}, \partial\bar{\psi})$, with two independent variables ψ and $\bar{\psi} = \psi^\dagger \gamma^0 = \psi^\dagger \boldsymbol{\beta}$ [see Eq. (D.16)] where ψ is the classical (i.e. non-quantized) Dirac matter field, and their associated derivatives. Considering that the Dirac field is a continuous function of the 4-position, the use of a matter Lagrangian density is mandatory and we thus express

$$L_{\text{mat}} = \int_{\Omega} \mathcal{L}_{\text{mat}} \, d\mathbf{r}. \quad (1.67)$$

In the same way as for Eq. (1.63) we can write the Euler-Lagrange equations for the matter Lagrangian density, in the case of the $\bar{\psi}$ field dynamical variable

$$\frac{\partial \mathcal{L}_{\text{mat}}}{\partial \bar{\psi}} - \partial^\nu \frac{\partial \mathcal{L}_{\text{mat}}}{\partial (\partial^\nu \bar{\psi})} = 0, \quad (1.68)$$

where the use of the $\bar{\psi}$ field makes for an easier determination of the matter Lagrangian density [see Appendix C.5], which is written as

$$\mathcal{L}_{\text{mat}}(\psi, \bar{\psi}) = \bar{\psi} (-i\hbar c \boldsymbol{\gamma}^\mu \partial_\mu + mc^2 \mathbf{1}_4) \psi. \quad (1.69)$$

This matter Lagrangian density is manifestly covariant, as the use of the 4-gradient ensures that time and space are treated identically.

1.5.3 Complete Lagrangian and quantization

From this, we can now write the full non-quantized QED Lagrangian density as

$$\begin{aligned}\mathcal{L}_{\text{QED}} &= \mathcal{L}_{\text{rad}}(\partial A, x) + \mathcal{L}_{\text{int}}(A, x, u) + \mathcal{L}_{\text{mat}}(\Psi, \bar{\Psi}) \\ &= -\frac{1}{16\pi} F^{\mu\nu} F_{\mu\nu} - \frac{1}{c} A_\mu(x) j^\mu(x) + \bar{\Psi} (-i\hbar c \boldsymbol{\gamma}^\mu \partial_\mu + mc^2 \mathbf{1}_4) \Psi.\end{aligned}\quad (1.70)$$

This Lagrangian formulation is the last step before quantization must be considered, after what excitations of the quantized Dirac field ψ can be interpreted as electrons and positrons [6]. While quantization of the Dirac matter field is rather straightforward [see the book from S. S. Schweber [12] (Quantization of the Dirac field, page 218)], quantization of the electromagnetic field is trouble from the start [13] with redundant degrees of freedom and the different possible choices of gauge condition [see the book from J. D. Bjorken and S. Drell [14] for the quantization in Coulomb gauge (Quantization of the electromagnetic field, page 69), and the book from F. Mandl and G. Shaw [15] for the quantization in Lorenz gauge (Covariant quantization page 86)]. Furthermore, quantization in QED comes with a heavy price, namely the need for renormalization. As such, quantization of the matter field requires charge renormalization of the electrons to account for the vacuum polarization [16], and quantization of the electromagnetic field requires mass renormalization of the electron.

This apparatus of renormalization, as well as the fact that the QED formalism is so heavy that calculations on chemical systems are all but out of reach for systems more complex than an atom with a couple of electrons [6, 17], thus motivating the use of methods less complete but more tractable. While one cannot abandon the quantization of particles for any kind of ab-initio quantum chemistry calculation, it is not so for the quantization of the electromagnetic field. The next chapter focuses on the Hamiltonian formulation rather than the Lagrangian formulation, mostly through the use of the Dirac equation where electromagnetic interactions are treated in a purely classical way.

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Chapter 2

Relativistic quantum chemistry

In this chapter we work out the first-quantized and second-quantized Dirac Hamiltonians used in quantum chemistry, starting from the momentum dispersion relation of special relativity. Additionally, we introduce the main equations of relativistic density-functional theory as well as some practical details about the implementation of a four-component relativistic quantum chemistry code.

2.1 Fundamental one-particle equation

While we already stated and used the Dirac equation in Section 1.5, it is interesting to see how and why this four-component equation is at the core of most relativistic quantum chemistry ab-initio developments. We first review some properties of the Klein-Gordon equation, as this equation emerges naturally from a quantization of the energy momentum dispersion relation [see Eq. (1.24)], before pointing out some of the flaws that historically led to the abandon of this equation to the profit of the Dirac equation.

2.1.1 The Klein-Gordon equation

We want to derive the Klein-Gordon equation. We start from the classical relativistic energy-momentum dispersion relation [see Eq. (1.24)]. It seems reasonable to isolate the expression of the positive energy root, which is usually understood as describing particles, yielding

$$E = \sqrt{\mathbf{p}^2 c^2 + m^2 c^4}. \quad (2.1)$$

In order to respect the correspondence principle, quantum mechanical equations can be derived from classical equations using the substitutions

$$E \rightarrow i\hbar \frac{\partial}{\partial t} \quad \text{and} \quad \mathbf{p} \rightarrow -i\hbar \nabla, \quad (2.2)$$

such that, when acting upon a wave function ψ we obtain from Eq. (2.1) the quantum mechanical equation

$$i\hbar \frac{\partial}{\partial t} \psi = \sqrt{-\hbar^2 c^2 \nabla^2 + m^2 c^4} \psi. \quad (2.3)$$

This equation features a square-root operator which may be expanded as a power series

$$\sqrt{-\hbar^2 c^2 \nabla^2 + m^2 c^4} = mc^2 \left(1 - \frac{1}{2} \frac{\hbar^2 \nabla^2}{m^2 c^2} - \frac{1}{8} \frac{\hbar^4 \nabla^4}{m^4 c^4} - \dots \right), \quad (2.4)$$

which would lead to an equation which is not manifestly covariant, as time and space are not treated identically. A way to circumvent this trouble is to start directly from the squared energy expression,

that is from the energy-momentum dispersion relation [see Eq. (1.24)] $E^2 = \mathbf{p}^2 c^2 + m^2 c^4$, such that the substitutions from Eq. (2.2) yield, after acting upon a wave function ψ , the Klein-Gordon equation [1, 2]

$$-\hbar^2 \frac{\partial^2}{\partial t^2} \psi = \left(-\hbar^2 c^2 \nabla^2 + m^2 c^4 \right) \psi, \quad (2.5)$$

which is manifestly covariant as it treats time and space identically, as second-order derivatives. One important consequence of having an equation with second-order derivative on time is that knowing the wave function at a time t does not give enough information to know the wave function at later times, and knowledge of the derivative of the wave function with respect to time at time t is also needed, setting this equation apart from general equations of quantum mechanics. The Klein-Gordon equation [see Eq. (2.5)] can be recast into a covariant formalism using the 4-gradient [see Eq. (1.17)], such that

$$\left(\hbar^2 \partial_\mu \partial^\mu + m^2 c^4 \right) \psi = 0, \quad (2.6)$$

which is somewhat more convenient for later manipulations.

Continuity equation of the 4-current

If one considers the wave function solutions of the Klein-Gordon equation to behave as probability amplitudes in the same way as a solution of the Schrödinger equation, it is possible to derive a continuity equation for a free particle by multiplying Eq. (2.6) by ψ^* on the left and subtracting its complex conjugate such that

$$\begin{aligned} 0 &= \psi^* \left(\hbar^2 \partial_\mu \partial^\mu + m^2 c^4 \right) \psi - \psi \left(\hbar^2 \partial_\mu \partial^\mu + m^2 c^4 \right) \psi^* \\ &= \hbar^2 \left(\psi^* \partial_\mu \partial^\mu \psi - \psi \partial_\mu \partial^\mu \psi^* \right) \\ &= \hbar^2 \partial_\mu \left(\psi^* \partial^\mu \psi - \psi \partial^\mu \psi^* \right), \end{aligned} \quad (2.7)$$

where we use the cancellation of the crossed terms $\partial_\mu \psi^* \partial^\mu \psi - \partial_\mu \psi \partial^\mu \psi^* = 0$. The \hbar^2 has been arbitrarily kept, and does not yield the correct dimension for a 4-current from this continuity equation. In order to obtain the correct dimension we arbitrarily choose the prefactor to be the same as for the non-relativistic current expression [3] for a free particle

$$\mathbf{j} = -\frac{i\hbar}{2m} \left(\psi^* \nabla \psi - \psi \nabla \psi^* \right), \quad (2.8)$$

such that, taking in account the minus sign entering the equations from $(\partial^i)_{i=1,3}$ we have the continuity equation for the Klein-Gordon equation written as

$$\begin{aligned} 0 &= \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} \\ &= \partial_\mu j^\mu \\ &= \partial_\mu \frac{i\hbar}{2m} \left(\psi^* \partial^\mu \psi - \psi \partial^\mu \psi^* \right). \end{aligned} \quad (2.9)$$

In particular, the particle density must be expressed as $\rho = j^0/c$ such that

$$\rho = \frac{1}{c} \frac{i\hbar}{2m} \left(\psi^* \partial^0 \psi - \psi \partial^0 \psi^* \right), \quad (2.10)$$

with the correct dimension.

Solution of the Klein-Gordon equation for a free particle

As the Klein-Gordon equation emerges from the energy-momentum dispersion relation [see Eq. (1.24)], the free particle solutions of this equation corresponds to plane waves with positive or negative energies [4] and a normalization constant \mathcal{N}

$$\Psi_{\mathbf{k}}^{\pm}(t, \mathbf{r}) = \mathcal{N} \exp \left[-i \left(\pm \frac{|E_{\mathbf{k}}|}{\hbar} t - \mathbf{k} \cdot \mathbf{r} \right) \right], \quad (2.11)$$

such that

$$E_{\mathbf{k}}^2 = (\hbar^2 c^2 \mathbf{k}^2 + m^2 c^4) \quad (2.12)$$

for a plane wave of wave vector \mathbf{k} . The positive energy solutions are usually associated to particles, while the negative energy solutions are less straightforwardly described in a wave function formalism. The particle density yielded by such a plane wave of wave vector \mathbf{k} would then be

$$\begin{aligned} \rho^{\pm} &= \frac{1}{c} \frac{i\hbar}{2m} (\Psi_{\mathbf{k}}^{\pm*} \partial^0 \Psi_{\mathbf{k}}^{\pm} - \Psi_{\mathbf{k}}^{\pm} \partial^0 \Psi_{\mathbf{k}}^{\pm*}) \\ &= \pm \mathcal{N}^2 \frac{|E_{\mathbf{k}}|}{mc^2}, \end{aligned} \quad (2.13)$$

where the particle probability density depends on the sign of the energy of the wave function, leading to what appears like negative probability density if the squared normalization constant is positive. This problem obviously propagates to the definition of the normalization constant, which requires that we choose an inner product between two solutions of the Klein-Gordon equation [4]. Such an inner product usually comes from the space integral of the continuity equation

$$\begin{aligned} 0 &= \int_{\Omega} d\mathbf{r} \left(\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} \right) \\ 0 &= \frac{\partial}{\partial t} \int_{\Omega} d\mathbf{r} \rho + \int_{\partial\Omega} dS \mathbf{n} \cdot \mathbf{j} \\ 0 &= \frac{\partial}{\partial t} \int_{\Omega} d\mathbf{r} \rho, \end{aligned} \quad (2.14)$$

where we re-expressed the space integral over the divergence of the current \mathbf{j} as a surface vanishing surface integral through Ostrogradsky's theorem. The vanishing of the time derivative of the space integral of the density ρ ensures that this space integral must be a constant, and this constant should logically be the number of particle described by the wave function. For two solutions of the Klein-Gordon equation $\Psi_{\mathbf{k}_m}(t, \mathbf{r})$ and $\Psi_{\mathbf{k}_n}(t, \mathbf{r})$, we define the inner product

$$\langle \Psi_{\mathbf{k}_m}, \Psi_{\mathbf{k}_n} \rangle = \int_{\Omega} d\mathbf{r} \frac{i\hbar}{2mc^2} \left(\Psi_{\mathbf{k}_m}^* \frac{\partial}{\partial t} \Psi_{\mathbf{k}_n} - \Psi_{\mathbf{k}_n} \frac{\partial}{\partial t} \Psi_{\mathbf{k}_m}^* \right), \quad (2.15)$$

such that for wave function $\Psi_{\mathbf{k}}^{\pm}(t, \mathbf{r})$ describing exactly one free particle inside a box of volume V , its squared norm is

$$\langle \Psi_{\mathbf{k}}^{\pm}, \Psi_{\mathbf{k}}^{\pm} \rangle = \pm \mathcal{N}^2 V \frac{|E_{\mathbf{k}}|}{2mc^2}. \quad (2.16)$$

Choosing a positive real normalization constant $\mathcal{N} = \left(V \frac{|E_{\mathbf{k}}|}{2mc^2} \right)^{-1/2}$ yields, for positive energy solution, squared norms of $+1$ and, for negative energy solutions, squared norms of -1 . This inconsistency led historically to the rejection of the Klein-Gordon equation, but may be reinterpreted as charge densities instead of particle densities [4]. Furthermore, as it does not explicitly take in account the spin the Klein-Gordon equation is usually considered as describing spinless particles [5].

2.1.2 The Dirac equation

In order to have an equation which describes particles of spin $1/2$, as the electrons we focus on in quantum chemistry, the Dirac equation [6,7] is usually favored. We derive this equation [see Appendix D] and write it using the mono-electronic free particle Dirac Hamiltonian $h_{\text{free}}^{\text{D}}$ such that

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi &= h_{\text{free}}^{\text{D}} \psi \\ &= (c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2) \psi, \end{aligned} \quad (2.17)$$

where $\mathbf{p} = -i\hbar\nabla$ is the three-dimensional momentum operator and $\boldsymbol{\alpha} = (\boldsymbol{\alpha}_1, \boldsymbol{\alpha}_2, \boldsymbol{\alpha}_3)$ is treated as a column vector with

$$\boldsymbol{\alpha}_1 = \begin{pmatrix} 0 & \boldsymbol{\sigma}_1 \\ \boldsymbol{\sigma}_1 & 0 \end{pmatrix}, \quad \boldsymbol{\alpha}_2 = \begin{pmatrix} 0 & \boldsymbol{\sigma}_2 \\ \boldsymbol{\sigma}_2 & 0 \end{pmatrix}, \quad \boldsymbol{\alpha}_3 = \begin{pmatrix} 0 & \boldsymbol{\sigma}_3 \\ \boldsymbol{\sigma}_3 & 0 \end{pmatrix} \quad \text{and} \quad \boldsymbol{\beta} = \begin{pmatrix} \mathbf{I}_2 & 0 \\ 0 & -\mathbf{I}_2 \end{pmatrix}, \quad (2.18)$$

featuring the Pauli matrices $\boldsymbol{\sigma}_1$, $\boldsymbol{\sigma}_2$ and $\boldsymbol{\sigma}_3$ [see Eq. (D.12)]. The use of the Pauli matrices is most significant and makes for an easy connection between the Dirac equation and the spin operator of the electron $\mathbf{s} = \frac{\hbar}{2}\boldsymbol{\sigma}$ [3], as electrons are fermions of spin quantum number $s = 1/2$. Contrary to the Klein-Gordon equation, the Dirac equation is manifestly covariant but contains only first-order derivatives, such that knowing the wave function at a given time t gives enough information to determine it at any later time. Furthermore, considering that the $\boldsymbol{\alpha}$'s and $\boldsymbol{\beta}$ are 4×4 matrices, the eigenfunctions ψ of the Dirac equation must be of dimension four and are called 4-spinors such that

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \begin{pmatrix} \psi^{\text{L}} \\ \psi^{\text{S}} \end{pmatrix} \quad (2.19)$$

where the block structures of the $\boldsymbol{\alpha}$'s and $\boldsymbol{\beta}$ matrices calls for a separation of the 4-spinor ψ into two 2-spinors ψ^{L} and ψ^{S} , respectively known the large (L) and small (S) components. In the same way as the Klein-Gordon equation [see Eq. (2.6)], the Dirac equation may be recast into a covariant form [see Eq. (D.14)], such that

$$0 = (-i\hbar c \partial_0 - i\hbar c \boldsymbol{\alpha}^i \partial_i + \beta mc^2) \psi. \quad (2.20)$$

Continuity equation of the 4-current

We derive a continuity equation for the Dirac equation by multiplying Eq. (2.20) by ψ^\dagger on the left and subtracting its transposed complex conjugate such that

$$\begin{aligned} 0 &= \psi^\dagger (-i\hbar c \partial_0 - i\hbar c \boldsymbol{\alpha}^i \partial_i + \beta mc^2) \psi - \left(\psi^\dagger (-i\hbar c \partial_0 - i\hbar c \boldsymbol{\alpha}^i \partial_i + \beta mc^2) \psi \right)^\dagger \\ &= -i\hbar [\psi^\dagger c \partial_0 \psi + \psi^\dagger c \boldsymbol{\alpha}^i \partial_i \psi + (c \partial_0 \psi^\dagger) \psi + (c \partial_i \psi^\dagger) \boldsymbol{\alpha}^{i\dagger} \psi] + mc^2 (\psi^\dagger \boldsymbol{\beta} \psi - \psi^\dagger \boldsymbol{\beta}^\dagger \psi) \\ &= c \partial_0 (\psi^\dagger \psi) + [\psi^\dagger c \boldsymbol{\alpha}^i \partial_i \psi + (\partial_i \psi^\dagger) c \boldsymbol{\alpha}^i \psi] \\ &= \frac{\partial}{\partial t} (\psi^\dagger \psi) + \nabla \cdot (\psi^\dagger c \boldsymbol{\alpha} \psi), \end{aligned} \quad (2.21)$$

where care has been taken to correctly consider ψ^\dagger as the conjugate transpose of the 4-spinor of ψ , i.e. a line vector and not a column vector, and remarking that $\boldsymbol{\alpha}^{i\dagger} = \boldsymbol{\alpha}^i$ and $\boldsymbol{\beta}^\dagger = \boldsymbol{\beta}$ as they are Hermitian

matrices [see Appendix D] before simplifying the remaining terms by $-i\hbar$. We have correctly obtained an equation of the form

$$0 = \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j}, \quad (2.22)$$

where the Dirac density distribution for a single particle is $\rho = \psi^\dagger \psi$ and the Dirac current density is $\mathbf{j} = \psi^\dagger c \boldsymbol{\alpha} \psi$. It is interesting to indicate that the vector $c \boldsymbol{\alpha}$ which gives its structure to the Dirac current density is known as the Dirac velocity operator, as the use of Heisenberg's equation of motion [3] for the position operator yields for a free particle, for $k = 1, 3$

$$x^k = \frac{i}{\hbar} [c \boldsymbol{\alpha} \cdot \mathbf{p}, x^k] = \frac{i}{\hbar} c \alpha^j [p_j, x^k] = c \alpha^k, \quad (2.23)$$

using the commutator relation between position and impulsion $[p_j, x^k] = -i\hbar \delta_{jk}$.

Solution of the Dirac equation for a free particle

The free particle solutions of this equation corresponds to plane waves [3] with a 4-spinor structure and a normalization constant \mathcal{N}

$$\Psi_{\mathbf{k}, \sigma}^\pm(t, \mathbf{r}) = \mathcal{N} \begin{pmatrix} \Phi_{\mathbf{k}, \sigma}^\pm \\ \chi_{\mathbf{k}, \sigma}^\pm \end{pmatrix} \exp \left[-i \left(\pm \frac{|E_k|}{\hbar} t - \mathbf{k} \cdot \mathbf{r} \right) \right], \quad (2.24)$$

for a wave vector \mathbf{k} and a "spin" index σ taking two values $\sigma_1, \sigma_2 = \uparrow, \downarrow$, with once more positive or negative energy eigenvalues, with

$$|E_k| = \sqrt{\hbar^2 k^2 c^2 + m^2 c^4}. \quad (2.25)$$

For positive energy solutions we have [3]

$$\begin{pmatrix} \Phi_{\mathbf{k}, \uparrow}^+ \\ \chi_{\mathbf{k}, \uparrow}^+ \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ \frac{\hbar k_z c}{|E_k| + mc^2} \\ \frac{\hbar(k_x + ik_y)c}{|E_k| + mc^2} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \Phi_{\mathbf{k}, \downarrow}^+ \\ \chi_{\mathbf{k}, \downarrow}^+ \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ \frac{\hbar(k_x - ik_y)c}{|E_k| + mc^2} \\ -\frac{\hbar k_z c}{|E_k| + mc^2} \end{pmatrix}, \quad (2.26)$$

while for negative energy solutions we have

$$\begin{pmatrix} \Phi_{\mathbf{k}, \uparrow}^- \\ \chi_{\mathbf{k}, \uparrow}^- \end{pmatrix} = \begin{pmatrix} \frac{\hbar k_z c}{-|E_k| - mc^2} \\ \frac{\hbar(k_x + ik_y)c}{-|E_k| - mc^2} \\ 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \Phi_{\mathbf{k}, \downarrow}^- \\ \chi_{\mathbf{k}, \downarrow}^- \end{pmatrix} = \begin{pmatrix} \frac{\hbar(k_x - ik_y)c}{-|E_k| - mc^2} \\ -\frac{\hbar k_z c}{-|E_k| - mc^2} \\ 0 \\ 1 \end{pmatrix}. \quad (2.27)$$

As Eq. (2.14) is general for all continuity equation, we define for two solutions of the Dirac equation $\Psi_{\mathbf{k}_m, \sigma_m}(t, \mathbf{r})$ and $\Psi_{\mathbf{k}_n, \sigma_n}(t, \mathbf{r})$ the inner product

$$\langle \Psi_{\mathbf{k}_m, \sigma_m}, \Psi_{\mathbf{k}_n, \sigma_n} \rangle = \int_{\Omega} d\mathbf{r} (\Psi_{\mathbf{k}_m, \sigma_m}^\pm)^\dagger \Psi_{\mathbf{k}_n, \sigma_n}^\pm, \quad (2.28)$$

such that for a wave function $\Psi_{\mathbf{k},\sigma}^{\pm}(t, \mathbf{r})$ describing one free particle inside a box of volume V , its normalization constant \mathcal{N} is determined by

$$\begin{aligned} 1 &= \int_{\Omega} d\mathbf{r} (\Psi_{\mathbf{k},\sigma}^{\pm})^{\dagger} \Psi_{\mathbf{k},\sigma}^{\pm} = \mathcal{N}^2 V \left(1 + \frac{\hbar^2 \mathbf{k}^2 c^2}{(\pm |E_{\mathbf{k}}| \pm mc^2)^2} \right) \\ &= \mathcal{N}^2 V \left(1 + \frac{\hbar^2 \mathbf{k}^2 c^2}{(|E_{\mathbf{k}}| + mc^2)^2} \right), \end{aligned} \quad (2.29)$$

yielding

$$\begin{aligned} \mathcal{N}^2 &= \frac{1}{V} \frac{1}{1 + \frac{\hbar^2 \mathbf{k}^2 c^2}{(|E_{\mathbf{k}}| + mc^2)^2}} \\ &= \frac{1}{V} \frac{|E_{\mathbf{k}}| + mc^2}{2|E_{\mathbf{k}}|}, \end{aligned} \quad (2.30)$$

which is a purely positive quantity. As this expression depends neither of the sign of the energy eigenvalue nor of the “spin” index σ , all four 4-spinors solutions of the Dirac equation for a free particle have the same positive normalization constant $\mathcal{N} = \left(V \frac{|E_{\mathbf{k}}| + mc^2}{2|E_{\mathbf{k}}|} \right)^{-1/2}$.

Dirac equation in the presence of external electromagnetic fields

In order to take in account the presence of non-quantized external electromagnetic potentials in a covariant formalism, it is better to rewrite the Dirac equation [see Eq. (D.15)] to make it manifestly covariant

$$0 = (-i\hbar c \boldsymbol{\gamma}^{\mu} \partial_{\mu} + mc^2 \mathbf{I}_4) \Psi, \quad (2.31)$$

introducing the $\boldsymbol{\gamma}$'s matrices such that

$$\boldsymbol{\gamma}^0 = \boldsymbol{\beta} = \begin{pmatrix} \mathbf{I}_2 & 0 \\ 0 & -\mathbf{I}_2 \end{pmatrix}, \quad (2.32)$$

and

$$\boldsymbol{\gamma}^1 = \boldsymbol{\beta} \boldsymbol{\alpha}^1 = \begin{pmatrix} 0 & \boldsymbol{\sigma}_1 \\ -\boldsymbol{\sigma}_1 & 0 \end{pmatrix}, \boldsymbol{\gamma}^2 = \boldsymbol{\beta} \boldsymbol{\alpha}^2 = \begin{pmatrix} 0 & \boldsymbol{\sigma}_2 \\ -\boldsymbol{\sigma}_2 & 0 \end{pmatrix}, \boldsymbol{\gamma}^3 = \boldsymbol{\beta} \boldsymbol{\alpha}^3 = \begin{pmatrix} 0 & \boldsymbol{\sigma}_3 \\ -\boldsymbol{\sigma}_3 & 0 \end{pmatrix}. \quad (2.33)$$

We start from the minimal coupling that was derived in Eq. (1.59) for a particle of charge q , such that

$$p^i \longrightarrow p^i + \frac{q}{c} A^i, \quad (2.34)$$

noting that $p^i = -p_i = i\hbar \partial_i$ and making a straightforward extension to the 4-momentum coupling to the gauge field for an electron of charge q_e we have

$$i\hbar \partial_{\mu} \longrightarrow i\hbar \partial_{\mu} - \frac{q_e}{c} A_{\mu}. \quad (2.35)$$

such that the Dirac equations with an external electromagnetic field becomes

$$0 = \left(-c \boldsymbol{\gamma}^{\mu} \left(i\hbar \partial_{\mu} - \frac{q_e}{c} A_{\mu} \right) + mc^2 \mathbf{I}_4 \right) \Psi, \quad (2.36)$$

which is manifestly covariant and also invariant under gauge transformations [see Appendix B]

$$\Psi(x) \longrightarrow \exp \left[i \frac{q_e}{\hbar c} g(x) \right] \Psi(x) \quad \text{and} \quad A_{\mu}(x) \rightarrow A_{\mu}(x) - \partial_{\mu} g(x). \quad (2.37)$$

Separating once more the time and space variables and multiplying by $\boldsymbol{\gamma}^0$ from the left yields

$$i\hbar \frac{\partial}{\partial t} \Psi = \left(c \boldsymbol{\alpha} \cdot \left(\mathbf{p} - \frac{q_e}{c} \mathbf{A} \right) + \boldsymbol{\beta} mc^2 + q_e \phi \mathbf{I}_4 \right) \Psi, \quad (2.38)$$

where the minimal coupling from Eq. (1.59) appears once more clearly.

Electrons and positrons

The 4-spinors [see Eq. (2.19)] solutions of the Dirac equation feature four degrees of freedom, corresponding to the descriptions of electrons and positrons with the spin considered explicitly, as both electrons and positrons are fermions of spin 1/2. We thus write

$$\Psi = \begin{pmatrix} \Psi^{L\alpha} \\ \Psi^{L\beta} \\ \Psi^{S\alpha} \\ \Psi^{S\beta} \end{pmatrix}, \quad (2.39)$$

with α and β denoting the two possible "spin" states. For a given external potential the positive-energy solutions are describing electronic states, and in the non-relativistic limit the small components ($\Psi^{S,\alpha}$ and $\Psi^{S,\beta}$) vanish while the large components ($\Psi^{L,\alpha}$ and $\Psi^{L,\beta}$) of the 4-spinor become the α and β components of a spin-orbital, each spatial part being solution of the Schrödinger equation. For the same external potential the negative-energy solutions describe [8] positronic states in an indirect fashion, as it requires charge-conjugation to have the correct description of these positronic solutions. The charge-conjugation operator can be written as [9]

$$C = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \mathcal{K}_0, \quad (2.40)$$

with \mathcal{K}_0 the complex conjugation operator, such that application of this charge-conjugation operator C on the Dirac equation in the presence of an electromagnetic field [see Eq. (2.38)] yields

$$i\hbar \frac{\partial}{\partial t} C\Psi = \left(c\boldsymbol{\alpha} \cdot (\mathbf{p} + \frac{q_e}{c}\mathbf{A}) + \boldsymbol{\beta}mc^2 - q_e\phi\mathbf{I}_4 \right) C\Psi, \quad (2.41)$$

where we used $C\boldsymbol{\beta} = -\boldsymbol{\beta}C$ and $C\boldsymbol{\alpha} = \boldsymbol{\alpha}C$ and multiplied both sides of the equation by -1 , which corresponds to the Dirac equation in the presence of an electromagnetic field for a particle having the same mass as the electron but the opposite charge. Thus, the solution of this equation are usually considered to be anti-particles of the electron, i.e. positrons. As the eigenvectors of this equation are written as $C\Psi$, we can deduce positronic solutions of the Dirac equation by applying the charge-conjugation operator on negative energy solutions of the Dirac equation [see Eq. (2.27)], yielding for example

$$\begin{aligned} C \left[\Psi_{\mathbf{k},\downarrow}^-(t, \mathbf{r}) \right] &= C \left[\mathcal{N} \begin{pmatrix} \frac{\hbar(k_x - ik_y)c}{-|E_k| - mc^2} \\ -\hbar k_z c \\ \frac{-\hbar k_z c}{-|E_k| - mc^2} \\ 0 \\ 1 \end{pmatrix} \exp \left[-i \left(\pm \frac{|E_k|}{\hbar} t - \mathbf{k} \cdot \mathbf{r} \right) \right] \right] \\ &= \mathcal{N} \begin{pmatrix} 1 \\ 0 \\ \frac{-\hbar(k_x + ik_y)c}{|E_k| + mc^2} \\ -\hbar k_z c \\ \frac{-\hbar k_z c}{|E_k| + mc^2} \end{pmatrix} \exp \left[+i \left(\pm \frac{|E_k|}{\hbar} t - \mathbf{k} \cdot \mathbf{r} \right) \right] \\ &= \Psi_{-\mathbf{k},\uparrow}^+(-t, \mathbf{r}), \end{aligned} \quad (2.42)$$

which would correspond to a 4-spinor solution of the Dirac equation, allowing us to interpret negative-energy electronic solutions as positive-energy positronic solution with opposite momentum and moving backwards in time.

Kramers' time-reversal symmetry

Considering that the Dirac Hamiltonian features spin-orbit coupling within its kinetic operator, the spin symmetry that existed with the Schrödinger Hamiltonian does not exist anymore. Yet, the double degeneracy of fermionic states in the absence of external magnetic field [3] still exists, and the 4-spinors describing such a pair of states are denoted as a Kramers pair ψ and $\bar{\psi}$, such that

$$\bar{\psi} = \mathcal{K}\psi, \quad (2.43)$$

with \mathcal{K} the Kramers time-reversal operator

$$\mathcal{K} = -i \begin{pmatrix} \boldsymbol{\sigma}_2 & 0 \\ 0 & \boldsymbol{\sigma}_2 \end{pmatrix} \mathcal{K}_0, \quad (2.44)$$

expressed using the Pauli matrix $\boldsymbol{\sigma}_2$ [see Eq. (D.12)] and \mathcal{K}_0 the complex conjugation operator. Writing

$$\psi = \begin{pmatrix} \psi^{L\alpha} \\ \psi^{L\beta} \\ \psi^{S\alpha} \\ \psi^{S\beta} \end{pmatrix}, \quad (2.45)$$

we derive the expression of $\bar{\psi}$ with respect to the four-components of ψ using first a two component decomposition as

$$\begin{aligned} \bar{\psi} &= \mathcal{K}\psi \\ &= -i \begin{pmatrix} \boldsymbol{\sigma}_2 & 0 \\ 0 & \boldsymbol{\sigma}_2 \end{pmatrix} \mathcal{K}_0 \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} \\ &= -i \begin{pmatrix} \boldsymbol{\sigma}_2 \psi^{L*} \\ \boldsymbol{\sigma}_2 \psi^{S*} \end{pmatrix}. \end{aligned} \quad (2.46)$$

Considering that, for $X=\{L,S\}$, we have

$$\boldsymbol{\sigma}_2 \psi^{X*} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \psi^{X\alpha*} \\ \psi^{X\beta*} \end{pmatrix} = \begin{pmatrix} -i\psi^{X\beta*} \\ i\psi^{X\alpha*} \end{pmatrix}, \quad (2.47)$$

we have then

$$\bar{\psi} = -i \begin{pmatrix} -i\psi^{L\beta*} \\ i\psi^{L\alpha*} \\ -i\psi^{S\beta*} \\ i\psi^{S\alpha*} \end{pmatrix} = \begin{pmatrix} -\psi^{L\beta*} \\ \psi^{L\alpha*} \\ -\psi^{S\beta*} \\ \psi^{S\alpha*} \end{pmatrix}. \quad (2.48)$$

Finally, we write some properties of products of the Kramers time-reversal operator

$$\mathcal{K}\mathcal{K} = -I_4, \quad (2.49)$$

$$\mathcal{K}^\dagger \mathcal{K} = I_4, \quad (2.50)$$

and some properties of mixed products of the Kramers time-reversal operator and the $\boldsymbol{\alpha}$ matrix

$$\mathcal{K}\boldsymbol{\alpha}\mathcal{K}^\dagger = -\boldsymbol{\alpha}, \quad (2.51)$$

$$\boldsymbol{\alpha} = -\mathcal{K}^\dagger \boldsymbol{\alpha} \mathcal{K}, \quad (2.52)$$

$$\boldsymbol{\alpha} \mathcal{K} = \mathcal{K}^\dagger \boldsymbol{\alpha}. \quad (2.53)$$

2.2 Hamiltonians for chemical systems in first quantization

Quantum chemistry is usually expressed in Coulomb gauge [see Eq. (B.5)], such that the classical interaction potential [3, 8] between two point-charge particles of charges q_1 and q_2 is, to the first non-zero relativistic correction, that is to the first-order in $1/c^2$,

$$V_{12} = \frac{q_1 q_2}{r_{12}} \left(1 - \frac{1}{2c^2} \left[\mathbf{v}_1 \cdot \mathbf{v}_2 + \frac{(\mathbf{r}_{12} \cdot \mathbf{v}_1)(\mathbf{r}_{12} \cdot \mathbf{v}_2)}{r_{12}^2} \right] \right) \quad (2.54)$$

with $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, \mathbf{r}_i and \mathbf{v}_i being respectively the position and speed of particle i . The first term corresponds to a charge-charge interaction and the second to a current-current interaction. We first look at the simplest physical system in quantum chemistry, with only one electron and one nucleus.

2.2.1 One-electron Hamiltonian

This section is evocated separately from the case featuring several electrons, as the Dirac equation can be solved analytically for a one-electron atom with fairly few approximations, while giving still quite good energy eigenvalues and wave functions and maintaining the correct non-relativistic limit [3, 9]. Both electron and nucleus are usually considered to be point-charges, interacting through an instantaneous Coulomb interaction corresponding to the scalar potential

$$v_{ne} = q_e \phi = \frac{q_e q_{\text{nucl}}}{|\mathbf{r} - \mathbf{R}|} = -\frac{Ze^2}{r}, \quad (2.55)$$

with $r = |\mathbf{r} - \mathbf{R}|$, \mathbf{r} denoting the position of the electron and \mathbf{R} the position of the nucleus. The charge of the electron is written as $q_e = -e$ while the charge of the nucleus is $q_{\text{nucl}} = Ze$, writing e as the unit of charge. This interaction potential corresponds to keeping only the charge-charge interaction term of Eq. (2.54), the nucleus being treated as an external source of scalar potential in what is called the clamped nucleus approximation. It is justified in the same spirit as the Born-Oppenheimer approximation, with a nucleus that is considered to be at rest as a single proton has already a mass around 2000 times larger than the mass of the electron and moves much more slowly under the same external forces, the electron density re-arranging around it adiabatically. Nevertheless, it corresponds to the choice of a frame of reference that is the rest-frame of the nucleus, thus invalidating the Lorentz covariance of the equations. The mass energy term of the nucleus is not considered as it is but an additive constant to the energy with no impact on the electronic wave-function. Such derivation relies on the ansatz

$$\Psi(t, \mathbf{r}) = \exp \left[-i \frac{E}{\hbar} t \right] \Psi(\mathbf{r}), \quad (2.56)$$

such that the Dirac equation in the presence of an external electromagnetic field [see Eq. (2.38)] for this model system is written, after simplification by the time-part of the ansatz, as a time-independent equation using the one-electron Dirac Hamiltonian h^D , comprised of the sum of the one-electron free particle Dirac Hamiltonian h_{free}^D and any mono-electronic external potential v_{ne} such that

$$\begin{aligned} E \Psi(\mathbf{r}) &= h^D \Psi(\mathbf{r}) \\ &= \left(h_{\text{free}}^D + v_{ne} \right) \Psi(\mathbf{r}) \\ &= \left(c \boldsymbol{\alpha} \cdot \mathbf{p} + \boldsymbol{\beta} m c^2 + v_{ne} \mathbf{I}_4 \right) \Psi(\mathbf{r}). \end{aligned} \quad (2.57)$$

This Hamiltonian in first quantization is usually taken as the basis for calculation on one-electron systems.

2.2.2 Many-electron Hamiltonian

For more general cases, several electrons and several nuclei are usually considered and new interactions appears such that the Dirac equation can no longer be solved analytically. For ground-state calculations, it is still possible to use the ansatz from Eq. (2.56) and write a time-independent Dirac equation using the many-electron Dirac Hamiltonian $H^D = \sum_i h^D(i)$ containing all one-electron terms, and adding the new nucleus-nucleus (zero-electron terms) and electron-electron (two-electron terms) interaction potentials such that

$$\begin{aligned} E \Psi &= (H^D + V_{ee} + V_{nn}) \Psi \\ &= \left(\sum_i [c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \boldsymbol{\beta}_i mc^2 + v_{ne}(i)(\mathbf{I}_4)_i] + V_{ee} + V_{nn} \right) \Psi, \end{aligned} \quad (2.58)$$

with $\boldsymbol{\alpha}_i$, \mathbf{p}_i , $\boldsymbol{\beta}_i$ and $(\mathbf{I}_4)_i$ acting only on electron i . The kinetic energy and the mass energy terms are explicitly written as simple sums over all electrons, while the electromagnetic potential terms V_{ne} , V_{ee} , and V_{nn} , corresponding respectively to the nucleus-electron and electron-electron and nucleus-nucleus interaction potential terms, are slightly more complicated and detailed in the following subsections.

Nucleus-nucleus interaction

Theoretically several nuclei interact through a nucleus-nucleus interaction potential, usually written [8] as an instantaneous Coulomb interaction between point-charges through the scalar potential as a sum over nuclei

$$V_{nn} = \sum_{A>B} \frac{Z_A Z_B e^2}{|\mathbf{R}_A - \mathbf{R}_B|}, \quad (2.59)$$

with $R = |\mathbf{R}_A - \mathbf{R}_B|$, \mathbf{R}_A and $Z_A e$ being respectively the position and charge of nucleus A , writing e as the unit of charge, and where double counting has been properly taken care of. In the clamped nucleus approximation these nuclei are supposed to be static sources of scalar potential, interacting with one another but not in a dynamical way. This nucleus-nucleus interaction term thus yields a constant repulsive energy term for adiabatic quantum chemistry calculations. It is interesting to mention that if, in the case of a single nucleus, choosing to work in the rest frame of the nucleus is enough to ensure the clamped nucleus approximation, no such frame can usually be found as nuclei will move relatively to each others [8].

Electron-nucleus interaction

In the case of a general chemical system featuring several electrons and nuclei in the clamped nucleus approximation one can still treat both electrons and nuclei as point-charges [8] such that a straightforward extension of Eq. (2.55) yields for an electron i

$$v_{ne}(i) = \sum_A \frac{-Z_A e^2}{|\mathbf{r}_i - \mathbf{R}_A|}, \quad (2.60)$$

with \mathbf{r}_i denoting the position of electron i , \mathbf{R}_A and $Z_A e$ denoting respectively the position and charge of nucleus A . Another possibility is to consider finite-size nucleus [8, 10] as considering point-charge nucleus causes weak singularity at the nucleus as the Dirac Hamiltonian contains only first-order space derivatives, making for slower basis set convergence. As theoretical nuclear physics does not provide [3] a unique charge distribution function for the nucleus, several charge distribution models [10] exist in quantum chemistry. A very popular one is the Gaussian charge distribution model, making for an easy implementation as electronic wave-function are usually also expanded in Gaussian type basis functions in

most quantum chemistry codes, such that electron-nucleus interaction potentials can be calculated using pre-existing primitive integrals. Several parameter choices exist for this one model, and L. Visscher and K. G. Dyall [10] prescribe the use of the root-mean-square radius of the nucleus as a parameter. It can be fitted as

$$\sqrt{\langle R^2 \rangle} = (0.8636A^{1/3} + 0.570) \text{ fm}, \quad (2.61)$$

where A is the mass number of the considered isotope. The charge distribution is then expressed as

$$\rho^G(R) = Ze \left(\frac{3}{2\pi\langle R^2 \rangle} \right) \exp \left[-\frac{3R^2}{2\langle R^2 \rangle} \right], \quad (2.62)$$

such that the scalar interaction potential of Eq. (2.60) becomes for an electron i

$$v_{\text{ne}}(i) = \sum_A \frac{-Z_A e^2}{|\mathbf{r}_i - \mathbf{R}_A|} \text{erf} \left(\sqrt{\frac{3}{2\langle R^2 \rangle}} |\mathbf{r}_i - \mathbf{R}_A| \right), \quad (2.63)$$

with the erf function removing the divergence at 0.

Electron-electron interaction

Interactions between electrons in relativistic quantum chemistry [8] are usually considered in the semi-classical limit, corresponding to a classical treatment of electromagnetic fields. This level of description can be obtained from a straightforward quantization of Eq. (2.54), yielding the Coulomb-Breit interaction potential as a sum over pair-interactions between electrons

$$V_{\text{ee}}^{\text{CB}} = \sum_{i>j} \mathbf{w}^{\text{CB}}(i, j) = \sum_{i>j} \frac{e^2}{r_{ij}} \left((\mathbf{1}_4)_i (\mathbf{1}_4)_j - \frac{1}{2c^2} \left[(c\boldsymbol{\alpha}_i \cdot c\boldsymbol{\alpha}_j) + \frac{(\mathbf{r}_{ij} \cdot c\boldsymbol{\alpha}_i)(\mathbf{r}_{ij} \cdot c\boldsymbol{\alpha}_j)}{r_{ij}^2} \right] \right), \quad (2.64)$$

with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, \mathbf{r}_i denoting the position of electron i and $(\mathbf{1}_4)_i$ and $\boldsymbol{\alpha}_i$ acting on electron i . We observe that such quantization implies that the particles velocities of Eq. (2.54) are replaced by the Dirac velocity operator [see Eq. (2.23)]. The Coulomb-Breit interaction can also be derived from the one-photon exchange two-electron interaction, usually treated in QED as the exchange of virtual photons between electrons through a photon propagator [11], by taking the zero-frequency limit. The first term of Eq. (2.64) corresponds to the zeroth order of the interaction, that is the instantaneous charge-charge Coulomb interaction,

$$V_{\text{ee}}^{\text{C}} = \sum_{i>j} \mathbf{w}^{\text{C}}(i, j) = \sum_{i>j} \frac{e^2}{r_{ij}} (\mathbf{1}_4)_i (\mathbf{1}_4)_j \quad (2.65)$$

also labelled as the longitudinal interaction as it corresponds to the time-like element of the QED photon propagator. The second term of Eq. (2.64) corresponds to the first-order in $1/c^2$ of the interaction, that is the retarded current-current Breit interaction. It corresponds to the sum of two sub-terms [12] in the Coulomb gauge, written as $V_{\text{ee}}^{\text{B}} = V_{\text{ee}}^{\text{G}} + V_{\text{ee}}^{\text{gauge}}$, where the first sub-term is the instantaneous current-current Gaunt interaction,

$$V_{\text{ee}}^{\text{G}} = \sum_{i>j} \mathbf{w}^{\text{G}}(i, j) = - \sum_{i>j} \frac{e^2}{r_{ij}} \frac{1}{c^2} (c\boldsymbol{\alpha}_i \cdot c\boldsymbol{\alpha}_j), \quad (2.66)$$

and the second sub-term is the retardation term in Coulomb gauge

$$V_{\text{ee}}^{\text{gauge}} = \sum_{i>j} \mathbf{w}^{\text{gauge}}(i, j) = - \sum_{i>j} \frac{e^2}{r_{ij}} \frac{1}{2c^2} \left[-(c\boldsymbol{\alpha}_i \cdot c\boldsymbol{\alpha}_j) + \frac{(\mathbf{r}_{ij} \cdot c\boldsymbol{\alpha}_i)(\mathbf{r}_{ij} \cdot c\boldsymbol{\alpha}_j)}{r_{ij}^2} \right], \quad (2.67)$$

which vanishes in the Lorenz gauge [8]. This retarded current-current interaction is also labelled as the transverse interaction, as it derives from the transverse part of the QED photon propagator. Although the Breit interaction potential has little impact on energetic and spectroscopic properties [13,14], it is needed in order to get spin-orbit splitting correctly. While the Breit retardation potential [see Eq. (2.67)] requires specific numerical integrals [15], the pure Gaunt current-current interaction potential [see Eq. (2.66)] can be implemented using the same two-electron integrals as the charge-charge Coulomb interaction, as is illustrated in section F.2, and thus makes for an easy implementation and a good choice to start relativistic quantum chemistry calculations. Furthermore, keeping only the Gaunt part of the interaction, that is considering instantaneous current-current interactions, is enough to introduce electron-electron spin-orbit, also denoted spin-other-orbit coupling, into the calculations.

Dirac-Coulomb-Breit Hamiltonian in configuration space

We explicitly write down the full many-electron configuration space (cs) Dirac-Coulomb-Breit (DCB) Hamiltonian in first quantization, removing from further expressions the nucleus-nucleus interaction potential which is but a constant repulsive energy term for a given chemical system, such that

$$H_{\text{cs}}^{\text{DCB}} = \sum_i \left[c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \boldsymbol{\beta}_i mc^2 + \sum_A \frac{-Z_A e^2}{|\mathbf{r}_i - \mathbf{R}_A|} (\mathbf{I}_4)_i \right] + \sum_{i>j} \frac{e^2}{r_{ij}} \left((\mathbf{I}_4)_i (\mathbf{I}_4)_j - \frac{1}{2c^2} \left[(c\boldsymbol{\alpha}_i \cdot c\boldsymbol{\alpha}_j) + \frac{(\mathbf{r}_{ij} \cdot c\boldsymbol{\alpha}_i)(\mathbf{r}_{ij} \cdot c\boldsymbol{\alpha}_j)}{r_{ij}^2} \right] \right), \quad (2.68)$$

this Hamiltonian having been constructed in order to describe mixed systems of electrons and point-charge nucleus, in the clamped nucleus approximation.

We saw in section 2.1.2 that the Dirac equation has positive and negative-energy solutions, with negative-energy electronic solutions being related to positive-energy positronic solutions. The existence of these negative energy electronic solution implies that there is a negative continuum of solutions for any electronic calculations starting from the Dirac Hamiltonian, which is not bounded from below. The impacts of this negative continuum are discussed in the next section.

2.3 Hamiltonians for chemical systems in second quantization

2.3.1 Configuration space

The one-electron Dirac Hamiltonian [see Eq. (2.57)] in first quantization has eigenvalues which can be positive or negative, where a positive eigenvalue means that the eigenfunction corresponds to an electronic state, and a negative eigenvalue that the eigenfunction corresponds to a positronic state. Thus, and only for a one-particle system, there is no indecision as to the type of particle as long as one knows the sign of the energy. For more than one particle considered, the sign of the energy of the total system does not give any informations on the type of particles any more [16]. Furthermore, the fact that this Hamiltonian is not bounded from below brings new difficulties for variational procedures compared to non-relativistic calculation based on the Schrödinger equation. In order to better understand these phenomena we rewrite the configuration-space DCB Hamiltonian in second quantization

$$\hat{H}_{\text{cs}}^{\text{DCB}} = \hat{H}_{\text{cs}}^{\text{D}} + \hat{W}_{\text{cs}}^{\text{CB}} = \int d\mathbf{r} \hat{\Psi}^\dagger(\mathbf{r}) h^{\text{D}}(\mathbf{r}) \hat{\Psi}(\mathbf{r}) + \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \hat{\Psi}^\dagger(\mathbf{r}_1) \hat{\Psi}^\dagger(\mathbf{r}_2) \mathbf{w}^{\text{CB}}(\mathbf{r}_{12}) \hat{\Psi}(\mathbf{r}_2) \hat{\Psi}(\mathbf{r}_1), \quad (2.69)$$

where $\hat{\Psi}(\mathbf{r})$ and $\hat{\Psi}^\dagger(\mathbf{r})$ are the annihilation and creation field operators

$$\hat{\Psi}(\mathbf{r}) = \sum_p \psi_p(\mathbf{r}) \hat{a}_p \quad \text{and} \quad \hat{\Psi}^\dagger(\mathbf{r}) = \sum_p \psi_p^\dagger(\mathbf{r}) \hat{a}_p^\dagger, \quad (2.70)$$

where the sum is over a set of orthonormal 4-component-spinor orbitals $\{\psi_p(\mathbf{r})\}$ which are eigenfunctions of a one-electron Dirac Hamiltonian, \hat{a}_p and \hat{a}_p^\dagger being the corresponding annihilation and creation operators of these orbitals such that [8, 16]

$$[\hat{a}_p^\dagger, \hat{a}_q]_+ = \hat{a}_p^\dagger \hat{a}_q + \hat{a}_q \hat{a}_p^\dagger = \delta_{pq} \quad \text{and} \quad [\hat{a}_p, \hat{a}_q]_+ = [\hat{a}_p^\dagger, \hat{a}_q^\dagger]_+ = 0 \quad (2.71)$$

No-pair Dirac-Coulomb-Breit Hamiltonian

The most usual approximation to remove difficulties coming from the existence of the negative-energy continuum is, in configuration space, to simply prevent negative-energy states to be occupied. It is usually done through the embedding of the Hamiltonian by a projection operator Λ_+ onto positive-energy states, and is known as the no-pair approximation [8, 17, 18], considering that negative-energy eigenfunctions of the Dirac Hamiltonian can be understood as positronic states and that such projectors prevent the apparition of any electron-positron pairs as positronic states are projected out. One thus writes the configuration space no-pair DCB Hamiltonian in second quantization as

$$\hat{H}_{\text{cs}}^{\text{no-pair DCB}} = \int d\mathbf{r} \hat{\Psi}_+^\dagger(\mathbf{r}) h^{\text{D}}(\mathbf{r}) \hat{\Psi}_+(\mathbf{r}) + \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \hat{\Psi}_+^\dagger(\mathbf{r}_1) \hat{\Psi}_+^\dagger(\mathbf{r}_2) \mathbf{w}^{\text{CB}}(\mathbf{r}_{12}) \hat{\Psi}_+(\mathbf{r}_2) \hat{\Psi}_+(\mathbf{r}_1), \quad (2.72)$$

where $\hat{\Psi}_+(\mathbf{r})$ and $\hat{\Psi}_+^\dagger(\mathbf{r})$ are the projected annihilation and creation field operators

$$\hat{\Psi}_+(\mathbf{r}) = \sum_{p^+} \psi_{p^+}(\mathbf{r}) \hat{a}_{p^+} \quad \text{and} \quad \hat{\Psi}_+^\dagger(\mathbf{r}) = \sum_{p^+} \psi_{p^+}^\dagger(\mathbf{r}) \hat{a}_{p^+}^\dagger, \quad (2.73)$$

where, compared to Eq. (2.70), the sum is over the positive-energy orthonormal 4-component-spinor orbitals $\{\psi_{p^+}(\mathbf{r})\}$ which are eigenfunctions of a chosen Dirac Hamiltonian (the choice of this Hamiltonian depending of the choice of the projector Λ_+ considered for the no-pair approximation). Several different projectors Λ_+ can be considered [12, 18, 19], among them the historical projectors Λ_+^{free} onto the free particle solutions of the Dirac Hamiltonian $h_{\text{free}}^{\text{D}}$ [See Eq. (2.17)], which is much too drastic an approximation and introduces quite important errors in the energy calculations even for two-electron atoms [18], and the projector Λ_+^{bare} onto the solutions of the one-electron Dirac Hamiltonian h^{D} [See Eq. (2.57)] which is often denoted as the Furry picture [20]. More efficient projectors would be Λ_+^{HF} onto the positive-energy solutions of the relativistic Hartree-Fock calculation, which is often denoted as the Fuzzy picture [19] as the projection operator is updated at each step of the self-consistent calculation, and Λ_+^{MCSCF} onto the positive-energy solutions of the relativistic MCSCF calculations [18], where the projection operator is self-consistently updated at the correlated level. One of the main consequences of the fact that the Dirac Hamiltonian [see Eq. (2.69)] is not bounded from below is the absence of a true minimization principle, the energy of the no-pair relativistic ground-state of a N -electron system being written using a minmax principle [8, 18, 21] such that

$$E = \min_{\Psi} \left[\max_{\{\psi_{p^+}\}} \langle \Psi | \hat{H}_{\text{cs}}^{\text{no-pair DCB}} | \Psi \rangle \right], \quad (2.74)$$

where the maximization is done with respect to the set of positive-energy orbitals $\{\psi_{p^+}\}$ [see Eq. (2.73)] by rotations with its complement set of negative-energy orbitals, and the minimization is done with respect to normalized wave function Ψ within the N -electron space generated by the set of positive-energy orbitals $\{\psi_{p^+}\}$.

Hartree-Fock level

In order to better understand this projected minmax principle we look at the Hartree-Fock variational ansatz [8, 18], which is written as

$$|\Phi^{\text{HF}}\rangle = \exp[-\hat{\kappa}] |\Phi\rangle \quad \text{with} \quad \hat{\kappa} = \sum_{p,q} \kappa_{pq} \hat{a}_p^\dagger \hat{a}_q, \quad (2.75)$$

where $\hat{\kappa}$ is the orbital rotation operator with $\kappa_{pq} = -\kappa_{qp}^*$, and $|\Phi\rangle$ a reference determinant which can be taken as the variational solution of the Dirac equation for non-interacting electrons, which corresponds to the Slater determinants $|\Psi_1, \Psi_2, \dots, \Psi_N\rangle$ for a system of N electrons with ψ_i a solution of the one-electron Dirac equation [see Eq. (2.57)] for electron i . This reference determinant is usually the lowest bound state instead of the state with the lowest energy possible, as the Dirac Hamiltonian is not bounded from below, which corresponds to an implicit projection by choosing ψ_i as a positive-energy bound state for each electron i . The use of Λ_+^{HF} is then done implicitly during a relativistic Dirac Hartree-Fock calculation by considering, at each step of the self-consistent calculation, the lowest positive-energy orbitals as occupied and corresponding to electronic bound states, and all the negative-energy orbitals as empty. This is easily done as long as there is an important energy gap between the bound states and the negative continuum states [3]. The minmax principle then takes the form of a minimization of the energy with respect to κ_{a+i+} rotations, i.e. rotations between positive-energy occupied orbitals and positive-energy virtual orbitals, which is exactly how a non-relativistic Hartree-Fock energy is minimized, but it is accompanied by a maximization of the energy with respect to κ_{a-i+} rotations, i.e. rotations between positive-energy occupied orbitals and negative-energy virtual orbitals, as virtual orbitals (denoted using the indices a, b, c, d, \dots) can be either positive-energy virtual orbitals with an energy greater than that of any occupied orbitals (denoted using the indices i, j, k, l, \dots), or negative-energy virtual orbitals with an energy lesser than that of any occupied orbitals. This minmax principle thus relates to a saddle point optimization, the lowest bound state corresponding to an excited determinant with respect to negative-energy states.

Correlated level

We make apparent the absolute necessity of the projection operators Λ_+ in configuration space with some insight from correlated level calculations, where it is necessary to go further than rotations between orbitals by mixing out determinants. Taking the same indices convention as in the previous section, the second-order Møller-Plesset correlation energy (MP2) [18, 22] is written, in all generality and using the physicists' notation convention, as

$$E_c^{\text{MP2}} = -\frac{1}{4} \sum_{i,j} \sum_{a,b} \frac{|\langle ij||ab\rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}, \quad (2.76)$$

where the denominator of the second term brings new complications for relativistic calculations due to spurious degeneracies linked to the very existence of the negative-energy virtual solutions of the Dirac equation. Indeed, for systems having at least two electrons, any positive-energy electronic determinant $|\Phi\rangle$ is degenerated with an infinity of doubly-excited determinants $|\Phi_{ij}^{ab}\rangle$, with one virtual orbital into the positive-energy continuum and one virtual orbital into the negative-energy continuum. This phenomenon, known as the Brown-Ravenhall disease [23], leads to a continuum dissolution [8] for any system containing two electrons or more as soon as one considers electronic interactions between determinants, such that no multiconfigurational electronic state could possibly be stable for the configuration-space Dirac-Coulomb-Breit Hamiltonian. In order to get rid of these degeneracies Brown and Ravenhall proposed the embedding of the Dirac-Coulomb-Breit Hamiltonian by projection operators onto the positive-energy states, leading to the no-pair approximation. The use of the Λ_+^{MCSCF} projector ensures the removal of any spurious degeneracy with a projector fully-optimized at the correlated level [18], such that

$$E_c^{\text{no-pair MP2}} = -\frac{1}{4} \sum_{i^+, j^+} \sum_{a^+, b^+} \frac{|\langle i^+ j^+||a^+ b^+\rangle|^2}{\epsilon_{a^+} + \epsilon_{b^+} - \epsilon_{i^+} - \epsilon_{j^+}}, \quad (2.77)$$

where the correlation energy now corresponds to the mixing of positive-energy determinants between themselves.

2.3.2 Fock space

In order to take care of the negative continuum in an Hamiltonian formalism without the use of projectors another possibility is to rewrite it in the so-called Fock space formalism [16, 24]. We start by replacing the annihilation and creation operators according to the particle-hole picture [8, 16], thus defining

$$\hat{b}_{p^+} = \hat{a}_{p^+} \quad \text{and} \quad \hat{b}_{p^+}^\dagger = \hat{a}_{p^+}^\dagger \quad \text{for } p^+ \text{ such that } E_{p^+} > 0, \quad (2.78)$$

and

$$\hat{b}_{p^-} = \hat{a}_{p^-}^\dagger \quad \text{and} \quad \hat{b}_{p^-}^\dagger = \hat{a}_{p^-} \quad \text{for } p^- \text{ such that } E_{p^-} < 0, \quad (2.79)$$

such that the field annihilation and creation operators are now written as

$$\hat{\Psi}(\mathbf{r}) = \sum_{p^+} \Psi_{p^+}(\mathbf{r}) \hat{b}_{p^+} + \sum_{p^-} \Psi_{p^-}(\mathbf{r}) \hat{b}_{p^-}^\dagger \quad \text{and} \quad \hat{\Psi}^\dagger(\mathbf{r}) = \sum_{p^+} \Psi_{p^+}^\dagger(\mathbf{r}) \hat{b}_{p^+}^\dagger + \sum_{p^-} \Psi_{p^-}^\dagger(\mathbf{r}) \hat{b}_{p^-} \quad (2.80)$$

where, compared to Eq. (2.70), the sum is over either positive-energy orthonormal 4-component-spinor orbitals $\{\Psi_{p^+}(\mathbf{r})\}$ or negative-energy orthonormal 4-component-spinor orbitals $\{\Psi_{p^-}(\mathbf{r})\}$ which are all eigenfunctions of a chosen one-electron Dirac Hamiltonian.

For an Hamiltonian to be labelled as Fock space it must be in normal order, that is with all creation operators on the left to all annihilation operators. Yet, once rewritten using the \hat{b}' s operators the configuration space DCB Hamiltonian [see Eq. (2.69)] is no longer in normal order as the field annihilation and creation operators feature each both annihilation (\hat{b}) and creation (\hat{b}^\dagger) operators. Re-ordering all creation and annihilation operators from the configuration space DCB Hamiltonian in the particle-hole picture leads to the Fock space (fs) DCB Hamiltonian

$$\hat{H}_{\text{fs}}^{\text{DCB}} = \int d\mathbf{r} : \hat{\Psi}^\dagger(\mathbf{r}) h^{\text{D}}(\mathbf{r}) \hat{\Psi}(\mathbf{r}) : + \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 : \hat{\Psi}^\dagger(\mathbf{r}_1) \hat{\Psi}^\dagger(\mathbf{r}_2) \mathbf{w}^{\text{CB}}(\mathbf{r}_{12}) \hat{\Psi}(\mathbf{r}_2) \hat{\Psi}(\mathbf{r}_1) :, \quad (2.81)$$

where we write for any operator product O its normal-ordered product as $: O :$. This Fock space Dirac-Coulomb-Breit Hamiltonian is the first step toward the effective QED Hamiltonian [24] and allows one to take in account the vacuum polarization [16] (also called photon self-energy in Ref. [24]) which the configuration space no-pair Dirac-Coulomb-Breit Hamiltonian neglected.

While the link between the two-electron parts of the Fock space and configuration space DCB Hamiltonians is quite complicated [8, 16], it is easy to grasp some understanding from the one-electron part for which the normal re-ordering corresponds just to the permutation of two operators, and can be understood physically as the removal of its infinite vacuum expectation value [8, 16, 24]. We therefore derive expressions and properties for the one-electron part of the Fock space DCB Hamiltonian in the next subsection.

Non-interacting electrons in Fock space

Considering non-interacting electrons reduces the Dirac-Coulomb-Breit Hamiltonian to only a one-electron Dirac Hamiltonian which may be written as

$$\begin{aligned} \hat{H}_{\text{cs}}^{\text{D}} &= \sum_{p,q} h_{pq}^{\text{D}} \hat{a}_p^\dagger \hat{a}_q = \sum_{p,q} \langle \Psi_p | h^{\text{D}} | \Psi_q \rangle \hat{a}_p^\dagger \hat{a}_q \\ &= \sum_{p,q} E_p \delta_{pq} \hat{a}_p^\dagger \hat{a}_q \\ &= \sum_p E_p \hat{a}_p^\dagger \hat{a}_p. \end{aligned} \quad (2.82)$$

in configuration space. Replacing the \hat{a}' s operators by the particle-hole picture \hat{b}' s operators [see Eq. (2.79)], this Hamiltonian can be rewritten as

$$\hat{H}_{\text{cs}}^{\text{D}} = \sum_{p^+} E_{p^+} \hat{b}_{p^+}^\dagger \hat{b}_{p^+} + \sum_{p^-} E_{p^-} \hat{b}_{p^-} \hat{b}_{p^-}^\dagger, \quad (2.83)$$

such that taking now the normal order of $\hat{H}_{\text{cs}}^{\text{D}}$ to obtain the Fock space Hamiltonian $\hat{H}_{\text{fs}}^{\text{D}}$ yields

$$\begin{aligned}\hat{H}_{\text{fs}}^{\text{D}} = : \hat{H}_{\text{cs}}^{\text{D}} : &= \sum_{p^+} E_{p^+} \hat{b}_{p^+}^\dagger \hat{b}_{p^+} - \sum_{p^-} E_{p^-} \hat{b}_{p^-}^\dagger \hat{b}_{p^-} \\ &= \sum_p |E_p| \hat{b}_p^\dagger \hat{b}_p,\end{aligned}\quad (2.84)$$

with the normal ordering adding a factor $(-1)^p$ with p the number of permutations between operators. We represent in Fig. 2.1 the eigenvalues for both the configuration space and Fock space Dirac Hamiltonians [16], with electronic bound states taking place between the positive-energy electronic continuum and the negative-energy positronic continuum in configuration space.

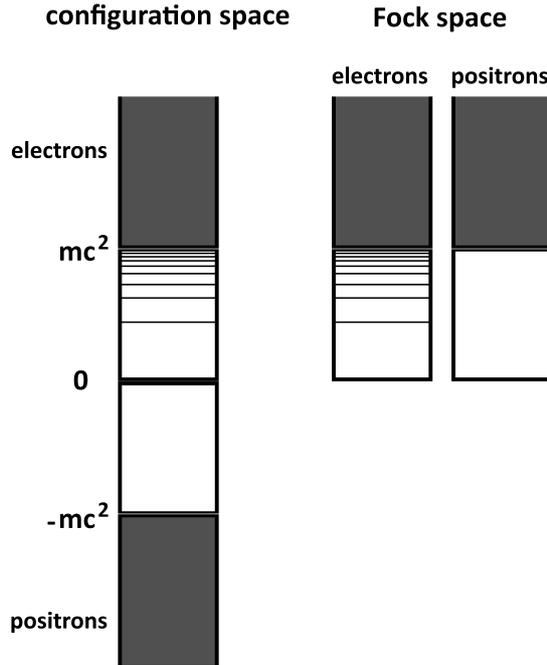


Figure 2.1: Comparison of the one-particle spectrum for the configuration and Fock space Dirac Hamiltonians

The Fock space Hamiltonian ensures that both electron and positron states have positive energies, such that there is no negative continuum anymore and the energy of an electronic system can be variationally minimized without need of a minmax principle. For such a Fock space Dirac Hamiltonian, the vacuum state $|0\rangle$ [16] is defined by

$$\hat{b}_p|0\rangle = 0, \quad (2.85)$$

for all possible state p , such that this vacuum state contains neither electrons nor positrons. It corresponds to a stable vacuum, corresponding to an eigenstate of $\hat{H}_{\text{fs}}^{\text{D}}$ as

$$\hat{H}_{\text{fs}}^{\text{D}}|0\rangle = 0, \quad (2.86)$$

with vanishing energy expectation value. Yet, this vacuum depends on the Dirac Hamiltonian h^{D} , that is the vacuum depends on the external potential, in what is known as the vacuum polarization [16]. Such a vacuum polarization exists even in the absence of electrons as long as there is an external potential, i.e. the presence of charged nuclei, and is closely related to the need for charge renormalization as a consequence of the quantization of the fermionic Dirac field [see Section 1.5.3].

It is possible to work within the no-pair approximation starting from the Fock space Hamiltonian, but as all states have positive energies it reduces to considering a variational subspace of electronic solutions, which is much like the restriction to an active orbital subspace in the complete active space self-consistent field (CASSCF) method.

The Dirac sea

In order to explain the importance of normal ordering more naturally, we write out the equations describing the Dirac Sea [3, 9, 16] as an historical first step toward the Fock space. In order to conciliate the observation of the physical world with the existence of an infinite negative continuum of solutions for the Dirac equation, which very existence should mean that any fermion would gain stability by falling into these negative-energy and high velocity states with emission of radiations, P. A. M. Dirac postulated [25, 26] the fact that the vacuum must be considered as a state where all negative-energy states are occupied by electrons, usually labeled as the Dirac sea [3, 9]. As such occupations would be completely homogeneous, it would be unobservable save for small variation from uniformity, as the excitation of an electron from such a negative-energy state to a positive-energy one, which would require an excitation energy greater than $2mc^2$, i.e. greater than 37500 Hartree in atomic units. Such excitation would correspond to the creation of an electron-positron pair [3], with an excited electron of positive energy and one positron of negative energy, the total charge of the system being the conserved quantity instead of the number of particle. Such a vacuum can be modeled by requiring

$$\hat{a}_{p^+}|0\rangle = 0 \quad \text{for } p^+ \text{ such that } E_{p^+} > 0, \quad (2.87)$$

and

$$\hat{a}_{p^-}^\dagger|0\rangle = 0 \quad \text{for } p^- \text{ such that } E_{p^-} < 0, \quad (2.88)$$

with an vacuum energy expectation value of $\sum_{p^-} E_{p^-}$ for the configuration space Dirac Hamiltonian [see Eq. (2.82)], which corresponds to an infinitely negative energy. Re-normalizing the configuration space Dirac Hamiltonian by removing this quantity, we get [16]

$$\begin{aligned} \hat{H}_{\text{cs}}^{\text{D}} - \sum_{p^-} E_{p^-} &= \sum_p E_p \hat{a}_p^\dagger \hat{a}_p - \sum_{p^-} E_{p^-} \\ &= \sum_{p^+} E_{p^+} \hat{a}_{p^+}^\dagger \hat{a}_{p^+} + \sum_{p^-} E_{p^-} (\hat{a}_{p^-}^\dagger \hat{a}_{p^-} - 1) \\ &= \sum_{p^+} E_{p^+} \hat{a}_{p^+}^\dagger \hat{a}_{p^+} - \sum_{p^-} E_{p^-} \hat{a}_{p^-} \hat{a}_{p^-}^\dagger, \end{aligned} \quad (2.89)$$

which corresponds to the Dirac Hamiltonian in Fock space [see Eq. (2.84)] if one introduces the \hat{b}' 's operators from the particle-hole picture [See Eq. (2.79)]. Nevertheless this Dirac sea picture makes for a very unbalanced description with a vacuum with infinite energy and infinite charge. The energy renormalization corresponds to a first bridge between the Dirac sea picture in configuration space and the Fock space, but one would also need to subtract an homogeneous charge distribution equal to the charge distribution from the filled negative-energy states to get a stable vacuum once the electron-electron interaction is turned on.

2.3.3 Hartree-Fock ansatz and the particle number

In the configuration space, we considered the Hartree-Fock ansatz [see Eq. (2.75)] using the orbital rotation operator

$$\hat{\mathbf{K}} = \sum_{p,q} \kappa_{pq} \hat{a}_p^\dagger \hat{a}_q. \quad (2.90)$$

Considering that the particle number operator [8] is written as

$$\hat{N} = \sum_p \hat{a}_p^\dagger \hat{a}_p, \quad (2.91)$$

we remark that $[\hat{\kappa}, \hat{N}] = 0$, such that the orbital rotation operator is commutative with the particle number operator. Relativistic quantum chemistry calculations starting from the Hartree-Fock ansatz in configuration space thus conserve the number of particles.

On the contrary, in the Fock space we rewrite the Hartree-Fock orbital rotation operator $\hat{\kappa}$ [8] in the particle-hole picture such that

$$\hat{\kappa} = \underbrace{\sum_{p^+, q^+} \kappa_{p^+ q^+} \hat{b}_{p^+}^\dagger \hat{b}_{q^+}}_{\hat{\kappa}^{++}} + \underbrace{\sum_{p^+, q^-} \kappa_{p^+ q^-} \hat{b}_{p^+}^\dagger \hat{b}_{q^-}^\dagger}_{\hat{\kappa}^{+-}} + \underbrace{\sum_{p^-, q^+} \kappa_{p^- q^+} \hat{b}_{p^-} \hat{b}_{q^+}}_{\hat{\kappa}^{-+}} + \underbrace{\sum_{p^-, q^-} \kappa_{p^- q^-} \hat{b}_{p^-} \hat{b}_{q^-}^\dagger}_{\hat{\kappa}^{--}}. \quad (2.92)$$

From this expression, and defining the electron and positron number operator [8] respectively as

$$\hat{N}^e = \sum_{p^+} \hat{b}_{p^+}^\dagger \hat{b}_{p^+} \quad \text{and} \quad \hat{N}^p = \sum_{p^-} \hat{b}_{p^-}^\dagger \hat{b}_{p^-}, \quad (2.93)$$

one gets the commutators $[\hat{\kappa}, \hat{N}^e] = [\hat{\kappa}, \hat{N}^p] = \hat{\kappa}^{-+} - \hat{\kappa}^{+-}$, such that the orbital rotation operator commutes with neither electron number operator nor the positron number operator. Instead, the charge operator

$$\hat{Q} = e (\hat{N}^p - \hat{N}^e), \quad (2.94)$$

does commute with the rotation operator, such that the charge of the system is conserved in the particle-hole picture [8, 24] but not the particle number. It corresponds to the possibility of creation or destruction of electron-positron pairs, such that applying the rotation operator onto a given state may produce a state having the same charge but with incremental or decremental electron-positron pairs.

2.4 Density functional theory

Non-relativistic density functional theory (DFT) relies on the Hohenberg-Kohn theorem [27], dating from 1964 and stating that any given ground-state electronic density $n(\mathbf{r})$ cannot be born from two potentials differing by more than a constant. The knowledge of the electronic density of the ground-state thus determines (up to a constant) the potential $v(\mathbf{r})$, which in turns determines the many-electron Schrödinger Hamiltonian such that the ground-state wave function ψ is a functional of the density $n(\mathbf{r})$ and written as $\psi[n]$. From this, Hohenberg and Kohn defined the universal functional (i.e. a functional that is independent of the external potential) $F[n]$ as

$$F[n] = \langle \psi[n] | \hat{T} + \hat{W}_{ee} | \psi[n] \rangle, \quad (2.95)$$

where \hat{T} is the kinetic operator and \hat{W}_{ee} the electron-electron interaction operator, such that the electronic energy functional is

$$E[n] = F[n] + \int d\mathbf{r} v_{ne}(\mathbf{r}) n(\mathbf{r}), \quad (2.96)$$

in all generality. This formalism has been extended to relativistic systems, first in the 70s' [28–30] using a QED Hamiltonian and the four-current j instead of the electronic density n but without all renormalization counter-terms, and then in the 90s' [31] with the correct renormalized quantities. The relativistic Hohenberg-Kohn existence theorem thus states that the ground-state energy is a unique functional of the ground-state four-current [11, 31, 32], including in the proof all radiative effects as well as relativistic ones. Relativistic density functional theory (RDFT) can thus be formulated using the full QED apparatus, electromagnetic interactions being treated using the photon propagator in a covariant formalism and taking care of all divergences through renormalization. It is also possible to use any approximation for the electron-electron interaction (i.e. keeping only the Coulomb-Breit [see Eq. (2.64)] or the Coulomb [see Eq. (2.65)] interaction). In practice for electronic structure calculations one usually works within

the no-pair approximation [32], by neglecting all renormalization terms for both kinetic energy and four-current, if RDFT calculations are to be tractable. It is interesting to specify that the use of the no-pair approximation introduces a gauge dependence for the photon propagator [32, 33], such that any correlation functional becomes gauge dependent. Nevertheless, the no-pair exchange energy remains gauge independent [34].

2.4.1 Kohn-Sham density functional theory

The DFT scheme that is the most widely used nowadays is the Kohn-Sham DFT formulation [35], which is an everyday method for electronic-structure calculations in condensed-matter physics and quantum chemistry. It is straightforwardly generalized for relativistic systems [29, 30], and corresponds to the separation of the universal functional into a kinetic part $T_S[n, \mathbf{j}]$, corresponding to the kinetic energy of a fictitious non-interacting electronic system, and an Hartree-exchange-correlation functional $E_{\text{Hxc}}[n, \mathbf{j}]$. Considering that the Hartree term corresponds to the direct interaction of the 4-current distribution with itself, it consists of a charge-charge interaction term plus a current-current interaction term. It is by definition a 4-current functional and as such usually explicitly used without approximations, while the exchange-correlation part, i.e. $E_{\text{xc}}[n, \mathbf{j}]$, has to be approximated and is for the moment written in all generality as an exchange-correlation functional. Within the no-pair approximation, using the clamped nucleus approximation such that we have the external electron-nucleus interaction potential [see Eq. (2.60)] written as $v_{\text{ne}}(\mathbf{r})$ and in the absence of external magnetic field [36], one writes the Kohn-Sham RDFT ground-state energy as

$$\begin{aligned} E[n, \mathbf{j}] &= T_S[n, \mathbf{j}] + \int d\mathbf{r} v_{\text{ne}}(\mathbf{r})n(\mathbf{r}) \\ &+ \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{2c^2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\mathbf{j}(\mathbf{r}_1) \cdot \mathbf{j}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &+ E_{\text{xc}}[n, \mathbf{j}], \end{aligned} \quad (2.97)$$

where $T_S[n, \mathbf{j}]$ corresponds to the kinetic energy of the electrons described by the Kohn-Sham orbitals, the 4-spinor eigenfunctions ψ_i of the one-particle Dirac equation in the presence of an effective electromagnetic field [see Eq. (2.38)] such that

$$\left(c\boldsymbol{\alpha} \cdot (\mathbf{p} - \frac{q_e}{c} \mathbf{A}_{\text{eff}}) + \boldsymbol{\beta}mc^2 + V_{\text{eff}}\mathbf{I}_4 \right) \psi_i = \varepsilon_i \psi_i, \quad (2.98)$$

with the effective Kohn-Sham scalar potential

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ne}}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})}, \quad (2.99)$$

and effective Kohn-Sham vector potential

$$\mathbf{A}_{\text{eff}}(\mathbf{r}) = -\frac{1}{c^2} \int d\mathbf{r}' \frac{\mathbf{j}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}}{\delta \mathbf{j}(\mathbf{r})}. \quad (2.100)$$

As only unpaired electrons are sources of current \mathbf{j} , the first term of the Kohn-Sham vector potential is usually neglected (and vanishes entirely for closed-shell calculations). Furthermore, for exchange-correlation functionals which are pure density functional, i.e. $E_{\text{xc}}[n]$, the second term also vanishes. Closed-shell calculations thus require only density exchange-correlation functionals instead of density-current exchange-correlation functionals, and in the absence of external magnetic field the effective Kohn-Sham vector potential vanishes entirely.

2.5 Practical relativistic quantum chemistry

Practical four-component relativistic quantum chemistry calculations are computationally costlier than non-relativistic ones, partly from the loss of spin-symmetry which removes some simplification and partly from the use of a 4×4 Hamiltonian and its 4-spinors eigenfunctions. The matrix structure of the Hamiltonian makes for more matrix elements, and the 4-spinor structure requires more complex basis sets [see Section 2.5.1] than the non-relativistic spin-orbitals. Nevertheless, the computational cost has the same scaling with the number of basis functions and the increase on computational cost is only a prefactor.

Furthermore, the use of Kramers symmetry can help restoring some simplification. In particular, for a ground-state closed-shell two-electron atom, that is two electrons described by one Kramers pair [see Eq. (2.43)], we have for the Coulomb interaction the usual relation between the Hartree and exchange energies as

$$E_x^C = -\frac{1}{2}E_H^C, \quad (2.101)$$

which is easily recovered [see Appendix E.1] with the use of Kramers symmetry. Considering that the Coulomb interaction is but the zeroth order of the electron-electron interaction in relativistic quantum chemistry, one can do the same derivation for the higher orders of interaction and obtain for the Gaunt interaction [see Appendix E.2] a vanishing Hartree energy and the appearance of a current-current exchange energy.

2.5.1 Basis sets for implementation

Four-component relativistic calculations making use of 4-spinor orbitals instead of spin-orbitals, there are several structures of basis sets that can be used [8, 9] for implementation.

2-spinor basis set

A first possibility is to write the 4-spinor ψ in a 2-spinor decomposition such that

$$\psi = \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = \begin{pmatrix} \sum_{\nu=1}^{N_L} a_{\nu}^L \chi_{\nu}^L \\ \sum_{\nu=1}^{N_S} a_{\nu}^S \chi_{\nu}^S \end{pmatrix}, \quad (2.102)$$

using a 2-spinors basis $\{\chi^L, \chi^S\}$ such that N_L and N_S corresponding to the number of 2-spinors in the large component basis set and small component basis set respectively.

Scalar basis set

Another possibility is to write the 4-spinor ψ in a scalar decomposition such that

$$\psi = \begin{pmatrix} \psi^{L\alpha} \\ \psi^{L\beta} \\ \psi^{S\alpha} \\ \psi^{S\beta} \end{pmatrix} = \begin{pmatrix} \sum_{\nu=1}^{N_L} a_{\nu}^{L\alpha} \chi_{\nu}^{L(\alpha)} \\ \sum_{\nu=1}^{N_L} a_{\nu}^{L\beta} \chi_{\nu}^{L(\beta)} \\ \sum_{\nu=1}^{N_S} a_{\nu}^{S\alpha} \chi_{\nu}^{S(\alpha)} \\ \sum_{\nu=1}^{N_S} a_{\nu}^{S\beta} \chi_{\nu}^{S(\beta)} \end{pmatrix}, \quad (2.103)$$

using a scalar basis $\{\chi^L, \chi^S\}$. The (“spin”) parenthesis are but indicative of the position of the scalar basis function within the 4-spinor, and are only kept to keep track. The basis functions are labelled between 1 and N_L or N_S , corresponding to the number of basis function for the expansion of the large and small components respectively. The same scalar basis functions are used to describe each “spin” component and are thus used twice with different coefficients $a_{\nu}^{\chi\tau}$.

Kinetic balance

We have considered the use of two different basis sets $\{\chi^L\}$ and $\{\chi^S\}$ for the large and small component respectively. It corresponds to a feature that is distinctive of relativistic quantum chemistry calculations and is denoted as the kinetic balance. Indeed, in order to avoid divergences of the kinetic energy, [3,9,16], it is necessary to use two different basis sets fulfilling some constraints, usually related to the expression of the small component as a function of the large component of the 4-spinor in the non-relativistic limit [3], which we write as

$$\psi^S \approx \frac{c\boldsymbol{\sigma} \cdot \mathbf{p}}{2mc^2} \psi^L. \quad (2.104)$$

As the small component of the 4-spinor is obtained from a differentiation of the large component, the small component basis set $\{\chi^S\}$ must be obtained from a differentiation of the large component basis set $\{\chi^L\}$. There are once more several choices, among them the two simplest being the restricted kinetic balance (RKB), for which all small component basis function obtained from the differentiation of the same large component basis-function are kept with only one variational coefficient, and the unrestricted kinetic balance (UKB), for which the variational coefficients of the small component basis functions all change freely. The UKB makes for an easier implementation but for a bigger variational space, slowing down calculations and increasing the risk of intruder states [37].

2.5.2 Application: four-component Hartree-Fock in a scalar basis set

The relativistic Hartree-Fock equations in the four-component formalism are most easily implemented using a scalar basis set, as they make use of exactly the same two-electron integrals as the non-relativistic equations even if the 4×4 structure of the Dirac Hamiltonian makes for a complicated block structure of the Fock matrix. In the spirit of the book from K. G. Dyall and K. Fægri Jr. [9] we write in Appendix F the relativistic Fock matrix elements in a scalar basis set for the Dirac-Coulomb-Gaunt Hamiltonian and without use of Kramers symmetry. In particular, we show in Appendix F.2 how the Gaunt two-electron integrals are rewritten using the same two-electron integrals as for the Coulomb interaction, which is the main reason why the Gaunt interaction is much more easily implemented and used in relativistic quantum chemistry calculations than the full Breit interaction.

The four-component Fock matrix explicitly written in Appendix F is the core of the four-component relativistic unrestricted Hartree-Fock (UHF) based on the Dirac-Coulomb-Gaunt Hamiltonian that we implemented as a plugin of the software QUANTUM PACKAGE 2.0 [38] in order to have a “sandbox” in which to test and experiment on short-range relativistic density functionals.

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Chapter 3

Four-component relativistic range-separated density-functional theory: Short-range exchange local-density approximation

This chapter corresponds to the article [J. Paquier and J. Toulouse, *J. Chem. Phys.* **149**, 174110 (2018)]. <https://doi.org/10.1063/1.5049773>

We lay out the extension of range-separated density-functional theory to a four-component relativistic framework using a Dirac-Coulomb-Breit Hamiltonian in the no-pair approximation. This formalism combines a wave-function method for the long-range part of the electron-electron interaction with a density(-current) functional for the short-range part of the interaction. We construct for this formalism a short-range exchange local-density approximation based on calculations on a relativistic homogeneous electron gas with a modified Coulomb-Breit electron-electron interaction. More specifically, we provide the relativistic short-range Coulomb and Breit exchange energies per particle of the relativistic homogeneous electron gas in the form of Padé approximants which are systematically improvable to arbitrary accuracy. These quantities, as well as the associated effective Coulomb-Breit exchange hole, show the important impact of relativity on short-range exchange effects for high densities.

3.1 Introduction

Range-separated density-functional theory (RS-DFT) (see, e.g., Refs. [1, 2]) is an alternative to Kohn-Sham density-functional theory (DFT) [3] for electronic-structure calculations of atoms, molecules, and solids. It permits to rigorously combine an explicit wave-function calculation for the long-range part of the electron-electron interaction with a compact density functional for the short-range part of the electron-electron interaction. RS-DFT leads to a faster basis convergence than standard wave-function methods [4] and can provide improvement over usual Kohn-Sham DFT approximations for the description of strong-correlation effects (see, e.g., Refs. [5, 6]), weak intermolecular interactions (see, e.g., Refs. [7–9]), fractionally charged subsystems (see, e.g., Refs. [10, 11]), and electronic excitation energies (see, e.g., Refs. [12–14]).

For the description of compounds with heavy elements, relativistic effects have to be incorporated into RS-DFT. A simple approach that has been used consists in using standard scalar-relativistic effective-core potentials in RS-DFT [15, 16]. A more sophisticated approach was developed by Kullie and Saue [17] who extended RS-DFT to a four-component relativistic Dirac-Coulomb Hamiltonian, using second-order Møller-Plesset (MP2) perturbation theory for the long-range part of the calculation and usual non-relativistic short-range semi-local exchange-correlation density-functional approximations.

To make this approach more rigorous and possibly more accurate, especially for core properties, relativistic short-range density-functional approximations should be used. A number of relativistic density-functional approximations have been proposed for four-component relativistic Kohn-Sham DFT (see, e.g., the review in Ref. [18]), but no relativistic short-range density-functional approximations has been developed yet. This is unfortunate since relativistic effects are most important in spatial regions of high density whose contribution to the energy in RS-DFT mainly comes from the short-range exchange-correlation density functional.

In the present work, we remedy to this limitation by constructing a relativistic short-range exchange local-density approximation (LDA) based on a relativistic homogeneous electron gas (RHEG) with a modified electron-electron interaction. The choice to focus on the exchange energy and not on the correlation energy is motivated by the fact that, at high densities where relativistic effects are important, exchange largely dominates correlation, at least in not very strongly correlated systems. The choice to target a LDA, as opposed to a generalized-gradient approximation (GGA), is motivated by the fact that LDA is the standard first-level approximation to consider in DFT. Moreover, gradient corrections beyond LDA for a short-range electron-electron interaction are much smaller than for the standard Coulomb interaction [2, 19]. Beyond the goal of using this relativistic short-range exchange LDA in RS-DFT calculations of molecular and solid-state systems, the present work also aims at analyzing the importance of relativistic effects on the short-range exchange energy.

The paper is organized as follows. In Section 3.2, we briefly lay out the formalism of RS-DFT for a four-component relativistic Dirac-Coulomb-Breit Hamiltonian. In Sections 3.3.1, 3.3.2, and 3.3.3, we review the calculation of the full-range exchange energy per particle of the RHEG with the standard Dirac-Coulomb-Breit Hamiltonian in a way that will prepare for the extension to the short-range case. We discuss the importance of the separate Coulomb and Breit contributions to the exchange energy per particle and to the exchange hole. In Section 3.3.4, we derive the exchange energy per particle of a RHEG with the short-range version of the Coulomb-Breit electron-electron interaction. Whereas the exchange energy per particle of a non-relativistic homogeneous electron gas with a short-range interaction can be obtained analytically quite easily [1, 20, 21], the calculation of the relativistic analogue turned out to be quite a formidable task. We did not manage to obtain a closed-form expression for the relativistic short-range exchange energy per particle, but we could express it as a divergent series in inverse powers of the speed of light that can be summed to high accuracy using Padé approximants, which is suitable for all practical purposes. In Section 3.3.5, we derive expansions of the relativistic short-range exchange energy per particle for small and large values of the range-separation parameter, and use them to construct a simple approximation to the relativistic short-range exchange energy per particle which can be used as an alternative to the Padé approximants. Finally, Section 4.7 contains our conclusions and prospects for future work.

3.2 Relativistic range-separated density-functional theory

3.2.1 No-pair Dirac-Coulomb-Breit wave-function theory

For relativistic electronic-structure calculations, a good starting point is the Dirac-Coulomb-Breit (DCB) electronic Hamiltonian in the no-pair approximation [22]

$$\hat{H}_+^{\text{DCB}} = \hat{H}_+^{\text{D}} + \hat{W}_+^{\text{CB}}, \quad (3.1)$$

where \hat{H}_+^{D} is the one-electron Dirac Hamiltonian and \hat{W}_+^{CB} is the two-electron Coulomb-Breit (CB) interaction. In second-quantized position representation, \hat{H}_+^{D} can be written as, in atomic units,

$$\hat{H}_+^{\text{D}} = \int d\mathbf{r} \hat{\psi}_+^\dagger(\mathbf{r}) [c(\boldsymbol{\alpha} \cdot \mathbf{p}) + \boldsymbol{\beta} mc^2 + v_{\text{ne}}(\mathbf{r})\mathbf{I}_4] \hat{\psi}_+(\mathbf{r}), \quad (3.2)$$

where $\mathbf{p} = -i\nabla_{\mathbf{r}}$ is the momentum operator, $c = 137.036$ a.u. is the speed of light, and $m = 1$ a.u. is the electron mass that has been kept for clarity, $v_{\text{ne}}(\mathbf{r})$ is the electron-nuclei scalar potential, \mathbf{I}_4 is the 4×4 identity matrix, and $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are the 4×4 Dirac matrices

$$\boldsymbol{\alpha} = \begin{pmatrix} \mathbf{0}_2 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0}_2 \end{pmatrix} \text{ and } \boldsymbol{\beta} = \begin{pmatrix} \mathbf{I}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & -\mathbf{I}_2 \end{pmatrix}, \quad (3.3)$$

where $\boldsymbol{\sigma} = (\boldsymbol{\sigma}_x, \boldsymbol{\sigma}_y, \boldsymbol{\sigma}_z)$ is the 3-dimensional vector of the 2×2 Pauli matrices, and $\mathbf{0}_2$ and \mathbf{I}_2 are the 2×2 zero and identity matrices, respectively. In Eq. (3.2), $\hat{\Psi}_+(\mathbf{r})$ and $\hat{\Psi}_+^\dagger(\mathbf{r})$ are the (projected) annihilation and creation field operators

$$\hat{\Psi}_+(\mathbf{r}) = \sum_p^+ \psi_p(\mathbf{r}) \hat{a}_p \text{ and } \hat{\Psi}_+^\dagger(\mathbf{r}) = \sum_p^+ \psi_p^\dagger(\mathbf{r}) \hat{a}_p^\dagger, \quad (3.4)$$

where the sum is over a set of orthonormal 4-component-spinor orbitals $\{\psi_p(\mathbf{r})\}$ which are positive-energy eigenfunctions of a Dirac Hamiltonian with some potential [23], and \hat{a}_p and \hat{a}_p^\dagger are the corresponding annihilation and creation operators of these orbitals. The restriction in the sum to positive-energy states corresponds to the no-pair approximation, in which negative-energy states corresponding to positronic states are disregarded. The two-electron Coulomb-Breit interaction term is written as

$$\hat{W}_+^{\text{CB}} = \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \hat{\Psi}_+^\dagger(\mathbf{r}_1) \hat{\Psi}_+^\dagger(\mathbf{r}_2) \mathbf{w}^{\text{CB}}(\mathbf{r}_{12}) \hat{\Psi}_+(\mathbf{r}_2) \hat{\Psi}_+(\mathbf{r}_1), \quad (3.5)$$

where $\mathbf{w}^{\text{CB}}(\mathbf{r}_{12})$ is the sum of the Coulomb and Breit contributions

$$\mathbf{w}^{\text{CB}}(\mathbf{r}_{12}) = \mathbf{w}^{\text{C}}(r_{12}) + \mathbf{w}^{\text{B}}(\mathbf{r}_{12}), \quad (3.6)$$

where $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ and $r_{12} = |\mathbf{r}_{12}|$. The Coulomb interaction is

$$\mathbf{w}^{\text{C}}(r_{12}) = w_{\text{ee}}(r_{12}) (\mathbf{I}_4)_1 (\mathbf{I}_4)_2, \quad (3.7)$$

where $w_{\text{ee}}(r_{12}) = 1/r_{12}$, and $(\mathbf{I}_4)_1$ and $(\mathbf{I}_4)_2$ are the 4×4 identity matrices acting on electron 1 and 2, respectively. The Breit interaction is

$$\mathbf{w}^{\text{B}}(\mathbf{r}_{12}) = -\frac{1}{2} w_{\text{ee}}(r_{12}) \left(\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + \frac{(\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})}{r_{12}^2} \right), \quad (3.8)$$

where the Dirac matrices $\boldsymbol{\alpha}_1$ and $\boldsymbol{\alpha}_2$ act on electron 1 and 2, respectively. The Coulomb-Breit interaction corresponds to the single-photon exchange electron-electron scattering amplitude in quantum-electrodynamics (QED) evaluated with the zero-frequency limit of the photon propagator in the Coulomb electromagnetic gauge. More specifically, the instantaneous Coulomb interaction corresponds to the longitudinal component of the photon propagator, whereas the Breit interaction is obtained from the zero-frequency transverse component of the photon propagator. The Breit interaction comprises the instantaneous magnetic Gaunt interaction and the lowest-order retardation correction (see, e.g., Ref. [24]). The no-pair Hamiltonian is not unique since it depends on the choice of the set of orbitals $\{\psi_p\}$. It has been proposed [25,26] to define the no-pair relativistic ground-state energy of a N -electron system using a minmax principle, that we will formally write as

$$E = \min_{\Psi} \left[\max_{\{\psi_p\}} \langle \Psi | \hat{H}_+^D + \hat{W}_+^{\text{CB}} | \Psi \rangle \right], \quad (3.9)$$

where the maximization is done with respect to the set of positive-energy orbitals $\{\psi_p\}$ [on which the Hamiltonian is projected via Eq. (3.4)] by rotations with its complement set of negative-energy orbitals, and the minimization is done with respect to normalized multideterminant wave functions Ψ within the

N -electron space generated by the set of positive-energy orbitals $\{\psi_p\}$. In practice, Eq. (4.6) can be realized with a multiconfiguration self-consistent-field (MCSCF) algorithm which targets a saddle point in the parameter space [26–28]. For one-electron Dirac Hamiltonians, this type of minmax principle appears well founded (see Refs. [29–32]). For the no-pair Dirac-Coulomb-Breit Hamiltonian with a correlated wave function, to the best of our knowledge this minmax principle has not been rigorously examined mathematically but the results of Ref. [26] on two-electron systems suggests that it is indeed a reasonable definition of the no-pair ground-state energy.

3.2.2 No-pair Dirac-Coulomb-Breit range-separated density-functional theory

The Dirac-Coulomb RS-DFT introduced by Kullie and Saue [17] can be readily extended to a Dirac-Coulomb-Breit Hamiltonian. We will do so using the general formalism of relativistic current-density-functional theory [33–35], even though we do not consider any external vector potential. The starting point is the following decomposition of the Coulomb-form electron-electron potential $w_{ee}(r_{12}) = 1/r_{12}$ appearing in Eqs. (3.7) and (3.8)

$$w_{ee}(r_{12}) = w_{ee}^{\text{lr},\mu}(r_{12}) + w_{ee}^{\text{sr},\mu}(r_{12}), \quad (3.10)$$

where $w_{ee}^{\text{lr},\mu}(r_{12}) = \text{erf}(\mu r_{12})/r_{12}$ and $w_{ee}^{\text{sr},\mu}(r_{12}) = \text{erfc}(\mu r_{12})/r_{12}$ are long-range and short-range potentials, respectively. Here, $\text{erf}(x) = (2/\sqrt{\pi}) \int_0^x e^{-t^2} dt$ is the error function, $\text{erfc}(x) = 1 - \text{erf}(x)$ is the complementary error function, and μ is the range-separation parameter acting like an inverse smooth cut-off radius. We then assume that the no-pair relativistic ground-state energy can be expressed as

$$E = \min_{\Psi} \left[\max_{\{\psi_p\}} \left\{ \langle \Psi | \hat{H}_+^D + \hat{W}_+^{\text{CB,lr},\mu} | \Psi \rangle + \bar{E}_{\text{Hxc}}^{\text{CB,sr},\mu}[n_{\Psi}, \mathbf{j}_{\Psi}] \right\} \right], \quad (3.11)$$

where, as before, the maximization is over the set of projecting positive-energy orbitals $\{\psi_p\}$ by rotations with its complement set of negative-energy orbitals and the minimization is over normalized multideterminant wave functions Ψ within the N -electron space generated by the set of positive-energy orbitals. In Eq. (3.11), $\hat{W}_+^{\text{CB,lr},\mu}$ is the long-range version of the two-electron Coulomb-Breit interaction as defined by Eqs. (3.5)-(3.8) but with the substitution $w_{ee}(r_{12}) \rightarrow w_{ee}^{\text{lr},\mu}(r_{12})$, and $\bar{E}_{\text{Hxc}}^{\text{CB,sr},\mu}[n_{\Psi}, \mathbf{j}_{\Psi}]$ is a complement short-range Coulomb-Breit Hartree-exchange-correlation functional of the electron density $n_{\Psi}(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$ and current electron density $\mathbf{j}_{\Psi}(\mathbf{r}) = \langle \Psi | \hat{\mathbf{j}}(\mathbf{r}) | \Psi \rangle$, where $\hat{n}(\mathbf{r}) = \int d\mathbf{r}' \hat{\psi}_+^{\dagger}(\mathbf{r}') \hat{\psi}_+(\mathbf{r})$ and $\hat{\mathbf{j}}(\mathbf{r}) = \int d\mathbf{r}' \hat{\psi}_+^{\dagger}(\mathbf{r}') c \boldsymbol{\alpha} \hat{\psi}_+(\mathbf{r})$ are the density and current density operators, respectively. We note that, even though Eq. (3.11) seems a natural extension of non-relativistic RS-DFT [1, 2], the existence of a universal density-current functional $\bar{E}_{\text{Hxc}}^{\text{CB,sr},\mu}[n, \mathbf{j}]$ giving the no-pair relativistic ground-state energy via the minmax procedure of Eq. (3.11) is not established. Indeed, similarly to the problem of defining static density functionals for excited-state energies (see, e.g., Refs. [36, 37]), it seems *a priori* only possible to define a no-pair relativistic functional which either is universal but satisfies only a stationary principle (instead of a minmax principle) or satisfies a minmax principle but is not universal (i.e., depending on an external potential via the projecting orbitals $\{\psi_p\}$). It might be necessary to go at the QED level to rigorously formulate a RS-DFT approach, as it was done for Kohn-Sham DFT [38]. These aspects are beyond the scope of the present work.

The limiting cases of the relativistic RS-DFT approach of Eq. (3.11) should be mentioned. For $\mu \rightarrow \infty$, the long-range interaction reduces to the Coulomb form, $w_{ee}^{\text{lr},\mu \rightarrow \infty}(r_{12}) = 1/r_{12}$, and the complement short-range functional vanishes, $\bar{E}_{\text{Hxc}}^{\text{CB,sr},\mu \rightarrow \infty}[n] = 0$, so Eq. (3.11) reduces to the wave-function theory of Eq. (4.6). For $\mu = 0$, the long-range interaction vanishes, $w_{ee}^{\text{lr},\mu=0}(r_{12}) = 0$, and the complement short-range functional reduces to a full-range density functional, $\bar{E}_{\text{Hxc}}^{\text{CB,sr},\mu=0}[n] = E_{\text{Hxc}}^{\text{CB}}[n]$, so it reduces to a no-pair relativistic Kohn-Sham DFT method (see, e.g., Ref. [39]), and the corresponding minimizing wave function in Eq. (3.11) is a single Slater determinant $\Psi^{\mu=0} = \Phi$. We decompose now the short-range

density-current functional into Hartree, exchange, and correlation contributions

$$\bar{E}_{\text{Hxc}}^{\text{CB,sr},\mu}[n,\mathbf{j}] = E_{\text{H}}^{\text{CB,sr},\mu}[n,\mathbf{j}] + E_{\text{x}}^{\text{CB,sr},\mu}[n,\mathbf{j}] + \bar{E}_{\text{c}}^{\text{CB,sr},\mu}[n,\mathbf{j}]. \quad (3.12)$$

The short-range Hartree contribution, containing Coulomb and Breit contributions, is an explicit functional of the density n and the current \mathbf{j}

$$E_{\text{H}}^{\text{CB,sr},\mu}[n,\mathbf{j}] = \frac{1}{2} \iint w_{\text{ee}}^{\text{sr},\mu}(r_{12}) n(\mathbf{r}_1) n(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 - \frac{1}{4c^2} \left[\iint w_{\text{ee}}^{\text{sr},\mu}(r_{12}) \mathbf{j}(\mathbf{r}_1) \cdot \mathbf{j}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 + \iint w_{\text{ee}}^{\text{sr},\mu}(r_{12}) \frac{\mathbf{j}(\mathbf{r}_1) \cdot \mathbf{r}_{12} \mathbf{j}(\mathbf{r}_2) \cdot \mathbf{r}_{12}}{r_{12}^2} d\mathbf{r}_1 d\mathbf{r}_2 \right]. \quad (3.13)$$

Note that, in relativistic Kohn-Sham DFT, the Hartree energy is usually defined with the full QED photon propagator in the Feynman gauge [38]. Here, instead, we define the short-range Hartree energy with the two-electron Coulomb-Breit interaction in the Coulomb gauge, in order to be consistent with the corresponding long-range wave-function contribution. The short-range exchange density-current functional is consequently defined by

$$E_{\text{x}}^{\text{CB,sr},\mu}[n,\mathbf{j}] = \langle \Phi[n,\mathbf{j}] | \hat{W}_{+}^{\text{CB,sr},\mu} | \Phi[n,\mathbf{j}] \rangle - E_{\text{H}}^{\text{CB,sr},\mu}[n,\mathbf{j}], \quad (3.14)$$

where $\Phi[n,\mathbf{j}]$ is the Kohn-Sham determinant associated with density n and current \mathbf{j} , and $\hat{W}_{+}^{\text{CB,sr},\mu}$ is the short-range version of the two-electron Coulomb-Breit interaction obtained as in Eqs. (3.5)-(3.8) but with the substitution $w_{\text{ee}}(r_{12}) \rightarrow w_{\text{ee}}^{\text{sr},\mu}(r_{12})$. In Eq. (3.12), $\bar{E}_{\text{c}}^{\text{CB,sr},\mu}[n,\mathbf{j}]$ is the complement short-range correlation functional including all interaction effects beyond Hartree and exchange. Finally, note that, for closed-shell systems, the current vanishes, $\mathbf{j} = \mathbf{0}$, and thus we have simply short-range functionals of the density only. We only consider this case in this work. In practice, the application of the relativistic RS-DFT approach of Eq. (3.11) requires to use approximations for the long-range wave-function part and for the short-range exchange and correlation functionals. For the long-range wave-function part, one can use standard approximations: Hartree-Fock, MP2, MCSCF, etc. For the short-range functionals, no approximation including the relativistic effects has been proposed so far. The rest of paper is devoted to the development of a relativistic LDA for the short-range exchange functional

$$E_{\text{x,LDA}}^{\text{CB,sr},\mu}[n] = \int n(\mathbf{r}) \varepsilon_{\text{x}}^{\text{CB,sr},\mu}(n(\mathbf{r})) d\mathbf{r}, \quad (3.15)$$

where $\varepsilon_{\text{x}}^{\text{CB,sr},\mu}(n)$ is the exchange energy per particle of a RHEG with the short-range two-electron Coulomb-Breit interaction. The calculation of the latter quantity is quite complicated and was performed with the help of the software Wolfram Mathematica [40].

3.3 Exchange effects in the relativistic homogeneous electron gas

We consider a homogeneous electron gas, i.e. a box of volume V containing N electrons with electronic density $n = N/V$ characteristic of the system and a uniform background of positive charges with density n_{b} equal to n in order to ensure the electroneutrality of the system. The electron gas is studied in the thermodynamic limit, i.e. $N \rightarrow \infty$ and $V \rightarrow \infty$ while $n = N/V$ is kept constant, the positive background cancelling the diverging Hartree energy term. Such an electron gas is considered to be relativistic when the Fermi wave vector $k_{\text{F}} = (3\pi^2 n)^{1/3}$ is non negligible compared to the speed of light c . This must really be understood as a comparison between the energy related to the Fermi wave vector $\hbar k_{\text{F}} c$ and the rest

energy mc^2 where we take these quantities in atomic units. In order to get an idea of the maximal value of k_F that one encounters in an heavy element, one may consider a 1s hydrogen-like orbital, $\psi_{1s}(r) = (Z^3/\pi)^{1/2} e^{-Zr}$ where Z is the atomic number, and calculate the density of this doubly occupied 1s orbital at the nucleus: $n = 2 |\psi_{1s}(0)|^2 = 2 Z^3/\pi$ corresponding to a Fermi wave vector of $k_F = (6\pi)^{1/3} Z = 2.66 Z$. The heaviest elements having atomic numbers Z of about 100, this corresponds to a maximal value of k_F of nearly 300 a.u..

3.3.1 One-electron part

The form of the one-electron Dirac equation for this homogeneous electron gas is

$$(c(\boldsymbol{\alpha} \cdot \mathbf{p}) + \boldsymbol{\beta}mc^2) \Psi_{\mathbf{k},\sigma}(\mathbf{r}) = E_k \Psi_{\mathbf{k},\sigma}(\mathbf{r}), \quad (3.16)$$

where $\Psi_{\mathbf{k},\sigma}(\mathbf{r})$ is a one-electron wave function with wave vector \mathbf{k} and “spin” index $\sigma = \uparrow, \downarrow$ associated with the positive-energy eigenvalue

$$E_k = \sqrt{k^2 c^2 + m^2 c^4}. \quad (3.17)$$

The wave functions $\Psi_{\mathbf{k},\sigma}(\mathbf{r})$ are four-component spinors of the form

$$\Psi_{\mathbf{k},\sigma}(\mathbf{r}) = \begin{pmatrix} \Phi_{\mathbf{k},\sigma}(\mathbf{r}) \\ \chi_{\mathbf{k},\sigma}(\mathbf{r}) \end{pmatrix}, \quad (3.18)$$

where each component is itself a two-component spinor. The large component $\Phi_{\mathbf{k},\sigma}(\mathbf{r})$ has a plane-wave form

$$\Phi_{\mathbf{k},\sigma}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sqrt{\frac{E_k + mc^2}{2E_k}} e^{-i\mathbf{k} \cdot \mathbf{r}} \varphi_\sigma, \quad (3.19)$$

and the small component is obtained from the large component by

$$\chi_{\mathbf{k},\sigma}(\mathbf{r}) = \frac{c(\boldsymbol{\sigma} \cdot \mathbf{k})}{E_k + mc^2} \Phi_{\mathbf{k},\sigma}(\mathbf{r}), \quad (3.20)$$

and φ_σ is a two-component spin part with $\varphi_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\varphi_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. What we call “spin” here really refers to the index σ identifying the two components of the large-component spinor. It is easy to prove in the non-relativistic formalism that the plane-wave solutions of the non-interacting Schrödinger equation are also solution of the exchange operator, but to the best of our knowledge such a demonstration has not been done for non-interacting plane-wave spinors. Nevertheless, we use these plane-wave spinors as is usually done in a non-relativistic scheme to determine exchange energies in the following.

3.3.2 Full-range Coulomb-Breit exchange energy

As the preparation for the case of the short-range Coulomb-Breit interaction, we recall the form of the full-range Coulomb-Breit exchange energy. The Coulomb exchange energy per particle can be expressed as [35, 41] (see Appendix G)

$$\begin{aligned} \epsilon_x^C = & -\frac{3 k_F}{4\pi} \left(\frac{5}{6} + \frac{1}{3} \tilde{c}^2 + \frac{2}{3} \sqrt{1 + \tilde{c}^2} \operatorname{arcsinh} \left(\frac{1}{\tilde{c}} \right) - \frac{1}{3} \left(1 + \tilde{c}^2 \right)^2 \ln \left(1 + \frac{1}{\tilde{c}^2} \right) \right. \\ & \left. - \frac{1}{2} \left(\sqrt{1 + \tilde{c}^2} - \tilde{c}^2 \operatorname{arcsinh} \left(\frac{1}{\tilde{c}} \right) \right)^2 \right), \quad (3.21) \end{aligned}$$

where $\tilde{c} = c/k_F$. The Breit exchange energy per particle has a similar form [42] (see Appendix G)

$$\begin{aligned} \epsilon_x^B = & \frac{3 k_F}{4\pi} \left(1 - 2(1 + \tilde{c}^2) \left(1 - \tilde{c}^2 \left(-2 \ln(\tilde{c}) + \ln(1 + \tilde{c}^2) \right) \right) \right) \\ & + 2 \left(\sqrt{1 + \tilde{c}^2} - \tilde{c}^2 \operatorname{arcsinh} \left(\frac{1}{\tilde{c}} \right) \right)^2. \end{aligned} \quad (3.22)$$

The Breit exchange energy per particle is an approximation to the exchange energy per particle obtained with the transverse component of the full QED photon propagator [34, 35, 41]. The exchange energy per particle obtained with the full QED photon propagator has in fact a simpler expression than the Coulomb-Breit one, thanks to the cancellation of many terms between the Coulomb and transverse components,

$$\epsilon_x^{\text{QED}} = -\frac{3 k_F}{4\pi} \left(1 - \frac{3}{2} \left(\sqrt{1 + \tilde{c}^2} - \tilde{c}^2 \operatorname{arcsinh} \left(\frac{1}{\tilde{c}} \right) \right)^2 \right). \quad (3.23)$$

It is interesting to consider the non-relativistic and ultra-relativistic limits of the Coulomb and Breit exchange energies. In the non-relativistic (NR) limit $\tilde{c} \rightarrow \infty$ (or equivalently the low-density limit), only the Coulomb contribution survives

$$\epsilon_x^{\text{C,NR}} = -\frac{3 k_F}{4\pi} \quad \text{and} \quad \epsilon_x^{\text{B,NR}} = 0, \quad (3.24)$$

which is consistent with the fact that the Breit interaction is a purely relativistic phenomenon. In the opposite ultra-relativistic (UR) limit $\tilde{c} \rightarrow 0$ (or equivalently the high-density limit), we have

$$\epsilon_x^{\text{C,UR}} = -\frac{(1 + \ln 4) k_F}{4\pi} \quad \text{and} \quad \epsilon_x^{\text{B,UR}} = \frac{3 k_F}{4\pi}, \quad (3.25)$$

i.e. the Breit contribution becomes the opposite of the non-relativistic Coulomb exchange energy, and is larger in absolute value than the Coulomb contribution, implying that the total exchange energy becomes positive. The different exchange energies per particle are plotted in Figure 3.1 as functions of the Fermi wave vector k_F , up to $k_F = 300$ a.u. which is about the largest value that could be encountered in an heavy element. We observe that, compared to the non-relativistic energy energy, relativity always reduces the exchange energy in absolute value, and this effect increases with the density. The relativistic effects for the Coulomb exchange contribution remain relatively small, even at high densities. By contrast, the Breit exchange contribution has a much larger effect at sufficiently high densities. The Coulomb-Breit exchange energy per particle is a good approximation to the exchange energy per particle obtained with the full QED photon propagator for $k_F \lesssim c \approx 137$ a.u., which is consistent with the fact that the Breit interaction constitutes only the leading term in the expansion of the QED photon propagator in $1/c$.

3.3.3 Effective Coulomb-Breit exchange hole

A convenient way of analyzing the exchange effects in terms of the interelectronic distance r_{12} is to introduce an effective Coulomb-Breit exchange hole $n_x^{\text{CB}}(r_{12})$ such that

$$\epsilon_x^{\text{CB}} = \frac{1}{2} \int n_x^{\text{CB}}(r_{12}) w_{ee}(r_{12}) \mathbf{d}\mathbf{r}_{12}. \quad (3.26)$$

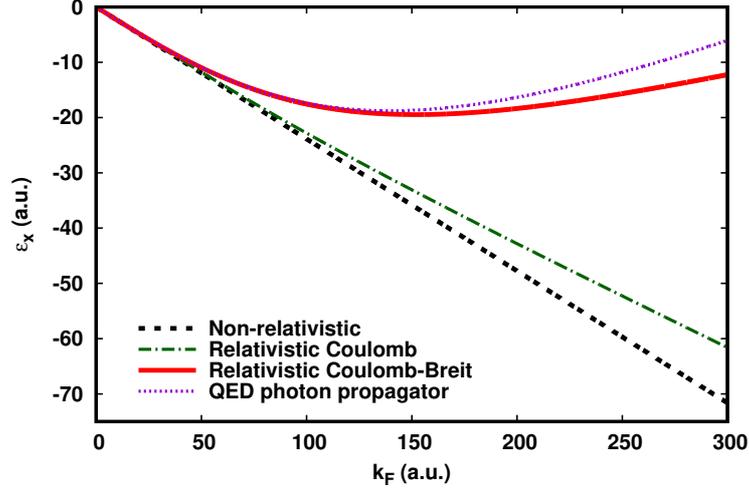


Figure 3.1: Non-relativistic and relativistic exchange energies per particle for the Coulomb, Coulomb-Breit, and QED photon propagator electron-electron interactions as functions of the Fermi wave vector k_F .

For the case of the Coulomb interaction, the associated exchange hole was derived by Ellis [43] and MacDonald and Vosko [35] (see Appendix G)

$$n_x^C(r_{12}) = -\frac{9}{4}n \frac{1}{(k_F r_{12})^2} \left[j_1(k_F r_{12})^2 + (1-\lambda)A_\lambda(k_F r_{12})^2 + \lambda B_\lambda(k_F r_{12})^2 \right], \quad (3.27)$$

with $\lambda = 1/(1+\tilde{c}^2)$ and

$$\begin{aligned} A_\lambda(k_F r_{12}) &= \sum_{\nu=0}^{\infty} \frac{(2\nu+1)!!}{(2\nu+1)} j_{\nu+1}(k_F r_{12}) \left(\frac{\lambda}{k_F r_{12}} \right)^\nu, \\ B_\lambda(k_F r_{12}) &= \sum_{\nu=0}^{\infty} \frac{(2\nu+1)!!}{(2\nu+1)} j_{\nu+2}(k_F r_{12}) \left(\frac{\lambda}{k_F r_{12}} \right)^\nu, \end{aligned} \quad (3.28)$$

where j_ν are the spherical Bessel functions. We have extended this result to the case of the Breit interaction. The associated exchange hole is (see Appendix G)

$$n_x^B(r_{12}) = -\frac{9}{2}n \frac{1}{(k_F r_{12})^2} \left[-j_1(k_F r_{12})^2 + (1-\lambda)A_\lambda(k_F r_{12})^2 \right]. \quad (3.29)$$

To the best of our knowledge this expression had not been derived before. This Breit exchange hole should not be interpreted as a modification of the pair density, but simply as giving after integration the Breit exchange energy. Like the non-relativistic exchange hole, the relativistic Coulomb exchange hole is normalized to -1

$$\int n_x^C(r_{12}) d\mathbf{r}_{12} = -1, \quad (3.30)$$

but the Breit exchange hole is not. When the density increases from the low-density limit to the high-density limit, its integral varies from 0 to 1

$$0 \leq \int n_x^B(r_{12}) d\mathbf{r}_{12} \leq 1, \quad (3.31)$$

which confirms that it should be considered as an effective exchange hole with only purpose to give the Breit exchange energy.

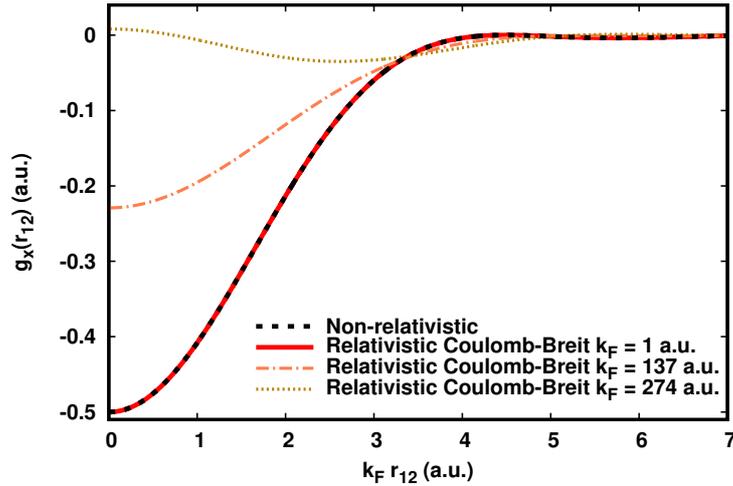


Figure 3.2: Effective Coulomb-Breit exchange pair-distribution function at different values of k_F as a function of $k_F r_{12}$.

In the non-relativistic limit, corresponding to $\lambda = 0$, the Coulomb exchange hole reduces to the well-known non-relativistic form and the Breit exchange hole vanishes

$$n_x^{\text{C,NR}}(r_{12}) = -\frac{9}{2}n \frac{j_1(k_F r_{12})^2}{(k_F r_{12})^2} \quad \text{and} \quad n_x^{\text{B,NR}}(r_{12}) = 0. \quad (3.32)$$

In the opposite ultra-relativistic limit, corresponding to $\lambda = 1$, we have

$$n_x^{\text{C,UR}}(r_{12}) = -\frac{9}{4}n \frac{1}{(k_F r_{12})^2} \left[j_1(k_F r_{12})^2 + B_1(k_F r_{12})^2 \right] \quad \text{and} \quad n_x^{\text{B,UR}}(r_{12}) = \frac{9}{2}n \frac{j_1(k_F r_{12})^2}{(k_F r_{12})^2}, \quad (3.33)$$

where we observe again the ultra-relativistic limit of the Breit term is the exact opposite of the non-relativistic limit of the Coulomb contribution.

In Figure 3.2, we plot the effective Coulomb-Breit exchange pair-distribution function

$$g_x^{\text{CB}}(r_{12}) = n_x^{\text{CB}}(r_{12})/n, \quad (3.34)$$

for different values of the density (or equivalently k_F). For a low value of the density, $k_F = 1$ a.u., $g_x^{\text{CB}}(r_{12})$ has the usual shape of the exchange hole and is indistinguishable from the non-relativistic calculation, with the on-top value being $g_x^{\text{CB}}(0) \approx -1/2$. For the higher values of the density, $k_F = 137$ and 274 a.u., we observe that the Coulomb-Breit exchange hole becomes shallower. In particular, for $k_F = 274$ a.u., the Coulomb-Breit exchange hole is almost flat, with a very small minimum not located at $r_{12} = 0$ anymore. These dramatic modifications of the exchange effects due to relativity underline the importance of considering relativistic effects when calculating short-range exchange energies in systems containing high-density regions.

3.3.4 Short-range Coulomb-Breit exchange energy per particle

Since we have previously calculated the Coulomb-Breit exchange hole, the most straightforward way of calculating the short-range Coulomb-Breit exchange energy per particle is to integrate the exchange hole with the short-range electron-electron interaction

$$\epsilon_x^{\text{CB,sr},\mu} = \frac{1}{2} \int n_x^{\text{CB}}(r_{12}) w_{ee}^{\text{sr},\mu}(r_{12}) \mathbf{d}r_{12}. \quad (3.35)$$

Unfortunately, we did not manage to calculate this integral analytically. We thus instead follow the same route as for the calculation of the full-range exchange energy (see Appendix G), i.e. integrating over space variables first. Similarly to Eq. (G.1), we obtain the short-range Coulomb exchange energy per particle as a Fourier-space integral where each wave vector spans the volume of the Fermi sphere V_{k_F}

$$\begin{aligned}
\varepsilon_x^{C, sr, \mu} &= -\frac{1}{2n(2\pi)^6} \iint_{V_{k_F}} \tilde{w}_{ee}^{sr, \mu}(k_{12}) \frac{E_{k_1} E_{k_2} + (\mathbf{k}_1 \cdot \mathbf{k}_2) c^2 + c^4}{E_{k_1} E_{k_2}} d\mathbf{k}_1 d\mathbf{k}_2 \\
&= \frac{3k_F}{4\pi} \int_0^1 \int_0^1 d\tilde{k}_1 d\tilde{k}_2 \tilde{k}_1 \tilde{k}_2 \left(\frac{1}{\sqrt{\tilde{c}^2 + \tilde{k}_1^2} \sqrt{\tilde{c}^2 + \tilde{k}_2^2}} \left[\tilde{k}_1 \tilde{k}_2 + \left(e^{-\left(\frac{\tilde{k}_1 + \tilde{k}_2}{2\tilde{\mu}}\right)^2} - e^{-\left(\frac{\tilde{k}_1 - \tilde{k}_2}{2\tilde{\mu}}\right)^2} \right) \tilde{\mu}^2 \right] \right. \\
&\quad + \frac{2\tilde{c}^2 + \tilde{k}_1^2 + \tilde{k}_2^2 + 2\sqrt{\tilde{c}^2 + \tilde{k}_1^2} \sqrt{\tilde{c}^2 + \tilde{k}_2^2}}{4\sqrt{\tilde{c}^2 + \tilde{k}_1^2} \sqrt{\tilde{c}^2 + \tilde{k}_2^2}} \left[\text{Ei} \left(-\left(\frac{\tilde{k}_1 + \tilde{k}_2}{2\tilde{\mu}}\right)^2 \right) - \text{Ei} \left(-\left(\frac{\tilde{k}_1 - \tilde{k}_2}{2\tilde{\mu}}\right)^2 \right) \right. \\
&\quad \left. \left. + \ln((\tilde{k}_1 - \tilde{k}_2)^2) - \ln((\tilde{k}_1 + \tilde{k}_2)^2) \right] \right), \quad (3.36)
\end{aligned}$$

where $\tilde{w}_{ee}^{sr, \mu}(k_{12}) = (4\pi/k_{12}^2)(1 - e^{-k_{12}^2/4\mu^2})$ is the Fourier transform of the short-range interaction in terms of the relative wave vector $k_{12} = |\mathbf{k}_{12}|$ with $\mathbf{k}_{12} = \mathbf{k}_1 - \mathbf{k}_2$, $\text{Ei}(x) = -\int_{-x}^{\infty} e^{-t}/t dt$ is the exponential integral function, and we have introduced the scaled variables $\tilde{\mu} = \mu/k_F$, $\tilde{k}_1 = k_1/k_F$, and $\tilde{k}_2 = k_2/k_F$. Unfortunately we were unable to straightforwardly calculate the double integral in Eq. (3.36). To circumvent this difficulty we first make an asymptotic expansion of the integrand for $\tilde{c} \rightarrow \infty$ and then integrate term by term to obtain the asymptotic series

$$\varepsilon_x^{C, sr, \mu} \sim k_F \sum_{i=0}^{\infty} \frac{\alpha_{2i}(\tilde{\mu})}{\tilde{c}^{2i}}, \quad (3.37)$$

where the coefficients $\alpha_{2i}(\tilde{\mu})$ can be obtained analytically. Their derivation being quite lengthy, it is discussed in detail in Appendix I.2. We give here the first three coefficients.

$$\begin{aligned}
\alpha_0(\tilde{\mu}) &= \frac{1}{4\pi} \left(-3 + 4\sqrt{\pi} \operatorname{erf}\left(\frac{1}{\tilde{\mu}}\right) \tilde{\mu} + 2\left(2e^{-\frac{1}{\tilde{\mu}^2}} - 3\right) \tilde{\mu}^2 - 2\left(e^{-\frac{1}{\tilde{\mu}^2}} - 1\right) \tilde{\mu}^4 \right), \\
\alpha_2(\tilde{\mu}) &= \frac{1}{12\pi} \left(1 - 6\sqrt{\pi} \operatorname{erf}\left(\frac{1}{\tilde{\mu}}\right) \tilde{\mu}^3 - 6\left(e^{-\frac{1}{\tilde{\mu}^2}} - 3\right) \tilde{\mu}^4 + 12\left(e^{-\frac{1}{\tilde{\mu}^2}} - 1\right) \tilde{\mu}^6 \right), \\
\alpha_4(\tilde{\mu}) &= \frac{1}{240\pi} \left(-13 + 12\sqrt{\pi} \operatorname{erf}\left(\frac{1}{\tilde{\mu}}\right) \left(8 + 45\tilde{\mu}^2\right) \tilde{\mu}^3 + 12\left(4e^{-\frac{1}{\tilde{\mu}^2}} - 45\right) \tilde{\mu}^4 \right. \\
&\quad \left. + 24\left(13e^{-\frac{1}{\tilde{\mu}^2}} - 40\right) \tilde{\mu}^6 - 648\left(e^{-\frac{1}{\tilde{\mu}^2}} - 1\right) \tilde{\mu}^8 \right). \quad (3.38)
\end{aligned}$$

However, the asymptotic series of Eq. (3.37) diverges for $\tilde{c} < 1$, i.e. for $k_F \gtrsim 137$ a.u.. To avoid this divergence, we use a diagonal Padé approximant [44] of even order M

$$\varepsilon_{x, \text{Padé}}^{C, sr, \mu} = k_F \frac{\sum_{i=0}^{M/2} A_{2i}(\tilde{\mu})/\tilde{c}^{2i}}{\sum_{i=0}^{M/2} B_{2i}(\tilde{\mu})/\tilde{c}^{2i}}, \quad (3.39)$$

with the choice $B_0(\tilde{\mu}) = 1$ without loss of generality, and the other coefficients $A_{2i}(\tilde{\mu})$ and $B_{2i}(\tilde{\mu})$ are uniquely determined, for a given M , from the coefficients $\alpha_{2i}(\tilde{\mu})$ so that the asymptotic expansion of the Padé approximant matches the asymptotic expansion of Eq. (3.37) up to order $2M$ (see Appendix H).

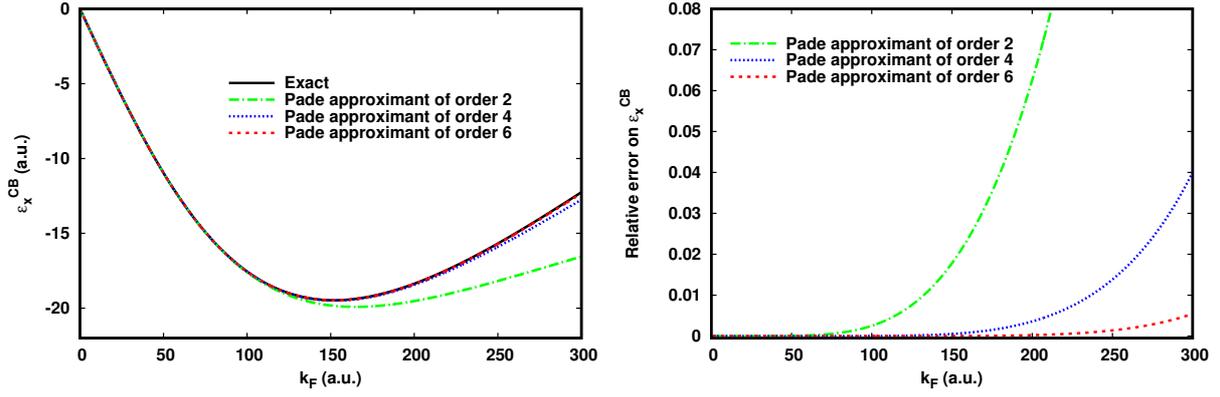


Figure 3.3: Left plot: Exact full-range Coulomb-Breit exchange energy per particle and its Padé approximants of orders 2, 4, and 6 as functions of the Fermi wave vector k_F . Right plot: Relative errors, $\Delta\epsilon_x^{\text{CB}} = \left| (\epsilon_{x,\text{Padé}}^{\text{CB}} - \epsilon_x^{\text{CB}}) / \epsilon_x^{\text{CB}} \right|$, of the Padé approximants compared to the exact full-range Coulomb-Breit exchange energy per particle.

For example, we give here the coefficients for the diagonal Padé approximant of order 2

$$\begin{aligned}
 A_0(\tilde{\mu}) &= \alpha_0(\tilde{\mu}) \quad \text{and} \quad A_2(\tilde{\mu}) = \alpha_2(\tilde{\mu}) - \frac{\alpha_0(\tilde{\mu})\alpha_4(\tilde{\mu})}{\alpha_2(\tilde{\mu})}, \\
 B_2(\tilde{\mu}) &= -\frac{\alpha_4(\tilde{\mu})}{\alpha_2(\tilde{\mu})}.
 \end{aligned} \tag{3.40}$$

We proceed similarly for the short-range Breit exchange energy per particle. Adapting Eq. (G.2) to the case of the short-range interaction gives the Fourier-space integral

$$\begin{aligned}
 \epsilon_x^{\text{B},\text{sr},\mu} &= \frac{1}{2n(2\pi)^6} \iint_{V_{k_F}} \tilde{w}_{ee}^{\text{sr},\mu}(k_{12}) \frac{c^2}{E_{k_1} E_{k_2}} \left(\frac{E_{k_2} + c^2}{E_{k_1} + c^2} k_1^2 + \frac{E_{k_1} + c^2}{E_{k_2} + c^2} k_2^2 \right) \mathbf{d}\mathbf{k}_1 \mathbf{d}\mathbf{k}_2 \\
 &= \frac{3k_F}{4\pi} \int_0^1 \int_0^1 d\tilde{k}_1 d\tilde{k}_2 \tilde{k}_1 \tilde{k}_2 \frac{\tilde{c}^2 - \sqrt{\tilde{c}^2 + \tilde{k}_1^2} \sqrt{\tilde{c}^2 + \tilde{k}_2^2}}{\sqrt{\tilde{c}^2 + \tilde{k}_1^2} \sqrt{\tilde{c}^2 + \tilde{k}_2^2}} \left[\text{Ei} \left(-\left(\frac{\tilde{k}_1 + \tilde{k}_2}{2\tilde{\mu}} \right)^2 \right) - \text{Ei} \left(-\left(\frac{\tilde{k}_1 - \tilde{k}_2}{2\tilde{\mu}} \right)^2 \right) \right. \\
 &\quad \left. + \ln((\tilde{k}_1 - \tilde{k}_2)^2) - \ln((\tilde{k}_1 + \tilde{k}_2)^2) \right], \tag{3.41}
 \end{aligned}$$

which, after asymptotically expanding the integrand for $\tilde{c} \rightarrow \infty$ and integrating term by term, turns into the asymptotic series

$$\epsilon_x^{\text{B},\text{sr},\mu} \sim k_F \sum_{i=0}^{\infty} \frac{\beta_{2i}(\tilde{\mu})}{\tilde{c}^{2i}}, \tag{3.42}$$

where the coefficients $\beta_{2i}(\tilde{\mu})$ can be obtained analytically. The first three of them are

$$\begin{aligned}
\beta_0(\tilde{\mu}) &= 0, \\
\beta_2(\tilde{\mu}) &= \frac{1}{60\pi} \left(25 - 12\sqrt{\pi} \left(3 + 5\tilde{\mu}^2 \right) \operatorname{erf}\left(\frac{1}{\tilde{\mu}}\right) \tilde{\mu} + 18 \left(5 - 2e^{-\frac{1}{\tilde{\mu}^2}} \right) \tilde{\mu}^2 \right. \\
&\quad \left. + 6 \left(15 - 7e^{-\frac{1}{\tilde{\mu}^2}} \right) \tilde{\mu}^4 - 48 \left(1 - e^{-\frac{1}{\tilde{\mu}^2}} \right) \tilde{\mu}^6 \right), \\
\beta_4(\tilde{\mu}) &= \frac{1}{280\pi} \left(-77 + 12\sqrt{\pi} \left(10 + 42\tilde{\mu}^2 + 105\tilde{\mu}^4 \right) \operatorname{erf}\left(\frac{1}{\tilde{\mu}}\right) \tilde{\mu} - 60 \left(7 - 2e^{-\frac{1}{\tilde{\mu}^2}} \right) \tilde{\mu}^2 \right. \\
&\quad \left. - 12 \left(140 - 37e^{-\frac{1}{\tilde{\mu}^2}} \right) \tilde{\mu}^4 - 24 \left(70 - 37e^{-\frac{1}{\tilde{\mu}^2}} \right) \tilde{\mu}^6 + 792 \left(1 - e^{-\frac{1}{\tilde{\mu}^2}} \right) \tilde{\mu}^8 \right). \quad (3.43)
\end{aligned}$$

The fact that $\beta_0(\tilde{\mu}) = 0$ corresponds to the fact that the Breit exchange energy vanishes in the non-relativistic limit. Again, the asymptotic series of Eq. (3.42) diverges for $\tilde{c} < 1$, so we construct a diagonal Padé approximant of even order M

$$\epsilon_{x,\text{Padé}}^{\text{B,sr},\mu} = k_{\text{F}} \frac{\sum_{i=0}^{M/2} C_{2i}(\tilde{\mu}) / \tilde{c}^{2i}}{\sum_{i=0}^{M/2} D_{2i}(\tilde{\mu}) / \tilde{c}^{2i}}, \quad (3.44)$$

with $D_0(\tilde{\mu}) = 1$ and the other coefficients $C_{2i}(\tilde{\mu})$ and $D_{2i}(\tilde{\mu})$ are uniquely determined, for a given M , from the coefficients $\beta_{2i}(\tilde{\mu})$. We give here the coefficients of the diagonal Padé approximant of order 2

$$\begin{aligned}
C_0(\tilde{\mu}) &= \beta_0(\tilde{\mu}) \quad \text{and} \quad C_2(\tilde{\mu}) = \beta_2(\tilde{\mu}) - \frac{\beta_0(\tilde{\mu})\beta_4(\tilde{\mu})}{\beta_2(\tilde{\mu})}, \\
D_2(\tilde{\mu}) &= -\frac{\beta_4(\tilde{\mu})}{\beta_2(\tilde{\mu})}. \quad (3.45)
\end{aligned}$$

The complete expressions of the large- \tilde{c} expansions in Eqs. (3.37) and (3.42) and their associated Padé approximants in Eqs. (3.39) and (3.44) are explicitly given up to an arbitrary order in the Mathematica notebook available in Appendix I. We want to check the accuracy of these Padé approximants to the short-range Coulomb-Breit exchange energy per particle and at which order M we can truncate the expansion. For this, we may check for the most demanding case of $\mu = 0$ corresponding to the full-range interaction and for which we know the exact exchange energy per particle [Eqs. (3.21) and (3.22)]. We thus plot in Figure 3.3 the exact full-range Coulomb-Breit exchange energy per particle and its Padé approximants of orders 2, 4, and 6, as well as their relative errors $\Delta\epsilon_x^{\text{CB}} = \left| (\epsilon_{x,\text{Padé}}^{\text{CB}} - \epsilon_x^{\text{CB}}) / \epsilon_x^{\text{CB}} \right|$, as functions of the Fermi wave vector k_{F} . We note in passing that the Padé approximants can be calculated either for the Coulomb and Breit exchange energies per particle separately, or directly for the total Coulomb-Breit exchange energy per particle, as done here for the plot. It turns out that these two ways of proceeding give very similar Padé approximants for the Coulomb-Breit exchange energy per particle, for example differing by at most about 10^{-4} % for the Padé approximants of order 6. As seen in Figure 3.3, the error of all Padé approximants naturally increases with the density. The error of the Padé approximant of order 2 increases most rapidly with the density, the relative error exceeding 5% as soon as $k_{\text{F}} \gtrsim 200$ a.u.. The relative error in the Padé approximant of order 4 is less than 0.5% until about $k_{\text{F}} = 200$ a.u. and increases to about 4% at $k_{\text{F}} = 300$ a.u.. The Padé approximant of order 6 has a maximal relative error of 0.5% at $k_{\text{F}} = 300$ a.u.. We thus conclude that the Padé approximant of order 6 provides an excellent approximation for all the density range in which we are interested. We have also explicitly checked that this accuracy of the Padé approximant of order 6 is preserved for the short-range Coulomb-Breit exchange energy per particle for a non-zero value of μ by comparing to results obtained by numerical integration in Eq. (3.35). Hence, numerically, the Padé approximants appear to rapidly converge to the correct limit as $M \rightarrow \infty$.

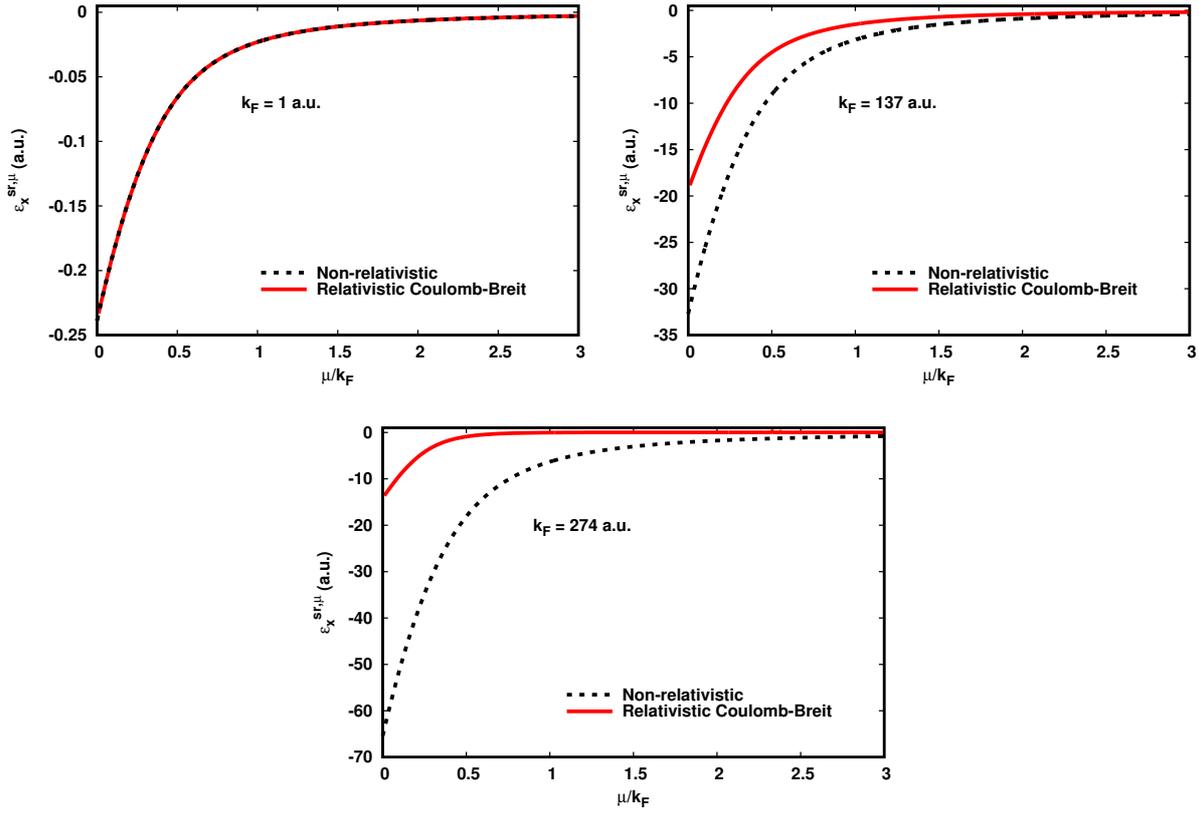


Figure 3.4: Non-relativistic and relativistic Coulomb-Breit short-range exchange energies per particle as functions of μ/k_F . The relativistic Coulomb-Breit short-range exchange energy is obtained from the Padé approximant of order 6.

In Figure 3.4 we plot the relativistic short-range Coulomb-Breit exchange energy per particle, using the Padé approximant of order 6, as a function of the scaled range-separation parameter μ/k_F for different values of k_F , and compare it to the non-relativistic short-range exchange energy per particle (whose expression can be found in Refs. [1, 21]). For $k_F = 1$ a.u., the relativistic exchange energy per particle is indistinguishable from its non-relativistic counterpart, for all values of μ . For higher values of the Fermi wave vector, $k_F = 137$ and 274 a.u., the relativistic short-range Coulomb-Breit exchange energy per particle becomes much smaller, in absolute value, than the non-relativistic short-range exchange energy per particle. Also, it appears that, for large k_F , the relativistic short-range exchange energy per particle goes to zero when increasing μ/k_F significantly faster than does its non-relativistic analogue.

3.3.5 Small- and large- μ expansions and simple approximation for the short-range Coulomb-Breit exchange energy per particle

We have determined the short-range Coulomb and Breit exchange energies per particle $\epsilon_x^{C, sr, \mu}$ and $\epsilon_x^{B, sr, \mu}$ in the form of Padé approximants with quite complicated coefficients. We now derive simple expressions valid for small and large values of the range-separation parameter μ and use them to construct simple approximations for $\epsilon_x^{C, sr, \mu}$ and $\epsilon_x^{B, sr, \mu}$. In order to obtain the expansions of $\epsilon_x^{C, sr, \mu}$ and $\epsilon_x^{B, sr, \mu}$ for $\mu \rightarrow 0$, we start from the asymptotic series in Eqs. (3.37) and (3.42), expand them with respect to μ , and extract the μ and μ^2 terms. For the short-range Coulomb exchange energy per particle, we obtain directly expressions independent of \tilde{c} for the linear and quadratic terms in μ

$$\epsilon_x^{C, sr, \mu} = \epsilon_x^C + \frac{\mu}{\sqrt{\pi}} - \frac{3\mu^2}{2\pi k_F} + O(\mu^3), \quad (3.46)$$

and for the short-range Breit exchange energy per particle we obtain expansions in \tilde{c} for the linear and quadratic terms in μ

$$\begin{aligned}\epsilon_x^{\text{B, sr}, \mu} &= \epsilon_x^{\text{B}} - \frac{\mu}{\sqrt{\pi}} \left(\frac{3}{5\tilde{c}^2} - \frac{3}{7\tilde{c}^4} + \frac{3}{9\tilde{c}^6} - \frac{3}{11\tilde{c}^8} + O\left(\frac{1}{\tilde{c}^{10}}\right) \right) \\ &+ \frac{3\mu^2}{2\pi k_{\text{F}}} \left(\frac{1}{\tilde{c}^2} - \frac{1}{\tilde{c}^4} + \frac{1}{\tilde{c}^6} - \frac{1}{\tilde{c}^8} + O\left(\frac{1}{\tilde{c}^{10}}\right) \right) + O(\mu^3).\end{aligned}\quad (3.47)$$

In this expression, the series in $1/\tilde{c}$ can be exactly summed, and we can write Eq. (3.47) as

$$\epsilon_x^{\text{B, sr}, \mu} = \epsilon_x^{\text{B}} - \frac{\mu}{\sqrt{\pi}} (1 - f(\tilde{c})) + \frac{3\mu^2}{2\pi k_{\text{F}}} (1 - g(\tilde{c})) + O(\mu^3), \quad (3.48)$$

where

$$f(\tilde{c}) = 3\tilde{c}^2 - 3\tilde{c}^3 \arctan\left(\frac{1}{\tilde{c}}\right) \quad \text{and} \quad g(\tilde{c}) = \frac{1}{1 + \frac{1}{\tilde{c}^2}}. \quad (3.49)$$

We note that the linear term in μ in Eq. (3.48) can also be found by inserting into Eq. (3.41) the Fourier transform of the linear term in μ of the expansion of the short-range interaction. However, such an approach cannot be used for higher-order terms in μ because these terms lead to divergences when inserting into Eq. (3.41). The expansion of the short-range Coulomb-Breit exchange energy per particle for $\mu \rightarrow 0$ is thus

$$\epsilon_x^{\text{CB, sr}, \mu} = \epsilon_x^{\text{CB}} + \frac{\mu}{\sqrt{\pi}} f(\tilde{c}) - \frac{3\mu^2}{2\pi k_{\text{F}}} g(\tilde{c}) + O(\mu^3). \quad (3.50)$$

Therefore, near $\mu = 0$, the linear and quadratic terms in μ of $\epsilon_x^{\text{CB, sr}, \mu}$ depend on \tilde{c} . In the non-relativistic limit, we have $f(\tilde{c} \rightarrow \infty) = 1$ and $g(\tilde{c} \rightarrow \infty) = 1$, and thus we correctly recover the non-relativistic expansion $\mu/\sqrt{\pi} - 3\mu^2/(2\pi k_{\text{F}})$ [2, 21]. In the ultra-relativistic limit, we have $f(\tilde{c} \rightarrow 0) = 0$ and $g(\tilde{c} \rightarrow 0) = 0$, and thus the linear and quadratic terms in μ vanish. In order to obtain the expansions of $\epsilon_x^{\text{C, sr}, \mu}$ and $\epsilon_x^{\text{B, sr}, \mu}$ for $\mu \rightarrow \infty$, we start from the asymptotic expansion of the Fourier transform of the short-range interaction

$$\tilde{w}_{\text{ee}}^{\text{sr}, \mu}(k_{12}) = \frac{\pi}{\mu^2} + O\left(\frac{1}{\mu^4}\right). \quad (3.51)$$

Inserting then Eq. (3.51) into Eq. (3.36) leads to the expansion of the short-range Coulomb exchange energy per particle

$$\epsilon_x^{\text{C, sr}, \mu} = -\frac{k_{\text{F}}^3}{24\pi\mu^2} (1 + h(\tilde{c})) + O\left(\frac{1}{\mu^4}\right), \quad (3.52)$$

with

$$h(\tilde{c}) = \frac{9}{4} (\tilde{c}^2 + \tilde{c}^4) - \frac{9}{4} \tilde{c}^4 \operatorname{arcsinh}\left(\frac{1}{\tilde{c}}\right) \left(2\sqrt{1 + \tilde{c}^2} - \tilde{c}^2 \operatorname{arcsinh}\left(\frac{1}{\tilde{c}}\right) \right). \quad (3.53)$$

Similarly, inserting Eq. (3.51) into Eq. (3.41) leads to the expansion of the short-range Breit exchange energy per particle

$$\epsilon_x^{\text{B, sr}, \mu} = \frac{k_{\text{F}}^3}{12\pi\mu^2} (1 - h(\tilde{c})) + O\left(\frac{1}{\mu^4}\right). \quad (3.54)$$

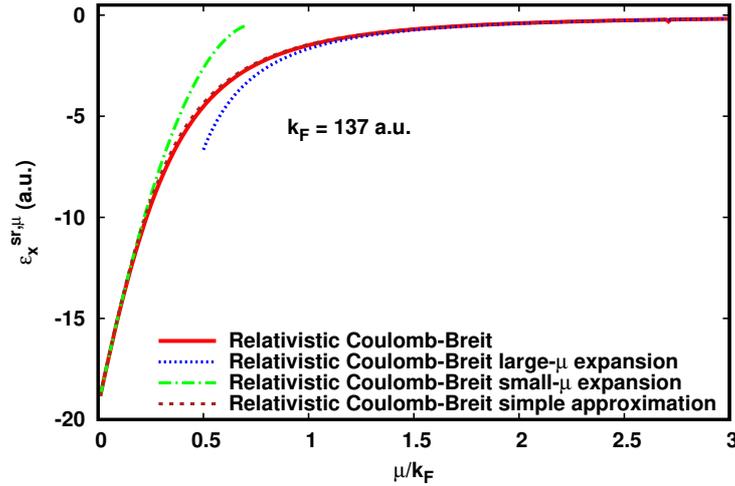


Figure 3.5: Relativistic Coulomb-Breit short-range exchange energy per particle, its small- and large- μ expansions of Eqs. (3.50) and (3.55), and its simple approximation of Eqs. (3.56) and (3.58) as functions of μ/k_F . The reference relativistic Coulomb-Breit short-range exchange energy per particle is obtained from the Padé approximant of order 6.

The asymptotic expansion of the short-range Coulomb-Breit exchange energy per particle for $\mu \rightarrow \infty$ is thus

$$\epsilon_x^{\text{CB},\text{sr},\mu} = -\frac{k_F^3}{24\pi\mu^2} (3h(\tilde{c}) - 1) + O\left(\frac{1}{\mu^4}\right). \quad (3.55)$$

In the non-relativistic limit, we have $h(\tilde{c} \rightarrow \infty) = 1$ and we thus recover the leading term of the asymptotic expansion of the non-relativistic short-range exchange energy per particle, $-k_F^3/(12\pi\mu^2)$ [2, 21]. In the ultra-relativistic limit, we have $h(\tilde{c} \rightarrow 0) = 0$ and thus the leading term is $k_F^3/(24\pi\mu^2)$. We can see on Figure 3.5 that these small- and large- μ expansions indeed reproduce well, at the scale of the plot, the short-range Coulomb-Breit exchange energy per particle for $\mu/k_F \lesssim 0.25$ and $\mu/k_F \gtrsim 1$, respectively.

We propose now simple approximations for $\epsilon_x^{\text{C},\text{sr},\mu}$ and $\epsilon_x^{\text{B},\text{sr},\mu}$ as rational interpolations between these small- and large- μ expansions. The short-range Coulomb exchange energy per particle can be approximated by

$$\epsilon_x^{\text{C},\text{sr},\mu} \approx \frac{\epsilon_x^{\text{C}} + d^{\text{C}}\mu}{1 + a^{\text{C}}\mu + b^{\text{C}}\mu^2 + c^{\text{C}}\mu^3}, \quad (3.56)$$

where the coefficients are determined to recover the μ and μ^2 terms of the small- μ expansion of Eq. (3.46) and the $1/\mu^2$ term and the vanishing $1/\mu^3$ term of the large- μ expansion of Eq. (3.52)

$$\begin{aligned} a^{\text{C}} &= \frac{3}{2\pi^{1/2}k_F} + \frac{24\pi^{3/2}}{k_F^3(1+h(\tilde{c}))}(\epsilon_x^{\text{C}})^2, \\ b^{\text{C}} &= -\frac{24\pi}{k_F^3(1+h(\tilde{c}))}\epsilon_x^{\text{C}}, \\ c^{\text{C}} &= -\frac{24\pi}{k_F^3(1+h(\tilde{c}))}d^{\text{C}}, \\ d^{\text{C}} &= \frac{1}{\pi^{1/2}} + a^{\text{C}}\epsilon_x^{\text{C}}. \end{aligned} \quad (3.57)$$

In a similar way, we propose to approximate the short-range Breit exchange energy per particle by

$$\epsilon_x^{\text{B},\text{sr},\mu} \approx \frac{\epsilon_x^{\text{B}} + d^{\text{B}}\mu}{1 + a^{\text{B}}\mu + b^{\text{B}}\mu^2 + c^{\text{B}}\mu^3}, \quad (3.58)$$

where the coefficients are again determined by imposing the small- μ expansion of Eq. (3.48) and the large- μ expansion of Eq. (3.54).

$$\begin{aligned}
a^B &= \frac{3(1-g(\tilde{c}))}{2\pi^{1/2}k_F(1-f(\tilde{c}))} + \frac{12\pi^{3/2}}{k_F^3(1-h(\tilde{c}))(1-f(\tilde{c}))}(\epsilon_x^B)^2, \\
b^B &= \frac{12\pi}{k_F^3(1-h(\tilde{c}))}\epsilon_x^B, \\
c^B &= \frac{12\pi}{k_F^3(1-h(\tilde{c}))}d^B, \\
d^B &= -\frac{(1-f(\tilde{c}))}{\pi^{1/2}} + a^B\epsilon_x^B.
\end{aligned} \tag{3.59}$$

Using the same form of approximation on directly the short-range Coulomb-Breit exchange energy per particle can lead to poles in μ , thus it is preferable to separately construct approximations for the Coulomb and Breit contributions and to sum them to get an approximation of the short-range Coulomb-Breit exchange energy per particle. This simple approximation is reported on Figure 3.5 where it can be seen that it is a quite good approximation to the accurate short-range Coulomb-Breit exchange energy per particle given by the Padé approximant of order 6. The relative error of this simple approximation is less than 5% for all values of k_F and μ . For higher accuracy, one could construct rational interpolations with more coefficients determined from higher-order terms in the small- and large- μ expansions. However, while the large- μ expansion could easily be obtained at an arbitrary order, higher-order terms in the small- μ expansion would be obtained as large- c asymptotic series that might not be always easy to sum into a closed form.

3.4 Conclusions

In this work, we have considered the extension of RS-DFT to a four-component relativistic framework using a Dirac-Coulomb-Breit Hamiltonian, and we have constructed a short-range LDA exchange density functional based on calculations on the RHEG with a modified electron-electron interaction. More specifically, we have provided the relativistic short-range Coulomb and Breit exchange energies per particle of the RHEG in the form of Padé approximants [Eqs. (3.39) and (3.44)], constructed from large- c asymptotic expansions (but without involving expansions with respect to μ) and which are systematically improvable to arbitrary accuracy. These quantities, as well as the associated effective Coulomb-Breit exchange hole of the RHEG, show the important impact of relativity on short-range exchange effects for high densities. We have also provided simpler approximations for the relativistic short-range Coulomb and Breit exchange energies per particle of the RHEG in the form of rational interpolations [Eqs. (3.56) and (3.58)] constructed from the exact small- and large- μ expansions (but without involving expansions with respect to c) of the short-range exchange energies per particle, which can also be used when a limited accuracy is sufficient (relative error less than 5%).

Possible continuation of this work includes the construction of a relativistic short-range LDA correlation density functional (even though relativistic effects are expected to be much smaller for correlation than for exchange), the construction of relativistic short-range GGA functionals, the inclusion of the dependence on the current for open-shell systems, and the implementation of these functionals in a four-component relativistic RS-DFT program for tests on atomic and molecular systems. In particular, for compounds with heavy elements, including relativistic effects in short-range functionals should have significant effects on quantities sensitive to atomic cores, such as total energies, NMR and EPR parameters, or X-ray spectra.

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Chapter 4

Relativistic short-range exchange energy functionals beyond the local-density approximation

This section corresponds to the article [J. Paquier, E. Giner and J.Toulouse, hal-02480263, to appear in J. Chem. Phys.].

<https://hal.sorbonne-universite.fr/hal-02480263>

We develop relativistic short-range exchange energy functionals for four-component relativistic range-separated density-functional theory using a Dirac-Coulomb Hamiltonian in the no-pair approximation. We show how to improve the short-range local-density approximation exchange functional for large range-separation parameters by using the on-top exchange pair density as a new variable. We also develop a relativistic short-range generalized-gradient approximation exchange functional which further increases the accuracy for small range-separation parameters. Tests on the helium, beryllium, neon, and argon isoelectronic series up to high nuclear charges show that this latter functional gives exchange energies with a maximal relative percentage error of 3%. The development of this exchange functional represents a step forward for the application of four-component relativistic range-separated density-functional theory to chemical compounds with heavy elements.

4.1 Introduction

Range-separated density-functional theory (RS-DFT) (see, e.g., Refs. [1, 2]) is an extension of Kohn-Sham density-functional theory (DFT) [3] which rigorously combines a wave-function method accounting for the long-range part of the electron-electron interaction with a complementary short-range density functional. RS-DFT has a faster basis convergence than standard wave-function methods [4] and can improve over usual Kohn-Sham density-functional approximations (DFAs) for the description of strong-correlation effects (see, e.g., Refs. [5, 6]) or weak intermolecular interactions (see, e.g., Refs. [7, 8]).

For the description of compounds with heavy elements, RS-DFT can be extended to a four-component relativistic framework [9–11]. In particular, in Refs. [9, 10], second-order Møller-Plesset perturbation theory and coupled-cluster theory based on a no-pair Dirac-Coulomb Hamiltonian with long-range electron-electron interaction were combined with short-range non-relativistic exchange-correlation DFAs and applied to heavy rare-gas dimers. One limitation, at least in principle, in these works is the neglect of relativity in the short-range density functionals. It is thus desirable to develop appropriate short-range relativistic exchange-correlation DFAs for four-component RS-DFT in order to quantify the error due to the neglect of relativity in the short-range density functionals and possibly increase the accuracy of these approaches. As a first step toward this, in Ref. [11] some of the present authors developed a short-range relativistic local density-functional approximation (srRLDA) exchange functional based on calculations

on the relativistic homogeneous electron gas (RHEG) with the Coulomb and Coulomb-Breit electron-electron interactions in the no-pair approximation.

In the present work we test this srRLDA exchange functional on atomic systems, namely the helium, beryllium, neon, and argon isoelectronic series up to high nuclear charges Z , using a four-component Dirac-Coulomb Hamiltonian in the no-pair approximation. We reveal that, for these relativistic ions with large Z , the srRLDA exchange functional is quite inaccurate even for large values of the range-separation parameter μ . We show how this functional can be improved by using the on-top exchange pair density as a new variable. Finally, we further improve the short-range relativistic exchange functional by constructing a generalized-gradient approximation (GGA), achieving a 3% maximal relative energy error.

The paper is organized as follows. In Section 4.2 we lay out the formalism of RS-DFT for a four-component relativistic Dirac-Coulomb Hamiltonian in the no-pair approximation. In Section 4.3 we give the computational details for our calculations. In Section 4.4 we test the srRLDA exchange functional and discuss its limitations. In Section 4.5 we improve the srRLDA exchange functional by using the on-top exchange pair density. In Section 4.6, we construct and test short-range relativistic exchange GGAs. Finally, Section 4.7 contains our conclusions.

4.2 Relativistic range-separated density-functional theory

Let us first discuss the choice of the relativistic quantum many-particle theory on which to base relativistic RS-DFT and the general strategy that we follow in this work. Clearly, since RS-DFT combines WFT and DFT, we need a relativistic framework which is convenient for both of them. Relativistic Kohn-Sham DFT has been formulated based on quantum electrodynamics (QED) [12–14], even though the no-pair approximation [15, 16] is normally introduced at a later stage for practical calculations. As regards WFT, the best tractable relativistic framework is the recently developed effective QED Hamiltonian [17–19] incorporating all QED effects obtained with non-retarded two-particle interactions. In the present work, we will stick however to the most common choice of the four-component Dirac-Coulomb Hamiltonian in the no-pair approximation, which can be used for both WFT and DFT. As explained in Ref. [20], this relativistic framework can be derived in several ways (see, e.g., Refs. [17–21]).

In the effective QED approach, the Hamiltonian is written in second quantization with normal ordering with respect to the vacuum state of empty positive-energy one-particle states and completely filled negative-energy one-particle states, while incorporating charge-conjugation symmetry. This Hamiltonian has a stable vacuum state and is physically meaningful. In this approach, the no-pair approximation, corresponding to projecting this Hamiltonian onto the many-electron subspace generated by positive-energy one-particle states, is just a convenient approximation (but in principle not necessary), akin to the idea of restricting the orbitals entering the wave function to an active orbital subspace in the complete-active-space self-consistent field method. The no-pair Dirac-Coulomb Hamiltonian is then obtained by further neglecting the effective QED one-particle potential corresponding to vacuum polarization and electron self-energy. By contrast, in the configuration-space approach, the Hamiltonian is written either in first quantization or, equivalently, in “naive” second quantization (i.e., without normal ordering with respect to a stable vacuum state). The resulting Hamiltonian has thus an unstable vacuum state, corresponding to empty positive-energy one-particle states and empty negative-energy one-particle states, it has no bound states (the electronic states that should be normally bound being embedded in the continuum of excitations to positive-energy states and deexcitations to negative-energy states), and hence is per se unphysical. However, by projecting this Hamiltonian onto the many-electron subspace generated by the positive-energy one-particle states, we recover the same physically relevant no-pair Dirac-Coulomb Hamiltonian as the one obtained by starting with the effective QED approach.

One drawback of the no-pair approximation is that the projector onto the subspace of electronic states depends on the separation between positive-energy and negative-energy one-particle states, and therefore depends on the potential used to generate these one-particle states. If the projector is applied to

the Hamiltonian, the whole resulting projected Hamiltonian is thus dependent on this potential. As mentioned in Ref. [14], this is problematic for formulating DFT since we cannot isolate, as normally done, an universal part of the Hamiltonian, and we thus cannot define universal density functionals. However, instead of thinking of the projector as being applied to the Hamiltonian, we can equivalently think of the projector as being applied to the considered many-body state and optimize the projector simultaneously with the wave function. In this way, we can introduce universal density functionals, similarly to non-relativistic DFT, defined such that for a given density a constrained-search optimization of the projected wave function will determine alone the optimal projector without the need of pre-choosing a particular potential, at least for systems for which positive-energy and negative-energy one-particle states can be unambiguously separated. Again, both the effective QED approach or the configuration-space approach can a priori be used for doing so. In the effective QED approach, the projector would be optimized (by rotations between positive-energy and negative-energy one-particle states) using an energy minimization principle. In the configuration-space approach, the projector is optimized (by rotations between positive-energy and negative-energy one-particle states) using a minmax principle [22–27].

In the present work, we follow the configuration-space approach and leave for future work the alternative formulation based on the effective QED approach. We thus start with the Dirac-Coulomb electronic Hamiltonian (see, e.g., Refs. [28, 29])

$$\hat{H} = \hat{T}_D + \hat{V}_{ne} + \hat{W}_{ee}, \quad (4.1)$$

where \hat{T}_D is the kinetic + rest mass Dirac operator, \hat{V}_{ne} is the nuclei-electron interaction operator, and \hat{W}_{ee} is the Coulomb electron-electron interaction operator. Using four-component creation and annihilation field operators $\hat{\Psi}^\dagger(\mathbf{r})$ and $\hat{\Psi}(\mathbf{r})$ without normal reordering with respect to a stable vacuum state. We thus write \hat{T}_D as

$$\hat{T}_D = \int \hat{\Psi}^\dagger(\mathbf{r}) [c(\boldsymbol{\alpha} \cdot \mathbf{p}) + \boldsymbol{\beta} mc^2] \hat{\Psi}(\mathbf{r}) \, d\mathbf{r}, \quad (4.2)$$

where $\mathbf{p} = -i\nabla_{\mathbf{r}}$ is the momentum operator, $c = 137.036$ a.u. is the speed of light, $m = 1$ a.u. is the electron mass, and $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are the 4×4 Dirac matrices

$$\boldsymbol{\alpha} = \begin{pmatrix} \mathbf{0}_2 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0}_2 \end{pmatrix} \text{ and } \boldsymbol{\beta} = \begin{pmatrix} \mathbf{I}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & -\mathbf{I}_2 \end{pmatrix}, \quad (4.3)$$

where $\boldsymbol{\sigma} = (\boldsymbol{\sigma}_x, \boldsymbol{\sigma}_y, \boldsymbol{\sigma}_z)$ is the 3-dimensional vector of the 2×2 Pauli matrices, and $\mathbf{0}_2$ and \mathbf{I}_2 are the 2×2 zero and identity matrices, respectively. Similarly, \hat{V}_{ne} and \hat{W}_{ee} have the expressions

$$\hat{V}_{ne} = \int v_{ne}(\mathbf{r}) \hat{n}(\mathbf{r}) \, d\mathbf{r}, \quad (4.4)$$

where $v_{ne}(\mathbf{r})$ is the nuclei-electron potential, and

$$\hat{W}_{ee} = \frac{1}{2} \iint w_{ee}(r_{12}) \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2, \quad (4.5)$$

where $w_{ee}(r_{12}) = 1/r_{12}$ is the Coulomb electron-electron potential, and $\hat{n}(\mathbf{r}) = \hat{\Psi}^\dagger(\mathbf{r})\hat{\Psi}(\mathbf{r})$ and $\hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) = \hat{\Psi}^\dagger(\mathbf{r}_1)\hat{\Psi}^\dagger(\mathbf{r}_2)\hat{\Psi}(\mathbf{r}_2)\hat{\Psi}(\mathbf{r}_1)$ are the density and pair density operators, respectively. Introducing a set of orthonormal 4-component-spinor orbitals $\{\psi_p(\mathbf{r})\}$ which are eigenfunctions of a one-particle Dirac Hamiltonian with some potential, and assuming that this set of orbitals can be partitioned into a set of positive-energy (electronic) orbitals and a set of negative-energy (positronic) orbitals, $\{\psi_p(\mathbf{r})\} = \{\psi_p(\mathbf{r})\}_{\epsilon_p > 0} \cup \{\psi_p(\mathbf{r})\}_{\epsilon_p < 0}$, the no-pair [15, 16] relativistic ground-state energy of a N -electron system can be defined using a minmax principle [22–27], that we will formally write as,

$$E_0 = \min_{\Psi_+} \max \langle \Psi_+ | \hat{T}_D + \hat{V}_{ne} + \hat{W}_{ee} | \Psi_+ \rangle. \quad (4.6)$$

In this equation, we search over normalized wave functions of the form $|\Psi_+\rangle = \hat{P}_+|\Psi\rangle$, where \hat{P}_+ is the projector on the N -electron-state space generated by the set of positive-energy orbitals $\{\psi_p(\mathbf{r})\}_{\varepsilon_p>0}$ and $|\Psi\rangle$ is a general N -electron antisymmetric wave function, and the notation $\min_{\Psi} \max_{\hat{P}_+} = \max_{\hat{P}_+} \min_{\Psi}$ means a minimization with respect to Ψ and a maximization with respect to \hat{P}_+ . This maximization must be done by rotations of the positive-energy orbitals $\{\psi_p(\mathbf{r})\}_{\varepsilon_p>0}$ with its complement set of negative-energy orbitals $\{\psi_p(\mathbf{r})\}_{\varepsilon_p<0}$. Here, we have assumed that the optimum of the minmax is a saddle point in the wave-function parameter space (which can be calculated with a multi-configuration self-consistent-field (MCSCF) algorithm [27, 30, 31]), so that the same energy is obtained whatever the order of \min_{Ψ} and $\max_{\hat{P}_+}$. Note that, in the non-relativistic limit ($c \rightarrow \infty$), the energy gap between positive- and negative-energy orbitals of order $2mc^2$ goes to infinity and the maximization over \hat{P}_+ becomes useless, and thus the minmax principle properly reduces to the non-relativistic minimization principle. Now we attempt to formulate a relativistic DFT within this no-pair approximation. Following the spirit of the constrained-search formulation of non-relativistic DFT [32, 33], we propose to define the no-pair relativistic universal density functional as

$$\begin{aligned} F[n] &= \min_{\Psi_+ \rightarrow n} \max \langle \Psi_+ | \hat{T}_D + \hat{W}_{ee} | \Psi_+ \rangle \\ &= \langle \Psi_+[n] | \hat{T}_D + \hat{W}_{ee} | \Psi_+[n] \rangle, \end{aligned} \quad (4.7)$$

where the minmax procedure is identical to that in Eq. (4.6) except for the additional constraint that Ψ_+ yields the density n , i.e. $\langle \Psi_+ | \hat{n}(\mathbf{r}) | \Psi_+ \rangle = n(\mathbf{r})$. In Eq. (4.7), $\Psi_+[n]$ is the optimal wave function for the density n . We will again assume that the optimum of the minmax is a saddle point in the density-constrained wave-function parameter subspace. Of course, this functional is only defined for densities which come from a wave function of the form of Ψ_+ , which we will refer to as Ψ_+ -representable densities. Note that, consistently with neglecting the Breit electron-electron interaction, we will only consider functionals of the density and not of the density current. The no-pair relativistic ground-state energy of Eq. (4.6) can be in principle obtained from $F[n]$ as a stationary point with respect to variations over Ψ_+ -representable densities

$$E_0 \in \text{stat}_n \left\{ F[n] + \int v_{ne}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right\}, \quad (4.8)$$

where we have introduced the notation stat_n to designate the set of stationary energies with respect to variations of n . Due to the minmax principle in Eqs. (4.6) and (4.7), we can only assume a stationary principle in Eq. (4.8), instead of the usual non-relativistic minimization principle over densities. This situation is in fact similar to the problem of formulating a pure-state time-independent variational extension of DFT for excited-state energies [34, 35]. We now define a no-pair relativistic long-range universal density functional, similarly to Eq. (4.7), as

$$\begin{aligned} F^{\text{lr},\mu}[n] &= \min_{\Psi_+ \rightarrow n} \max \langle \Psi_+ | \hat{T}_D + \hat{W}_{ee}^{\text{lr},\mu} | \Psi_+ \rangle \\ &= \langle \Psi_+^\mu[n] | \hat{T}_D + \hat{W}_{ee}^{\text{lr},\mu} | \Psi_+^\mu[n] \rangle, \end{aligned} \quad (4.9)$$

with the long-range electron-electron interaction operator $\hat{W}_{ee}^{\text{lr},\mu} = (1/2) \iint w_{ee}^{\text{lr},\mu}(r_{12}) \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$ where $w_{ee}^{\text{lr},\mu}(r_{12}) = \text{erf}(\mu r_{12})/r_{12}$ is the long-range electron-electron potential and μ is the range-separation parameter. In Eq. (4.9) $\Psi_+^\mu[n]$ is the optimal wave function for the density n and range-separation parameter μ . We can thus decompose the density functional $F[n]$ as

$$F[n] = F^{\text{lr},\mu}[n] + \bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n], \quad (4.10)$$

which defines the complement relativistic short-range Hartree-exchange-correlation density functional $\bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n]$. Plugging Eq. (4.10) into Eq. (4.8), we conclude that the no-pair relativistic ground-state energy

of Eq. (4.6) corresponds to a stationary point of the following range-separated energy expression over Ψ_+ wave functions

$$E_0 \in \text{stat}_{\Psi_+} \left\{ \langle \Psi_+ | \hat{T}_D + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr}, \mu} | \Psi_+ \rangle + \bar{E}_{\text{Hxc}}^{\text{sr}, \mu}[n_{\Psi_+}] \right\}, \quad (4.11)$$

where n_{Ψ_+} is the density of Ψ_+ . For practical calculations, we will *assume* that the no-pair relativistic ground-state energy corresponds in fact to the minmax search over Ψ_+

$$E_0 = \text{minmax}_{\Psi_+} \left\{ \langle \Psi_+ | \hat{T}_D + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr}, \mu} | \Psi_+ \rangle + \bar{E}_{\text{Hxc}}^{\text{sr}, \mu}[n_{\Psi_+}] \right\}. \quad (4.12)$$

Even though we do not see any guarantee that this is always true, it seems a reasonable working assumption for practical calculations. In fact, it corresponds to what is done in practice in no-pair Kohn-Sham DFT calculations [36–45], which corresponds to Eq. (4.12) in the special case of $\mu = 0$, i.e.

$$E_0 = \text{minmax}_{\Phi_+} \left\{ \langle \Phi_+ | \hat{T}_D + \hat{V}_{\text{ne}} | \Phi_+ \rangle + E_{\text{Hxc}}[n_{\Phi_+}] \right\}, \quad (4.13)$$

where the wave function can be restricted to a single determinant Φ_+ and $E_{\text{Hxc}}[n]$ is the relativistic Kohn-Sham Hartree-exchange-correlation density functional. Another special case of Eq. (4.12) is for $\mu \rightarrow \infty$ for which we correctly recover the wave-function theory of Eq. (4.6). As usual, we can decompose the complement relativistic short-range Hartree-exchange-correlation density functional into separate components

$$\bar{E}_{\text{Hxc}}^{\text{sr}, \mu}[n] = E_{\text{H}}^{\text{sr}, \mu}[n] + E_{\text{x}}^{\text{sr}, \mu}[n] + \bar{E}_{\text{c}}^{\text{sr}, \mu}[n]. \quad (4.14)$$

In this expression, $E_{\text{H}}^{\text{sr}, \mu}[n]$ is the short-range Hartree density functional (which has the same expression as in the non-relativistic case)

$$E_{\text{H}}^{\text{sr}, \mu}[n] = \frac{1}{2} \iint w_{\text{ee}}^{\text{sr}, \mu}(r_{12}) n(\mathbf{r}_1) n(\mathbf{r}_2) \mathbf{d}\mathbf{r}_1 \mathbf{d}\mathbf{r}_2, \quad (4.15)$$

where $w_{\text{ee}}^{\text{sr}, \mu}(r_{12}) = w_{\text{ee}}(r_{12}) - w_{\text{ee}}^{\text{lr}, \mu}(r_{12})$ is the short-range electron-electron potential, $E_{\text{x}}^{\text{sr}, \mu}[n]$ is the relativistic short-range exchange density functional

$$E_{\text{x}}^{\text{sr}, \mu}[n] = \langle \Phi_+[n] | \hat{W}_{\text{ee}}^{\text{sr}, \mu} | \Phi_+[n] \rangle - E_{\text{H}}^{\text{sr}, \mu}[n], \quad (4.16)$$

where $\Phi_+[n] = \Psi_+^{\mu=0}[n]$ is the relativistic Kohn-Sham single-determinant wave function and $\hat{W}_{\text{ee}}^{\text{sr}, \mu} = (1/2) \iint w_{\text{ee}}^{\text{sr}, \mu}(r_{12}) \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) \mathbf{d}\mathbf{r}_1 \mathbf{d}\mathbf{r}_2$ is the short-range electron-electron interaction operator, and $\bar{E}_{\text{c}}^{\text{sr}, \mu}[n]$ is the complement relativistic short-range correlation density functional. In Appendix J, we show that the relativistic short-range exchange density functional $E_{\text{x}}^{\text{sr}, \mu}[n]$ satisfies a uniform coordinate scaling relation [Eq. (J.7)] which represents an important constraint to impose in approximations.

Even though the present formulation of relativistic range-separated DFT seems reasonable for practical chemical applications, it obviously calls for a closer mathematical examination of its domain of validity. In particular, it is clear that the minmax principle of the no-pair approximation in the configuration-space approach breaks down in the strong relativistic regime (i.e., for nuclear charges $Z \gtrsim c$). Of course, in the non-relativistic limit ($c \rightarrow \infty$), relativistic RS-DFT properly reduces to non-relativistic RS-DFT.

4.3 Computational setup

We consider the helium, beryllium, neon, and argon isoelectronic series, up to the uranium nuclear charge $Z = 92$. The electronic density $n(\mathbf{r})$ naturally increases at the nucleus with Z and can be conveniently measured with k_{Fmax} , i.e. the maximal value taken at the nucleus by the local Fermi wave vector $k_{\text{F}}(\mathbf{r}) = (3\pi^2 n(\mathbf{r}))^{1/3}$. The strength of the relativistic effects can be measured by comparing the local Fermi wave

vector $k_F(\mathbf{r})$ to the speed of light $c \simeq 137.036$ a.u. (with $\hbar = m_e = 1$ a.u.): very little relativistic effects are expected in regions where $k_F(\mathbf{r}) \ll c$, while strong relativistic effects are expected in regions where $k_F(\mathbf{r}) \gtrsim c$.

To test the different functionals, we have first performed four-component Dirac Hartree-Fock (DHF) calculations based on the relativistic Dirac-Coulomb Hamiltonian with point-charge nucleus, using our own program implemented as a plugin of the software QUANTUM PACKAGE 2.0 [46]. For the helium series, we use the dyall_1s2.3z basis set of Ref. [27] except for Yb⁶⁸⁺ and U⁹⁰⁺ for which the basis set was not available. For these systems, as well as for the beryllium, neon, and argon series, we construct uncontracted even-tempered Gaussian-type orbital basis sets [47], following the primitive structure of the dyall-cvdz basis sets for He, Be, Ne, and Ar [48]. For each system and angular momentum, the exponents of the large-component basis functions are taken as the geometric series

$$\zeta_v = \zeta_1 q^{v-1}, \quad (4.17)$$

where ζ_1 is chosen among the largest exponents from the dyall-cvdz basis set for the given element and angular momentum [48, 49], and the parameter q is optimized by minimizing the DHF total energy. The small-component basis functions are generated from the unrestricted kinetic-balance scheme [?]. The basis-set parameters are given in Appendix L. Using the previously obtained DHF orbitals, we then estimate the short-range exact exchange energy

$$E_x^{\text{sr},\mu} = \frac{1}{2} \iint w_{ee}^{\text{sr},\mu}(r_{12}) n_{2,x}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (4.18)$$

where $n_{2,x}(\mathbf{r}_1, \mathbf{r}_2)$ is the exchange pair density

$$n_{2,x}(\mathbf{r}_1, \mathbf{r}_2) = -\text{Tr}[\gamma(\mathbf{r}_1, \mathbf{r}_2)\gamma(\mathbf{r}_2, \mathbf{r}_1)], \quad (4.19)$$

and $\gamma(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^N \psi_i(\mathbf{r}_1)\psi_i^\dagger(\mathbf{r}_2)$ is the 4×4 one-electron density matrix written with the four-component spinor occupied orbitals $\{\psi_i(\mathbf{r})\}$. This short-range DHF exchange energy is used as the reference for testing the different exchange energy functionals, which are evaluated with the DHF density $n(\mathbf{r}) = \text{Tr}[\gamma(\mathbf{r}, \mathbf{r})]$ (and the DHF exchange on-top pair density for some of them, see below) using a SG-2-type quadrature grid [50] with the radial grid of Ref. [51].

4.4 Short-range exchange local-density approximations

The non-relativistic short-range local-density approximation (srLDA) for the exchange functional has the expression

$$E_x^{\text{sr,LDA},\mu}[n] = \int n(\mathbf{r}) \epsilon_x^{\text{sr,HEG},\mu}(n(\mathbf{r})) d\mathbf{r}, \quad (4.20)$$

where the non-relativistic short-range homogeneous electron gas (HEG) exchange energy per particle $\epsilon_x^{\text{sr,HEG},\mu}(n)$ can be found in Refs. [1, 52, 53]. The relativistic generalization of this functional, referred to as srRLDA, is

$$E_x^{\text{sr,RLDA},\mu}[n] = \int n(\mathbf{r}) \epsilon_x^{\text{sr,RHEG},\mu}(n(\mathbf{r})) d\mathbf{r}, \quad (4.21)$$

where the short-range RHEG exchange energy per particle $\epsilon_x^{\text{sr,RHEG},\mu}(n)$ is given in Ref. [11] with arbitrary accuracy as systematic Padé approximants with respect to the dimensionless variable $\tilde{c} = c/k_F = c/(3\pi^2 n)^{1/3}$ (we employ here the Padé approximant of order 6) with coefficients written as functions of the dimensionless range-separation parameter μ/k_F . The dependence of $\epsilon_x^{\text{sr,RHEG},\mu}(n)$ on the dimensionless parameters \tilde{c} and μ/k_F is a consequence of the uniform coordinate scaling relation of Eq. (J.7) which is valid of the RHEG.

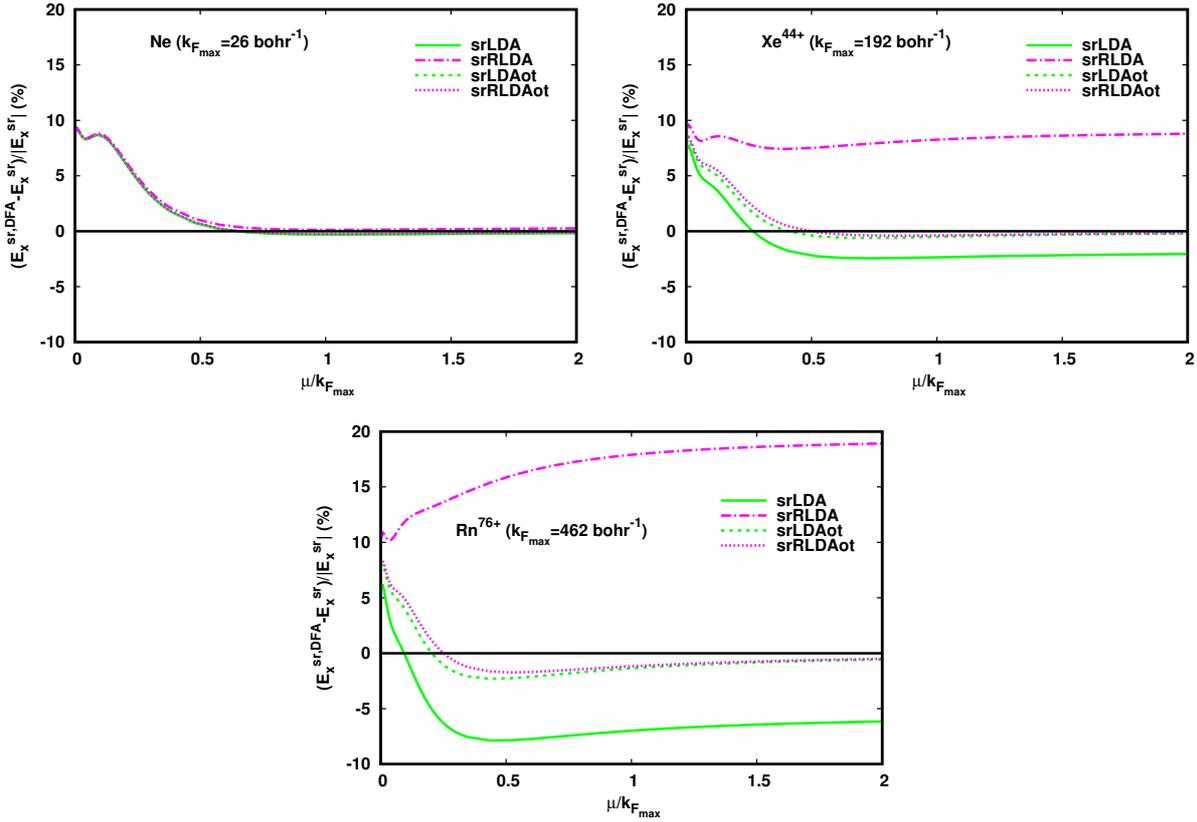


Figure 4.1: Relative percentage error on the short-range exchange energy calculated with the srLDA, srRLDA, srLDAot, srRLDAot functionals for three representative members of the neon isoelectronic series (Ne, Xe⁴⁴⁺, and Rn⁷⁶⁺).

The relative percentage errors of the srLDA and srRLDA exchange functionals with respect to the short-range DHF exchange energy, i.e. $100 \times (E_x^{\text{sr,DFA},\mu} - E_x^{\text{sr},\mu}) / |E_x^{\text{sr},\mu}|$, are plotted in Fig. 4.1 as a function of the dimensionless range-separation parameter $\mu/k_{F_{\text{max}}}$ for three representative members of the neon isoelectronic series (Ne, Xe⁴⁴⁺ and Rn⁷⁶⁺). The relativistic effects go from very small for Ne to very large for Rn⁷⁶⁺. For $\mu = 0$, the short-range interaction reduces to the full-range Coulomb interaction, and we observe that both the non-relativistic and relativistic LDA exchange functionals underestimate (in absolute value) the DHF exchange energy by 5% to 10%. As previously noted [54], the non-relativistic LDA exchange functional (evaluated with a relativistic density) fortuitously gives exchange energies with lower errors than the relativistic LDA exchange functional for systems with significant relativistic effects (Xe⁴⁴⁺, and Rn⁷⁶⁺). When μ increases, the srLDA and srRLDA exchange functionals show quite different behaviors for these relativistic systems. The relative error of the srLDA exchange energy changes sign with μ and eventually goes to a negative constant for $\mu \rightarrow \infty$, corresponding to an overestimation in absolute value. By contrast, the relative error of the srRLDA exchange energy always remains positive and goes to a positive constant for $\mu \rightarrow \infty$, corresponding to an underestimation in absolute value. The more relativistic the system is, the largest this overestimation or underestimation is. While for Ne at large μ both the srLDA and srRLDA exchange functionals have almost vanishing relative errors, for Rn⁷⁶⁺ at large μ the srLDA exchange energy is too negative by a little more than 5% and the srRLDA exchange energy is too positive by almost 20%. Clearly, both the srLDA and srRLDA exchange functionals are not accurate for relativistic systems.

In non-relativistic theory, it is known that the srLDA exchange functional becomes exact for large μ [2], which is one of the key advantages of RS-DFT. As apparent from Figure 4.1, for relativistic systems, this nice property does not hold anymore for both the srLDA and srRLDA exchange functionals.

This observation can be understood by using the distributional asymptotic expansion of the short-range interaction for large μ [2]

$$w_{ee}^{\text{sr},\mu}(r_{12}) = \frac{\pi}{\mu^2} \delta(\mathbf{r}_{12}) + O\left(\frac{1}{\mu^3}\right), \quad (4.22)$$

which directly leads to the asymptotic expansion of the short-range exact exchange energy

$$E_x^{\text{sr},\mu} = \frac{\pi}{2\mu^2} \int n_{2,x}(\mathbf{r}, \mathbf{r}) \, d\mathbf{r} + O\left(\frac{1}{\mu^4}\right), \quad (4.23)$$

where $n_{2,x}(\mathbf{r}, \mathbf{r})$ is the on-top exchange pair density. In the non-relativistic theory, considering the case of closed-shell systems for the sake of simplicity, the on-top exchange pair density is simply given in terms of the density as [55]

$$n_{2,x}^{\text{NR}}(\mathbf{r}, \mathbf{r}) = -\frac{n(\mathbf{r})^2}{2}, \quad (4.24)$$

and the srLDA exchange functional becomes indeed exact for large μ

$$E_x^{\text{sr,LDA},\mu}[n] = \frac{\pi}{2\mu^2} \int n_{2,x}^{\text{HEG},0}(n(\mathbf{r})) \, d\mathbf{r} + O\left(\frac{1}{\mu^4}\right), \quad (4.25)$$

with the on-top exchange pair density of the non-relativistic HEG

$$n_{2,x}^{\text{HEG},0}(n) = -\frac{n^2}{2}. \quad (4.26)$$

In the relativistic theory, the on-top exchange pair density is no longer a simple function of the density

$$n_{2,x}(\mathbf{r}, \mathbf{r}) = -\text{Tr}[\gamma(\mathbf{r}, \mathbf{r})^2], \quad (4.27)$$

which is not equal to $-n(\mathbf{r})^2/2$, except in the special case of two electrons in a unique Kramers pair (see Appendix K). Therefore, for relativistic systems with more than two electrons, we see that the srLDA exchange functional is not exact for large μ [Eq. (4.25)]. The srRLDA exchange functional is also not exact for large μ . It takes the form

$$E_x^{\text{sr,RLDA},\mu}[n] = \frac{\pi}{2\mu^2} \int n_{2,x}^{\text{RHEG},0}(n(\mathbf{r})) \, d\mathbf{r} + O\left(\frac{1}{\mu^4}\right), \quad (4.28)$$

with the on-top exchange pair density of the RHEG

$$n_{2,x}^{\text{RHEG},0}(n) = -\frac{n^2}{4}(1 + h(\tilde{c})), \quad (4.29)$$

and the function [11]

$$h(\tilde{c}) = \frac{9}{4} \left[\tilde{c}^2 + \tilde{c}^4 - \tilde{c}^4 \text{arcsinh}\left(\frac{1}{\tilde{c}}\right) \left(2\sqrt{1 + \tilde{c}^2} - \tilde{c}^2 \text{arcsinh}\left(\frac{1}{\tilde{c}}\right) \right) \right]. \quad (4.30)$$

For an alternative but equivalent expression for $n_{2,x}^{\text{RHEG},0}(n)$, see Eq. (A1) of Ref. [38]. The srRLDA exchange functional is in fact not even exact at large μ for two electrons in a unique Kramers pair. In Section 4.5, we show how to impose the large- μ behavior on the srLDA and srRLDA exchange functionals.

4.5 Short-range exchange local-density approximations with on-top exchange pair density

In order to impose the correct large- μ behavior of the srLDA and srRLDA exchange functionals for relativistic systems, we need to introduce a new ingredient in these functionals, namely the exact (relativistic) on-top exchange pair density $n_{2,x}(\mathbf{r}, \mathbf{r})$, or equivalently the on-top exchange hole

$$n_x(\mathbf{r}, \mathbf{r}) = \frac{n_{2,x}(\mathbf{r}, \mathbf{r})}{n(\mathbf{r})}. \quad (4.31)$$

A simple way to use $n_x(\mathbf{r}, \mathbf{r})$ to correct the srLDA exchange functional is to find, at each position \mathbf{r} , the effective density $n_{\text{eff}}(\mathbf{r})$ at which the on-top exchange hole of the HEG, $n_x^{\text{HEG},0}(n) = n_{2,x}^{\text{HEG},0}(n)/n = -n/2$, is equal to the on-top exchange hole of the inhomogeneous system considered, $n_x(\mathbf{r}, \mathbf{r})$, i.e.

$$n_x^{\text{HEG},0}(n_{\text{eff}}(\mathbf{r})) = n_x(\mathbf{r}, \mathbf{r}), \quad (4.32)$$

which simply gives $n_{\text{eff}}(\mathbf{r}) = -2n_x(\mathbf{r}, \mathbf{r})$. We then define the srLDA exchange functional with the on-top exchange pair density (srLDAot) using this effective density as

$$E_x^{\text{sr,LDAot},\mu}[n] = \int n(\mathbf{r}) \epsilon_x^{\text{sr,HEG},\mu}(n_{\text{eff}}(\mathbf{r})) \, d\mathbf{r}. \quad (4.33)$$

This approximation could be considered either as an implicit functional of the density alone since $n_x(\mathbf{r}, \mathbf{r})$ is an implicit functional of the density through the orbitals, or as an explicit functional of both the density and the on-top exchange hole $n_x(\mathbf{r}, \mathbf{r})$. This approximation corresponds to changing the transferability criterion in the LDA: at a given point \mathbf{r} , instead of taking the exchange energy per particle of the HEG having the same density than the inhomogeneous system at that point, we now take the exchange energy per particle of the HEG having the same on-top exchange hole than the inhomogeneous system at that point. Interestingly, this approximation can be thought of as a particular application of the recently formalized connector theory [56, 57]. Similarly, we can correct the srRLDA exchange functional by finding, at each position \mathbf{r} , the effective density $n_{\text{eff}}^{\text{R}}(\mathbf{r})$ at which the on-top exchange hole of the RHEG, $n_x^{\text{RHEG},0}(n) = n_{2,x}^{\text{RHEG},0}(n)/n = -(n/4)(1 + h(\tilde{c}))$, is equal to the on-top exchange hole of the inhomogeneous system considered, $n_x(\mathbf{r}, \mathbf{r})$, i.e.

$$n_x^{\text{RHEG},0}(n_{\text{eff}}^{\text{R}}(\mathbf{r})) = n_x(\mathbf{r}, \mathbf{r}). \quad (4.34)$$

This equation is less trivial to solve than Eq. (4.32) since $n_x^{\text{RHEG},0}(n)$ is a complicated nonlinear function of n (through \tilde{c}). However, at each point \mathbf{r} , a unique solution $n_{\text{eff}}^{\text{R}}(\mathbf{r})$ exists since the function $n \mapsto n_x^{\text{RHEG},0}(n)$ is monotonically decreasing and spans the domain $] -\infty, 0]$ in which $n_x(\mathbf{r}, \mathbf{r})$ necessarily belongs. In practice, we easily find $n_{\text{eff}}^{\text{R}}(\mathbf{r})$ by a numerical iterative method, and we use it to define the srRLDA exchange functional with the on-top exchange pair density (srRLDAot) as

$$E_x^{\text{sr,RLDAot},\mu}[n] = \int n(\mathbf{r}) \epsilon_x^{\text{sr,RHEG},\mu}(n_{\text{eff}}^{\text{R}}(\mathbf{r})) \, d\mathbf{r}. \quad (4.35)$$

Both the srLDAot and srRLDAot exchange functionals now fulfil the exact asymptotic expansion for large μ [Eq. (4.23)]. In fact, restoring the correct on-top value of the exchange hole could be beneficial for any value of μ , given the fact that the accuracy of non-relativistic Kohn-Sham exchange DFAs has been justified by the exactness of the underlying LDA on-top exchange hole (in addition to fulfilling the correct sum rule of the exchange hole) [58]. Finally, we note that, in the non-relativistic limit ($c \rightarrow \infty$), we have $n_{\text{eff}}(\mathbf{r}) = n_{\text{eff}}^{\text{R}}(\mathbf{r}) = n(\mathbf{r})$ and all these short-range exchange functionals reduce to the non-relativistic srLDA exchange functional (i.e., srLDAot = srRLDAot = srRLDA = srLDA).

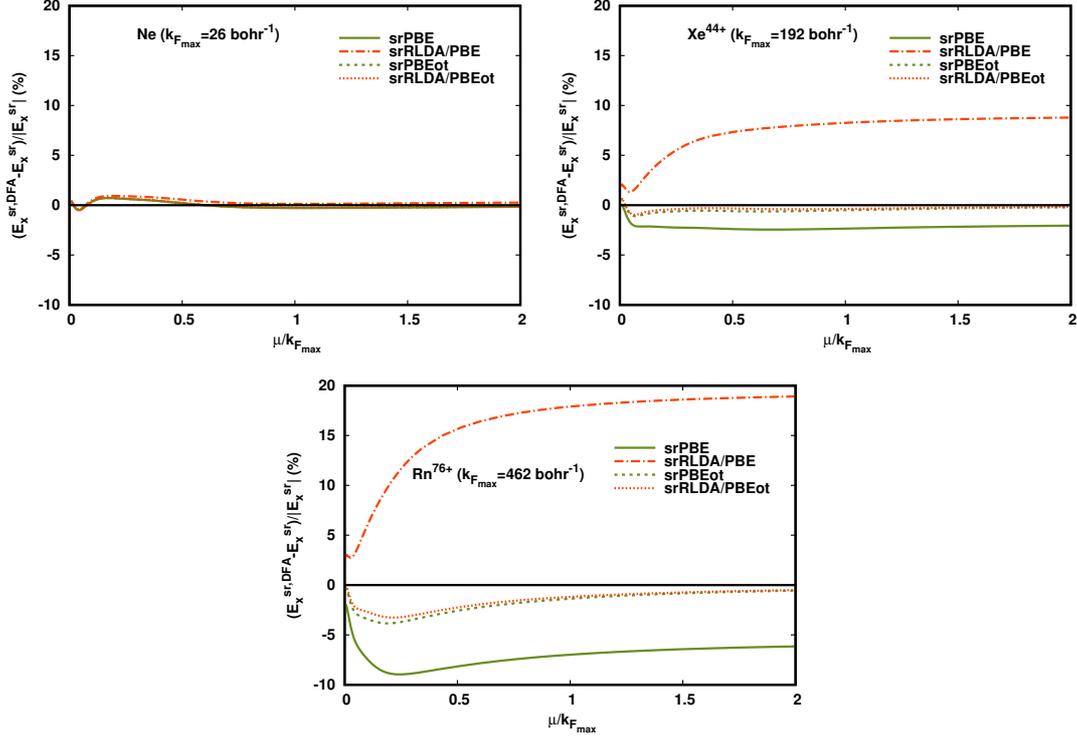


Figure 4.2: Relative percentage error on the short-range exchange energy calculated with the srPBE, srRLDA/PBE, srPBEot, srRLDA/PBEot functionals for three representative members of the neon isoelectronic series (Ne, Xe⁴⁴⁺, and Rn⁷⁶⁺).

The relative percentage errors of the srLDAot and srRLDAot exchange functionals for Ne, Xe⁴⁴⁺, and Rn⁷⁶⁺ are reported in Figure 4.1. The most prominent feature is of course the correct recovery of the large- μ asymptotic behavior for both the srLDAot and srRLDAot exchange functionals. It turns out the srLDAot and srRLDAot exchange functionals give very similar exchange energies for all values of μ . This comes from the fact that when going from srLDA to srLDAot Eq. (4.32) tends to make the LDA exchange hole shallower and when going from srRLDA to srRLDAot Eq. (4.34) tends to make the relativistic LDA exchange hole deeper, making finally for very close descriptions. The absolute relative percentage errors of the srLDAot and srRLDAot exchange functionals are always below 10%, and below about 2% for $\mu/k_{F_{\text{max}}} \geq 0.5$.

4.6 Short-range exchange generalized-gradient approximations

In order to improve over the short-range LDA exchange functionals at small values of the range-separation parameter μ , we now consider short-range GGA exchange functionals. We start with the non-relativistic short-range extension of the Perdew-Burke-Ernzerhof (PBE) [59] of Refs. [60, 61], referred to as srPBE,

$$E_x^{\text{sr,PBE},\mu}[n] = \int n(\mathbf{r}) \varepsilon_x^{\text{sr,HEG},\mu}(n(\mathbf{r})) [1 + f_x^\mu(n(\mathbf{r}), \nabla n(\mathbf{r}))] d\mathbf{r}, \quad (4.36)$$

with the function

$$f_x^\mu(n, \nabla n) = \kappa - \frac{\kappa}{1 + b(\tilde{\mu})s^2/\kappa}, \quad (4.37)$$

where $s = |\nabla n|/(2k_F n)$ is the reduced density gradient and $\tilde{\mu} = \mu/(2k_F)$ is a dimensionless range-separation parameter. In this expression, $\kappa = 0.840$ is a constant fixed by imposing the Lieb-Oxford

bound (for $\mu = 0$) and $b(\tilde{\mu}) = b^{\text{PBE}}[b^{\text{T}}(\tilde{\mu})/b^{\text{T}}(0)]e^{-\alpha_x \tilde{\mu}^2}$ where $b^{\text{PBE}} = 0.21951$ is the second-order gradient-expansion coefficient of the standard PBE exchange functional, $b^{\text{T}}(\tilde{\mu})$ is a function coming from the second-order gradient-expansion approximation (GEA) of the short-range exchange energy and given in Refs. [62, 63], and $\alpha_x = 19.0$ is a damping parameter optimized on the He atom. For $\mu = 0$, this srPBE exchange functional reduces to the standard PBE exchange functional [59], and for large μ it reduces to the srLDA exchange functional. A simple relativistic extension of this srPBE exchange functional can be obtained by replacing the srLDA part by the srRLDA one while using the same density-gradient correction $f_x^\mu(n, \nabla n)$, to which we will refer as srRLDA/PBE,

$$E_x^{\text{sr,RLDA/PBE},\mu}[n] = \int n(\mathbf{r}) \varepsilon_x^{\text{sr,RHEG},\mu}(n(\mathbf{r})) [1 + f_x^\mu(n(\mathbf{r}), \nabla n(\mathbf{r}))] d\mathbf{r}, \quad (4.38)$$

which reduces to the srRLDA exchange functional for large μ . The srPBE and srRLDA/PBE exchange functionals have the same (incorrect) asymptotic expansions as the srLDA and srRLDA exchange functionals [Eqs. (4.25) and (4.28)], and we can thus use the same effective densities in Eqs. (4.32) and (4.34) to restore their large- μ behaviors, which defines the srPBEot and srRLDA/PBEot exchange functionals

$$E_x^{\text{sr,PBEot},\mu}[n] = \int n(\mathbf{r}) \varepsilon_x^{\text{sr,RHEG},\mu}(n_{\text{eff}}(\mathbf{r})) [1 + f_x^\mu(n_{\text{eff}}(\mathbf{r}), \nabla n_{\text{eff}}(\mathbf{r}))] d\mathbf{r}, \quad (4.39)$$

where $\nabla n_{\text{eff}}(\mathbf{r}) = -2\nabla n_x(\mathbf{r}, \mathbf{r})$, and

$$E_x^{\text{sr,RLDA/PBEot},\mu}[n] = \int n(\mathbf{r}) \varepsilon_x^{\text{sr,RHEG},\mu}(n_{\text{eff}}^{\text{R}}(\mathbf{r})) [1 + f_x^\mu(n_{\text{eff}}^{\text{R}}(\mathbf{r}), \nabla n_{\text{eff}}^{\text{R}}(\mathbf{r}))] d\mathbf{r}, \quad (4.40)$$

where $\nabla n_{\text{eff}}^{\text{R}}(\mathbf{r}) = [dn_x^{\text{RHEG},0}(n_{\text{eff}}^{\text{R}}(\mathbf{r}))/dn_{\text{eff}}^{\text{R}}]^{-1} \nabla n_x(\mathbf{r}, \mathbf{r})$. In Figure 4.2, we report the relative percentage errors of the srPBE, srRLDA/PBE, srPBEot, and srRLDA/PBEot exchange energies for Ne, Xe⁴⁴⁺, and Rn⁷⁶⁺. For Ne, where the relativistic effects are very small, all these functionals give almost the same exchange energy, as expected. For Xe⁴⁴⁺ and Rn⁷⁶⁺, even though the srPBE and srRLDA/PBE exchange functionals are more accurate than the srLDA and srRLDA exchange functionals at $\mu = 0$ (see Figure 4.1), they eventually suffer from the same large inaccuracy as srLDA and srRLDA as μ increases. This problem is solved by using the effective densities from the on-top exchange pair density, the srPBEot and srRLDA/PBEot exchange functionals giving vanishing errors at large μ . Similarly to what was observed for srLDAot and srRLDAot, the srPBEot and srRLDA/PBEot functionals give very close exchange energies for all values of μ . Interestingly, we see that using the effective densities also reduces the errors of srPBE and srRLDA/PBE at $\mu = 0$, making srPBEot and srRLDA/PBEot quite accurate in this full-range limit. Thus, the srPBEot and srRLDA/PBEot exchange functionals are definitely an improvement over srLDAot and srRLDAot. We observe a maximal absolute percentage error of about 3% for Rn⁷⁶⁺ for $\mu/k_{\text{F,max}} \approx 0.2$.

In order to further reduce the errors, in particular for intermediate values of μ , we now consider a relativistic correction to the density-gradient term in the srRLDA/PBEot exchange functional. We define a short-range relativistic PBE exchange functional using the on-top exchange pair density, referred to as srRPBEot,

$$E_x^{\text{sr,RPBEot},\mu}[n] = \int n(\mathbf{r}) \varepsilon_x^{\text{sr,RHEG},\mu}(n_{\text{eff}}^{\text{R}}(\mathbf{r})) [1 + f_x^\mu(n_{\text{eff}}^{\text{R}}(\mathbf{r}), \nabla n_{\text{eff}}^{\text{R}}(\mathbf{r})) \phi^\mu(n_{\text{eff}}^{\text{R}}(\mathbf{r}))] d\mathbf{r}, \quad (4.41)$$

where, in the spirit of the work of Engel *et al.* [54], we have introduced a multiplicative relativistic correction $\phi^\mu(n)$ to the term $f_x^\mu(n, \nabla n)$ of the form

$$\phi^\mu(n) = \frac{1 + \frac{a_1(\mu/c)}{\tilde{c}^2} + \frac{a_2(\mu/c)}{\tilde{c}^4}}{1 + \frac{b_1(\mu/c)}{\tilde{c}^2} + \frac{b_2(\mu/c)}{\tilde{c}^4}}. \quad (4.42)$$

Since $\phi^\mu(n)$ only depends on the dimensionless parameters \tilde{c} and μ/c , it does not change the uniform coordinate scaling of the functional which still fulfils the scaling relation of Eq. (J.7).

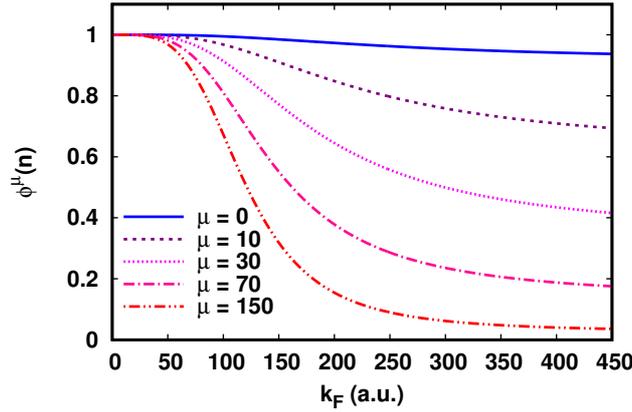


Figure 4.3: Relativistic correction factor $\phi^\mu(n)$ to the density-gradient term [Eq. (4.42)] as a function of k_F for several values of μ .

After some tests, we chose to impose $a_1(\mu/c) = b_1(\mu/c)$ to avoid overcorrections in low-density regions which have very small relativistic effects. We started to determine the coefficients for $\mu = 0$ by minimizing the mean squared relative percentage error of the exchange energy with respect to the reference DHF exchange energy for 7 systems of the neon isoelectronic series (Ne, Ar⁸⁺, Kr²⁶⁺, Xe⁴⁴⁺, Yb⁶⁰⁺, Rn⁷⁶⁺, U⁸²⁺), giving $a_1(0) = b_1(0) = 1.3824$, $a_2(0) = 0.3753$, and $b_2 = 0.4096$. The resulting relativistic correction factor $\phi^{\mu=0}(n)$ can be seen in Figure 4.3. It correctly tends to 1 in the low-density ($k_F \rightarrow 0$) or non-relativistic ($c \rightarrow \infty$) limit, and remains very close to 1 for $k_F \ll c$. In regions with very high densities, the relativistic correction factor $\phi^{\mu=0}(n)$ induces a slight reduction of the effective density-gradient correction term in the functional, reducing a bit the relative error on the exchange energy for the heaviest systems. For $\mu \neq 0$, we have searched for coefficients in Eq. (4.42) which reduce the largest errors of the srRLDA/PBEot exchange energy observed at intermediate values of μ (see Figure 4.2). We chose coefficients depending on μ/c of the form

$$a_1(\mu/c) = b_1(\mu/c) = a_1(0)[1 - \text{erf}(\mu/c)], \quad (4.43)$$

$$a_2(\mu/c) = a_2(0)[1 - \text{erf}(\mu/c)], \quad (4.44)$$

$$b_2(\mu/c) = b_2(0)[1 - \beta \text{erf}(\mu/c)], \quad (4.45)$$

with $\beta = -4.235$ which has been found by minimizing the mean squared relative percentage error of the short-range exchange energy for the same 7 systems of the neon isoelectronic series and for 4 intermediate values of the range-separation parameter ($\mu/k_{F_{\max}} = 0.05; 0.1; 0.2; 0.4$). The resulting relativistic correction factor $\phi^\mu(n)$ is reported in Figure 4.3. It still tends to 1 in the low-density limit, but goes down to 0 when $\mu \gg c$ in the high-density limit. The higher the value of μ the faster it decreases as a function of k_F . In Figure 4.4, we report the relative percentage errors of the srRPBEot exchange functional for systems of the helium, beryllium, neon, and argon series. For $\mu = 0$, this functional achieves an error of at most about 1% for all systems, and it has the correct large- μ limit. The maximum absolute percentage errors, which are found for intermediate values of μ , tend to grow with Z but remain at most about 3% for the heavier systems. The srRPBEot exchange functional represents a significant improvement over the srPBEot and srRLDA/PBEot exchange functionals for the heavier systems.

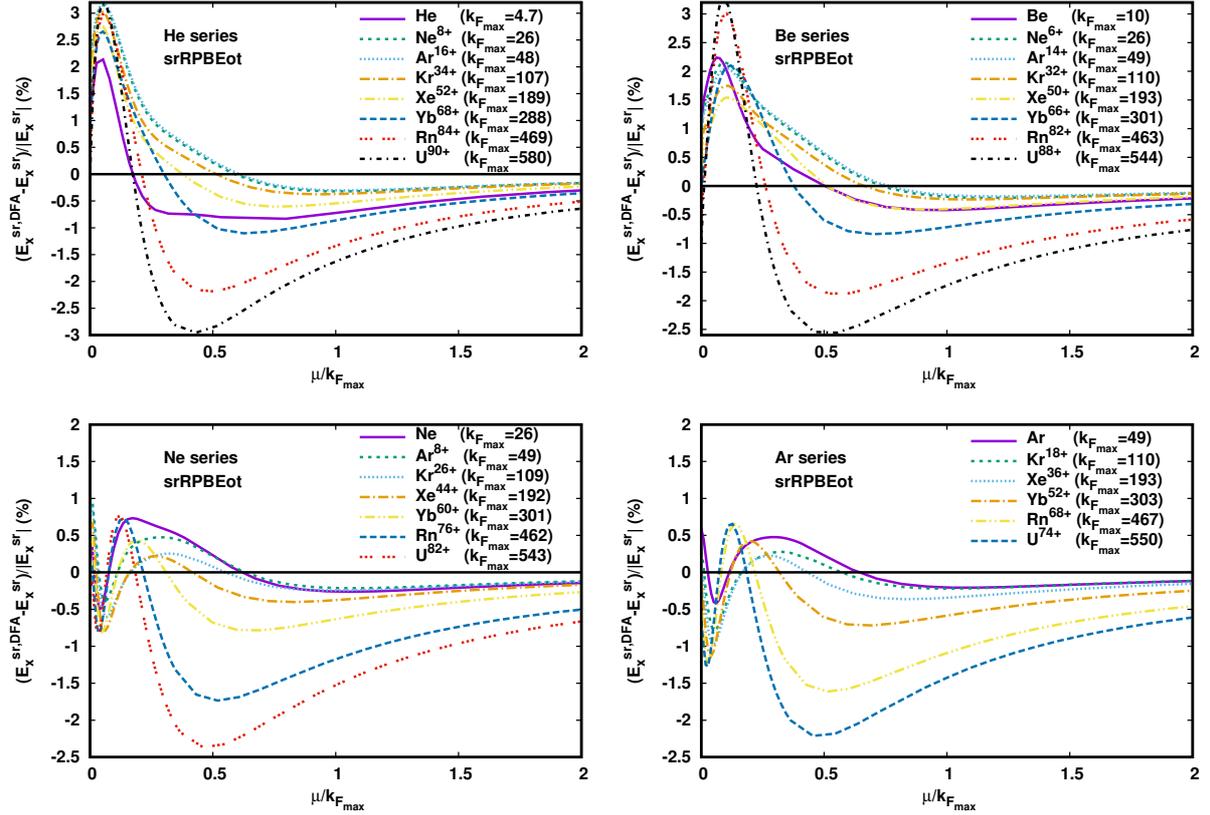


Figure 4.4: Relative percentage error on the short-range exchange energy calculated with the srRPBEot functional for systems of helium, beryllium, neon, and argon isoelectronic series.

4.7 Conclusions

In this work, we have tested the srRLDA exchange functional developed in Ref. [11] on three systems of the neon isoelectronic series (Ne, Xe⁴⁴⁺, and Rn⁷⁶⁺) and compared it to the usual non-relativistic srLDA exchange functional. Both functionals are quite inaccurate for relativistic systems and do not have the correct asymptotic behavior for large range-separation parameter μ . In order to fix this large- μ behavior, we have then defined the srLDAot and srRLDAot exchange functionals by introducing the exact on-top exchange pair density as a new variable. These functionals recover the correct asymptotic behavior for large μ but remain inaccurate for small values of μ . To improve the accuracy for small values of μ , we have then developed a relativistic short-range GGA exchange functional also using the on-top exchange pair density as an extension of the non-relativistic srPBE exchange functional. Tests on the systems of the isoelectronic series of He, Be, Ne, and Ar up to $Z = 92$ show that this srRPBEot exchange functional gives a maximal relative percentage error of 3% for intermediate values of μ and less than 1% relative error for $\mu = 0$. Of course, in the non-relativistic limit ($c \rightarrow \infty$), all the relativistic functionals introduced in this work properly reduce to their non-relativistic counterparts.

Possible continuations of this work include further tests on atoms and molecules, extension to the Gaunt or Breit electron-electron interactions, development of the short-range relativistic correlation functionals, and use of a local range-separation parameter.

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Chapter 5

Four-component relativistic range-separated density-functional theory: Short-range correlation local-density approximation

In this chapter we work out a relativistic complementary short-range correlation density functional scheme in the local density approximation (LDA), making use of a long-range correlation correction factor parameterized at the random phase approximation (RPA) level to introduce relativistic effects locally.

5.1 Short-range correlation local density approximation

We want to build a short-range relativistic LDA (SR-RLDA) Coulomb correlation density functional in order to have the correlation counterpart of the SR-RLDA Coulomb exchange density functional that was developed within Chapter 3 as well as tested and improved within Chapter 4. Such a short-range correlation functional must be defined as the complementary part of a long-range correlation functional with respect to the full-range one, due the non-linearity of the correlation energy with respect to the range-separation parameter. As such, we define the complementary short-range Coulomb correlation density functional as

$$E_c^{\text{sr,RLDA},\mu}[n] = E_c^{\text{RLDA}}[n] - E_c^{\text{lr,RLDA},\mu}[n]. \quad (5.1)$$

Both in the spirit of Schmid *et al.* [1] and of the extension of the SR-RLDA to a short-range exchange relativistic generalized gradient approximation (SR-RGGA) [see Chapter 4], we express the relativistic correlation functional at the RLDA level using a relativistic correlation correction factor $\phi_c(n)$ in order to introduce relativistic effects at the local level. We therefore write

$$\begin{aligned} E_c^{\text{RLDA}}[n] &= \int_{\Omega} d\mathbf{r} n(\mathbf{r}) \varepsilon_c^{\text{RHEG}}(n) \\ &= \int_{\Omega} d\mathbf{r} n(\mathbf{r}) \varepsilon_c^{\text{HEG}}(n) \phi_c(n), \end{aligned} \quad (5.2)$$

and

$$\begin{aligned} E_c^{\text{lr,RLDA},\mu}[n] &= \int_{\Omega} d\mathbf{r} n(\mathbf{r}) \varepsilon_c^{\text{lr,RHEG},\mu}(n) \\ &= \int_{\Omega} d\mathbf{r} n(\mathbf{r}) \varepsilon_c^{\text{lr,HEG},\tilde{\mu}}(n) \phi_c^{\text{lr},\tilde{\mu}}(n), \end{aligned} \quad (5.3)$$

where ϵ_c^{RHEG} stands for the full-range correlation energy per particle of the relativistic homogeneous electron gas (RHEG), ϵ_c^{HEG} for the full-range correlation energy per particle of the homogeneous electron gas (HEG) and where we require $\phi_c^{\text{lr},\tilde{\mu}} \rightarrow \phi_c$ when $\tilde{\mu} \rightarrow \infty$ for the sake of consistency, as the long-range interaction reduces to the full-range one in this limit. We write $\phi_c^{\text{lr},\tilde{\mu}}$ using a superscript $\tilde{\mu} = \mu/k_F = \mu/(3\pi^2 n)^{1/3}$, the scaled range-separation parameter which is the natural adimensional quantity reflecting the link between the electronic density n and the range-separation parameter μ at a local scale. This approach allows us to make use of the existing non-relativistic correlation functionals, both for the full-range interaction [2] and short-range interaction [3, 4]. In the spirit of Schmid *et al.* [1] we define the relativistic correlation correction factor ϕ_c using the correlation energies of the RHEG and HEG at the RPA level, such that

$$\phi_c^{\text{lr},\tilde{\mu}} = \phi_c^{\text{lr,RPA},\tilde{\mu}} = \frac{\epsilon_c^{\text{lr,RRPA},\tilde{\mu}}}{\epsilon_c^{\text{lr,RPA},\tilde{\mu}}}, \quad (5.4)$$

where $\epsilon_c^{\text{lr,RRPA},\tilde{\mu}}$ stands for the long-range Coulomb correlation energy of the RHEG at the relativistic RPA (RRPA) level and $\epsilon_c^{\text{lr,RPA},\tilde{\mu}}$ stands for the long-range Coulomb correlation energy of the HEG at the RPA level. The use of the RPA correlation energy appears consistent considering that relativistic effects are important in the high-density regions of a system, which also correspond to regions where RPA is a correct approximation to the correlation energy. In order to have a tractable expression for $\phi_c^{\text{lr,RPA},\tilde{\mu}}$ we need to parameterize it, as there is no possibility to obtain an analytical expression of the correlation energies per particle. We choose a Padé-like structure [see Chapter 3] for our parameterization, even though the coefficients must be fitted instead of analytically derived

$$\phi_c^{\text{lr,RPA},\tilde{\mu}} = \frac{\sum_{i=0}^M A_i(\tilde{\mu})/\tilde{c}^i}{\sum_{i=0}^M B_i(\tilde{\mu})/\tilde{c}^i}, \quad (5.5)$$

with $\tilde{c} = mc/\hbar k_F$, which is the natural adimensional quantity reflecting the impact of relativistic effects at a local scale. Indeed, relativistic effects are usually negligible when $mc \gg \hbar k_F$ [see Chapter 3], i.e. when $\tilde{c} \gg 1$, and relativistic effects increase when \tilde{c} decreases. In the spirit of Schmid *et al.* [1] we take for the highest degree term of the numerator the opposite of the high-density limit of the long-range Coulomb correlation energy of the RHEG at the RPA level, such that

$$A_M = -\epsilon_c^{\text{lr,RRPA},\tilde{\mu}} \Big|_{k_F \gg 1}, \quad (5.6)$$

and for the highest degree term of the denominator the opposite of the high-density limit of the long-range Coulomb correlation energy of the HEG at the RPA level, such that

$$B_M = -\epsilon_c^{\text{lr,RPA},\tilde{\mu}} \Big|_{k_F \gg 1}. \quad (5.7)$$

It is important to specify that although we write the high-density limit of the long-range Coulomb correlation energy of the RHEG using the subscript $k_F \gg 1$, it corresponds in practice to the ultra-relativistic limit of the correlation energy, i.e. $\hbar k_F \gg mc$. The choice of the opposite of the correlation energies ensures the use of positive quantities and reduces the risk of introducing poles within the parameterization.

5.2 Long-range correlation random phase approximation

We want to derive the no-pair long-range Coulomb correlation energy per particle of the RHEG at the RPA level, that is the RRPA energy per particle $\epsilon_c^{\text{lr,RRPA},\tilde{\mu}}$. We consider thus only the Coulomb interaction, that is the longitudinal part of the electron-electron interaction in QED parlance [see Section 2.2.2], and neglect all transversal interactions as well as all renormalization terms due to the no-pair approximation.

As we consider only the instantaneous Coulomb charge-charge interaction, it corresponds to working in Coulomb gauge. We start from the expression of the no-pair long-range correlation energy per particle [3, 5, 6] at the RPA level using only the Hartree kernel, such that

$$\epsilon_c^{\text{lr,RRPA},\tilde{\mu}} = -\frac{\hbar e^2}{2\pi n} \int \frac{d\mathbf{q}}{(2\pi)^3} v^{\text{lr},\tilde{\mu}}(q) \int_{u=0}^{\infty} du \int_{\lambda=0}^1 d\lambda \frac{[\chi^0(\mathbf{q}, i u)]^2 f_H^{\text{lr},\tilde{\mu},\lambda}(q)}{1 - \chi^0(\mathbf{q}, i u) f_H^{\text{lr},\tilde{\mu},\lambda}(q)}, \quad (5.8)$$

where χ^0 is the non-interacting linear-response function of the RHEG in the no-pair approximation [see Appendix N] such that for the wave-vector \mathbf{q} and the imaginary frequency $i u$ we have

$$\begin{aligned} \chi^0(\mathbf{q}, i u) &= -\frac{m k_F}{\hbar^2} \int \frac{d\mathbf{k}'}{(2\pi)^3} \theta(1 - k') \frac{\left(\sqrt{k'^2 + \tilde{c}^2} + \sqrt{|\mathbf{k}' + \mathbf{q}'|^2 + \tilde{c}^2}\right)^2 - q'^2}{\sqrt{k'^2 + \tilde{c}^2} \sqrt{|\mathbf{k}' + \mathbf{q}'|^2 + \tilde{c}^2}} \\ &\quad \frac{\tilde{c} \left(\sqrt{|\mathbf{k}' + \mathbf{q}'|^2 + \tilde{c}^2} - \sqrt{k'^2 + \tilde{c}^2}\right)}{v^2 + \tilde{c}^2 \left(\sqrt{|\mathbf{k}' + \mathbf{q}'|^2 + \tilde{c}^2} - \sqrt{k'^2 + \tilde{c}^2}\right)^2} \\ &= -\frac{m k_F}{\hbar^2} \int_{k'=0}^1 \frac{dk'}{(2\pi)^2} k'^2 \int_{\theta=0}^{\pi} d\theta \frac{\left(\sqrt{k'^2 + \tilde{c}^2} + \sqrt{k'^2 + q'^2 + 2k'q'\cos\theta + \tilde{c}^2}\right)^2 - q'^2}{\sqrt{k'^2 + \tilde{c}^2} \sqrt{k'^2 + q'^2 + 2k'q'\cos\theta + \tilde{c}^2}} \\ &\quad \frac{\tilde{c} \left(\sqrt{k'^2 + q'^2 + 2k'q'\cos\theta + \tilde{c}^2} - \sqrt{k'^2 + \tilde{c}^2}\right)}{v^2 + \tilde{c}^2 \left(\sqrt{k'^2 + q'^2 + 2k'q'\cos\theta + \tilde{c}^2} - \sqrt{k'^2 + \tilde{c}^2}\right)^2}, \quad (5.9) \end{aligned}$$

which depends only on $|\mathbf{q}| = q = q'k_F$ such that we write now $\chi^0(q, i u)$, and where $f_H^{\text{lr},\mu,\lambda}$ is the long-range Hartree kernel such that for the wave-vector \mathbf{q} it corresponds to the scaled Fourier transform of the Coulomb interaction

$$f_H^{\text{lr},\tilde{\mu},\lambda}(q) = \lambda v^{\text{lr},\tilde{\mu}}(q) = \lambda \frac{4\pi}{q'^2 k_F^2} \exp\left[\frac{-q'^2}{4\tilde{\mu}^2}\right], \quad (5.10)$$

using the adimensional variables $\mathbf{k}' = \mathbf{k}/k_F$, $\mathbf{q}' = \mathbf{q}/k_F$, $\tilde{\mu} = \mu/k_F$, $\tilde{c} = mc/\hbar k_F$ and $v = m u/\hbar k_F^2$. This linear-response function of the RHEG must, to the best of our knowledge, be integrated numerically if one uses imaginary frequencies, its evaluation requiring two numerical integrals. On the contrary, it reduces to the Lindhard function at imaginary frequency [7] in the non-relativistic limit, i.e. by taking $\tilde{c} \rightarrow \infty$, which is analytically integrable and does not require any numerical integration.

Analytical integrations

The integrals over the two angular variables of \mathbf{q} in Eq. (5.8) yield a factor 4π as the integrand only depends on $|\mathbf{q}|$ and the integral over the coupling constant λ is analytical, yielding

$$\begin{aligned} \epsilon_c^{\text{lr,RRPA},\tilde{\mu}} &= -\frac{\hbar e^2}{4\pi^3 n} \int_{q=0}^{\infty} dq q^2 v^{\text{lr},\tilde{\mu}}(q) \int_{u=0}^{\infty} du \frac{v^{\text{lr},\tilde{\mu}}(q) \chi^0(q, i u) + \ln\left[1 - v^{\text{lr},\tilde{\mu}}(q) \chi^0(q, i u)\right]}{v^{\text{lr},\tilde{\mu}}(q)} \\ &= -\frac{\hbar^2 e^2}{m} \frac{3}{4\pi} \int_{q'=0}^{\infty} dq' \int_{u=0}^{\infty} dv \left(4\pi \exp\left[\frac{-q'^2}{4\tilde{\mu}^2}\right] \chi^0(q'k_F, i u) \right. \\ &\quad \left. + q'^2 k_F^2 \ln\left[1 - \frac{4\pi}{q'^2 k_F^2} \exp\left[\frac{-q'^2}{4\tilde{\mu}^2}\right] \chi^0(q'k_F, i u)\right] \right), \quad (5.11) \end{aligned}$$

using the adimensional variables and having explicitly written the Fourier transform of the Coulomb interaction [see Eq. (5.10)] and expressed the electronic density as a function of k_F in the last line. As the no-pair long-range Coulomb correlation energy per particle of the RHEG at the RPA level contains two integrals with no analytical solution, and recalling that the linear-response function of the RHEG [see Eq. (5.9)] requires itself two numerical integrals, any evaluation of $\epsilon_c^{\text{lr,RRPA},\tilde{\mu}}(k_F)$ thus requires four simultaneous numerical integrations. Considering the non-relativistic limit brings simplifications as the linear-response function has now an analytical expression, thus making for only two simultaneous numerical integrations to evaluate $\epsilon_c^{\text{lr,RPA},\tilde{\mu}}(k_F)$. The full-range Coulomb correlation energy can be seen as a specific case of the long-range as it comes straightforwardly by taking $\tilde{\mu} \rightarrow \infty$ within Eq. (5.11), thus simply removing the exponential functions.

Numerical Integrations

The evaluation of Eq. (5.11) requiring four simultaneous numerical integrals. This brings some complications and increases the computational cost. As such, we calculated the numerical integrals using the software Wolfram Mathematica [8] with only six digits of accuracy in order to have tractable numerical integrations for the relativistic correlation energies. For consistency we used the same precision for non-relativistic calculations. We decided to sample the long-range correlation energies per particle with respect to two variables, the Fermi wave vector $k_F = (3\pi^2 n)^{1/3}$ and the scaled range-separation parameter $\tilde{\mu} = \mu/k_F$. For the Fermi wave vector k_F we considered 41 different values [see Table 5.1].

Table 5.1: Fermi wave vectors sampling.

0.005	0.01	0.05	0.1	0.25	0.5	0.75	1.0	1.75	2.5	3.75	5.0	7.5
10	15	20	25	30	35	40	50	60	80	100	137.0359998	150
200	250	300	350	400	450	500	550	600	700	800	900	1000
1100	1200											

This sampling of Fermi wave vectors ranges up to more than twice the core electronic densities of heavy ions we studied in the previous chapter [see Fig. 4.2] with our four-component Hartree-Fock code [see Section 2.5.2], thus encompassing all electronic density chemically relevant for the creation of a relativistic long-range correction factor $\phi_c^{\text{lr,RPA},\tilde{\mu}}$. In order to better understand this sampling of Fermi wave vectors we recall the formula

$$\begin{aligned}
 k_F &= (3\pi^2 n)^{1/3} = \left(3\pi^2 \frac{3}{4\pi r_s^3}\right)^{1/3} \\
 &= \left(\frac{3}{2}\right)^{2/3} \pi^{1/3} \frac{1}{r_s},
 \end{aligned} \tag{5.12}$$

such that a Fermi wave vector of $k_F = 0.005$ a.u. corresponds to a Wigner-Seitz radius $r_s \approx 384$ a.u. and a Fermi wave vector of $k_F = 1200$ a.u. corresponds to a Wigner-Seitz radius $r_s \approx 0.0016$ a.u., yet even though most non-relativistic correlation energy functionals are usually discussed using the Wigner-Seitz radius as variable, we favor the use of k_F for its easy comparison in the relativistic formalism with the speed of light $c = 137.035998$ a.u.. For the scaled range-separation parameter $\tilde{\mu} = \mu/k_F$ we considered 26 different values [see Table 5.2].

Table 5.2: Scaled range-separation parameter sampling.

0.005	0.01	0.025	0.05	0.075	0.1	0.15	0.2	0.3	0.4	0.5	0.6	0.7
0.8	0.9	1.0	1.25	1.5	2.0	3.0	5.0	7.5	10.0	15.0	20.0	$\rightarrow \infty$

We denote as $\tilde{\mu} \rightarrow \infty$ the use of the full-range Coulomb interaction. These two-variable samplings make for $41 * 26 = 1066$ reference points that we use for the following parameterizations.

5.2.1 Non-relativistic long-range correlation energy

We represent in Fig. 5.1 the long-range Coulomb RPA correlation energy per particle of the HEG for several values of $\tilde{\mu}$ and we recall the usual high-density expansion of the full-range Coulomb RPA correlation energy per particle of the HEG [3, 9, 10] as a logarithmic expansion

$$\begin{aligned}\epsilon_c^{\text{RPA}} &= \frac{1 - \ln 2}{\pi^2} \ln r_s - 0.071100 + O(r_s \ln r_s) \\ &= -\frac{1 - \ln 2}{\pi^2} \ln k_F - 0.0508324 + O\left(\frac{1}{k_F} \ln k_F\right),\end{aligned}\quad (5.13)$$

for the full-range Coulomb interaction in non-relativistic formalism at the RPA level, where we made use of Eq. (5.12) to introduce the Fermi wave vector as a new variable.

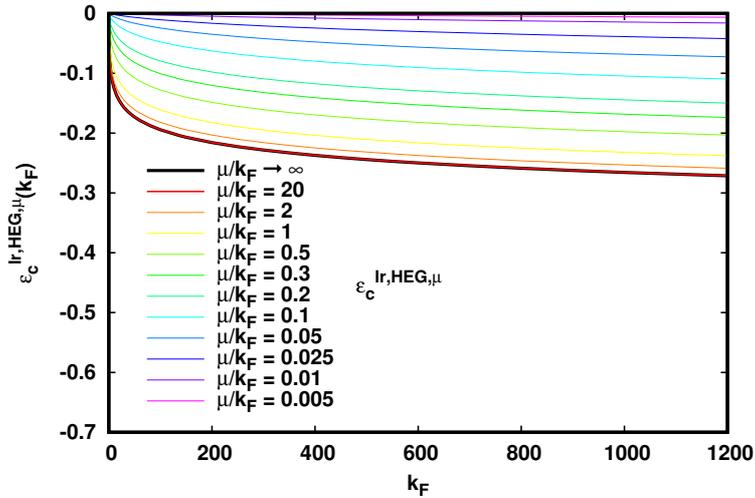


Figure 5.1: Non-relativistic long-range Coulomb RPA correlation energy per particle of the HEG.

We observe neatly the logarithmic behaviour and remark that when $\tilde{\mu}$ goes from infinity down to 20 there is barely any variations on the actual correlation energy per particle. Furthermore, the high-density logarithmic behaviour seems to be conserved on this range of Fermi wave vector for values of $\tilde{\mu}$ higher than 0.1.

5.2.2 Relativistic long-range correlation energy

We represent in Fig. 5.2 the no-pair long-range Coulomb RPA correlation energy per particle of the RHEG. We observe a very different behaviour than its non-relativistic counterpart as it appears to become almost linear with respect to k_F in the high-density limit. This behaviour is a known feature of the relativistic RPA correlation energy [1, 11] for the full-range two-electron Coulomb interaction, and it appears to be conserved for the long-range interaction when $\tilde{\mu}$ decreases. We once more observe that when $\tilde{\mu}$ goes from infinity down to 20 there is barely any variations on the actual correlation energy per particle.

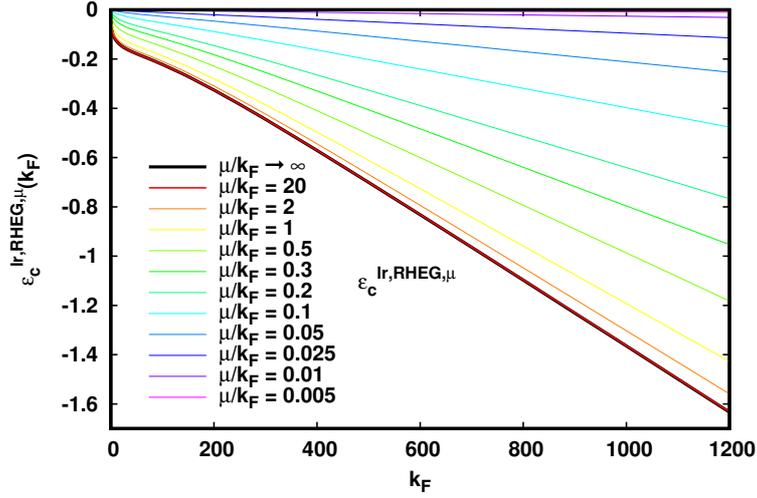


Figure 5.2: Relativistic long-range Coulomb RPA correlation energy per particle of the RHEG.

5.2.3 Relativistic long-range correlation factor

We represent in Fig. 5.3 the coefficient $\phi_c^{\text{lr,RPA},\tilde{\mu}}$ as a function of k_F for several values of $\tilde{\mu}$.

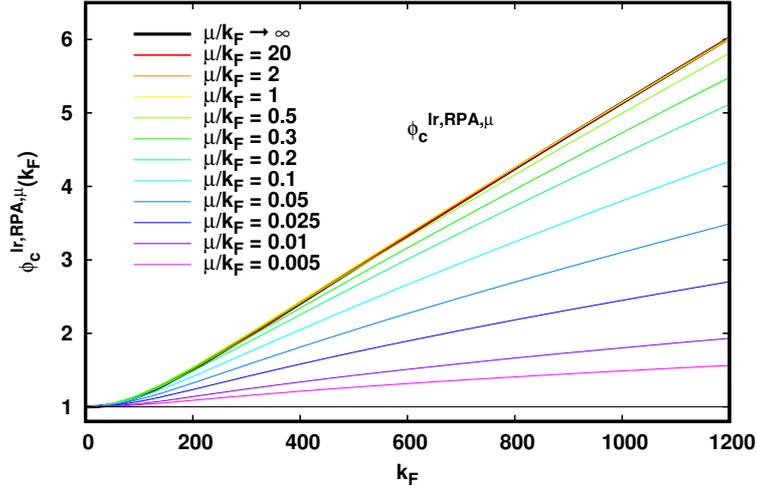


Figure 5.3: Relativistic correlation correction factor $\phi_c^{\text{lr,RPA},\tilde{\mu}}$ as a function of k_F

While it appears at first sight that $\phi^{\text{lr,RPA},\tilde{\mu}}$ is a monotonic decreasing function of $\tilde{\mu}$, it is in fact more complicated and best understood with the use of a representation in Fig. 5.4 of $\phi_c^{\text{lr,RPA},\tilde{\mu}}$ as a function of $\tilde{\mu}$ for several values of k_F . For clarity, we represent only the correction coefficient for values of k_F lower than 200, but the behaviour is similar for the whole range of Fermi wave vectors considered. It appears that, and for any value of k_F , $\phi^{\text{lr,RPA},\tilde{\mu}}$ starts as an increasing function of $\tilde{\mu}$ until it reaches a maximum value, which we will denote as $\tilde{\mu}^{\text{max}}(k_F)$, after which it becomes a decreasing function of $\tilde{\mu}$ converging to a constant value for the full-range Coulomb interaction.

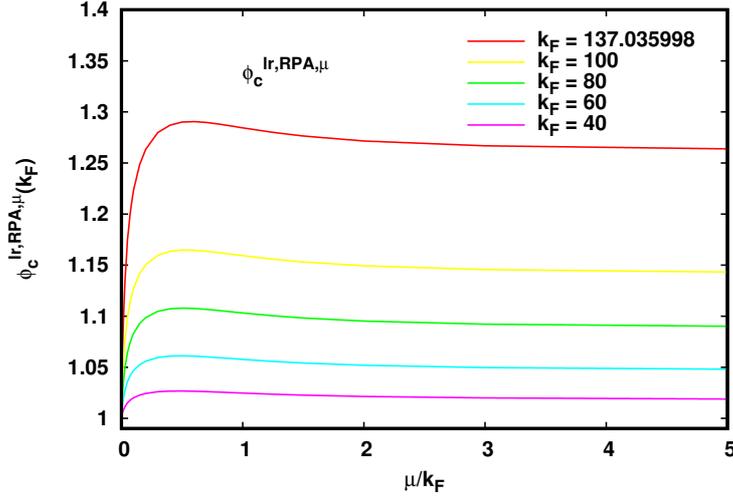


Figure 5.4: Relativistic correlation correction factor $\phi_c^{\text{lr,RPA},\tilde{\mu}}$ as a function of $\tilde{\mu}$

The value of $\tilde{\mu}^{\text{max}}$ is itself an increasing function of k_F , going from $\tilde{\mu}^{\text{max}}(10) \approx 0.5$ to $\tilde{\mu}^{\text{max}}(1200) \approx 1.5$. Furthermore, while $\phi_c^{\text{lr,RPA},\tilde{\mu}}$ increases greatly before $\tilde{\mu}^{\text{max}}$, its variations close to it are much smaller and its value decreases only slightly afterward. This behaviour explains why all curves for $\tilde{\mu}$ higher than 1 appear to be superposed in Fig. 5.3 as there is little variation of $\phi_c^{\text{lr,RPA},\tilde{\mu}}$ with respect to $\tilde{\mu}$ for these values, and why we observe such a neat separation of the coefficients $\phi_c^{\text{lr,RPA},\tilde{\mu}}$ and a monotonic decreasing behaviour with respect to $\tilde{\mu}$ only for lower values of $\tilde{\mu}$. This non-linear behaviour of $\phi_c^{\text{lr,RPA},\tilde{\mu}}$ with respect to $\tilde{\mu}$ can be understood as a very slight increase of the relativistic effects on the long-range correlation energy when goes $\tilde{\mu}$ goes from infinity down to $\tilde{\mu}^{\text{max}}(k_F)$, and then as a decrease of the relativistic effects on the long-range correlation energy as $\tilde{\mu}$ decreases further. It appears that for $\tilde{\mu} \rightarrow 0$ the correction factor goes to 1 for all values of k_F , such that relativistic effects on the long-range correlation all but disappear. Obviously, as the long-range correlation energy vanishes when $\tilde{\mu} \rightarrow 0$, this property will not dominate and relativistic effects will only be reduced for non-negligible values of the long-range correlation energy.

5.3 High-density limit of the long-range correlation energy

We now look in detail at the high-density limit in order to have the first building blocks for a parameterization of $\phi_c^{\text{lr,RPA},\tilde{\mu}}$.

5.3.1 High-density limit of the non-relativistic long-range correlation energy

The high-density limit parameterization for the non-relativistic correlation energy is done through the combination of two separate parameterizations, the first one for high values of $\tilde{\mu}$ and the second one for low values of $\tilde{\mu}$.

High values of $\tilde{\mu}$

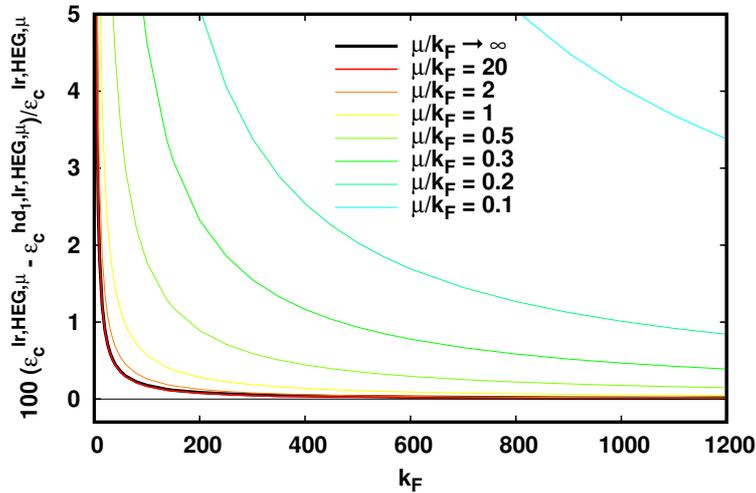
For values of the scaled range-separation parameter higher than 0.1 the logarithmic behaviour of the non-relativistic long-range correlation energy of the HEG [see Eq. (5.13)] appears to be conserved, and we found out that its dependence on the scaled range-separation parameter is accurately approximated in the high-density limit by

$$\epsilon_c^{\text{lr,RPA},\tilde{\mu}} \underset{k_F \gg 1}{\approx} \epsilon_c^{\text{hd1,lr,RPA},\tilde{\mu}} = -\frac{1 - \ln 2}{\pi^2} \ln k_F + \left(-0.0508324 + \frac{1 + a_1 \tilde{\mu}}{a_2 + a_3 \tilde{\mu} + a_4 \tilde{\mu}^2 + a_5 \tilde{\mu}^3} \right). \quad (5.14)$$

Table 5.3: Parameters for the high-density limit $\epsilon_c^{\text{hd}_1, \text{lr}, \text{RPA}, \tilde{\mu}}$ valid for high values of $\tilde{\mu}$

x	a_x
1	3.72862
2	3.53869
3	43.4382
4	40.2625
5	53.1731

The notation hd_1 stands for the first part of the high-density limit parameterization, which is the high- $\tilde{\mu}$ part. The parameters from Table 5.4 have been fitted using the software Wolfram Mathematica [8], on values obtained through numerical integration of $\epsilon_c^{\text{lr}, \text{RPA}, \tilde{\mu}} + \frac{1 - \ln 2}{\pi^2} \ln k_F$ at a “high enough” Fermi wave vector to reach the high-density limit and for the scaled range-separation parameters from Table 5.2 higher or equal to 0.1, thus making for a sampling of 21 points over which the root-mean-square deviation of the absolute error in percentage of the fitted function is 0.225%. We chose the “high enough” Fermi wave vector to be $k_F = 9600$ a.u. in order to make similar calculations on the relativistic correlation energy tractable. The absolute error in percentage of the parameterized high-density formula $\epsilon_c^{\text{hd}_1, \text{lr}, \text{RPA}, \tilde{\mu}}$ [see Eq. (5.14)] with respect to the numerically integrated $\epsilon_c^{\text{lr}, \text{RPA}, \tilde{\mu}}$ is represented in Fig. 5.5. We observe that the establishment of the logarithmic behaviour with less than 1% of absolute error for the high-density limit is reached around $k_F = 20$ a.u. for the full-range interaction, while it is not reached before $k_F = 200$ a.u. for the long-range interaction with $\tilde{\mu} = 0.5$ and it is barely reached at $k_F = 1200$ a.u. for the long-range interaction with $\tilde{\mu} = 0.2$.

Figure 5.5: Non-relativistic high-density limit absolute errors: high $\tilde{\mu}$ approximation.

For values of the scaled range-separation parameter lower than 0.2, the logarithmic behaviour is not established in the studied range of Fermi wave vector. This justifies the use of only the scaled range-separation parameters from Table 5.2 higher than 0.1 for our parameterization, as Eq. (5.14) is no longer a good approximation of the high-density limit for values of $\tilde{\mu} < 0.2$ in the chemically relevant range of electronic densities. This can be perceived as a change of regime, such that a change of parametrization is required for lower values of the scaled range-separation parameter.

Low values of $\tilde{\mu}$

In order to have a high-density formula which remains correct at low values of $\tilde{\mu}$, we make use of a parameterization from Paziani *et al.* [4], which is correct for small $\mu\sqrt{r_s}$, that is for small μ and/or small r_s . This can be understood, once re-expressed in our variables, as a parameterization correct for small $\sqrt{k_F}\tilde{\mu}$, that is for small values of $\tilde{\mu}$ and high values of k_F . Their parameterized expression of the high-density long-range correlation energy of an unpolarized HEG corresponds to

$$\varepsilon_c^{\text{lr}}(r_s, \mu) \Big|_{\mu, r_s \rightarrow 0} = \frac{2\ln 2 - 2}{\pi^2} \ln \left[\frac{1 + b_1 x + b_2 x^2 + b_3 x^3}{1 + b_1 x + b_4 x^2} \right], \quad (5.15)$$

with $x = \mu\sqrt{r_s}$, such that once rewritten with our variables it yields

$$\varepsilon_c^{\text{hd}_2, \text{lr}, \text{RPA}, \tilde{\mu}} = \frac{2\ln 2 - 2}{\pi^2} \ln \left[\frac{1 + b_1 \left(\frac{3\sqrt{\pi}}{2}\right)^{1/3} \sqrt{k_F}\tilde{\mu} + b_2 \left(\frac{3\sqrt{\pi}}{2}\right)^{2/3} (\sqrt{k_F}\tilde{\mu})^2 + b_3 \frac{3\sqrt{\pi}}{2} (\sqrt{k_F}\tilde{\mu})^3}{1 + b_1 \left(\frac{3\sqrt{\pi}}{2}\right)^{1/3} \sqrt{k_F}\tilde{\mu} + b_4 \left(\frac{3\sqrt{\pi}}{2}\right)^{2/3} (\sqrt{k_F}\tilde{\mu})^2} \right]. \quad (5.16)$$

Table 5.4: Parameters for the high-density limit $\varepsilon_c^{\text{hd}_2, \text{lr}, \text{RPA}, \tilde{\mu}}$ valid for low values of $\tilde{\mu}$, taken from Ref. [4].

x	b_x
1	5.84605
2	7.44953
3	3.91744
4	3.44851

The notation hd_2 stands for the second part of the high-density limit parameterization, which is the low- $\tilde{\mu}$ part. The absolute error in percentage of the parameterized high-density formula $\varepsilon_c^{\text{hd}_2, \text{lr}, \text{RPA}, \tilde{\mu}}$ [see Eq. (5.16)] with respect to the numerically integrated $\varepsilon_c^{\text{lr}, \text{RPA}, \tilde{\mu}}$ is represented in Fig. 5.6.

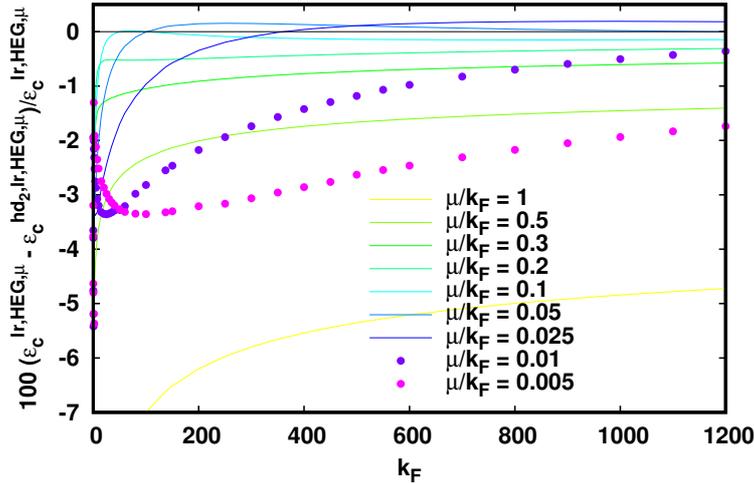


Figure 5.6: Non-relativistic high-density limit absolute errors : low $\tilde{\mu}$ approximation.

We first observe that the absolute error decreases with $\tilde{\mu}$ between 1 and 0.025 (full lines in Fig. 5.6). For values of the scaled range-separation parameter higher than 1 this parameterization is not a correct approximation to the long-range correlation energy, and for values of the scaled range-separation parameter lower than 0.025 (dotted lines in Fig. 5.6) the absolute error slightly increases up to 3% of absolute

error for $\tilde{\mu} = 0.005$. This behaviour mostly comes from the very low value of the correlation energy per particle [see Fig. 5.1] at such low values of the scaled range-separation parameter which magnifies the absolute error for a similar accuracy of the parameterization. This parameterization from Paziani *et al.* [4] appears thus to be complementary to our parameterization [see Eq. (5.14)] with respect to the scaled range-separation parameter. In order to have a high-density parameterization correct for the whole range of $\tilde{\mu}$ we found out that a continuation using a power of the error function works quite correctly, and settled on the use of $\text{erf}[3\tilde{\mu}]^4$ which is represented in Fig. 5.7.

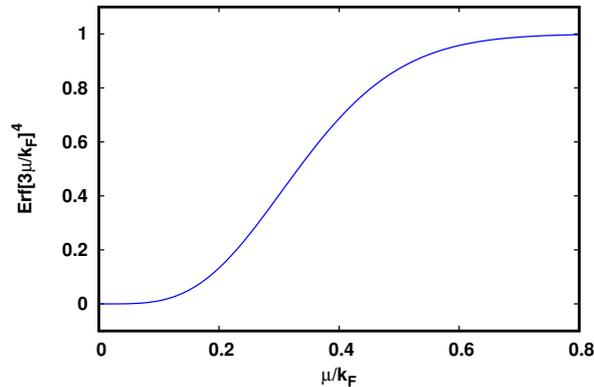


Figure 5.7: Continuation function for the two parts of the non-relativistic high-density correlation energy.

The use of the fourth power of the error function allows for a steep enough continuation, and taking $3\tilde{\mu}$ as the variable makes for a transition between the two different parameterizations around $\tilde{\mu} = 0.3$. We thus propose for the high-density non-relativistic long-range correlation energy of the HEG the parameterization

$$\epsilon_c^{\text{hd,lr,RPA},\tilde{\mu}} = \text{erf}[3\tilde{\mu}]^4 \epsilon_c^{\text{hd}_1,\text{lr,RPA},\tilde{\mu}} + (1 - \text{erf}[3\tilde{\mu}]^4) \epsilon_c^{\text{hd}_2,\text{lr,RPA},\tilde{\mu}}, \quad (5.17)$$

which allows for a very neat transition between the previous two parameterizations [see Eq. (5.14) and Eq. (5.16)]. This expression correctly reduces to the usual logarithmic expansion

$$\epsilon_c^{\text{hd,RPA}} = -\frac{1 - \ln 2}{\pi^2} \ln k_F - 0.0508324, \quad (5.18)$$

for the full-range Coulomb interaction. The absolute error in percentage of the parameterized high-density formula $\epsilon_c^{\text{hd,lr,RPA},\tilde{\mu}}$ [see Eq. (5.17)] with respect to the numerically integrated $\epsilon_c^{\text{lr,RPA},\tilde{\mu}}$ is represented in Fig. 5.8. We observe that for high electronic densities we have now a parameterization with less than 0.2% of absolute error for all values of $\tilde{\mu}$ higher than 0.025. We do not represent the graphs for $\tilde{\mu}$ equal to 0.01 and 0.005 as they would be strictly similar to those represented in Fig. 5.6 with around 3% of absolute error due to the very low values of the correlation energies per particle. Any improvement of the precision for values of the scaled range-separation parameter lower than 0.025 would require to rework the parameterization that was done by Paziani *et al.* [4], and does not appear to be necessary as the behaviour of the long-range correlation energy is still correct albeit with slightly lesser precision.

5.3.2 High-density limit of the relativistic long-range correlation energy

For the relativistic long-range correlation energy of the RHEG, it appears that a linear behaviour emerges for k_F high enough [1], which we observe in Fig. 5.2. Due to the computational cost of the numerical integrations we decided on the use of a “high enough” Fermi wave vector for parameterizing the high-density limit of the relativistic long-range correlation energy of the RHEG.

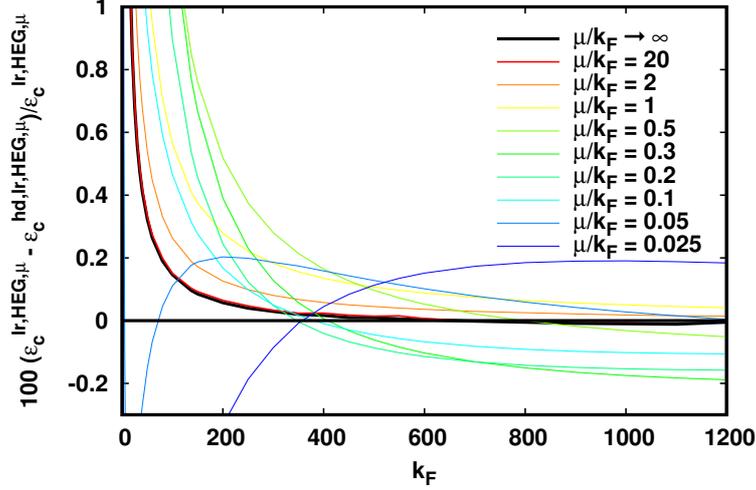


Figure 5.8: Non-relativistic high-density limit absolute errors.

To determine such a “high enough” Fermi wave vector we calculated the full-range correlation energy per particle ϵ_c^{RHEG} at three values of k_F high enough to observe the establishment of the linear behaviour. Calculations for k_F in $\{2400, 4800, 9600\}$ allowed us to check the variation in slopes, and while there is 0.6% of variations in absolute value of the slope between 1200 and 9600, there is less than 0.03% between 4800 and 9600, thus validating the use of $k_F = 9600$ a.u. as a “high enough” Fermi wave vector for the range that interests us. We found out that the high-density limit of the relativistic long-range correlation energy per particle is accurately approximated by

$$\epsilon_c^{\text{hd,Ir,RRPA},\tilde{\mu}} = -0.185345 \left(1 - \frac{1 + c_1\tilde{\mu} + c_2\tilde{\mu}^2 + c_3\tilde{\mu}^3 + c_4\tilde{\mu}^4}{1 + c_5\tilde{\mu} + c_6\tilde{\mu}^2 + c_7\tilde{\mu}^3 + c_8\tilde{\mu}^4 + c_9\tilde{\mu}^5} \right) / \tilde{c}, \quad (5.19)$$

and reduces to

$$\epsilon_c^{\text{hd,RRPA}} = -0.185345 / \tilde{c}. \quad (5.20)$$

for the full-range Coulomb interaction.

Table 5.5: Parameters for the high-density limit $\epsilon_c^{\text{hd,Ir,RRPA},\tilde{\mu}}$.

x	c_x
1	63.6213
2	161.703
3	58.4589
4	-0.55375
5	63.7034
6	467.578
7	624.653
8	952.370
9	159.956

The parameters from Table 5.5 have been fitted using the software Wolfram Mathematica [8], on values obtained through numerical integration of $\epsilon_c^{\text{Ir,RRPA},\tilde{\mu}} / \tilde{c}$ at $k_F = 9600$ a.u. and for all scaled range-separation parameters from Table 5.2, thus making for a sampling of 26 points over which the root-mean-square deviation of the absolute error in percentage of the fitted function is 0.033%. The absolute error in

percentage of the parameterized high-density formula $\epsilon_c^{\text{hd,lr,RRPA},\tilde{\mu}}$ [see Eq. (5.19)] with respect to the numerically integrated $\epsilon_c^{\text{lr,RRPA},\tilde{\mu}}$ is represented in Fig. 5.9.

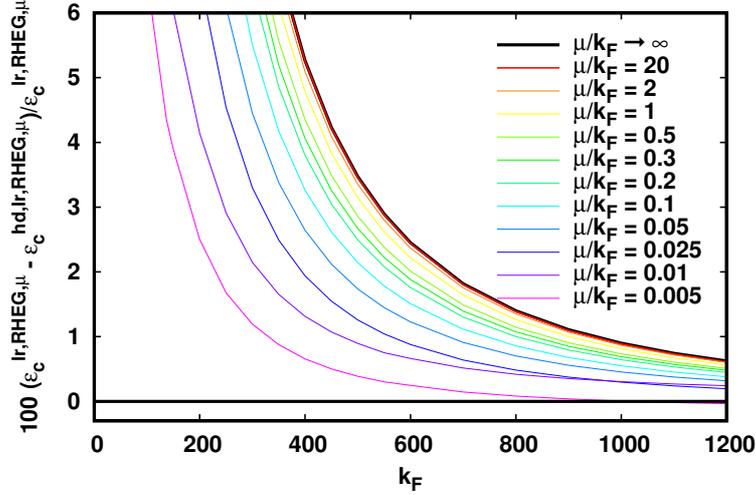


Figure 5.9: Relativistic high-density limit absolute errors.

We observe that the establishment of the linear behaviour with less than 1% of absolute error for the high-density limit is reached around $k_F = 1000$ a.u. for the full-range interaction. Contrary to the non-relativistic case, the high-density limit behaviour is established for lower values of k_F for the long-range Coulomb interaction, such that we reach less than 1% of absolute error for the parameterized high-density limit around $k_F = 300$ a.u. for a long-range interaction with $\tilde{\mu} = 0.005$. The relativistic long-range high-density limit appears to be simpler than the non-relativistic one as there is seemingly no change of regime and we thus have a unique parameterization working for all values of $\tilde{\mu}$.

5.4 Parameterization of the relativistic correlation correction factor

Having worked out parameterizations for the high-density limit of the long-range correlation energy per particle of both the HEG and RHEG, we now use these expressions to build the Padé-like expression of the relativistic correlation correction factor $\phi_c^{\text{lr,RPA},\tilde{\mu}}$ [see Eq. (5.5)]. We found out that the relativistic long-range correlation energy correction at the no-pair RPA level is accurately approximated by

$$\phi_c^{\text{lr,RPA},\tilde{\mu}} = \frac{1 + \frac{a_{1,1} + a_{1,2}\tilde{\mu}}{a_{1,4} + \tilde{\mu}}/\tilde{c} + \frac{a_{2,1} + a_{2,2}\tilde{\mu} + a_{2,3}\tilde{\mu}^2}{a_{2,4} + a_{2,5}\tilde{\mu} + \tilde{\mu}^2}/\tilde{c}^2 + \frac{a_{3,1} + a_{3,2}\tilde{\mu} + a_{3,3}\tilde{\mu}^2}{a_{3,4} + a_{3,5}\tilde{\mu} + \tilde{\mu}^2}/\tilde{c}^3 - \epsilon_c^{\text{hd,lr,RRPA},\tilde{\mu}}/\tilde{c}^4}{1 + \frac{a_{1,1} + b_{1,2}\tilde{\mu}}{a_{1,4} + \tilde{\mu}}/\tilde{c} + \frac{a_{2,1} + b_{2,2}\tilde{\mu} + b_{2,3}\tilde{\mu}^2}{a_{2,4} + b_{2,5}\tilde{\mu} + \tilde{\mu}^2}/\tilde{c}^2 + \frac{a_{3,1} + b_{3,2}\tilde{\mu} + b_{3,3}\tilde{\mu}^2}{a_{3,4} + b_{3,5}\tilde{\mu} + \tilde{\mu}^2}/\tilde{c}^3 - \epsilon_c^{\text{hd,lr,RPA},\tilde{\mu}}/\tilde{c}^4}. \quad (5.21)$$

The parameters from Table 5.6 have been fitted using the software Wolfram Mathematica [8], on values obtained through numerical integration of $\epsilon_c^{\text{lr,RRPA},\tilde{\mu}}/\epsilon_c^{\text{lr,RPA},\tilde{\mu}}$ for all Fermi wave vectors from Table 5.1 and all scaled range-separation parameters from Table 5.2, thus making for a sampling of 1066 points over which the root-mean-square deviation of the absolute error in percentage of the fitted function is 0.053%, with a maximum absolute error in percentage reaching less than 0.4% for the smallest values of $\tilde{\mu}$ considered. We emphasize that the relativistic full-range Coulomb correlation energy correction at the no-pair RPA level reduces to

$$\phi_c^{\text{RPA}} = \frac{1 + a_{1,2}/\tilde{c} + a_{2,3}/\tilde{c}^2 + a_{3,3}/\tilde{c}^3 - \epsilon_c^{\text{hd,RRPA}}/\tilde{c}^4}{1 + b_{1,2}/\tilde{c} + b_{2,3}/\tilde{c}^2 + b_{3,3}/\tilde{c}^3 - \epsilon_c^{\text{hd,RPA}}/\tilde{c}^4}, \quad (5.22)$$

Table 5.6: Parameters for correlation correction factor $\phi_c^{\text{lr,RPA},\tilde{\mu}}$.

x	$a_{1,x}$	$a_{2,x}$	$a_{3,x}$	$b_{1,x}$	$b_{2,x}$	$b_{3,x}$
1	2.22080 d-2	9.66045 d-2	1.59065 d-4	-	-	-
2	7.04721 d-1	2.66457	9.62993 d-2	7.09439 d-1	2.91597 d-1	-2.40333 d-3
3	-	9.24891 d-1	6.30881 d-1	-	5.62594 d-1	6.077222 d-3
4	1.16165 d-1	1.50127 d-1	5.30353 d-3	-	-	-
5	-	3.07852	5.32685 d-1	-	7.56679 d-1	8.30363 d-1

with a root-mean-square deviation of the absolute error in percentage of 0.039% over the full range of Fermi wave vectors from Table 5.1, and with a maximum absolute error in percentage reaching less than 0.1%. It is important that the full-range correction factor be as precise as possible, as this coefficient multiplies the full-range non-relativistic Coulomb correlation energy [see Eq. (5.2)], which is always bigger than its long-range counterpart. As such, a small loss of precision of the long-range correction factor for the lowest values of $\tilde{\mu}$ is acceptable as it multiplies only very reduced long-range correlation energies and has a smaller impact on the overall correlation energy.

5.5 Conclusion

We have extended the complementary short-range correlation density functional scheme to a relativistic framework, with the use of a relativistic correlation correction factor. This correction factor has been constructed from ratio of the correlation energy per particle of the RHEG and HEG at the RPA level of theory, and requires a parametrization as these correlation energies have no analytical expressions. In particular, the parametrization we built relies heavily on the high-density limit of both relativistic and non-relativistic RPA correlation energies, which we studied as function of k_F and $\tilde{\mu}$. We first emphasize that both correlation energies per particle share the common traits of being monotonic decreasing functions of k_F for any given value of $\tilde{\mu}$ and monotonic decreasing functions of $\tilde{\mu}$ for any given values of k_F . We found out that the known linear behaviour of the relativistic high-density limit of the full-range Coulomb correlation energy at the RPA level extends to its long-range counterpart with a slope being a simple monotonic decreasing function of $\tilde{\mu}$, making for an easy parametrization. On the contrary, the known logarithmic behaviour of the non-relativistic high-density limit of the full-range Coulomb correlation energy at the RPA level does not straightforwardly extend to its long-range counterpart, and requires for our purpose the linear combination of two separate parametrizations with the use of a continuation function. The long-range correlation correction factor constructed is, for any given value of $\tilde{\mu}$, an increasing function of k_F starting from 1 for very low values of k_F , such that relativistic effects increase the correlation energy per particle in absolute value at the RPA level. Nevertheless, the variations with respect to $\tilde{\mu}$ of this correction factor is not simply a monotonic decrease but reaches a maximum at a value $\tilde{\mu}^{\text{max}}(k_F)$, which is itself an increasing function of k_F . For any values of k_F a decrease of the scaled range-separation parameter from infinity, that is going from full-range interaction to a long-range interaction, leads to a slight increase of the correlation energy per particle until $\tilde{\mu}^{\text{max}}(k_F)$ is reached, after which the correlation energy per particle decreases quickly to zero when $\tilde{\mu} \rightarrow 0$. We have parameterized this relativistic correlation correction factor at the RPA level with a Padé-like formula yielding a root-mean-square deviation of the absolute error in percentage of 0.053% with respect to our numerical integrations.

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General conclusion

This PhD thesis constitutes a contribution to the relativistic extension of the range-separated density functional theory scheme, by combining a relativistic four-component wave function calculation for the long-range contribution with a complementary relativistic short-range exchange-correlation density functional based on the no-pair Dirac-Coulomb or Dirac-Coulomb-Breit Hamiltonian.

We have developed four-component relativistic short-range exchange Coulomb and Coulomb-Breit density functionals at the local density approximation (LDA) level, based on the relativistic homogeneous electron gas. The most precise functionals are expressed as Padé approximants, making no approximation on the dependence on the scaled range-separation parameter μ/k_F and being systematically improvable to arbitrary accuracy with respect to the parameter c/k_F as we explicitly derived the analytical expression of the corresponding expansion coefficients.

Numerical tests of the relativistic short-range exchange Coulomb functional with respect to the exact Dirac-Hartree-Fock short-range exchange Coulomb energy have been realized using the four-component range-separated density functional code that we implemented as a plugin in the software QUANTUM PACKAGE 2.0. We found out that, within the four-component relativistic framework, the local density approximation does not become exact in the very short-range limit but instead shows an increasing discrepancy when relativistic effects increase. This phenomenon comes from the explicit dependence of the exact short-range exchange Coulomb energy on the on-top exchange pair density, which reduces to a dependence on the electronic density only in the non-relativistic limit. As such, it is necessary to consider the on-top exchange pair density as a separate variable from the electronic density to recover the correct very short-range behaviour of the local density approximation in a relativistic framework, and we proposed for correction the use of a local density approximation “on top” (LDAot) with a modified transferability criterion, such that the short-range exchange energy is now calculated by integrating over the short-range exchange energy per particle of an homogeneous system having locally the same on-top exchange pair density as the inhomogeneous system, instead of the same electronic density.

In order to go further than the LDAot approximation, which is only exact in the very-short range limit and is no more accurate than the standard local density approximation for low values of the range-separation parameter, we extended the proposed density functional up to the generalized gradient approximation (GGA) level, using the non-relativistic short-range PBE gradient correction corrected by a parameterized multiplicative relativistic correction factor, and we proposed a short-range relativistic PBE “on top” (srRPBEot) exchange Coulomb density functional with less than 1% of absolute error with respect to the exact Dirac-Hartree-Fock short-range exchange Coulomb energy for low values of the range-separation parameter according to our calculations on the isoelectronic series of He, Be, Ne, and Ar up to atomic number $Z = 92$.

We have developed a relativistic complementary short-range correlation Coulomb density functional scheme at the local-density approximation level, introducing relativistic effects locally by correcting the non-relativistic correlation energy per particle with a parameterized multiplicative relativistic correction factor at the random phase approximation level. The proposed correction factor has a root-mean-square deviation of the absolute error in percentage of 0.053% with respect to numerical integrations over our

parameterization set and shows less than 0.5% of absolute error for any chemically relevant values of the scaled parameters μ/k_F and c/k_F .

Possible continuations of this work include implementation and tests of the relativistic short-range exchange Coulomb-Breit LDA functional, which would require the implementation of the Breit two-electron integrals to compute the exact Dirac-Hartree-Fock short-range exchange Coulomb-Breit energy, implementation and tests of the relativistic complementary short-range correlation Coulomb LDA functional, tests on heavy ions to observe the impact of the relativistic correction factor on the correlation energy of inhomogeneous systems, and a generalization to a relativistic complementary short-range correlation Coulomb GGA functional. Considering the importance of the on-top exchange pair density for the short-range Coulomb exchange density functional we expect the very short-range Coulomb-Breit exchange and correlation energies to show the same kind of discrepancy and to require some further corrections.

One of the obvious limitations of the relativistic range-separated density functional theory that was worked out within this PhD thesis is the use of a constant range-separation parameter μ . Indeed, compared to non-relativistic systems containing only light atoms where the electronic densities in terms of k_F range usually from 0 a.u. up to 50 a.u., in the case of relativistic systems containing heavy atoms the electronic densities in terms of k_F range rather from 0 a.u. up to 500 a.u. (in the presence of a uranium atom for example). This increase in electronic density range implies that for any given constant value of μ , if there is to be any range separation in the valence regions, then the core electrons will be treated with almost pure density functional theory, and on the contrary if there is to be any range separation in the core regions, then the valence electrons will be treated with almost pure wave function theory. To ensure that we do not lose the benefit of range separation in any regions of space the use of a local range-separation parameter $\mu(\mathbf{r})$ appears to be a possible solution, albeit not straightforward to implement in an computationally efficient fashion.

Appendices

Appendix A

Lorentz transformations

A.1 Lorentz transformation of position and time

We want to derive the explicit form of the Lorentz transformation of position and time for a general Lorentz boost (see, e.g., Ref. [1]). We start with two inertial frames \mathbf{J} and \mathbf{J}' coinciding at $t = t' = 0$, the motion of \mathbf{J}' relative to \mathbf{J} being the constant velocity $\mathbf{v} = v \mathbf{e}_x$ along the x axis such that the y and z directions are unaffected. The homogeneity of space and time enforces linearity between the old and new sets of coordinates, with only the time and the x axis being affected

$$\begin{pmatrix} ct' \\ x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \Lambda_0^0 & \Lambda_0^1 & 0 & 0 \\ \Lambda_1^0 & \Lambda_1^1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} ct \\ x \\ y \\ z \end{pmatrix}. \quad (\text{A.1})$$

In order to determine explicitly the four remaining Λ_μ^ν parameters we consider two light signals emitted at $t = t' = 0$ from the origin of the inertial frames $x = x' = 0$, a first one in the negative x direction and a second one in the positive x direction. At a time t_1 , the first light signal defines an event E_1 given by

$$x_1 + ct_1 = 0 \quad (\text{A.2})$$

$$x'_1 + ct'_1 = (\Lambda_1^1 + \Lambda_1^0) x_1 + (\Lambda_0^0 + \Lambda_0^1) ct_1 = 0, \quad (\text{A.3})$$

such that multiplication of Eq. (A.2) by $(\Lambda_0^0 + \Lambda_0^1)$ and subtraction of Eq. (A.3) leads to

$$\begin{aligned} 0 &= (\Lambda_0^0 + \Lambda_0^1)(x_1 + ct_1) - [(\Lambda_1^1 + \Lambda_1^0) x_1 + (\Lambda_0^0 + \Lambda_0^1) ct_1] \\ &= (\Lambda_0^0 + \Lambda_0^1 - \Lambda_1^1 - \Lambda_1^0) x_1. \\ &= \Lambda_0^0 + \Lambda_0^1 - \Lambda_1^1 - \Lambda_1^0, \end{aligned} \quad (\text{A.4})$$

where $x_1 \neq 0$ has been simplified in the last line. At a time t_2 , the second light signal defines an event E_2 given by

$$x_2 - ct_2 = 0 \quad (\text{A.5})$$

$$x'_2 - ct'_2 = (\Lambda_1^1 - \Lambda_1^0) x_2 - (\Lambda_0^0 - \Lambda_0^1) ct_2 = 0, \quad (\text{A.6})$$

such that multiplication of Eq. (A.5) by $(\Lambda_0^0 - \Lambda_0^1)$ and subtraction of Eq. (A.6) leads to

$$\begin{aligned} 0 &= (\Lambda_0^0 - \Lambda_0^1)(x_2 - ct_2) - [(\Lambda_1^1 - \Lambda_1^0) x_2 - (\Lambda_0^0 - \Lambda_0^1) ct_2] \\ &= (\Lambda_0^0 - \Lambda_0^1 - \Lambda_1^1 + \Lambda_1^0) x_2, \\ &= \Lambda_0^0 - \Lambda_0^1 - \Lambda_1^1 + \Lambda_1^0, \end{aligned} \quad (\text{A.7})$$

where $x_2 \neq 0$ has been simplified in the last line. Addition of Eq. (A.4) and Eq. (A.7) yields $\Lambda_0^0 = \Lambda_1^1$ while subtraction of Eq. (A.4) from Eq. (A.7) yields $\Lambda_0^1 = \Lambda_1^0$, reducing the problem to only two parameters. We can determine relations between these parameters by considering O' the origin of \mathbf{J}' . We have $x'_{O'} = 0$ and $x_{O'} = vt$, such that

$$x'_{O'} = \Lambda_0^1 ct + \Lambda_1^1 x_{O'} = \Lambda_0^1 ct + \Lambda_1^1 vt = 0, \quad (\text{A.8})$$

yielding $\Lambda_0^1 = -v/c \Lambda_0^0$ and the relevant Lorentz transformation

$$\begin{pmatrix} ct' \\ x' \end{pmatrix} = \begin{pmatrix} \Lambda_0^0 & -v/c \Lambda_0^0 \\ -v/c \Lambda_0^0 & \Lambda_0^0 \end{pmatrix} \begin{pmatrix} ct \\ x \end{pmatrix}. \quad (\text{A.9})$$

The relativity principle implies that the Lorentz coordinate transformation from \mathbf{J}' to \mathbf{J} must have the same form with an opposite velocity, yielding

$$\begin{pmatrix} ct \\ x \end{pmatrix} = \begin{pmatrix} \Lambda_0^0 & v/c \Lambda_0^0 \\ v/c \Lambda_0^0 & \Lambda_0^0 \end{pmatrix} \begin{pmatrix} ct' \\ x' \end{pmatrix}. \quad (\text{A.10})$$

We can now write the back and forth coordinate transformation (from \mathbf{J} to \mathbf{J}' to \mathbf{J} again) as

$$\begin{aligned} x &= \Lambda_0^0(x' + vt') \\ &= \Lambda_0^0 \left(\Lambda_0^0(x - vt) + v\Lambda_0^0 \left(t - \frac{v}{c^2}x \right) \right) \\ &= (\Lambda_0^0)^2 \left(1 - \frac{v^2}{c^2} \right) x, \end{aligned} \quad (\text{A.11})$$

such that

$$\Lambda_0^0 = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \equiv \gamma, \quad (\text{A.12})$$

with γ a coefficient called the Lorentz factor. We thus express the Lorentz transformation of the 4-position as

$$\begin{pmatrix} ct' \\ x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \gamma \left(ct - \frac{v x}{c} \right) \\ \gamma(x - vt) \\ y \\ z \end{pmatrix}. \quad (\text{A.13})$$

Considering that a three-dimensional position \mathbf{r} can be split into a parallel part plus an orthogonal part $\mathbf{r} = \mathbf{r}_{\parallel} + \mathbf{r}_{\perp}$ where the parallel part has the same direction as the Lorentz boost, we have

$$\begin{pmatrix} ct' \\ \mathbf{r}' \end{pmatrix} = \begin{pmatrix} \gamma \left(ct - \frac{\mathbf{v} \cdot \mathbf{r}_{\parallel}}{c} \right) \\ \mathbf{r}_{\perp} + \gamma(\mathbf{r}_{\parallel} - \mathbf{v}t) \end{pmatrix}, \quad (\text{A.14})$$

or, re-writing $\mathbf{r}_{\perp} = \mathbf{r} - \mathbf{r}_{\parallel}$ and $\mathbf{r}_{\parallel} = [\mathbf{r} \cdot \mathbf{v}] \mathbf{v} / v^2$

$$\begin{pmatrix} ct' \\ \mathbf{r}' \end{pmatrix} = \begin{pmatrix} \gamma \left(ct - \frac{\mathbf{v} \cdot \mathbf{r}}{c} \right) \\ \mathbf{r} + (\gamma - 1) \frac{[\mathbf{r} \cdot \mathbf{v}] \mathbf{v}}{v^2} - \gamma \mathbf{v}t \end{pmatrix}, \quad (\text{A.15})$$

which reduces to the Galilei transformation when $c \rightarrow \infty$, in the non-relativistic limit.

A.2 Lorentz transformation of electric and magnetic fields

We want to derive the explicit form of the Lorentz transformation for the electromagnetic field for a general Lorentz boost (see, e.g., Ref. [1]). As neither the electric nor the magnetic fields are Lorentz 4-vectors, we have to consider the Lorentz transformation of the field strength tensor which determine both fields uniquely. We start with two inertial frames \mathbf{J} and \mathbf{J}' which coincide at $t = t' = 0$, the motion of \mathbf{J}' relative to \mathbf{J} is the constant velocity $\mathbf{v} = v \mathbf{e}_x$ along the x axis so that the y and z directions are unaffected. The transformation of the second-rank tensor $F^{\mu\nu}$ is given by

$$F' = \Lambda F \Lambda^T \iff F'^{\mu\nu} = \Lambda^\mu_\sigma F^{\sigma\tau} \Lambda^\nu_\tau \quad (\text{A.16})$$

Considering the results of Section A.1 we have thus

$$\begin{aligned} & \begin{pmatrix} \gamma & -v/c\gamma & 0 & 0 \\ -v/c\gamma & \gamma & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & -E_x & -E_y & -E_z \\ E_x & 0 & -B_z & B_y \\ E_y & B_z & 0 & -B_x \\ E_z & -B_y & B_x & 0 \end{pmatrix} \begin{pmatrix} \gamma & -v/c\gamma & 0 & 0 \\ -v/c\gamma & \gamma & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \\ = & \begin{pmatrix} 0 & \gamma^2(1 - \frac{v^2}{c^2})E_x & -\gamma(E_y - \frac{v}{c}B_z) & -\gamma(E_z + \frac{v}{c}B_y) \\ -\gamma^2(1 - \frac{v^2}{c^2})E_x & 0 & -\gamma(B_z - \frac{v}{c}E_y) & \gamma(B_y + \frac{v}{c}E_z) \\ \gamma(E_y - \frac{v}{c}B_z) & \gamma(B_z - \frac{v}{c}E_y) & 0 & -B_x \\ \gamma(E_z + \frac{v}{c}B_y) & -\gamma(B_y + \frac{v}{c}E_z) & B_x & 0 \end{pmatrix} \\ = & \begin{pmatrix} 0 & -E'_x & -E'_y & -E'_z \\ E'_x & 0 & -B'_z & B'_y \\ E'_y & B'_z & 0 & -B'_x \\ E'_z & -B'_y & B'_x & 0 \end{pmatrix}, \end{aligned} \quad (\text{A.17})$$

and using $\gamma^2(1 - \frac{v^2}{c^2}) = 1$ we obtain the transformation behaviours, under an x direction Lorentz boost, of the electric and magnetic fields respectively

$$\begin{pmatrix} E'_x \\ E'_y \\ E'_z \end{pmatrix} = \begin{pmatrix} E_x \\ \gamma(E_y - \frac{v}{c}B_z) \\ \gamma(E_z + \frac{v}{c}B_y) \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} B'_x \\ B'_y \\ B'_z \end{pmatrix} = \begin{pmatrix} B_x \\ \gamma(B_y + \frac{v}{c}E_z) \\ \gamma(B_z - \frac{v}{c}E_y) \end{pmatrix}. \quad (\text{A.18})$$

For a general motion of \mathbf{J}' relative to \mathbf{J} with a speed \mathbf{v} we have thus

$$\mathbf{E}'_{\parallel} = \mathbf{E}_{\parallel} \quad \text{and} \quad \mathbf{E}'_{\perp} = \gamma(\mathbf{E}_{\perp} + \frac{1}{c}\mathbf{v} \times \mathbf{B}) \quad (\text{A.19})$$

as well as

$$\mathbf{B}'_{\parallel} = \mathbf{B}_{\parallel} \quad \text{and} \quad \mathbf{B}'_{\perp} = \gamma(\mathbf{B}_{\perp} - \frac{1}{c}\mathbf{v} \times \mathbf{E}). \quad (\text{A.20})$$

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Appendix B

Electromagnetic gauge conditions

We want to derive the explicit electromagnetic gauge conditions (see, e.g., Ref. [1]). We start by highlighting the gauge invariance of the electric and magnetic fields, rewriting Eq. (1.32) and explicitly introducing a gauge transformation $A^\mu \rightarrow A'^\mu = A^\mu - \partial^\mu g$ where $g = g(x)$ is any sufficiently smooth gauge function, such that for the electric field we have

$$\begin{aligned}
 \mathbf{E}' &= -\nabla\phi' - \frac{1}{c} \frac{\partial \mathbf{A}'}{\partial t} \\
 &= -\nabla \left(\phi - \frac{1}{c} \frac{\partial g}{\partial t} \right) - \frac{1}{c} \frac{\partial (\mathbf{A} + \nabla g)}{\partial t} \\
 &= -\nabla\phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} + \frac{1}{c} \left(\nabla \frac{\partial g}{\partial t} - \frac{\partial \nabla g}{\partial t} \right) \\
 &= -\nabla\phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \\
 &= \mathbf{E},
 \end{aligned} \tag{B.1}$$

where the order of the derivatives, being arbitrary according to Young's theorem, can be inverted such that the gauge terms cancel each other. For the magnetic field we have

$$\begin{aligned}
 \mathbf{B}' &= \nabla \times \mathbf{A}' \\
 &= \nabla \times (\mathbf{A} + \nabla g) \\
 &= \nabla \times \mathbf{A} + \nabla \times \nabla g \\
 &= \nabla \times \mathbf{A} \\
 &= \mathbf{B},
 \end{aligned} \tag{B.2}$$

where the curl of a gradient $\nabla \times \nabla g$ vanishes according to the vector calculus identities, whatever the properties of the gauge function g .

Rewriting Gauss's law [see Eq. (1.35)] and Ampère's circuital law [see Eq. (1.36)] using the scalar potential ϕ and vector potential \mathbf{A} yield respectively

$$\begin{aligned}
 \nabla \cdot \mathbf{E} = 4\pi\rho &\iff \nabla \cdot \left(-\nabla\phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \right) = 4\pi\rho \\
 -\Delta\phi - \frac{1}{c} \frac{\partial}{\partial t} (\nabla \cdot \mathbf{A}) &= 4\pi\rho,
 \end{aligned} \tag{B.3}$$

and

$$\begin{aligned}
 \nabla \times \mathbf{B} - \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} = \frac{4\pi}{c} \mathbf{j} &\iff \nabla \times (\nabla \times \mathbf{A}) - \frac{1}{c} \frac{\partial}{\partial t} \left(-\nabla\phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \right) = \frac{4\pi}{c} \mathbf{j} \\
 -\Delta\mathbf{A} + \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} + \nabla \left(\frac{1}{c} \frac{\partial \phi}{\partial t} + \nabla \cdot \mathbf{A} \right) &= \frac{4\pi}{c} \mathbf{j},
 \end{aligned} \tag{B.4}$$

where we used the vector calculus identities $\nabla \cdot \nabla \phi = \Delta \phi$ and $\nabla \times (\nabla \times \mathbf{A}) = \nabla(\nabla \cdot \mathbf{A}) - \Delta \mathbf{A}$. Equations (B.3) and (B.4) are thus equivalent to the Maxwell equations, and valid for each and any gauge transformations of the gauge field A . This makes for redundant degrees of freedom, which can be restricted by the choice of a gauge. Among the many existing gauges, two of the most prominent ones are the Coulomb gauge and the Lorenz gauge, respectively

$$\nabla \cdot \mathbf{A} = 0, \quad (\text{B.5})$$

and

$$\frac{1}{c} \frac{\partial \phi}{\partial t} + \nabla \cdot \mathbf{A} = \partial_\mu A^\mu = 0. \quad (\text{B.6})$$

B.1 Coulomb gauge

The use of the Coulomb gauge [see Eq. (B.5)] simplifies Eq. (B.3) into Poisson's equation

$$-\Delta \phi = 4\pi\rho, \quad (\text{B.7})$$

which solution is Poisson's integral

$$\phi(t, \mathbf{r}) = \int_{\Omega} d\mathbf{r}' \frac{\rho(t, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (\text{B.8})$$

The scalar potential ϕ at time t is thus defined by the instantaneous Coulomb potential created by the charge density ρ at time t , making for no retardation in the transmission of the scalar potential. This propriety comes from the removal of the time derivative of Eq. (B.3), and as the time derivatives of Eq. (B.4) have not been removed retardation effects still show up within the scalar potential in Coulomb gauge. The Coulomb gauge condition and Poisson's equation makes for two constraints on the gauge field A , such that it has only two independent dynamical variables instead of four.

B.2 Lorenz gauge

The use of the Lorenz gauge [see Eq. (B.6)] simplifies Eq. (B.3) and Eq. (B.4) into wave equations, respectively

$$-\Delta \phi + \frac{1}{c^2} \frac{\partial^2 \phi}{\partial t^2} = \partial_\mu \partial^\mu \phi = 4\pi\rho, \quad (\text{B.9})$$

and

$$-\Delta \mathbf{A} + \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = \partial_\mu \partial^\mu \mathbf{A} = \frac{4\pi}{c} \mathbf{j}, \quad (\text{B.10})$$

separating neatly the scalar potential ϕ and vector potential \mathbf{A} . The Lorenz gauge condition makes for one constraint on the gauge field A , such that it has only three independent dynamical variables instead of four. As such, the Lorenz gauge does not completely fix the potentials and restricted gauge transformations of the form $A'^\mu = A^\mu - \partial^\mu g$ are still possible for constrained gauge functions such that

$$\partial_\mu \partial^\mu g = 0. \quad (\text{B.11})$$

Indeed, applying the 4-gradient onto such a gauge field (A'^μ) yields

$$\begin{aligned} \partial_\mu A'^\mu &= \partial_\mu (A^\mu - \partial^\mu g) \\ &= \partial_\mu A^\mu - \partial_\mu \partial^\mu g \\ &= \partial_\mu A^\mu, \end{aligned} \quad (\text{B.12})$$

thus satisfying the Lorenz gauge as long as the gauge function fulfils Eq. (B.11).

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Appendix C

Derivations of covariant Lagrangians

C.1 Lagrangian of a relativistic massive particle

We want to derive the covariant Lagrangian of a relativistic free particle of mass m (see, e.g., Ref. [1]). Due to translational invariance in time-space it cannot depend on the 4-position x , and due to rotational invariance it cannot depend on the direction of the 4-velocity u , the only remaining parameter is thus the norm of the 4-velocity $\sqrt{u^\mu u_\mu}$, such that $L = L(u) = L(\sqrt{u^\mu u_\mu})$. The covariant Euler-Lagrange equations [see Eq. (1.54)] for the massive free particle reduces to

$$\left(\frac{d}{d\tau} \frac{\partial L}{\partial u^\mu} \right)_{\mu=0,3} = 0, \quad (\text{C.1})$$

such that, for $\mu = 0, 3$, we have

$$\frac{d}{d\tau} \left(\frac{u_\mu}{\sqrt{u^\mu u_\mu}} L'(\sqrt{u^\mu u_\mu}) \right) = \frac{L'(c)}{c} \frac{du_\mu}{d\tau} = 0, \quad (\text{C.2})$$

where L' is the derivative of the function L with respect to its variable, and we take the norm of the 4-velocity $\sqrt{u^\mu u_\mu} = c$, which is independent of time, to evaluate the function after differentiation. The equation of motion of the relativistic free particle is thus

$$\frac{du_\mu}{d\tau} = 0, \quad (\text{C.3})$$

which corresponds, up to a trivial multiplication by the mass of the particle, exactly to the one that derives from Eq. (1.45) for a particle with vanishing Minkowski force. Considering that this equation gives no information as to the form of the function L as it does not depend on it, we gain informations by re-expressing the Lagrangian as a function of the three-dimensional velocity \mathbf{v} such that $L(\mathbf{v})$ describes the same trajectory as before, and must therefore have the same action. The Euler-Lagrange equations for the free particle are now written as

$$\left(\frac{d}{dt} \frac{\partial L}{\partial v_i} \right)_{i=1,3} = 0, \quad (\text{C.4})$$

which must correspond to the spatial component of Eq. (1.45) for a particle with vanishing Minkowski force which we rewrite, for $i = 1, 3$, as

$$\frac{dm u_i}{d\tau} = \gamma \frac{d}{dt} \frac{\gamma(\mathbf{v}(t)) m v_i(t)}{dt} = \gamma \frac{d}{dt} \left(\frac{m v_i(t)}{\sqrt{1 - \frac{v^2(t)}{c^2}}} \right) = 0, \quad (\text{C.5})$$

yielding the equality

$$\frac{d}{dt} \frac{\partial L}{\partial v_i} = \frac{d}{dt} \left(\frac{m v_i(t)}{\sqrt{1 - \frac{v^2(t)}{c^2}}} \right), \quad (\text{C.6})$$

such that after integrations we have

$$L(\mathbf{v}) = -mc^2 \sqrt{1 - \frac{\mathbf{v}^2}{c^2}}, \quad (\text{C.7})$$

where the prefactor mc^2 is kept arbitrarily to recover the correct Lagrangian for a free particle in the non-relativistic limit, which corresponds to the kinetic energy (up to the rest mass energy). We can now determine the structure of our covariant Lagrangian, since any infinitesimal action has to be the same for a given trajectory whatever the variables we express the Lagrangian with, such that

$$\begin{aligned} L(\mathbf{v})dt &= -mc^2 \sqrt{1 - \frac{\mathbf{v}^2}{c^2}} dt \\ &= -mc \sqrt{\gamma^2 c^2 - \gamma^2 \mathbf{v}^2} d\tau \\ &= -mc \sqrt{u^\mu u_\mu} d\tau \\ &= L(u) d\tau, \end{aligned} \quad (\text{C.8})$$

and we can write the covariant Lagrangian of a free particle as

$$L_{\text{free}}(u) = -mc \sqrt{u^\mu u_\mu}, \quad (\text{C.9})$$

where we recover correctly the dependency in $\sqrt{u^\mu u_\mu}$.

C.2 Interaction Lagrangian of a relativistic massive charged particle

We want to derive the covariant interaction Lagrangian of a particle of mass m and charge q within an external electromagnetic field (see, e.g., Ref. [1]). Once inserted within the Euler-Lagrange equations the Lagrangian must yield the equation of motion taking in account the Lorentz electromagnetic force, which is linear in the fields \mathbf{E} and \mathbf{B} and the velocity of the particle \mathbf{v} . Considering that the electromagnetic field is not a Lorentz invariant quantity, the interaction term of the covariant Lagrangian must depend on the gauge field A directly. We propose as an interaction term, up to an undetermined constant prefactor Cst , $L_{\text{int}} = \text{Cst} A_\mu u^\mu$, where A_μ is only an external potential on which the Lagrangian does not depend dynamically. The Lagrangian of a massive charged particle is thus

$$L(x, u) = -mc \sqrt{u^\mu u_\mu} + \text{Cst} A_\mu(x) u^\mu. \quad (\text{C.10})$$

We evaluate the two terms of the covariant Euler-Lagrange equations [see Eq. (1.54)] for such a massive charged particle

$$\frac{\partial L}{\partial x^\mu} = \text{Cst} \frac{\partial A_\nu}{\partial x^\mu} u^\nu \quad (\text{C.11})$$

$$-\frac{d}{d\tau} \frac{\partial L}{\partial u^\mu} = m \frac{du_\mu}{d\tau} - \text{Cst} \frac{dA_\mu}{d\tau} = m \frac{du_\mu}{d\tau} - \text{Cst} \frac{\partial A_\mu}{\partial x^\nu} u^\nu, \quad (\text{C.12})$$

such that, considering that the sum of the two previous terms must vanish, we have

$$\begin{aligned} m \frac{du_\mu}{d\tau} &= \text{Cst} \left(\frac{\partial A_\mu}{\partial x^\nu} - \frac{\partial A_\nu}{\partial x^\mu} \right) u^\nu \\ &= \text{Cst} (\partial_\nu A_\mu - \partial_\mu A_\nu) u^\nu \\ &= \text{Cst} F_{\nu\mu} u^\nu, \end{aligned} \quad (\text{C.13})$$

where we recovered the covariant field strength tensor

$$(\partial_\nu A_\mu - \partial_\mu A_\nu) = (F_{\nu\mu}) = (g_{\nu\lambda} g_{\mu\sigma} F^{\lambda\sigma}) = \begin{pmatrix} 0 & E_x & E_y & E_z \\ -E_x & 0 & -B_z & B_y \\ -E_y & B_z & 0 & -B_x \\ -E_z & -B_y & B_x & 0 \end{pmatrix}. \quad (\text{C.14})$$

The prefactor Cst can now be extracted by calculation of any component of this equation of motion. We use $\mu = 0$

$$m \frac{du_0}{d\tau} = \text{Cst } F_{\nu 0} u^\nu = \text{Cst } \gamma (-E_x v_x - E_y v_y - E_z v_z) = -\text{Cst } \gamma \mathbf{E} \cdot \mathbf{v}. \quad (\text{C.15})$$

From a comparison to the Lorentz force from Eq. (1.51), we extract $\text{Cst} = -q/c$ such that the covariant Lagrangian of a particle of mass m and charge q within an external electromagnetic field determined by the gauge field A is written as

$$L(x, u) = -mc \sqrt{u^\mu u_\mu} - \frac{q}{c} A_\mu(x) u^\mu. \quad (\text{C.16})$$

C.3 Electromagnetic field interaction Lagrangian density

We want to derive the covariant interaction Lagrangian density of an electromagnetic field (see, e.g., Ref. [1]). Considering that the usual current \mathbf{j} can be written as $(j^i = qv^i)_{i=1,3}$, we propose as an interaction term

$$\mathcal{L}_{\text{int}}(A, \partial A, x, u) = -\frac{1}{c} A_\mu(x) j^\mu(x), \quad (\text{C.17})$$

which corresponds to an extension of Eq. (C.16) using the 4-current. To test the validity of this interaction Lagrangian density, we want to check if it correctly yields the same action as the interaction Lagrangian [see Eq. (C.16)] for a moving charged particle. As a first step, we express the 4-current j for one charged particle of charge q moving with a velocity \mathbf{v} , its position as a function of time t being denoted $\mathbf{r}_1(t)$. At the 4-position x corresponding to the time $t = x^0/c$ and position \mathbf{r} we have

$$\begin{aligned} j(x) = \begin{pmatrix} c\rho(t, \mathbf{r}) \\ \mathbf{j}(t, \mathbf{r}) \end{pmatrix} &= q \delta^{(3)}(\mathbf{r} - \mathbf{r}_1(t)) \begin{pmatrix} c \\ \mathbf{v}(t) \end{pmatrix} \\ &= \frac{q}{\gamma} \delta^{(3)}(\mathbf{r} - \mathbf{r}_1(t)) u(x^0) \\ &= \frac{q}{\gamma} \delta^{(3)}(\mathbf{r} - \mathbf{r}_1(t)) \int dx_1^0 \delta(x^0 - x_1^0) u(x_1^0) \\ &= \frac{q}{\gamma} \delta^{(3)}(\mathbf{r} - \mathbf{r}_1(t)) \int d\tau_1 c \gamma \delta(x^0 - x_1^0(\tau_1)) u(x_1^0(\tau_1)) \\ &= c q \int d\tau_1 \delta^{(4)}(x - x_1(\tau_1)) u(\tau_1) \end{aligned} \quad (\text{C.18})$$

where we first used the definitions of the charge density [see Eq. (1.28)] and current density [see Eq. (1.30)] before re-writing the 4-velocity as an integral over the proper time τ_1 of the particle. We now express the

action of the interaction Lagrangian density, such that

$$\begin{aligned}
S_{\text{int}} &= \frac{1}{c} \int dx \left(-\frac{1}{c} A_\mu(x) j^\mu(x) \right) \\
&= -\frac{1}{c^2} \int dx A_\mu(x) c \int d\tau_1 \delta^{(4)}(x - x_1(\tau_1)) u^\mu(\tau_1) \\
&= -\frac{q}{c} \int d\tau_1 \left(\int dx A_\mu(x) \delta^{(4)}(x - x_1(\tau_1)) \right) u^\mu(\tau_1) \\
&= -\frac{q}{c} \int d\tau_1 A_\mu(x_1(\tau_1)) u^\mu(\tau_1) \\
&= \int d\tau_1 \left(-\frac{q}{c} A_\mu(x_1(\tau_1)) u^\mu(\tau_1) \right), \tag{C.19}
\end{aligned}$$

which is the exact definition of the action of the interaction Lagrangian from Eq. (C.16), thus validating the interaction Lagrangian density proposed. We show explicitly the gauge invariance of this interaction Lagrangian density through

$$\begin{aligned}
S'_{\text{int}} &= \frac{1}{c} \int dx \mathcal{L}_{\text{int}}(A', \partial A', x, u) \\
&= \frac{1}{c} \int dx \left(-\frac{1}{c} A'_\mu j^\mu \right) \\
&= \frac{1}{c} \int dx \left(-\frac{1}{c} A_\mu j^\mu \right) + \frac{1}{c} \int dx \left(\frac{1}{c} \partial_\mu g j^\mu \right) \\
&= S_{\text{int}} - \frac{1}{c} \int dx \left(\frac{1}{c} g \partial_\mu j^\mu \right) + 0 \\
&= S_{\text{int}}, \tag{C.20}
\end{aligned}$$

where we expressed A'^μ using the gauge transformation $A'^\mu = A^\mu - \partial^\mu g$ [see Eq. (1.38)] before doing an integration by parts, with the surface term vanishing because it is proportional to the 4-current which is an integrable quantity and must therefore vanish at the boundaries of the available space, and the remaining integral vanishing due to the continuity equation of the 4-current [see Eq. (1.37)].

C.4 Electromagnetic field radiation Lagrangian density

We want to derive the covariant radiation Lagrangian density of an electrodynamic field (see, e.g., Ref. [1]). We start from the decomposition of the electromagnetic Lagrangian density

$$\begin{aligned}
\mathcal{L}_{\text{em}}(A, \partial A, x, u) &= \mathcal{L}_{\text{rad}}(\partial A, x) + \mathcal{L}_{\text{int}}(A, x, u) \\
&= \mathcal{L}_{\text{rad}}(\partial A, x) - \frac{q}{c} A_\mu(x) u^\mu, \tag{C.21}
\end{aligned}$$

such that inserting this Lagrangian density within the Euler-Lagrange equations [see Eq. (1.63)] must yield the equations of motion for the gauge field A [see Eq. (1.42)]. We first rewrite these equations in compact form with indices suiting Eq. (1.63), abandoning Einstein's summation convention for the sake of clarity during the rest of this section.

$$\sum_{\nu=0}^3 \partial_\nu F^{\nu\mu} = \frac{4\pi}{c} j^\mu, \tag{C.22}$$

and then insert the expression of our electromagnetic Lagrangian density Eq. (C.21) within the Euler-Lagrange equations such that

$$\begin{aligned} \frac{\partial \mathcal{L}_{\text{em}}}{\partial A^\mu} - \sum_{\nu=0}^3 \partial^\nu \frac{\partial \mathcal{L}_{\text{em}}}{\partial (\partial^\nu A^\mu)} = 0 &\iff \sum_{\nu=0}^3 \partial^\nu \frac{\partial \mathcal{L}_{\text{rad}}}{\partial (\partial^\nu A^\mu)} = \frac{\partial \mathcal{L}_{\text{int}}}{\partial (\sum_{\alpha=0}^3 A_\alpha g^{\alpha\mu})} \\ &= \frac{\partial \mathcal{L}_{\text{int}}}{\partial A_\mu} \frac{1}{g^{\mu\mu}} \\ &= -\frac{1}{c} j^\mu \frac{1}{g^{\mu\mu}} \end{aligned} \quad (\text{C.23})$$

as only the radiation part depends dynamically on derivatives of the gauge field, and only the interaction part depends dynamically on the gauge field itself, and where we made use of the metric tensor to raise indices and then kept only the non-zero coefficients of the metric tensor. The right-hand sides of Eq. (C.22) and Eq. (C.23) are equal up to a coefficient $-4\pi g^{\mu\mu}$, such that the radiation Lagrangian density must verify

$$\sum_{\nu=0}^3 \partial^\nu \frac{\partial \mathcal{L}_{\text{rad}}}{\partial (\partial^\nu A^\mu)} = -\frac{1}{4\pi g^{\mu\mu}} \sum_{\nu=0}^3 \partial_\nu F^{\nu\mu}. \quad (\text{C.24})$$

As the field strength tensor is $F^{\nu\mu} = \partial^\nu A^\mu - \partial^\mu A^\nu$, it is linear in the derivative of the gauge field. Therefore, this equality requires \mathcal{L}_{rad} to be quadratic in the derivative of the gauge field in order for its derivative to be proportional to the field strength tensor. In order to have a radiation Lagrangian density which is Lorentz invariant, gauge invariant and quadratic in the derivative of the gauge field, we propose, up to an undetermined constant prefactor Cst, $\mathcal{L}_{\text{rad}} = \text{Cst} F^{\lambda\sigma} F_{\lambda\sigma}$. We have thus

$$\begin{aligned} F^{\lambda\sigma} F_{\lambda\sigma} &= \sum_{\lambda,\sigma=0}^3 (\partial^\lambda A^\sigma - \partial^\sigma A^\lambda) (\partial_\lambda A_\sigma - \partial_\sigma A_\lambda) \\ &= \sum_{\lambda,\sigma=0}^3 (\partial^\lambda A^\sigma - \partial^\sigma A^\lambda) \sum_{\alpha,\beta=0}^3 (\partial^\alpha A^\beta - \partial^\beta A^\alpha) g_{\alpha\lambda} g_{\beta\sigma} \\ &= \sum_{\lambda,\sigma=0}^3 (\partial^\lambda A^\sigma - \partial^\sigma A^\lambda)^2 g_{\lambda\lambda} g_{\sigma\sigma}, \end{aligned} \quad (\text{C.25})$$

where we once more made use of the metric tensor to raise indices and then kept only the non-zero coefficients of the metric tensor, such that for any ν and μ between 0 and 3 both $(\partial^\mu A^\nu - \partial^\nu A^\mu)^2$ and $(\partial^\nu A^\mu - \partial^\mu A^\nu)^2$ have non-vanishing derivatives with respect to $(\partial^\nu A^\mu)$. Therefore, for any μ between 0 and 3 we have

$$\begin{aligned} \sum_{\nu=0}^3 \partial^\nu \frac{\partial \mathcal{L}_{\text{rad}}}{\partial (\partial^\nu A^\mu)} &= \sum_{\nu=0}^3 \partial^\nu \text{Cst} \left[2(\partial^\nu A^\mu - \partial^\mu A^\nu) - 2(\partial^\mu A^\nu - \partial^\nu A^\mu) \right] g_{\nu\nu} g_{\mu\mu} \\ &= \text{Cst} 4 g_{\mu\mu} \sum_{\nu=0}^3 \partial^\nu g_{\nu\nu} (\partial^\nu A^\mu - \partial^\mu A^\nu) \\ &= \text{Cst} 4 g_{\mu\mu} \sum_{\nu=0}^3 \partial_\nu F^{\nu\mu}, \end{aligned} \quad (\text{C.26})$$

The equality of Eq. (C.24) and Eq. (C.26) determines the prefactor Cst, such that $\text{Cst} = -g^{\mu\mu}/(16\pi g_{\mu\mu}) = -1/(16\pi)$ due to the structure of the metric tensor. We thus have the covariant radiation Lagrangian density

$$\mathcal{L}_{\text{rad}}(\partial A, x) = -\frac{1}{16\pi} F^{\mu\nu} F_{\mu\nu}. \quad (\text{C.27})$$

C.5 Matter Lagrangian density

We want to derive the covariant matter Lagrangian density (see, e.g., Ref. [1, 2]). The insertion of \mathcal{L}_{mat} into the Euler-Lagrange equations [see Eq. (1.68)] must yield the Dirac equation [see Eq. (D.15)], which we rewrite here

$$0 = (-i\hbar c \boldsymbol{\gamma}^\mu \partial_\mu + mc^2) \psi, \quad (\text{C.28})$$

and as this equation does not depend on $\bar{\psi}$ nor on its derivative, it is enough to consider as a matter Lagrangian density

$$\mathcal{L}_{\text{mat}}(\psi, \bar{\psi}) = \bar{\psi} (-i\hbar c \boldsymbol{\gamma}^\mu \partial_\mu + mc^2 \mathbf{I}_4) \psi, \quad (\text{C.29})$$

such that the Euler-Lagrange equations [see Eq. (1.68)] yield

$$\begin{aligned} \frac{\partial \mathcal{L}_{\text{mat}}}{\partial \bar{\psi}} - \partial^\nu \frac{\partial \mathcal{L}_{\text{em}}}{\partial (\partial^\nu \bar{\psi})} = 0 &\iff 0 = \frac{\partial \mathcal{L}_{\text{mat}}}{\partial \bar{\psi}} \\ 0 &= (-i\hbar c \boldsymbol{\gamma}^\mu \partial_\mu + mc^2 \mathbf{I}_4) \psi, \end{aligned} \quad (\text{C.30})$$

as the matter Lagrangian density depends only on $\bar{\psi}$ and ψ and not on their derivatives, thus recovering correctly the Dirac equation as the equation of motion for the Dirac field ψ .

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Appendix D

Derivation of the Dirac equation

We want to derive the Dirac equation (see, e.g., Ref. [1, 2]). This equation can be derived starting from an ansatz containing first order derivatives in time and space to ensure covariance,

$$i\hbar \frac{\partial}{\partial t} \Psi = (c\boldsymbol{\alpha} \cdot \mathbf{p} + \boldsymbol{\beta} mc^2) \Psi, \quad (\text{D.1})$$

where $\mathbf{p} = -i\hbar \nabla$ is the three-dimensional momentum operator and writing $\boldsymbol{\alpha}$ as

$$\boldsymbol{\alpha} = \begin{pmatrix} \boldsymbol{\alpha}^1 \\ \boldsymbol{\alpha}^2 \\ \boldsymbol{\alpha}^3 \end{pmatrix}, \quad (\text{D.2})$$

such that this ansatz features four matrices as parameters, $(\boldsymbol{\alpha}^i)_{(i=1,3)}$ and $\boldsymbol{\beta}$. These matrices have to be Hermitian in order for the eigenvalues of this equation to describe real-valued energies of particles. Considering that the energy-momentum dispersion relation [see Eq. (1.24)] must be satisfied by this equation, conditions on these parameters can be determined through

$$\begin{aligned} (\mathbf{p}^2 c^2 + m^2 c^4) \Psi &= E^2 \Psi = -\hbar^2 \frac{\partial^2}{\partial t^2} \Psi \\ &= i\hbar \frac{\partial}{\partial t} (c\boldsymbol{\alpha} \cdot \mathbf{p} + \boldsymbol{\beta} mc^2) \Psi \\ &= (c\boldsymbol{\alpha} \cdot \mathbf{p} + \boldsymbol{\beta} mc^2) i\hbar \frac{\partial}{\partial t} \Psi \\ &= (c\boldsymbol{\alpha} \cdot \mathbf{p} + \boldsymbol{\beta} mc^2)^2 \Psi, \end{aligned} \quad (\text{D.3})$$

which must hold for all and any function Ψ . We have thus, writing the sums explicitly for the sake of clarity,

$$\begin{aligned} \sum_{i=1}^3 (p_i)^2 c^2 + m^2 c^4 &= \left(\sum_{i=1}^3 c\boldsymbol{\alpha}^i p_i + \boldsymbol{\beta} mc^2 \right)^2 \\ &= \boldsymbol{\beta}^2 m^2 c^4 + \sum_{i,j=1}^3 c^2 \boldsymbol{\alpha}^i \boldsymbol{\alpha}^j p_i p_j + \sum_{i=1}^3 c(\boldsymbol{\alpha}^i \boldsymbol{\beta} + \boldsymbol{\beta} \boldsymbol{\alpha}^i) p_i mc^2 \\ &= \boldsymbol{\beta}^2 m^2 c^4 + \frac{1}{2} \sum_{i,j=1}^3 c^2 (\boldsymbol{\alpha}^i \boldsymbol{\alpha}^j + \boldsymbol{\alpha}^j \boldsymbol{\alpha}^i) p_i p_j + \sum_{i=1}^3 c(\boldsymbol{\alpha}^i \boldsymbol{\beta} + \boldsymbol{\beta} \boldsymbol{\alpha}^i) p_i mc^2. \end{aligned} \quad (\text{D.4})$$

This equation yields constraints on the parameters $(\boldsymbol{\alpha}^i)_{(i=1,3)}$ and $\boldsymbol{\beta}$, such that

$$\boldsymbol{\beta}^2 = 1 \quad \iff \quad \boldsymbol{\beta} = \boldsymbol{\beta}^{-1}, \quad (\text{D.5})$$

$$(\boldsymbol{\alpha}^i \boldsymbol{\alpha}^j + \boldsymbol{\alpha}^j \boldsymbol{\alpha}^i)_{i=1,3} = 2\delta_{ij} \quad \implies \quad (\boldsymbol{\alpha}^i)_{i=1,3}^2 = 1, \quad (\text{D.6})$$

$$(\boldsymbol{\alpha}^i \boldsymbol{\beta} + \boldsymbol{\beta} \boldsymbol{\alpha}^i)_{i=1,3} = 0. \quad (\text{D.7})$$

These constraints allow us to determine properties of these four matrices. Considering that they are Hermitian matrices, the equations $(\boldsymbol{\alpha}^i)_{i=1,3}^2 = 1$ [see Eq. (D.6)] and $\boldsymbol{\beta}^2 = 1$ [see Eq. (D.5)] yields that eigenvalues of both $\boldsymbol{\alpha}^i$'s and $\boldsymbol{\beta}$ matrices are necessarily $+1$ or -1 . Furthermore, by multiplying Eq. (D.7) by $\boldsymbol{\beta}^{-1}$ from the left, we have for $i = 1, 3$

$$\begin{aligned} \boldsymbol{\alpha}^i \boldsymbol{\beta} + \boldsymbol{\beta} \boldsymbol{\alpha}^i = 0 &\iff \boldsymbol{\beta}^{-1} \boldsymbol{\alpha}^i \boldsymbol{\beta} + \boldsymbol{\beta}^{-1} \boldsymbol{\beta} \boldsymbol{\alpha}^i = 0 \\ &\boldsymbol{\beta}^{-1} \boldsymbol{\alpha}^i \boldsymbol{\beta} + \boldsymbol{\alpha}^i = 0 \\ &\boldsymbol{\alpha}^i = -\boldsymbol{\beta}^{-1} \boldsymbol{\alpha}^i \boldsymbol{\beta} \\ &\boldsymbol{\alpha}^i = -\boldsymbol{\beta} \boldsymbol{\alpha}^i \boldsymbol{\beta} \end{aligned} \quad (\text{D.8})$$

where the last line makes use of $\boldsymbol{\beta} = \boldsymbol{\beta}^{-1}$ [see Eq. (D.5)]. Taking the trace of Eq. (D.8) yields

$$\begin{aligned} \text{Tr}[\boldsymbol{\alpha}^i] &= \text{Tr}[-\boldsymbol{\beta} \boldsymbol{\alpha}^i \boldsymbol{\beta}] \\ &= -\text{Tr}[\boldsymbol{\beta} \boldsymbol{\alpha}^i \boldsymbol{\beta}] \\ &= -\text{Tr}[\boldsymbol{\alpha}^i \boldsymbol{\beta} \boldsymbol{\beta}] \\ &= -\text{Tr}[\boldsymbol{\alpha}^i], \end{aligned} \quad (\text{D.9})$$

such that necessarily $\text{Tr}[\boldsymbol{\alpha}^i] = 0$. In the same way, by multiplying Eq. (D.7) by $(\boldsymbol{\alpha}^i)^{-1}$ from the left, we have for $i = 1, 3$

$$\begin{aligned} \boldsymbol{\alpha}^i \boldsymbol{\beta} + \boldsymbol{\beta} \boldsymbol{\alpha}^i = 0 &\iff (\boldsymbol{\alpha}^i)^{-1} \boldsymbol{\alpha}^i \boldsymbol{\beta} + (\boldsymbol{\alpha}^i)^{-1} \boldsymbol{\beta} \boldsymbol{\alpha}^i = 0 \\ &\boldsymbol{\beta} + (\boldsymbol{\alpha}^i)^{-1} \boldsymbol{\beta} \boldsymbol{\alpha}^i = 0 \\ &\boldsymbol{\beta} = -(\boldsymbol{\alpha}^i)^{-1} \boldsymbol{\beta} \boldsymbol{\alpha}^i \\ &\boldsymbol{\beta} = -\boldsymbol{\alpha}^i \boldsymbol{\beta} \boldsymbol{\alpha}^i \end{aligned} \quad (\text{D.10})$$

where the last line makes use of $\boldsymbol{\alpha}^i = (\boldsymbol{\alpha}^i)^{-1}$ [see Eq. (D.6)]. Taking the trace of Eq. (D.10) yields

$$\begin{aligned} \text{Tr}[\boldsymbol{\beta}] &= \text{Tr}[-\boldsymbol{\alpha}^i \boldsymbol{\beta} \boldsymbol{\alpha}^i] \\ &= -\text{Tr}[\boldsymbol{\alpha}^i \boldsymbol{\beta} \boldsymbol{\alpha}^i] \\ &= -\text{Tr}[\boldsymbol{\beta} \boldsymbol{\alpha}^i \boldsymbol{\alpha}^i] \\ &= -\text{Tr}[\boldsymbol{\beta}], \end{aligned} \quad (\text{D.11})$$

such that necessarily $\text{Tr}[\boldsymbol{\beta}] = 0$. The fact that all four Hermitian matrices have vanishing traces implies that they each have an equal number of positive and negative eigenvalues, which means that these matrices are of an even dimension. We may consider dimension two, where we know exactly four independent Hermitian matrices forming a basis of the vector-space of 2×2 matrices, the identity matrix of order 2 and the three Pauli matrices $(\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, \boldsymbol{\sigma}_3)$, corresponding respectively to

$$\mathbf{I}_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{and} \quad \boldsymbol{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (\text{D.12})$$

but as only the three Pauli matrices possess a vanishing trace, one cannot find four independent 2×2 matrices fulfilling the constraints from Eq. (D.5) to Eq. (D.7). The next possible dimension is four, with a vector-space of 4×4 matrices being described by a basis of sixteen independent Hermitian matrices, among which one can find four independent 4×4 matrices fulfilling these constraints. The standard representation of the Dirac equation [3, 4] uses the four following 4×4 matrices

$$\boldsymbol{\alpha}^1 = \begin{pmatrix} 0 & \boldsymbol{\sigma}_1 \\ \boldsymbol{\sigma}_1 & 0 \end{pmatrix}, \quad \boldsymbol{\alpha}^2 = \begin{pmatrix} 0 & \boldsymbol{\sigma}_2 \\ \boldsymbol{\sigma}_2 & 0 \end{pmatrix}, \quad \boldsymbol{\alpha}^3 = \begin{pmatrix} 0 & \boldsymbol{\sigma}_3 \\ \boldsymbol{\sigma}_3 & 0 \end{pmatrix} \quad \text{and} \quad \boldsymbol{\beta} = \begin{pmatrix} \mathbf{I}_2 & 0 \\ 0 & -\mathbf{I}_2 \end{pmatrix}, \quad (\text{D.13})$$

written using the 2×2 matrices of Eq. (D.12) and such that these four matrices correctly satisfy the constraints from Eq. (D.5) to Eq. (D.7). The Dirac equation can be recast into a covariant formalism using the 4-gradient [see Eq. (1.17)] such that it becomes

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \Psi = (c\boldsymbol{\alpha} \cdot \mathbf{p} + \boldsymbol{\beta} mc^2) \Psi &\iff 0 = \left(-i\hbar \frac{\partial}{\partial t} - i\hbar c \boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + \boldsymbol{\beta} mc^2 \right) \Psi \\ 0 &= (-i\hbar c \partial_0 - i\hbar c \boldsymbol{\alpha}^i \partial_i + \boldsymbol{\beta} mc^2) \Psi, \end{aligned} \quad (\text{D.14})$$

or, by multiplying from the left by $\boldsymbol{\beta}$

$$\begin{aligned} 0 &= (-i\hbar c \boldsymbol{\beta} \partial_0 - i\hbar c \boldsymbol{\beta} \boldsymbol{\alpha}^i \partial_i + mc^2 \mathbf{I}_4) \Psi \\ 0 &= (-i\hbar c \boldsymbol{\gamma}^\mu \partial_\mu + mc^2 \mathbf{I}_4) \Psi, \end{aligned} \quad (\text{D.15})$$

where we defined for $i = 1, 3$

$$\boldsymbol{\gamma}^0 = \boldsymbol{\beta} = \begin{pmatrix} \mathbf{I}_2 & 0 \\ 0 & -\mathbf{I}_2 \end{pmatrix} \quad \text{and} \quad \boldsymbol{\gamma}^i = \boldsymbol{\beta} \boldsymbol{\alpha}^i = \begin{pmatrix} 0 & \boldsymbol{\sigma}_i \\ -\boldsymbol{\sigma}_i & 0 \end{pmatrix}. \quad (\text{D.16})$$

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Appendix E

Hartree and exchange energies for two-electron systems

We want to prove some simple results on ground-state two-electrons systems by making use of the Kramers symmetry [see section (2.1.2)], such that the two electrons are described by two spinors forming a Kramers' pair.

E.1 Coulomb interaction

E.1.1 Hartree energy

We start with the expression of the Coulomb Hartree energy as

$$\begin{aligned}
 E_{\text{H}}^{\text{C}} &= +\frac{1}{2} \iint_{\Omega} \frac{1}{r_{12}} \sum_{i,j=1}^2 \psi_i^\dagger(\mathbf{r}_1) \mathbf{I}_4 \psi_i(\mathbf{r}_1) \psi_j^\dagger(\mathbf{r}_2) \mathbf{I}_4 \psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\
 &= +\frac{1}{2} \iint_{\Omega} \frac{1}{r_{12}} \left(\psi_1^\dagger(\mathbf{r}_1) \psi_1(\mathbf{r}_1) \left[\psi_1^\dagger(\mathbf{r}_2) \psi_1(\mathbf{r}_2) + \psi_1^\dagger(\mathbf{r}_2) \mathcal{K}^\dagger \mathcal{K} \psi_1(\mathbf{r}_2) \right] \right. \\
 &\quad \left. + \psi_1^\dagger(\mathbf{r}_1) \mathcal{K}^\dagger \mathcal{K} \psi_1(\mathbf{r}_1) \left[\psi_1^\dagger(\mathbf{r}_2) \psi_1(\mathbf{r}_2) + \psi_1^\dagger(\mathbf{r}_2) \mathcal{K}^\dagger \mathcal{K} \psi_1(\mathbf{r}_2) \right] \right) d\mathbf{r}_1 d\mathbf{r}_2 \\
 &= +\frac{1}{2} \iint_{\Omega} \frac{1}{r_{12}} 4 \psi_1^\dagger(\mathbf{r}_1) \psi_1(\mathbf{r}_1) \psi_1^\dagger(\mathbf{r}_2) \psi_1(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \tag{E.1}
 \end{aligned}$$

where we used Kramers' time inversion operator [see Eq. (2.44)], such that $\mathcal{K}^\dagger \mathcal{K} = \mathbf{I}_4$.

E.1.2 Exchange energy

We continue with the expression of the Coulomb exchange energy as

$$\begin{aligned}
 E_{\text{X}}^{\text{C}} &= -\frac{1}{2} \iint_{\Omega} \frac{1}{r_{12}} \sum_{i,j=1}^2 \psi_i^\dagger(\mathbf{r}_1) \mathbf{I}_4 \psi_j(\mathbf{r}_1) \psi_j^\dagger(\mathbf{r}_2) \mathbf{I}_4 \psi_i(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\
 &= -\frac{1}{2} \iint_{\Omega} \frac{1}{r_{12}} \left(\psi_1^\dagger(\mathbf{r}_1) \psi_1(\mathbf{r}_1) \psi_1^\dagger(\mathbf{r}_2) \psi_1(\mathbf{r}_2) + \psi_1^\dagger(\mathbf{r}_1) \mathcal{K}^\dagger \mathcal{K} \psi_1(\mathbf{r}_1) \psi_1^\dagger(\mathbf{r}_2) \mathcal{K}^\dagger \mathcal{K} \psi_1(\mathbf{r}_2) \right. \\
 &\quad \left. + (\mathcal{K} \psi_1)^\dagger(\mathbf{r}_1) \psi_1(\mathbf{r}_1) \psi_1^\dagger(\mathbf{r}_2) (\mathcal{K} \psi_1)(\mathbf{r}_2) + \psi_1^\dagger(\mathbf{r}_1) (\mathcal{K} \psi_1)(\mathbf{r}_1) (\mathcal{K} \psi_1)^\dagger(\mathbf{r}_2) \psi_1(\mathbf{r}_2) \right) d\mathbf{r}_1 d\mathbf{r}_2 \\
 &= -\frac{1}{2} \iint_{\Omega} \frac{1}{r_{12}} 2 \psi_1^\dagger(\mathbf{r}_1) \psi_1(\mathbf{r}_1) \psi_1^\dagger(\mathbf{r}_2) \psi_1(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \tag{E.2}
 \end{aligned}$$

with

$$\begin{aligned} \psi_1^\dagger(\mathcal{K}\psi_1) &= \begin{pmatrix} \psi_1^{L\alpha*} & \psi_1^{L\beta*} & \psi_1^{S\alpha*} & \psi_1^{S\beta*} \end{pmatrix} \begin{pmatrix} -\psi_1^{L\beta*} \\ \psi_1^{L\alpha*} \\ -\psi_1^{S\beta*} \\ \psi_1^{S\alpha*} \end{pmatrix} \\ &= 0, \end{aligned} \tag{E.3}$$

such that we correctly find that $E_x^C = -\frac{1}{2}E_H^C$ for two electrons described by one Kramers pair.

E.2 Gaunt interaction

E.2.1 Hartree energy

We start with the expression of the Gaunt Hartree energy as

$$\begin{aligned} E_H^G &= +\frac{1}{2} \iint_{\Omega} \frac{1}{r_{12}} \sum_{i,j=1}^2 \psi_i^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \psi_i(\mathbf{r}_1) \cdot \psi_j^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= -\frac{1}{2} \iint_{\Omega} \frac{1}{r_{12}} \left(\psi_1^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \psi_1(\mathbf{r}_2) + \psi_1^\dagger(\mathbf{r}_1) \mathcal{K}^\dagger \boldsymbol{\alpha}_1 \mathcal{K} \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \mathcal{K}^\dagger \boldsymbol{\alpha}_2 \mathcal{K} \psi_1(\mathbf{r}_2) \right. \\ &\quad \left. + \psi_1^\dagger(\mathbf{r}_1) \mathcal{K}^\dagger \boldsymbol{\alpha}_1 \mathcal{K} \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \psi_1(\mathbf{r}_2) + \psi_1^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \mathcal{K}^\dagger \boldsymbol{\alpha}_2 \mathcal{K} \psi_1(\mathbf{r}_2) \right) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= -\frac{1}{2} \iint_{\Omega} \frac{1}{r_{12}} \left(\psi_1^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \psi_1(\mathbf{r}_2) + \psi_1^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \psi_1(\mathbf{r}_2) \right. \\ &\quad \left. - \psi_1^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \psi_1(\mathbf{r}_2) - \psi_1^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \psi_1(\mathbf{r}_2) \right) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= 0, \end{aligned} \tag{E.4}$$

where, using the relations of the Kramers operator with the $\boldsymbol{\alpha}$ matrices [see Eq. (2.53)], we correctly find that for the Hartree energy for the Gaunt interaction vanishes. It corresponds, in all generality, to the vanishing of the current-current direct interaction for any closed-shell system.

E.2.2 Exchange energy

We continue with the expression of the Gaunt exchange energy as

$$\begin{aligned} E_X^G &= -\frac{1}{2} \iint_{\Omega} \frac{1}{r_{12}} \sum_{i,j=1}^2 \psi_i^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \psi_j(\mathbf{r}_1) \cdot \psi_j^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \psi_i(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= -\frac{1}{2} \iint_{\Omega} \frac{1}{r_{12}} \left(\psi_1^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \psi_1(\mathbf{r}_2) + \psi_1^\dagger(\mathbf{r}_1) \mathcal{K}^\dagger \boldsymbol{\alpha}_1 \mathcal{K} \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \mathcal{K}^\dagger \boldsymbol{\alpha}_2 \mathcal{K} \psi_1(\mathbf{r}_2) \right. \\ &\quad \left. + \psi_1^\dagger \mathcal{K}^\dagger \boldsymbol{\alpha}_1(\mathbf{r}_1) \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \mathcal{K} \psi_1(\mathbf{r}_2) + \psi_1^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \mathcal{K} \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \mathcal{K}^\dagger \boldsymbol{\alpha}_2 \psi_1(\mathbf{r}_2) \right) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= -\frac{1}{2} \iint_{\Omega} \frac{1}{r_{12}} 2 \left(\psi_1^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \psi_1(\mathbf{r}_2) + \psi_1^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \mathcal{K} \psi_1(\mathbf{r}_1) \cdot \psi_1^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \mathcal{K} \psi_1(\mathbf{r}_2) \right) d\mathbf{r}_1 d\mathbf{r}_2, \end{aligned} \tag{E.5}$$

which does not vanish but corresponds to current-current exchange interactions between the two electrons described by one Kramers pair.

Appendix F

Four-component Dirac-Hartree-Fock

F.1 One-electron Fock matrix

We wish to express the one-electron Fock matrix in four-component formalism for the Dirac Hamiltonian using a scalar Gaussian basis set (see, e.g., Ref. [1]). We first rewrite the one-electron Dirac Hamiltonian h^D [see Eq. (2.57)] in explicit 4×4 matrix form after having removed the mass energy term of the electron, such that

$$h_{-mc^2}^D = h^D - mc^2 \mathbf{I}_4 = \begin{pmatrix} V & 0 & c\Pi_z & c\Pi_- \\ 0 & V & c\Pi_+ & -c\Pi_z \\ c\Pi_z & c\Pi_- & V - 2mc^2 & 0 \\ c\Pi_+ & -c\Pi_z & 0 & V - 2mc^2 \end{pmatrix} \quad (\text{F.1})$$

where V is the external scalar potential, and using the notation

$$\Pi_z = -i\hbar \frac{\partial}{\partial z} \quad \text{and} \quad \Pi_{\pm} = -i\hbar \left(\frac{\partial}{\partial x} \pm i \frac{\partial}{\partial y} \right). \quad (\text{F.2})$$

The Dirac equation, shifted by the mass energy term of the electron, is written for a 4-spinor Ψ_p as

$$h_{-mc^2}^D \Psi_p = \Psi_p \varepsilon_p, \quad (\text{F.3})$$

such that using the scalar basis set decomposition for a spinor Ψ_p [see Eq. (2.103)] yields

$$\begin{pmatrix} V & 0 & c\Pi_z & c\Pi_- \\ 0 & V & c\Pi_+ & -c\Pi_z \\ c\Pi_z & c\Pi_- & V - 2mc^2 & 0 \\ c\Pi_+ & -c\Pi_z & 0 & V - 2mc^2 \end{pmatrix} \begin{pmatrix} \sum_{v=1}^{N_L} a_v^{L\alpha} \chi_v^{L(\alpha)} \\ \sum_{v=1}^{N_L} a_v^{L\beta} \chi_v^{L(\beta)} \\ \sum_{v=1}^{N_S} a_v^{S\alpha} \chi_v^{S(\alpha)} \\ \sum_{v=1}^{N_S} a_v^{S\beta} \chi_v^{S(\beta)} \end{pmatrix} = \begin{pmatrix} \sum_{v=1}^{N_L} a_v^{L\alpha} \chi_v^{L(\alpha)} \\ \sum_{v=1}^{N_L} a_v^{L\beta} \chi_v^{L(\beta)} \\ \sum_{v=1}^{N_S} a_v^{S\alpha} \chi_v^{S(\alpha)} \\ \sum_{v=1}^{N_S} a_v^{S\beta} \chi_v^{S(\beta)} \end{pmatrix} \varepsilon_p. \quad (\text{F.4})$$

Following the development from the book of A. Szabo and N. S. Ostlund [2] we want to transform the integro-differential equation into a pure matrix equation by multiplication by a single Gaussian basis function χ_μ^* on the left and integrating over the available space. Care has to be taken to consider this basis function within the spinor structure, i.e. as a four-dimensional vector with only one non-vanishing component. Using the labels X and Y running over L,S and the labels τ and ν running over α, β , we write for any 4×4 operator O its matrix element in the scalar basis set $\{\chi^L, \chi^S\}$ as $O_{\mu\nu}^{X\tau Y\nu}$ for the $O^{X\tau Y\nu}$ operator element. Its decomposition on the scalar basis set is then

$$\begin{aligned} O_{\mu\nu}^{X\tau Y\nu} &= \langle \chi_\mu^{X(\tau)} | O | \chi_\nu^{Y(\nu)} \rangle \\ &= \int d\mathbf{r} \left(\chi_\mu^{X(\tau)} \right)^\dagger O \chi_\nu^{Y(\nu)}. \end{aligned} \quad (\text{F.5})$$

In order not to do the work four times we shall consider basis functions for all four components at once, with $1 \leq \mu_1 \leq N_L$, $1 \leq \mu_2 \leq N_L$, $1 \leq \mu_3 \leq N_S$, $1 \leq \mu_4 \leq N_S$ such that

$$\begin{aligned} & \int d\mathbf{r} \begin{pmatrix} \chi_{\mu_1}^{L(\alpha)} \\ \chi_{\mu_2}^{L(\beta)} \\ \chi_{\mu_3}^{S(\alpha)} \\ \chi_{\mu_4}^{S(\beta)} \end{pmatrix}^\dagger \begin{pmatrix} V & 0 & c\Pi_z & c\Pi_- \\ 0 & V & c\Pi_+ & -c\Pi_z \\ c\Pi_z & c\Pi_- & V - 2mc^2 & 0 \\ c\Pi_+ & -c\Pi_z & 0 & V - 2mc^2 \end{pmatrix} \begin{pmatrix} \sum_{v=1}^{N_L} a_v^{L\alpha} \chi_v^{L(\alpha)} \\ \sum_{v=1}^{N_L} a_v^{L\beta} \chi_v^{L(\beta)} \\ \sum_{v=1}^{N_S} a_v^{S\alpha} \chi_v^{S(\alpha)} \\ \sum_{v=1}^{N_S} a_v^{S\beta} \chi_v^{S(\beta)} \end{pmatrix} \\ &= \int d\mathbf{r} \begin{pmatrix} \chi_{\mu_1}^{L(\alpha)} \\ \chi_{\mu_2}^{L(\beta)} \\ \chi_{\mu_3}^{S(\alpha)} \\ \chi_{\mu_4}^{S(\beta)} \end{pmatrix}^\dagger \begin{pmatrix} \sum_{v=1}^{N_L} a_v^{L\alpha} \chi_v^{L(\alpha)} \\ \sum_{v=1}^{N_L} a_v^{L\beta} \chi_v^{L(\beta)} \\ \sum_{v=1}^{N_S} a_v^{S\alpha} \chi_v^{S(\alpha)} \\ \sum_{v=1}^{N_S} a_v^{S\beta} \chi_v^{S(\beta)} \end{pmatrix} \epsilon_p. \end{aligned} \quad (\text{F.6})$$

Expanding the left-hand side of Eq. (F.6) yields

$$\begin{aligned} & \sum_{v=1}^{N_L} a_{v,p}^{L\alpha} \left(V_{\mu_1 v}^{L\alpha L\alpha} + c(\Pi_z)_{\mu_3 v}^{S\alpha L\alpha} + c(\Pi_+)_{\mu_4 v}^{S\beta L\alpha} \right) + \sum_{v=1}^{N_L} a_{v,p}^{L\beta} \left(V_{\mu_2 v}^{L\beta L\beta} + c(\Pi_-)_{\mu_3 v}^{S\alpha L\beta} - c(\Pi_z)_{\mu_4 v}^{S\beta L\beta} \right) \\ &+ \sum_{v=1}^{N_S} a_{v,p}^{S\alpha} \left(c(\Pi_z)_{\mu_1 v}^{L\alpha S\alpha} + c(\Pi_+)_{\mu_2 v}^{L\beta S\alpha} + V_{\mu_3 v}^{S\alpha S\alpha} - 2mc^2 S_{\mu_3 v}^{S\alpha S\alpha} \right) \\ &+ \sum_{v=1}^{N_S} a_{v,p}^{S\beta} \left(c(\Pi_-)_{\mu_1 v}^{L\alpha S\beta} - c(\Pi_z)_{\mu_2 v}^{L\beta S\beta} + V_{\mu_4 v}^{S\beta S\beta} - 2mc^2 S_{\mu_4 v}^{S\beta S\beta} \right), \end{aligned} \quad (\text{F.7})$$

and expanding the right-hand side of Eq. (F.6) yields

$$\left(\sum_{v=1}^{N_L} a_{v,p}^{L\alpha} S_{\mu_1 v}^{L\alpha L\alpha} + \sum_{v=1}^{N_L} a_{v,p}^{L\beta} S_{\mu_2 v}^{L\beta L\beta} + \sum_{v=1}^{N_S} a_{v,p}^{S\alpha} S_{\mu_3 v}^{S\alpha S\alpha} + \sum_{v=1}^{N_S} a_{v,p}^{S\beta} S_{\mu_4 v}^{S\beta S\beta} \right) \epsilon_p, \quad (\text{F.8})$$

such that we may rewrite this system of equations, which is a four-component version of the Roothaan equations in scalar basis set, in a matrix form as

$$\mathbf{F}^D \mathbf{A} = \mathbf{S} \mathbf{A} \boldsymbol{\epsilon} \quad (\text{F.9})$$

with the one-electron four-component Fock matrix written as

$$\mathbf{F}^D = \begin{pmatrix} \mathbf{V}^{L\alpha L\alpha} & 0 & c\Pi_z^{L\alpha S\alpha} & c\Pi_-^{L\alpha S\beta} \\ 0 & \mathbf{V}^{L\beta L\beta} & c\Pi_+^{L\beta S\alpha} & -c\Pi_z^{L\beta S\beta} \\ c\Pi_z^{S\alpha L\alpha} & c\Pi_-^{S\alpha L\beta} & \mathbf{V}^{S\alpha S\alpha} - 2mc^2 \mathbf{S}^{S\alpha S\alpha} & 0 \\ c\Pi_+^{S\beta L\alpha} & -c\Pi_z^{S\beta L\beta} & 0 & \mathbf{V}^{S\beta S\beta} - 2mc^2 \mathbf{S}^{S\beta S\beta} \end{pmatrix} \quad (\text{F.10})$$

where all α and β have been kept for clarity but may be removed due to the use of the same basis set for each ‘‘spin’’ component. The eigenvectors matrix (with each column corresponding to the coefficients of an eigenfunction ψ_p) is written as

$$\mathbf{A} = \begin{pmatrix} a_{1,1}^{L\alpha} & \cdots & a_{1,2(N_L+N_S)}^{L\alpha} \\ \vdots & \ddots & \vdots \\ a_{N_S,1}^{S\beta} & \cdots & a_{N_S,2(N_L+N_S)}^{S\beta} \end{pmatrix}, \quad (\text{F.11})$$

emphasizing the fact that we use $2(N_L + N_S)$ basis functions even though there is only $N_L + N_S$ which are different from one another. We thus describe $2(N_L + N_S)$ eigenvectors, $2N_L$ positive-energy ones and $2N_S$ negative-energy ones. The overlap matrix is written as

$$\mathbf{S} = \begin{pmatrix} \mathbf{S}^{L\alpha L\alpha} & 0 & 0 & 0 \\ 0 & \mathbf{S}^{L\beta L\beta} & 0 & 0 \\ 0 & 0 & \mathbf{S}^{S\alpha S\alpha} & 0 \\ 0 & 0 & 0 & \mathbf{S}^{S\beta S\beta} \end{pmatrix} \quad \text{with} \quad \mathbf{S}^{X\tau X\tau} = \begin{pmatrix} S_{1,1}^{X\tau X\tau} & \dots & S_{1,N_X}^{X\tau X\tau} \\ \vdots & \ddots & \vdots \\ S_{N_X,1}^{X\tau X\tau} & \dots & S_{N_X,N_X}^{X\tau X\tau} \end{pmatrix}, \quad (\text{F.12})$$

where there is no overlap between basis functions which do not describe the same component, and the diagonal matrix of orbital energies is written as

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_1 & & 0 \\ & \ddots & \\ 0 & & \varepsilon_{2(N_L+N_S)} \end{pmatrix}. \quad (\text{F.13})$$

Implementation technicalities

In practice, within an implementation the eigenvectors matrix would appear as

$$\mathbf{A} = \begin{pmatrix} a_{1,1} & \dots & a_{1,2(N_L+N_S)} \\ \vdots & \ddots & \vdots \\ a_{2(N_L+N_S),1} & \dots & a_{2(N_L+N_S),2(N_L+N_S)} \end{pmatrix}, \quad (\text{F.14})$$

describing $2(N_L + N_S)$ eigenvectors ψ_p written as

$$\psi_p = \begin{pmatrix} \sum_{v=1}^{N_L} a_{v,p} \chi_v^{L(\alpha)} \\ \sum_{v=N_L+1}^{2N_L} a_{v,p} \chi_v^{L(\beta)} \\ \sum_{v=2N_L+1}^{2N_L+N_S} a_{v,p} \chi_v^{S(\alpha)} \\ \sum_{v=2N_L+N_S+1}^{2(N_L+N_S)} a_{v,p} \chi_v^{S(\beta)} \end{pmatrix}, \quad (\text{F.15})$$

where we removed all ‘‘spin’’ labels as all information is contained within the number v of $a_{v,p}$.

F.2 Two-electron Fock matrix

We wish to express the two-electron Fock matrix in four-component formalism for the Dirac-Coulomb-Gaunt Hamiltonian using a scalar Gaussian basis set (see, e.g., Ref. [1]).

F.2.1 Coulomb interaction

We start with the two-electron Fock matrix for the Coulomb interaction. We first rewrite the 4-spinor ψ_p such that

$$\Psi_p = \mathbf{P} = \begin{pmatrix} \sum_{v=1}^{N_L} a_v^{L\alpha} \chi_v^{L(\alpha)} \\ \sum_{v=1}^{N_L} a_v^{L\beta} \chi_v^{L(\beta)} \\ \sum_{v=1}^{N_S} a_v^{S\alpha} \chi_v^{S(\alpha)} \\ \sum_{v=1}^{N_S} a_v^{S\beta} \chi_v^{S(\beta)} \end{pmatrix} \quad (\text{F.16})$$

The indices p,q,r,s denoting 4-spinors and the indices $\mu, \nu, \kappa, \lambda$ denoting Gaussian basis functions, the general two electrons integral for the Coulomb interaction is written as

$$\begin{aligned}
(pq | rs) &= \int d\mathbf{r}_1 \int d\mathbf{r}_2 \Psi_p^\dagger(\mathbf{r}_1) \Psi_q(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \Psi_r^\dagger(\mathbf{r}_2) \Psi_s(\mathbf{r}_2) \\
&= \sum_{X,Y,\tau,\nu} \sum_{\mu,\nu,\kappa,\lambda} (a_{\mu,p}^{X\tau})^* a_{\nu,q}^{X\tau} (a_{\kappa,r}^{Y\nu})^* a_{\lambda,s}^{Y\nu} \\
&\quad \int d\mathbf{r}_1 \int d\mathbf{r}_2 \left(\chi_\mu^{X(\tau)} \right)^\dagger(\mathbf{r}_1) \chi_\nu^{X(\tau)}(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \left(\chi_\kappa^{Y(\nu)} \right)^\dagger(\mathbf{r}_2) \chi_\lambda^{Y(\nu)}(\mathbf{r}_2) \\
&= \sum_{X,Y,\tau,\nu} \sum_{\mu,\nu,\kappa,\lambda} (a_{\mu,p}^{X\tau})^* a_{\nu,q}^{X\tau} (a_{\kappa,r}^{Y\nu})^* a_{\lambda,s}^{Y\nu} \left(\mu^{X(\tau)} \nu^{X(\tau)} | \kappa^{Y(\nu)} \lambda^{Y(\nu)} \right). \tag{F.17}
\end{aligned}$$

where X and Y run over $\{L, S\}$ and τ and ν run over $\{\alpha, \beta\}$. Writing $(F^C)_{\mu\nu}^{X\tau Y\nu}$ the general formula for a specific matrix element of a specific block, we have for the diagonal blocks

$$\begin{aligned}
(F^C)_{\mu\nu}^{X\tau X\tau} &= \sum_{p=1}^N \left[\left(\mu^{X(\tau)} \nu^{X(\tau)} | pp \right) - \left(\mu^{X(\tau)} p | p \nu^{X(\tau)} \right) \right] \\
&= \sum_{Y,\nu,\kappa,\lambda} \sum_{p=1}^N \left[\sum_{\mu,\nu} a_{\lambda,p}^{Y\nu} (a_{\kappa,p}^{Y\nu})^* \right] \left(\mu^{X(\tau)} \nu^{X(\tau)} | \kappa^{Y(\nu)} \lambda^{Y(\nu)} \right) \\
&\quad - \sum_{\kappa,\lambda} \left[\sum_{p=1}^N a_{\lambda,p}^{X\tau} (a_{\kappa,p}^{X\tau})^* \right] \left(\mu^{X(\tau)} \lambda^{X(\tau)} | \kappa^{X(\tau)} \nu^{X(\tau)} \right) \\
&= \sum_{Y,\nu,\kappa,\lambda} D_{\lambda,\kappa}^{Y\nu Y\nu} \left(\mu^{X(\tau)} \nu^{X(\tau)} | \kappa^{Y(\nu)} \lambda^{Y(\nu)} \right) \\
&\quad - \sum_{\kappa,\lambda} D_{\lambda,\kappa}^{X\tau X\tau} \left(\mu^{X(\tau)} \lambda^{X(\tau)} | \kappa^{X(\tau)} \nu^{X(\tau)} \right), \tag{F.18}
\end{aligned}$$

writing for a system containing N electrons the density matrix elements as

$$D_{\lambda,\kappa}^{X\tau Y\nu} = \sum_{p=1}^N a_{\lambda,p}^{X\tau} (a_{\kappa,p}^{Y\nu})^*, \tag{F.19}$$

with the sum running over the N lower positive-energy eigenfunctions. For $\tau \neq \nu$, we have

$$\begin{aligned}
(F^C)_{\mu\nu}^{X\tau X\nu} &= \sum_{p=1}^N \left[0 - \left(\mu^{X(\tau)} p | p \nu^{X(\nu)} \right) \right] \\
&= - \sum_{\kappa,\lambda} D_{\lambda,\kappa}^{X\tau X\nu} \left(\mu^{X(\tau)} \lambda^{X(\tau)} | \kappa^{X(\nu)} \nu^{X(\nu)} \right). \tag{F.20}
\end{aligned}$$

For $X \neq Y$, we have

$$\begin{aligned}
(F^C)_{\mu\nu}^{X\tau Y\tau} &= \sum_{p=1}^N \left[0 - \left(\mu^{X(\tau)} p | p \nu^{Y(\tau)} \right) \right] \\
&= - \sum_{\kappa,\lambda} D_{\lambda,\kappa}^{X\tau Y\tau} \left(\mu^{X(\tau)} \lambda^{X(\tau)} | \kappa^{Y(\tau)} \nu^{Y(\tau)} \right). \tag{F.21}
\end{aligned}$$

For $X \neq Y$ and $\tau \neq \nu$, we have

$$\begin{aligned}
(F^C)_{\mu\nu}^{X\tau Y\nu} &= \sum_{p=1}^N \left[0 - \left(\mu^{X(\tau)} p | p \nu^{Y(\nu)} \right) \right] \\
&= - \sum_{\kappa,\lambda} D_{\lambda,\kappa}^{X\tau Y\nu} \left(\mu^{X(\tau)} \lambda^{X(\tau)} | \kappa^{Y(\nu)} \nu^{Y(\nu)} \right). \tag{F.22}
\end{aligned}$$

F.2.2 Gaunt interaction

We first show that the two-electron Fock matrix for the Gaunt interaction can be expressed using the same two-electron integral as for the Coulomb interaction [see Eq. (F.17)]. The two-electron integral for the Gaunt interaction is written as

$$(p\alpha q | r\alpha s), \quad (\text{F.23})$$

such that we have in a two-spinor form

$$\psi_p^\dagger \alpha \psi_q = \begin{pmatrix} \psi_p^L \\ \psi_p^S \end{pmatrix}^\dagger \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \begin{pmatrix} \psi_q^L \\ \psi_q^S \end{pmatrix} = (\psi_p^L)^\dagger \sigma \psi_q^S + (\psi_p^S)^\dagger \sigma \psi_q^L. \quad (\text{F.24})$$

For each of the three Pauli matrices we have

$$(\psi_p^X)^\dagger \sigma_1 \psi_q^Y = \begin{pmatrix} \psi_p^{X\alpha} \\ \psi_p^{X\beta} \end{pmatrix}^\dagger \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \psi_q^{Y\alpha} \\ \psi_q^{Y\beta} \end{pmatrix} = (\psi_p^{X\beta})^* \psi_q^{Y\alpha} + (\psi_p^{X\alpha})^* \psi_q^{Y\beta}, \quad (\text{F.25})$$

$$(\psi_p^X)^\dagger \sigma_2 \psi_q^Y = \begin{pmatrix} \psi_p^{X\alpha} \\ \psi_p^{X\beta} \end{pmatrix}^\dagger \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \psi_q^{Y\alpha} \\ \psi_q^{Y\beta} \end{pmatrix} = i(\psi_p^{X\beta})^* \psi_q^{Y\beta} - i(\psi_p^{X\alpha})^* \psi_q^{Y\alpha}, \quad (\text{F.26})$$

$$(\psi_p^X)^\dagger \sigma_3 \psi_q^Y = \begin{pmatrix} \psi_p^{X\alpha} \\ \psi_p^{X\beta} \end{pmatrix}^\dagger \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \psi_q^{Y\alpha} \\ \psi_q^{Y\beta} \end{pmatrix} = (\psi_p^{X\alpha})^* \psi_q^{Y\alpha} - (\psi_p^{X\beta})^* \psi_q^{Y\beta}. \quad (\text{F.27})$$

We then rewrite the two-electron integral for the Gaunt interaction as

$$\begin{aligned} & (p\alpha q | r\alpha s) \\ &= \left(p^{L\beta} q^{S\alpha} + p^{L\alpha} q^{S\beta} + p^{S\beta} q^{L\alpha} + p^{S\alpha} q^{L\beta} \mid r^{L\beta} s^{S\alpha} + r^{L\alpha} s^{S\beta} + r^{S\beta} s^{L\alpha} + r^{S\alpha} s^{L\beta} \right) \\ & - \left(p^{L\beta} q^{S\alpha} - p^{L\alpha} q^{S\beta} + p^{S\beta} q^{L\alpha} - p^{S\alpha} q^{L\beta} \mid r^{L\beta} s^{S\alpha} - r^{L\alpha} s^{S\beta} + r^{S\beta} s^{L\alpha} - r^{S\alpha} s^{L\beta} \right) \\ & + \left(p^{L\alpha} q^{S\alpha} - p^{L\beta} q^{S\beta} + p^{S\alpha} q^{L\alpha} - p^{S\beta} q^{L\beta} \mid r^{L\alpha} s^{S\alpha} - r^{L\beta} s^{S\beta} + r^{S\alpha} s^{L\alpha} - r^{S\beta} s^{L\beta} \right) \\ &= 2 \left(p^{L\beta} q^{S\alpha} + p^{S\beta} q^{L\alpha} \mid r^{L\alpha} s^{S\beta} + r^{S\alpha} s^{L\beta} \right) \\ & + 2 \left(p^{L\alpha} q^{S\beta} + p^{S\alpha} q^{L\beta} \mid r^{L\beta} s^{S\alpha} + r^{S\beta} s^{L\alpha} \right) \\ & + \left(p^{L\alpha} q^{S\alpha} - p^{L\beta} q^{S\beta} + p^{S\alpha} q^{L\alpha} - p^{S\beta} q^{L\beta} \mid r^{L\alpha} s^{S\alpha} - r^{L\beta} s^{S\beta} + r^{S\alpha} s^{L\alpha} - r^{S\beta} s^{L\beta} \right), \end{aligned} \quad (\text{F.28})$$

which indeed corresponds to combinations of the same two-electron integrals as for the Coulomb interaction. Writing $(F^G)_{\mu\nu}^{X\tau Y\upsilon}$ the general formula for a specific matrix element of a specific block, and considering $X \neq Y$ and $\tau \neq \upsilon$, we have for the diagonal elements

$$\begin{aligned} (F^G)_{\mu\nu}^{X\tau X\tau} &= - \sum_{p=1}^N \left[0 - (\mu^{X(\tau)} \alpha p \mid p \alpha \nu^{X(\tau)}) \right] \\ &= - \left(- \sum_{\kappa, \lambda} \left(2D_{\lambda, \kappa}^{Y\upsilon Y\upsilon} + D_{\lambda, \kappa}^{Y\tau Y\tau} \right) (\mu^X \lambda^Y \mid \kappa^Y \nu^X) \right), \end{aligned} \quad (\text{F.29})$$

where we removed the ("spin") from the expression to allow factorization. The following formulas corresponds to all off-diagonal elements, with

$$\begin{aligned}
(\mathbf{F}^G)_{\mu\nu}^{X\tau X\nu} &= -\sum_{p=1}^N \left[0 - (\mu^{X(\tau)} \boldsymbol{\alpha} p \mid p \boldsymbol{\alpha} \nu^{X(\tau)}) \right] \\
&= -\left(\sum_{\kappa, \lambda} D_{\lambda, \kappa}^{Y\tau Y\nu} (\mu^X \lambda^Y \mid \kappa^Y \nu^X) \right), \tag{F.30}
\end{aligned}$$

$$\begin{aligned}
(\mathbf{F}^G)_{\mu\nu}^{X\tau Y\tau} &= -\sum_{p=1}^N \left[(\mu^{X(\tau)} \boldsymbol{\alpha} \nu^{X(\tau)} \mid p \boldsymbol{\alpha} p) - (\mu^{X(\tau)} \boldsymbol{\alpha} p \mid p \boldsymbol{\alpha} \nu^{X(\tau)}) \right] \\
&= -\left(\sum_{\kappa, \lambda} \left[(D_{\lambda, \kappa}^{S\tau L\tau} - D_{\lambda, \kappa}^{S\nu L\nu}) (\mu^X \nu^Y \mid \kappa^L \lambda^S) + (D_{\lambda, \kappa}^{L\tau S\tau} - D_{\lambda, \kappa}^{L\nu S\nu}) (\mu^X \nu^Y \mid \kappa^S \lambda^L) \right. \right. \\
&\quad \left. \left. - (2D_{\lambda, \kappa}^{Y\nu X\nu} + D_{\lambda, \kappa}^{Y\tau X\tau}) (\mu^X \lambda^Y \mid \kappa^X \nu^Y) \right] \right), \tag{F.31}
\end{aligned}$$

$$\begin{aligned}
(\mathbf{F}^G)_{\mu\nu}^{X\tau Y\nu} &= -\sum_{p=1}^N \left[(\mu^{X(\tau)} \boldsymbol{\alpha} \nu^{X(\tau)} \mid p \boldsymbol{\alpha} p) - (\mu^{X(\tau)} \boldsymbol{\alpha} p \mid p \boldsymbol{\alpha} \nu^{X(\tau)}) \right] \\
&= -\left(\sum_{\kappa, \lambda} \left[2D_{\lambda, \kappa}^{S\tau L\nu} (\mu^X \nu^Y \mid \kappa^L \lambda^S) + 2D_{\lambda, \kappa}^{L\tau S\nu} (\mu^X \nu^Y \mid \kappa^S \lambda^L) + D_{\lambda, \kappa}^{Y\tau X\nu} (\mu^X \lambda^Y \mid \kappa^X \nu^Y) \right] \right). \tag{F.32}
\end{aligned}$$

Bibliography

- [1] K. G. Dyall and K. Faegri, Jr., *Introduction to Relativistic Quantum Chemistry* (Oxford University Press, 2007).
- [2] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Dover, New York, 1996).

Appendix G

Coulomb-Breit exchange energy per particle and exchange hole of the relativistic homogeneous electron gas

In this appendix, we review the calculation of the Coulomb-Breit exchange energy per particle and the exchange hole of the relativistic homogeneous electron gas (RHEG) that we used in Chapter 3.

G.1 Coulomb-Breit exchange energy per particle

The Coulomb exchange energy per particle of the RHEG can be straightforwardly calculated by summing over spins [see Appendix I.1], integrating over each space coordinates in the volume V , and finally integrating over each wave vector in the volume of the Fermi sphere V_{k_F}

$$\begin{aligned}
\varepsilon_x^C &= -\frac{1}{2N} \frac{V^2}{(2\pi)^6} \iint_{V_{k_F}} \iint_V \sum_{\sigma_1, \sigma_2 = \downarrow, \uparrow} w_{ee}(r_{12}) \Psi_{\mathbf{k}_1, \sigma_1}^\dagger(\mathbf{r}_1) \Psi_{\mathbf{k}_2, \sigma_2}(\mathbf{r}_1) \Psi_{\mathbf{k}_2, \sigma_2}^\dagger(\mathbf{r}_2) \Psi_{\mathbf{k}_1, \sigma_1}(\mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{k}_1 d\mathbf{k}_2 \\
&= -\frac{1}{2N(2\pi)^6} \iint_{V_{k_F}} \iint_V w_{ee}(r_{12}) e^{-i\mathbf{k}_{12} \cdot \mathbf{r}_{12}} \frac{E_{k_1} E_{k_2} + (\mathbf{k}_1 \cdot \mathbf{k}_2) c^2 + c^4}{E_{k_1} E_{k_2}} \, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{k}_1 d\mathbf{k}_2 \\
&= -\frac{1}{2n(2\pi)^6} \iint_{V_{k_F}} \tilde{w}_{ee}(k_{12}) \frac{E_{k_1} E_{k_2} + (\mathbf{k}_1 \cdot \mathbf{k}_2) c^2 + c^4}{E_{k_1} E_{k_2}} \, d\mathbf{k}_1 d\mathbf{k}_2 \\
&= -\frac{3 k_F}{4\pi} \left(\frac{5}{6} + \frac{1}{3} \tilde{c}^2 + \frac{2}{3} \sqrt{1 + \tilde{c}^2} \operatorname{arcsinh} \left(\frac{1}{\tilde{c}} \right) - \frac{1}{3} (1 + \tilde{c}^2)^2 \ln \left(1 + \frac{1}{\tilde{c}^2} \right) \right. \\
&\quad \left. - \frac{1}{2} \left(\sqrt{1 + \tilde{c}^2} - \tilde{c}^2 \operatorname{arcsinh} \left(\frac{1}{\tilde{c}} \right) \right)^2 \right), \tag{G.1}
\end{aligned}$$

where we have introduced $\mathbf{k}_{12} = \mathbf{k}_1 - \mathbf{k}_2$, $k_{12} = |\mathbf{k}_{12}|$, $\tilde{w}_{ee}(k_{12}) = 4\pi/k_{12}^2$ which is the Fourier transform of the Coulomb interaction potential, and $\tilde{c} = c/k_F$. The final expression in Eq. (G.1) corresponds to the expression given in Refs. [1, 2]. The Breit exchange energy per particle of the RHEG can be calculated

in a similar way

$$\begin{aligned}
\varepsilon_x^B &= \frac{1}{4N} \frac{V^2}{(2\pi)^6} \iint_{V_{k_F}} \iint_V \sum_{\sigma_1, \sigma_2 = \downarrow, \uparrow} w_{ee}(r_{12}) \left(\Psi_{\mathbf{k}_1, \sigma_1}^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \Psi_{\mathbf{k}_2, \sigma_2}(\mathbf{r}_1) \cdot \Psi_{\mathbf{k}_2, \sigma_2}^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \Psi_{\mathbf{k}_1, \sigma_1}(\mathbf{r}_2) \right. \\
&\quad \left. + \frac{\Psi_{\mathbf{k}_1, \sigma_1}^\dagger(\mathbf{r}_1) (\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12}) \Psi_{\mathbf{k}_2, \sigma_2}(\mathbf{r}_1) \Psi_{\mathbf{k}_2, \sigma_2}^\dagger(\mathbf{r}_2) (\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12}) \Psi_{\mathbf{k}_1, \sigma_1}(\mathbf{r}_2)}{r_{12}^2} \right) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{k}_1 d\mathbf{k}_2 \\
&= \frac{1}{2N(2\pi)^6} \iint_{V_{k_F}} \iint_V w_{ee}(r_{12}) e^{-i\mathbf{k}_{12} \cdot \mathbf{r}_{12}} \frac{c^2}{E_{k_1} E_{k_2}} \left(\frac{E_{k_2} + c^2}{E_{k_1} + c^2} k_1^2 + \frac{E_{k_1} + c^2}{E_{k_2} + c^2} k_2^2 \right) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{k}_1 d\mathbf{k}_2 \\
&= \frac{1}{2n(2\pi)^6} \iint_{V_{k_F}} \tilde{w}_{ee}(k_{12}) \frac{c^2}{E_{k_1} E_{k_2}} \left(\frac{E_{k_2} + c^2}{E_{k_1} + c^2} k_1^2 + \frac{E_{k_1} + c^2}{E_{k_2} + c^2} k_2^2 \right) d\mathbf{k}_1 d\mathbf{k}_2 \\
&= \frac{3 k_F}{4\pi} \left(1 - 2(1 + \tilde{c}^2) \left(1 - \tilde{c}^2 \left(-2 \ln(\tilde{c}) + \ln(1 + \tilde{c}^2) \right) \right) \right) \\
&\quad + 2 \left(\sqrt{1 + \tilde{c}^2} - \tilde{c}^2 \operatorname{arcsinh} \left(\frac{1}{\tilde{c}} \right) \right)^2, \tag{G.2}
\end{aligned}$$

which corresponds to the expression given in Ref. [3]. The sums over spins in Eqs. (G.1) and (G.2) are explicitly calculated in the Supplementary Information [see Appendix I.1].

G.2 Effective Coulomb-Breit exchange hole

The Coulomb exchange hole can be written as an integral over the wave vectors

$$\begin{aligned}
n_x^C(r_{12}) &= -\frac{1}{(2\pi)^6 n} \iint_{V_{k_F}} e^{-i\mathbf{k}_{12} \cdot \mathbf{r}_{12}} \frac{E_{k_1} E_{k_2} + (\mathbf{k}_1 \cdot \mathbf{k}_2) c^2 + c^4}{E_{k_1} E_{k_2}} d\mathbf{k}_1 d\mathbf{k}_2 \\
&= -\frac{2}{16\pi^4 n} \left(\left[\int_0^{k_F} k^2 j_0(kr_{12}) \left(1 + \frac{c}{\sqrt{k^2 + c^2}} \right) dk \right]^2 + \left[\int_0^{k_F} k^2 j_0(kr_{12}) \left(1 - \frac{c}{\sqrt{k^2 + c^2}} \right) dk \right]^2 \right. \\
&\quad \left. + 2 \left[\int_0^{k_F} \frac{k^3}{\sqrt{k^2 + c^2}} j_1(kr_{12}) dk \right]^2 \right), \tag{G.3}
\end{aligned}$$

where the last expression is obtained after integration over the angle coordinates, and j_ν are the spherical Bessel functions. After repeated integrations by parts, using for a general function f ,

$$\int_0^{k_F} k^{\nu+2} j_\nu(kr_{12}) f(k) dk = \left[\frac{k^{\nu+2}}{r_{12}} j_{\nu+1}(kr_{12}) f(k) \right]_0^{k_F} - \int_0^{k_F} \frac{k^{\nu+2}}{r_{12}} j_{\nu+1}(kr_{12}) f'(k) dk, \tag{G.4}$$

we obtain the expression of the Coulomb exchange hole as

$$n_x^C(r_{12}) = -\frac{9}{4} n \frac{1}{(k_F r_{12})^2} \left[j_1(k_F r_{12})^2 + (1 - \lambda) A_\lambda(k_F r_{12})^2 + \lambda B_\lambda(k_F r_{12})^2 \right], \tag{G.5}$$

where $\lambda = 1/(1 + \tilde{c}^2)$ and

$$\begin{aligned}
A_\lambda(k_F r_{12}) &= \sum_{\nu=0}^{\infty} \frac{(2\nu+1)!!}{(2\nu+1)} j_{\nu+1}(k_F r_{12}) \left(\frac{\lambda}{k_F r_{12}} \right)^\nu, \\
B_\lambda(k_F r_{12}) &= \sum_{\nu=0}^{\infty} \frac{(2\nu+1)!!}{(2\nu+1)} j_{\nu+2}(k_F r_{12}) \left(\frac{\lambda}{k_F r_{12}} \right)^\nu. \tag{G.6}
\end{aligned}$$

This is the expression given in Refs. [2, 4]. Note that there are some typos in the expression given in Ref. [4]. We now extend the previous derivation to the case of the Breit interaction. The associated exchange hole can be expressed as

$$\begin{aligned}
 n_x^B(r_{12}) &= \frac{1}{(2\pi)^6 n} \iint_{V_{k_F}} e^{-i\mathbf{k}_{12} \cdot \mathbf{r}_{12}} \frac{c^2}{E_{k_1} E_{k_2}} \left(\frac{E_{k_2} + c^2}{E_{k_1} + c^2} k_1^2 + \frac{E_{k_1} + c^2}{E_{k_2} + c^2} k_2^2 \right) d\mathbf{k}_1 d\mathbf{k}_2 \\
 &= \frac{1}{2\pi^4 n} \int_0^{k_F} k_1^2 j_0(k_1 r_{12}) \left(1 - \frac{c}{\sqrt{k_1^2 + c^2}} \right) dk_1 \times \int_0^{k_F} k_2^2 j_0(k_2 r_{12}) \left(1 + \frac{c}{\sqrt{k_2^2 + c^2}} \right) dk_2 \quad (\text{G.7})
 \end{aligned}$$

which, after using the same integration by parts as before, gives

$$n_x^B(r_{12}) = -\frac{9}{2} n \frac{1}{(k_F r_{12})^2} \left[-j_1(k_F r_{12})^2 + (1 - \lambda) A_\lambda(k_F r_{12})^2 \right]. \quad (\text{G.8})$$

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Appendix H

Padé approximants

In this appendix, we recall how to calculate diagonal Padé approximants [1] that we used in Chapter 3 to express the short-range relativistic exchange energy per particle of the relativistic homogeneous electron gas. For a general (divergent) power series

$$\sum_{i=0}^{\infty} \alpha_i x^i, \quad (\text{H.1})$$

the diagonal Padé approximant of order M is

$$P_M^M(x) = \frac{\sum_{i=0}^M A_i x^i}{\sum_{i=0}^M B_i x^i}, \quad (\text{H.2})$$

where $B_0 = 1$ without loss of generality, and the other $2M + 1$ coefficients A_i and B_i are determined so that the power expansion of Eq. (H.2) matches the power series of Eq. (H.1) up to order $2M$. This gives the following matrix equation for the determining the coefficients B_1, B_2, \dots, B_M

$$\begin{pmatrix} \alpha_M & \alpha_{M-1} & \dots & \alpha_1 \\ \alpha_{M+1} & \alpha_M & \dots & \alpha_2 \\ \vdots & \vdots & \ddots & \vdots \\ \alpha_{2M-1} & \alpha_{2M-2} & \dots & \alpha_M \end{pmatrix} \begin{pmatrix} B_1 \\ B_2 \\ \vdots \\ B_M \end{pmatrix} = - \begin{pmatrix} \alpha_{M+1} \\ \alpha_{M+2} \\ \vdots \\ \alpha_{2M} \end{pmatrix}, \quad (\text{H.3})$$

and then the coefficients A_0, A_1, \dots, A_M are simply given by

$$A_i = \sum_{j=0}^i \alpha_{i-j} B_j. \quad (\text{H.4})$$

In order to have some insight as to the convergence of the Padé approximants used in this paper and noting that the range-separation scheme does not modify the convergence of the large \tilde{c} expansions we express the full-range Coulomb and Breit exchange energies as large- \tilde{c} expansions to see if they are Stieltjes series, as prescribed in [1] and make full use of the known analytical expressions of the full-range interactions. We define F_x^C as the opposite of the Coulomb exchange energy per particle with the asymptotic series

$$F_x^C(\tilde{c}) = -\epsilon_x^C \sim - \sum_{i=0}^{\infty} \frac{\alpha_{2i}}{\tilde{c}^{2i}} \quad (\text{H.5})$$

and F_x^B as the Breit exchange energy per particle with the asymptotic series

$$F_x^B(\tilde{c}) = \epsilon_x^B \sim \sum_{i=0}^{\infty} \frac{\beta_{2i}}{\tilde{c}^{2i}}. \quad (\text{H.6})$$

After careful numerical investigations it appears safe to say that both F_x^C and F_x^B are analytic in the cut plane, that both have positive limit values for $\tilde{c} \rightarrow 0$ and that both asymptotic series is alternating. Furthermore $-F_x^C$ appears to be Herglotz and thus F_x^C is a Stieltjes function. We have thus

$$\lim_{M \rightarrow \infty} P_{M+1}^M(\tilde{c}) \leq F_x^C(\tilde{c}) \leq \lim_{M \rightarrow \infty} P_M^M(\tilde{c}) \quad (\text{H.7})$$

and we observe numerically that there is a unique limit to these Padé approximants. On the contrary $-F_x^B$ appears not to be Herglotz and thus F_x^B is not a Stieltjes function, yet we observe numerically the same unique convergence of its Padé approximants. This does not come as a surprise given that the Padé approximants are known to converge for functions which are not Stieltjes.

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Appendix I

Calculations of the Coulomb-Breit exchange energy per particle of the relativistic homogeneous electron gas

In this appendix, we review mathematical steps of the calculation of the full-range and short-range Coulomb-Breit exchange energy per particle of the relativistic homogeneous electron gas (RHEG) that we used in Chapter 3 and Appendix G.

A mathematica [1] notebook containing all calculations related to the Padé approximants used to express the short-range Coulomb-Breit exchange energy per particle of the RHEG [see chapter 3 and appendix H] has been published [2] and can be downloaded at:

<https://aip.scitation.org/doi/suppl/10.1063/1.5049773>

Care has to be taken to change its extension from .tex to .nb before opening it with Mathematica.

I.1 Sums over spin combinations

We give here the expressions of the sums over the “spin” combinations that are needed to calculate the exchange energy per particle of the relativistic homogeneous electron gas for the Coulomb-Breit electron-electron interaction [Eq. (A1) of the main paper]. The notations used here are the same as in the main paper [see in particular Section III A]. We first consider the Coulomb contribution, and then the Breit contribution which contains the α matrices and is thus slightly more complex to calculate.

I.1.1 Coulomb contribution

We wish to calculate the expression

$$\sum_{\sigma_1, \sigma_2 = \downarrow, \uparrow} \psi_{\mathbf{k}_1, \sigma_1}^\dagger(\mathbf{r}_1) \psi_{\mathbf{k}_2, \sigma_2}(\mathbf{r}_1) \psi_{\mathbf{k}_2, \sigma_2}^\dagger(\mathbf{r}_2) \psi_{\mathbf{k}_2, \sigma_1}(\mathbf{r}_2), \quad (\text{I.1})$$

which means that we have to consider four spin combinations, and contrary to the non-relativistic case none of these combinations is zero.

Calculation of the $\uparrow/\uparrow/\uparrow/\uparrow$ and $\downarrow/\downarrow/\downarrow/\downarrow$ terms for the Coulomb interaction: We consider the expression of the product of two \uparrow -spinors

$$\begin{aligned}\Psi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\Psi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) &= \begin{pmatrix} \Phi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1) & \chi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1) \end{pmatrix} \begin{pmatrix} \Phi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \\ \chi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \end{pmatrix} \\ &= \left(\Phi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\Phi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) + \chi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\chi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \right) \\ &= \frac{1}{V} \sqrt{\frac{E_{k_1} + c^2}{2E_{k_1}}} \sqrt{\frac{E_{k_2} + c^2}{2E_{k_2}}} e^{-i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}_1} \left(1 + \frac{c^2(\mathbf{k}_1 \cdot \mathbf{k}_2 + i(\mathbf{k}_1 \times \mathbf{k}_2)_z)}{(E_{k_1} + c^2)(E_{k_2} + c^2)} \right), \quad (I.2)\end{aligned}$$

so that

$$\begin{aligned}\Psi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\Psi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1)\Psi_{\mathbf{k}_2,\uparrow}^\dagger(\mathbf{r}_2)\Psi_{\mathbf{k}_1,\uparrow}(\mathbf{r}_2) \\ = \frac{1}{V^2} e^{-i(\mathbf{k}_2 - \mathbf{k}_1) \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \left(\frac{(E_{k_1} + c^2)(E_{k_2} + c^2)}{4E_{k_1}E_{k_2}} + \frac{c^2(\mathbf{k}_1 \cdot \mathbf{k}_2)}{2E_{k_1}E_{k_2}} + \frac{c^4((\mathbf{k}_1 \cdot \mathbf{k}_2)^2 + (\mathbf{k}_1 \times \mathbf{k}_2)_z^2)}{4(E_{k_1} + c^2)(E_{k_2} + c^2)E_{k_1}E_{k_2}} \right), \quad (I.3)\end{aligned}$$

with the $\downarrow/\downarrow/\downarrow/\downarrow$ term being equal to this one.

Calculation of the $\uparrow/\downarrow/\downarrow/\uparrow$ and $\downarrow/\uparrow/\uparrow/\downarrow$ terms for the Coulomb interaction: We consider the expression of the product of a \uparrow -spinor and a \downarrow -spinor

$$\begin{aligned}\Psi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\Psi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) &= \begin{pmatrix} \Phi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1) & \chi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1) \end{pmatrix} \begin{pmatrix} \Phi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \\ \chi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \end{pmatrix} \\ &= \left(\Phi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\Phi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) + \chi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\chi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \right) \\ &= \frac{1}{V} \sqrt{\frac{E_{k_1} + c^2}{2E_{k_1}}} \sqrt{\frac{E_{k_2} + c^2}{2E_{k_2}}} e^{-i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}_1} \frac{c^2 i((\mathbf{k}_1 \times \mathbf{k}_2)_x - i(\mathbf{k}_1 \times \mathbf{k}_2)_y)}{(E_{k_1} + c^2)(E_{k_2} + c^2)}, \quad (I.4)\end{aligned}$$

thus giving us

$$\begin{aligned}\Psi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\Psi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1)\Psi_{\mathbf{k}_2,\downarrow}^\dagger(\mathbf{r}_2)\Psi_{\mathbf{k}_1,\uparrow}(\mathbf{r}_2) \\ = \frac{1}{V^2} e^{-i(\mathbf{k}_2 - \mathbf{k}_1) \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \left(\frac{c^4((\mathbf{k}_1 \times \mathbf{k}_2)_x^2 + (\mathbf{k}_1 \times \mathbf{k}_2)_y^2)}{4(E_{k_1} + mc^2)(E_{k_2} + mc^2)E_{k_1}E_{k_2}} \right), \quad (I.5)\end{aligned}$$

with the $\downarrow/\uparrow/\uparrow/\downarrow$ term being equal to this one.

Sum of the four Coulomb spin combinations: The sum of the four spin combinations previously determined is, using the relative variables $\mathbf{k}_{12} = \mathbf{k}_1 - \mathbf{k}_2$ and $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$,

$$\begin{aligned}\sum_{\sigma_1, \sigma_2 = \downarrow, \uparrow} \Psi_{\mathbf{k}_1, \sigma_1}^\dagger(\mathbf{r}_1)\Psi_{\mathbf{k}_2, \sigma_2}(\mathbf{r}_1)\Psi_{\mathbf{k}_2, \sigma_2}^\dagger(\mathbf{r}_2)\Psi_{\mathbf{k}_1, \sigma_1}(\mathbf{r}_2) \\ = \frac{1}{V^2} e^{-i\mathbf{k}_{12} \cdot \mathbf{r}_{12}} \left(\frac{(E_{k_1} + c^2)(E_{k_2} + c^2)}{4E_{k_1}E_{k_2}} + \frac{c^2(\mathbf{k}_1 \cdot \mathbf{k}_2)}{2E_{k_1}E_{k_2}} + \frac{c^4((\mathbf{k}_1 \cdot \mathbf{k}_2)^2 + (\mathbf{k}_1 \times \mathbf{k}_2)^2)}{4(E_{k_1} + c^2)(E_{k_2} + c^2)E_{k_1}E_{k_2}} \right) \\ = \frac{1}{V^2} e^{-i\mathbf{k}_{12} \cdot \mathbf{r}_{12}} \frac{E_{k_1}E_{k_2} + (\mathbf{k}_1 \cdot \mathbf{k}_2)c^2 + c^4}{E_{k_1}E_{k_2}}. \quad (I.6)\end{aligned}$$

I.1.2 Breit contribution

We wish to calculate the expression

$$\begin{aligned}\sum_{\sigma_1, \sigma_2 = \downarrow, \uparrow} \left(\Psi_{\mathbf{k}_1, \sigma_1}^\dagger(\mathbf{r}_1)\boldsymbol{\alpha}_1\Psi_{\mathbf{k}_2, \sigma_2}(\mathbf{r}_1) \cdot \Psi_{\mathbf{k}_2, \sigma_2}^\dagger(\mathbf{r}_2)\boldsymbol{\alpha}_2\Psi_{\mathbf{k}_1, \sigma_1}(\mathbf{r}_2) \right. \\ \left. + \frac{\Psi_{\mathbf{k}_1, \sigma_1}^\dagger(\mathbf{r}_1)(\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})\Psi_{\mathbf{k}_2, \sigma_2}(\mathbf{r}_1) \Psi_{\mathbf{k}_2, \sigma_2}^\dagger(\mathbf{r}_2)(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})\Psi_{\mathbf{k}_1, \sigma_1}(\mathbf{r}_2)}{r_{12}^2} \right). \quad (I.7)\end{aligned}$$

We work in two steps: first, we calculate the four spin combinations for the first Gaunt-type part (which we shall simply refer to as Gaunt in the following), and then we calculate the four spin combinations for the Gauge retardation part (which we shall simply refer to as Gauge in the following).

Calculation of the $\uparrow/\uparrow/\uparrow/\uparrow$ and $\downarrow/\downarrow/\downarrow/\downarrow$ terms for the Gaunt part of the Breit interaction: We consider the expression of the product of two \uparrow -spinors

$$\begin{aligned}
\Psi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\boldsymbol{\alpha}_1\Psi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) &= \begin{pmatrix} \Phi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1) & \chi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1) \\ \sigma & 0 \end{pmatrix} \begin{pmatrix} \Phi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \\ \chi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \end{pmatrix} \\
&= \left(\chi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\boldsymbol{\sigma}\Phi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) + \Phi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\boldsymbol{\sigma}\chi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \right) \\
&= \frac{1}{V} \sqrt{\frac{E_{k_1} + c^2}{2E_{k_1}}} \sqrt{\frac{E_{k_2} + c^2}{2E_{k_2}}} e^{-i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}_1} \\
&\quad \left[\frac{c}{E_{k_1} + c^2} \begin{pmatrix} (k_1)_x - i(k_1)_y \\ i(k_1)_x + (k_1)_y \\ (k_1)_z \end{pmatrix} + \frac{c}{E_{k_2} + c^2} \begin{pmatrix} (k_2)_x + i(k_2)_y \\ -i(k_2)_x + (k_2)_y \\ (k_2)_z \end{pmatrix} \right], \quad (\text{I.8})
\end{aligned}$$

thus we have

$$\begin{aligned}
&\Psi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\boldsymbol{\alpha}_1\Psi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \cdot \Psi_{\mathbf{k}_2,\uparrow}^\dagger(\mathbf{r}_2)\boldsymbol{\alpha}_2\Psi_{\mathbf{k}_1,\uparrow}(\mathbf{r}_2) \\
&= \frac{1}{V^2} \frac{e^{-i\mathbf{k}_{12} \cdot \mathbf{r}_{12}}}{4E_{k_1}E_{k_2}} \left(\frac{c^2(E_{k_2} + c^2)}{(E_{k_1} + c^2)} (2k_1^2 - (k_1)_z^2) + \frac{c^2(E_{k_1} + c^2)}{(E_{k_2} + c^2)} (2k_2^2 - (k_2)_z^2) + 2c^2(k_1)_z(k_2)_z \right), \quad (\text{I.9})
\end{aligned}$$

with the $\downarrow/\downarrow/\downarrow/\downarrow$ term equal to this one.

Calculation of the $\uparrow/\downarrow/\downarrow/\uparrow$ and $\downarrow/\uparrow/\uparrow/\downarrow$ terms for the Gaunt part of the Breit interaction: We consider the expression of the product of a \uparrow -spinor and a \downarrow -spinor

$$\begin{aligned}
\Psi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\boldsymbol{\alpha}_1\Psi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) &= \begin{pmatrix} \Phi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1) & \chi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1) \\ \sigma & 0 \end{pmatrix} \begin{pmatrix} \Phi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \\ \chi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \end{pmatrix} \\
&= \left(\chi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\boldsymbol{\sigma}\Phi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) + \Phi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\boldsymbol{\sigma}\chi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \right) \\
&= \frac{1}{V} \sqrt{\frac{E_{k_1} + c^2}{2E_{k_1}}} \sqrt{\frac{E_{k_2} + c^2}{2E_{k_2}}} e^{-i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}_1} \\
&\quad \left[\frac{c}{E_{k_1} + c^2} \begin{pmatrix} (k_1)_z \\ -i(k_1)_z \\ -(k_1)_x + i(k_1)_y \end{pmatrix} + \frac{c}{E_{k_2} + c^2} \begin{pmatrix} -(k_2)_z \\ i(k_2)_z \\ (k_2)_x - i(k_2)_y \end{pmatrix} \right], \quad (\text{I.10})
\end{aligned}$$

so that

$$\begin{aligned}
&\Psi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)\boldsymbol{\alpha}_1\Psi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \cdot \Psi_{\mathbf{k}_2,\downarrow}^\dagger(\mathbf{r}_2)\boldsymbol{\alpha}_2\Psi_{\mathbf{k}_1,\uparrow}(\mathbf{r}_2) \\
&= \frac{1}{V^2} \frac{e^{-i\mathbf{k}_{12} \cdot \mathbf{r}_{12}}}{4E_{k_1}E_{k_2}} \left(\frac{c^2(E_{k_1} + c^2)}{(E_{k_1} + c^2)} (k_1^2 + (k_1)_z^2) + \frac{c^2(E_{k_1} + c^2)}{(E_{k_2} + c^2)} (k_2^2 + (k_2)_z^2) - 2c^2(\mathbf{k}_1 \cdot \mathbf{k}_2 + (k_1)_z(k_2)_z) \right), \quad (\text{I.11})
\end{aligned}$$

with the $\downarrow/\uparrow/\uparrow/\downarrow$ term equal to this one.

Calculation of the $\uparrow/\uparrow/\uparrow/\uparrow$ and $\downarrow/\downarrow/\downarrow/\downarrow$ term for the Gauge part of the Breit interaction: We consider the expression of the product of two \uparrow -spinors

$$\begin{aligned}
\Psi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)(\boldsymbol{\alpha}_1 \cdot \mathbf{r})\Psi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) &= \begin{pmatrix} \Phi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1) & \chi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1) \end{pmatrix} \begin{pmatrix} 0 & \boldsymbol{\sigma} \cdot \mathbf{r} \\ \boldsymbol{\sigma} \cdot \mathbf{r} & 0 \end{pmatrix} \begin{pmatrix} \Phi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \\ \chi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \end{pmatrix} \\
&= \left(\chi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)(\boldsymbol{\sigma} \cdot \mathbf{r})\Phi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) + \Phi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)(\boldsymbol{\sigma} \cdot \mathbf{r})\chi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \right) \\
&= \frac{1}{V} \sqrt{\frac{E_{k_1} + c^2}{2E_{k_1}}} \sqrt{\frac{E_{k_2} + c^2}{2E_{k_2}}} e^{-i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}_1} \\
&\quad \left(\frac{c}{E_{k_1} + c^2} (\mathbf{k}_1 \cdot \mathbf{r} + i(\mathbf{k}_1 \times \mathbf{r})_z) + \frac{c}{E_{k_2} + c^2} (\mathbf{k}_2 \cdot \mathbf{r} - i(\mathbf{k}_2 \times \mathbf{r})_z) \right), \quad (\text{I.12})
\end{aligned}$$

so that

$$\begin{aligned}
&\Psi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)(\boldsymbol{\alpha}_1 \cdot \mathbf{r})\Psi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1)\Psi_{\mathbf{k}_2,\uparrow}^\dagger(\mathbf{r}_2)(\boldsymbol{\alpha}_2 \cdot \mathbf{r})\Psi_{\mathbf{k}_1,\uparrow}(\mathbf{r}_2) \\
&= \frac{1}{V^2} \frac{e^{-i\mathbf{k}_{12} \cdot \mathbf{r}_{12}}}{4E_{k_1}E_{k_2}} \left(\frac{c^2(E_{k_2} + c^2)}{(E_{k_1} + c^2)} ((\mathbf{k}_1 \cdot \mathbf{r})^2 + (\mathbf{k}_1 \times \mathbf{r})_z^2) \right. \\
&\quad \left. + \frac{c^2(E_{k_1} + c^2)}{(E_{k_2} + c^2)} ((\mathbf{k}_2 \cdot \mathbf{r})^2 + (\mathbf{k}_2 \times \mathbf{r})_z^2) + 2c^2 ((\mathbf{k}_1 \cdot \mathbf{r})(\mathbf{k}_2 \cdot \mathbf{r}) - (\mathbf{k}_1 \times \mathbf{r})_z(\mathbf{k}_2 \times \mathbf{r})_z) \right), \quad (\text{I.13})
\end{aligned}$$

with the $\downarrow/\downarrow/\downarrow/\downarrow$ term being equal to this one.

Calculation of the $\uparrow/\downarrow/\downarrow/\uparrow$ and $\downarrow/\uparrow/\uparrow/\downarrow$ term for the Gauge part of the Breit interaction: We consider the expression of the product of a \uparrow -spinor and a \downarrow -spinor

$$\begin{aligned}
\Psi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)(\boldsymbol{\alpha}_1 \cdot \mathbf{r})\Psi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) &= \begin{pmatrix} \Phi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1) & \chi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1) \end{pmatrix} \begin{pmatrix} 0 & \boldsymbol{\sigma} \cdot \mathbf{r} \\ \boldsymbol{\sigma} \cdot \mathbf{r} & 0 \end{pmatrix} \begin{pmatrix} \Phi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \\ \chi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \end{pmatrix} \\
&= \left(\chi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)(\boldsymbol{\sigma} \cdot \mathbf{r})\Phi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) + \Phi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)(\boldsymbol{\sigma} \cdot \mathbf{r})\chi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \right) \\
&= \frac{1}{V} \sqrt{\frac{E_{k_1} + c^2}{2E_{k_1}}} \sqrt{\frac{E_{k_2} + c^2}{2E_{k_2}}} e^{-i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}_1} \\
&\quad \left(\frac{c}{E_{k_1} + c^2} (i(\mathbf{k}_1 \times \mathbf{r})_x + (\mathbf{k}_1 \times \mathbf{r})_y) + \frac{c}{E_{k_2} + c^2} (-i(\mathbf{k}_2 \times \mathbf{r})_x - (\mathbf{k}_2 \times \mathbf{r})_y) \right), \quad (\text{I.14})
\end{aligned}$$

so that

$$\begin{aligned}
&\Psi_{\mathbf{k}_1,\uparrow}^\dagger(\mathbf{r}_1)(\boldsymbol{\alpha}_1 \cdot \mathbf{r})\Psi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1)\Psi_{\mathbf{k}_2,\downarrow}^\dagger(\mathbf{r}_2)(\boldsymbol{\alpha}_2 \cdot \mathbf{r})\Psi_{\mathbf{k}_1,\uparrow}(\mathbf{r}_2) \\
&= \frac{1}{V^2} \frac{e^{-i\mathbf{k}_{12} \cdot \mathbf{r}_{12}}}{4E_{k_1}E_{k_2}} \left(\frac{c^2(E_{k_2} + c^2)}{(E_{k_1} + c^2)} ((\mathbf{k}_1 \times \mathbf{r})_x^2 + (\mathbf{k}_1 \times \mathbf{r})_y^2) \right. \\
&\quad \left. + \frac{c^2(E_{k_1} + c^2)}{(E_{k_2} + c^2)} ((\mathbf{k}_2 \times \mathbf{r})_x^2 + (\mathbf{k}_2 \times \mathbf{r})_y^2) - 2c^2 ((\mathbf{k}_1 \times \mathbf{r})_x(\mathbf{k}_2 \times \mathbf{r})_x + (\mathbf{k}_1 \times \mathbf{r})_y(\mathbf{k}_2 \times \mathbf{r})_y) \right), \quad (\text{I.15})
\end{aligned}$$

with the $\downarrow/\uparrow/\uparrow/\downarrow$ term equal to this one.

Sum of the four Gaunt and four Gauge terms: The sum of the eight spins combinations previously determined is

$$\begin{aligned}
& \sum_{\sigma_1, \sigma_2 = \downarrow, \uparrow} \left(\Psi_{\mathbf{k}_1, \sigma_1}^\dagger(\mathbf{r}_1) \boldsymbol{\alpha}_1 \Psi_{\mathbf{k}_2, \sigma_2}(\mathbf{r}_1) \cdot \Psi_{\mathbf{k}_2, \sigma_2}^\dagger(\mathbf{r}_2) \boldsymbol{\alpha}_2 \Psi_{\mathbf{k}_1, \sigma_1}(\mathbf{r}_2) \right. \\
& \quad \left. + \frac{\Psi_{\mathbf{k}_1, \sigma_1}^\dagger(\mathbf{r}_1) (\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12}) \Psi_{\mathbf{k}_2, \sigma_2}(\mathbf{r}_1) \Psi_{\mathbf{k}_2, \sigma_2}^\dagger(\mathbf{r}_2) (\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12}) \Psi_{\mathbf{k}_1, \sigma_1}(\mathbf{r}_2)}{r_{12}^2} \right) \\
& = 2 \frac{e^{-i\mathbf{k}_{12} \cdot \mathbf{r}_{12}}}{V^2} \frac{c^2}{4E_{k_1} E_{k_2}} \left(\frac{E_{k_2} + c^2}{E_{k_1} + c^2} \left(3k_1^2 + \frac{(\mathbf{k}_1 \cdot \mathbf{r})^2 + (\mathbf{k}_1 \times \mathbf{r})^2}{r^2} \right) + \frac{E_{k_1} + c^2}{E_{k_2} + c^2} \left(3k_2^2 + \frac{(\mathbf{k}_2 \cdot \mathbf{r})^2 + (\mathbf{k}_2 \times \mathbf{r})^2}{r^2} \right) \right. \\
& \quad \left. + 2 \left(-\mathbf{k}_1 \cdot \mathbf{k}_2 + \frac{(\mathbf{k}_1 \cdot \mathbf{r})(\mathbf{k}_2 \cdot \mathbf{r})}{r^2} - \frac{(\mathbf{k}_1 \times \mathbf{r})(\mathbf{k}_2 \times \mathbf{r})}{r^2} \right) \right) \\
& = 2 \frac{e^{-i\mathbf{k}_{12} \cdot \mathbf{r}_{12}}}{V^2} \frac{c^2}{E_{k_1} E_{k_2}} \left(\frac{E_{k_2} + c^2}{E_{k_1} + c^2} k_1^2 + \frac{E_{k_1} + c^2}{E_{k_2} + c^2} k_2^2 \right), \tag{I.16}
\end{aligned}$$

where the last expression has been simplified considering that

$$\left(-\mathbf{k}_1 \cdot \mathbf{k}_2 + \frac{(\mathbf{k}_1 \cdot \mathbf{r})(\mathbf{k}_2 \cdot \mathbf{r})}{r^2} - \frac{(\mathbf{k}_1 \times \mathbf{r})(\mathbf{k}_2 \times \mathbf{r})}{r^2} \right) = -2k_1 k_2 \sin(\theta_1) \sin(\theta_2) \cos(\phi_1 - \phi_2), \tag{I.17}$$

reduces to zero once integrated over ϕ_1 or ϕ_2 on $[0, 2\pi]$, and therefore this term can be removed with the understanding that the expression must always be used in an integral over ϕ_1 or ϕ_2 .

I.2 Large- \tilde{c} asymptotic expansion

We explain here the key steps involved in the analytical calculation of the coefficients of the large- \tilde{c} asymptotic expansions of the short-range Coulomb [see Eq. (3.37)] and Breit [see Eq. (3.42)] exchange energies per particle. The Coulomb and Breit terms being of similar forms, we only explicitly consider the short-range Coulomb exchange energy per particle. We start from its expression in Eq. (3.36)

$$\begin{aligned} \varepsilon_x^{C, sr, \mu} = & \frac{3k_F}{4\pi} \int_{\tilde{k}_1=0}^1 \int_{\tilde{k}_2=0}^1 d\tilde{k}_1 d\tilde{k}_2 \tilde{k}_1 \tilde{k}_2 \left(\frac{1}{\sqrt{\tilde{c}^2 + \tilde{k}_1^2} \sqrt{\tilde{c}^2 + \tilde{k}_2^2}} \left[\tilde{k}_1 \tilde{k}_2 + \left(e^{-\left(\frac{\tilde{k}_1 + \tilde{k}_2}{2\tilde{\mu}}\right)^2} - e^{-\left(\frac{\tilde{k}_1 - \tilde{k}_2}{2\tilde{\mu}}\right)^2} \right) \tilde{\mu}^2 \right] \right. \\ & + \frac{2\tilde{c}^2 + \tilde{k}_1^2 + \tilde{k}_2^2 + 2\sqrt{\tilde{c}^2 + \tilde{k}_1^2} \sqrt{\tilde{c}^2 + \tilde{k}_2^2}}{4\sqrt{\tilde{c}^2 + \tilde{k}_1^2} \sqrt{\tilde{c}^2 + \tilde{k}_2^2}} \left[\text{Ei} \left(-\left(\frac{\tilde{k}_1 + \tilde{k}_2}{2\tilde{\mu}}\right)^2 \right) - \text{Ei} \left(-\left(\frac{\tilde{k}_1 - \tilde{k}_2}{2\tilde{\mu}}\right)^2 \right) \right. \\ & \left. \left. + \ln((\tilde{k}_1 - \tilde{k}_2)^2) - \ln((\tilde{k}_1 + \tilde{k}_2)^2) \right] \right). \quad (\text{I.18}) \end{aligned}$$

From now on, for simplicity, we drop the tilde notation and it will be implicit that k_1, k_2, c , and μ are in units of k_F . We want to find the expansion for $c \rightarrow \infty$. The expansion of the first part of the integrand is

$$\frac{\frac{1}{c^2}}{\sqrt{1 + \frac{k_1^2}{c^2}} \sqrt{1 + \frac{k_2^2}{c^2}}} = \frac{1}{c^2} - \left(\frac{k_1^2}{2} + \frac{k_2^2}{2} \right) \frac{1}{c^4} + \left(\frac{3k_1^4}{8} + \frac{k_1^2 k_2^2}{4} + \frac{3k_2^4}{8} \right) \frac{1}{c^6} + O\left(\frac{1}{c^8}\right), \quad (\text{I.19})$$

and the expansion of the second part of the integrand is

$$\frac{2 + (k_1^2 + k_2^2) \frac{1}{c^2} + 2\sqrt{1 + \frac{k_1^2}{c^2}} \sqrt{1 + \frac{k_2^2}{c^2}}}{4\sqrt{1 + \frac{k_1^2}{c^2}} \sqrt{1 + \frac{k_2^2}{c^2}}} = 1 + \left(\frac{k_1^4}{16} - \frac{k_1^2 k_2^2}{8} + \frac{k_2^4}{16} \right) \frac{1}{c^4} + O\left(\frac{1}{c^6}\right). \quad (\text{I.20})$$

Permuting the sum and the integrals, we integrate the general term of the large- \tilde{c} expansion. For the first part of the exchange energy, we need to calculate the general term

$$\frac{a_{m,n}}{c^{2m+2n+2}} \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \left[k_1 k_2 + \left(e^{-\left(\frac{k_1+k_2}{2\mu}\right)^2} - e^{-\left(\frac{k_1-k_2}{2\mu}\right)^2} \right) \mu^2 \right] dk_2 dk_1, \quad (\text{I.21})$$

and for the second part of the exchange energy, we need to calculate the general term

$$\begin{aligned} \frac{b_{m,n}}{c^{2m+2n}} \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \left[\text{Ei} \left(-\left(\frac{k_1+k_2}{2\mu}\right)^2 \right) - \text{Ei} \left(-\left(\frac{k_1-k_2}{2\mu}\right)^2 \right) \right. \\ \left. + \ln((k_1 - k_2)^2) - \ln((k_1 + k_2)^2) \right] dk_2 dk_1, \quad (\text{I.22}) \end{aligned}$$

with m and n positive integers, $a_{m,n}$ and $b_{m,n}$ being expressed using the coefficients of Eqs. (I.19) and (I.20) and are determined uniquely by the pair $\{m, n\}$. We observe a symmetry in m and n , so that only half the terms needs to be calculated.

These integrals are analytically calculated in the following pages because, although they can be calculated using the program Wolfram Mathematica [1] for a given value of $2m + 2n$, the general term for an unspecified value of $2m + 2n$ cannot be directly integrated by the program. It is convenient to have the analytical expression of the general term in order to calculate the expansion for large orders. The final complete expressions of the large- \tilde{c} expansions and their associated Padé approximants are explicitly given up to an arbitrary order in the accompanying Mathematica notebook.

I.2.1 First part of the exchange energy (I)

$$I = \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \left[k_1 k_2 + \left(e^{-\left(\frac{k_1+k_2}{2\mu}\right)^2} - e^{-\left(\frac{k_1-k_2}{2\mu}\right)^2} \right) \mu^2 \right] dk_2 dk_1. \quad (\text{I.23})$$

First integral of the first part (I_1)

The first integral of the first part gives

$$I_1 = \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{2+2m} k_2^{2+2n} dk_2 dk_1 = \frac{1}{9 + 6m + 6n + 4mn}. \quad (\text{I.24})$$

which is about the only easy integral in all this glorious mess.

Second integral of the first part (I_2)

The second integral of the first part is

$$I_2 = \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} e^{-\left(\frac{k_1+k_2}{2\mu}\right)^2} dk_2 dk_1, \quad (\text{I.25})$$

which can be calculated using changes of variables, binomial expansions, and integrations by parts. It will be more or less the same procedure for all the following integral calculations, we shall do it once in full. We start with a change of variable, $k_2 = 2\mu k - k_1$, so that we have

$$I_2 = 2\mu \int_{k_1=0}^1 \int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k_1^{1+2m} (2\mu k - k_1)^{1+2n} e^{-k^2} dk dk_1, \quad (\text{I.26})$$

then we use a binomial expansion to express our integral as

$$I_2 = \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1-i} (2\mu)^{1+i} \int_{k_1=0}^1 k_1^{2+2(m+n)-i} \left(\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i e^{-k^2} dk \right) dk_1. \quad (\text{I.27})$$

We now consider the two last integrals successively, first the one over k and then the one over k_1 .

Integration over k in I_2 : We calculate the integral over k with repeated integrations by parts using at each step

$$\frac{d}{dk} k^{i-1} = (i-1)k^{i-2} \quad \text{and} \quad \int^k x e^{-x^2} dx = -\frac{1}{2} e^{-k^2}. \quad (\text{I.28})$$

For the first step of the integration by parts, we have

$$\begin{aligned} & \int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^{i-1} k e^{-k^2} dk \\ &= -\frac{1}{2} \left[\left(\frac{1+k_1}{2\mu} \right)^{i-1} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - \left(\frac{k_1}{2\mu} \right)^{i-1} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] + \frac{i-1}{2} \int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^{i-3} k e^{-k^2} dk. \end{aligned} \quad (\text{I.29})$$

The repeated integrations by parts lead to two different cases for the last integral, depending on the parity of the integer i .

If i is even, the final integral obtained is

$$\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} e^{-k^2} dk = \frac{\sqrt{\pi}}{2} \left[\operatorname{erf}\left(\frac{1+k_1}{2\mu}\right) - \operatorname{erf}\left(\frac{k_1}{2\mu}\right) \right], \quad (\text{I.30})$$

so that we have

$$\begin{aligned} \int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i e^{-k^2} dk &= - \sum_{l_p=0}^{\frac{i}{2}-1} \frac{1}{2^{l_p+1}} \frac{(i-1)!!}{(i-1-2l_p)!!} \left[\left(\frac{1+k_1}{2\mu}\right)^{i-1-2l_p} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - \left(\frac{k_1}{2\mu}\right)^{i-1-2l_p} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \\ &\quad + \frac{(i-1)!!}{2^{\frac{i}{2}}} \frac{\sqrt{\pi}}{2} \left[\operatorname{erf}\left(\frac{1+k_1}{2\mu}\right) - \operatorname{erf}\left(\frac{k_1}{2\mu}\right) \right]. \quad (\text{I.31}) \end{aligned}$$

If i is odd, the final integral obtained is

$$\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k e^{-k^2} dk = \frac{-1}{2} \left[e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - e^{-\left(\frac{k_1}{2\mu}\right)^2} \right], \quad (\text{I.32})$$

so that we have

$$\begin{aligned} \int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i e^{-k^2} dk &= - \sum_{l_i=0}^{\frac{i-1}{2}-1} \frac{1}{2^{l_i+1}} \frac{(i-1)!!}{(i-1-2l_i)!!} \left[\left(\frac{1+k_1}{2\mu}\right)^{i-1-2l_i} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - \left(\frac{k_1}{2\mu}\right)^{i-1-2l_i} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \\ &\quad + \frac{(i-1)!!}{2^{\frac{i-1}{2}}} \frac{-1}{2} \left[e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - e^{-\left(\frac{k_1}{2\mu}\right)^2} \right]. \quad (\text{I.33}) \end{aligned}$$

Integration over k_1 in I_2 : We calculate the remaining integral as the sum of two sums over two different indices, i_p and i_i with $i = 2i_p$ if i is even and $i = 2i_i + 1$ if i is odd, which both run between 0 and n so that we have indeed $2 + 2n$ terms

$$\begin{aligned} I_2 &= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1-i} (2\mu)^{1+i} \int_{k_1=0}^1 k_1^{2+2(m+n)-i} \left(\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i e^{-k^2} dk \right) dk_1 \\ &= - \sum_{i_p=0}^n \binom{1+2n}{2i_p} (2\mu)^{1+2i_p} \int_{k_1=0}^1 k_1^{2+2(m+n)-2i_p} \left(\frac{(2i_p-1)!!}{2^{i_p}} \frac{\sqrt{\pi}}{2} \left[\operatorname{erf}\left(\frac{1+k_1}{2\mu}\right) - \operatorname{erf}\left(\frac{k_1}{2\mu}\right) \right] \right. \\ &\quad \left. - \sum_{l_p=0}^{i_p-1} \frac{1}{2^{l_p+1}} \frac{(2i_p-1)!!}{(2i_p-1-2l_p)!!} \frac{1}{(2\mu)^{2i_p-1-2l_p}} \left[(1+k_1)^{2i_p-1-2l_p} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - k_1^{2i_p-1-2l_p} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \right) dk_1 \\ &\quad + \sum_{i_i=0}^n \binom{1+2n}{2i_i+1} (2\mu)^{2+2i_i} \int_{k_1=0}^1 k_1^{1+2(m+n)-2i_i} \left(\frac{(2i_i)!!}{2^{i_i}} \frac{-1}{2} \left[e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \right. \\ &\quad \left. - \sum_{l_i=0}^{i_i-1} \frac{1}{2^{l_i+1}} \frac{(2i_i)!!}{(2i_i-2l_i)!!} \frac{1}{(2\mu)^{2i_i-2l_i}} \left[(1+k_1)^{2i_i-2l_i} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - k_1^{2i_i-2l_i} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \right) dk_1. \quad (\text{I.34}) \end{aligned}$$

Sum over i_p : There are four sub-integrals in the sum over i_p .

- First sub-integral:

$$\begin{aligned}
& -\frac{\sqrt{\pi}}{2} \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} \operatorname{erf}\left(\frac{k_1}{2\mu}\right) dk_1 \\
= & -\int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} \int_{t=0}^{\frac{k_1}{2\mu}} e^{-t^2} dt dk_1 \\
= & -\int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} \int_{k=0}^{k_1} e^{-\left(\frac{k}{2\mu}\right)^2} \frac{1}{2\mu} dk dk_1 \\
= & \frac{1}{3+2(m+n-i_p)} \left(-\frac{\sqrt{\pi}}{2} \operatorname{erf}\left(\frac{1}{2\mu}\right) + \frac{1}{2\mu} \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} k_1 e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 \right) \\
= & \frac{1}{3+2(m+n-i_p)} \left(-\frac{\sqrt{\pi}}{2} \operatorname{erf}\left(\frac{1}{2\mu}\right) + \frac{1}{2\mu} \left((2\mu^2)^{1+m+n-i_p} (2+2(m+n-i_p))!! (-2\mu^2) \left[e^{-\left(\frac{1}{2\mu}\right)^2} - 1 \right] \right. \right. \\
& \left. \left. - \sum_{\lambda_i=0}^{m+n-i_p} (2\mu^2)^{\lambda_i+1} \frac{(2+2(m+n-i_p))!!}{(2+2(m+n-i_p)-2\lambda_i)!!} e^{-\left(\frac{1}{2\mu}\right)^2} \right) \right) \\
= & \frac{1}{3+2(m+n-i_p)} \left(-\frac{\sqrt{\pi}}{2} \operatorname{erf}\left(\frac{1}{2\mu}\right) + \frac{1}{2\mu} S_i[1+m+n-i_p] \right), \tag{I.35}
\end{aligned}$$

where we used first the change of variable $t = \frac{k}{2\mu}$, then an integration by parts with

$$\frac{d}{dk_1} \frac{\sqrt{\pi}}{2} \operatorname{erf}\left(\frac{k_1}{2\mu}\right) = \frac{d}{dk_1} \int_{k=0}^{k_1} e^{-\left(\frac{k}{2\mu}\right)^2} \frac{1}{2\mu} dk = \frac{e^{-\left(\frac{k_1}{2\mu}\right)^2}}{2\mu} \quad \text{and} \quad \int^{k_1} x^{2+2(m+n-i_p)} dx = \frac{k_1^{3+2(m+n-i_p)}}{3+2(m+n-i_p)}, \tag{I.36}$$

to get rid of the error function. We then used repeated integrations by parts with the first step being

$$\frac{d}{dk} k^{2+2(m+n-i_p)} = (2+2(m+n-i_p))k^{1+2(m+n-i_p)} \quad \text{and} \quad \int^{k_1} x e^{-\left(\frac{x}{2\mu}\right)^2} dx = -2\mu^2 e^{-\left(\frac{k_1}{2\mu}\right)^2}, \tag{I.37}$$

and the final step is

$$\int_{k_1=0}^1 k_1 e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 = (-2\mu^2) \left[e^{-\left(\frac{1}{2\mu}\right)^2} - 1 \right]. \tag{I.38}$$

We also define a convenient notation for the result of the repeated integrations by parts over k_1 as

$$\int_{k_1=0}^1 k_1^{2N} e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 = S_p[N] \quad \text{and} \quad \int_{k_1=0}^1 k_1^{2N+1} e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 = S_i[N]. \tag{I.39}$$

- Second sub-integral:

$$\begin{aligned}
& \frac{\sqrt{\pi}}{2} \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} \operatorname{erf}\left(\frac{1+k_1}{2\mu}\right) dk_1 \\
&= \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} \int_{t=0}^{\frac{1+k_1}{2\mu}} e^{-t^2} dt dk_1 \\
&= \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} \int_{k=0}^{k_1} e^{-\left(\frac{1+k}{2\mu}\right)^2} \frac{1}{2\mu} dk dk_1 \\
&= \frac{1}{3+2(m+n-i_p)} \left(\frac{\sqrt{\pi}}{2} \operatorname{erf}\left(\frac{1}{\mu}\right) - \frac{1}{2\mu} \int_{k_1=0}^1 k_1^{3+2(m+n-i_p)} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 \right) \\
&= \frac{1}{3+2(m+n-i_p)} \left(\frac{\sqrt{\pi}}{2} \operatorname{erf}\left(\frac{1}{\mu}\right) - \frac{1}{2\mu} \sum_{j=0}^{3+2(m+n-i_p)} \binom{3+2(m+n-i_p)}{j} (-1)^{3-j} \int_{k_1=0}^1 (1+k_1)^j e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 \right) \\
&= \frac{1}{3+2(m+n-i_p)} \left(\frac{\sqrt{\pi}}{2} \operatorname{erf}\left(\frac{1}{\mu}\right) \right. \\
&\quad \left. + \frac{1}{2\mu} \sum_{j_p=0}^{1+m+n-i_p} \binom{3+2(m+n-i_p)}{2j_p} \left[(2\mu^2)^{j_p} (2j_p-1)!! \frac{\sqrt{\pi}}{2} \left[\operatorname{erf}\left(\frac{1}{\mu}\right) - \operatorname{erf}\left(\frac{1}{2\mu}\right) \right] \right. \right. \\
&\quad \left. \left. - \sum_{\lambda_p=0}^{j_p-1} (2\mu^2)^{\lambda_p+1} \frac{(2j_p-1)!!}{(2j_p-1-2\lambda_p)!!} \left[2^{2j_p-1-2\lambda_p} e^{-\left(\frac{1}{\mu}\right)^2} - e^{-\left(\frac{1}{2\mu}\right)^2} \right] \right] \right) \\
&\quad - \frac{1}{2\mu} \sum_{j_i=0}^{1+m+n-i_p} \binom{3+2(m+n-i_p)}{2j_i+1} \left[(2\mu^2)^{j_i} (2j_i)!! (-2\mu^2) \left[e^{-\left(\frac{1}{\mu}\right)^2} - e^{-\left(\frac{1}{2\mu}\right)^2} \right] \right. \\
&\quad \left. - \sum_{\lambda_i=0}^{j_i-1} (2\mu^2)^{\lambda_i+1} \frac{(2j_i)!!}{(2j_i-2\lambda_i)!!} \left[2^{2j_i-2\lambda_i} e^{-\left(\frac{1}{\mu}\right)^2} - e^{-\left(\frac{1}{2\mu}\right)^2} \right] \right] \left. \right) \\
&= \frac{1}{3+2(m+n-i_p)} \left(\frac{\sqrt{\pi}}{2} \operatorname{erf}\left(\frac{1}{\mu}\right) + \frac{1}{2\mu} \sum_{j_p=0}^{1+m+n-i_p} \binom{3+2(m+n-i_p)}{2j_p} S_p^+[j_p] \right. \\
&\quad \left. - \frac{1}{2\mu} \sum_{j_i=0}^{1+m+n-i_p} \binom{3+2(m+n-i_p)}{2j_i+1} S_i^+[j_i] \right), \tag{I.40}
\end{aligned}$$

where we used the binomial expansion

$$k_1^{3+2(m+n-i_p)} = \sum_{j=0}^{3+2(m+n-i_p)} \binom{3+2(m+n-i_p)}{j} (-1)^{3-j} (1+k_1)^j, \tag{I.41}$$

and split the sum over j into two sums over j_p and j_i . We also introduced the definitions

$$\int_{k_1=0}^1 (1+k_1)^{2N} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 = S_p^+[N] \quad \text{and} \quad \int_{k_1=0}^1 (1+k_1)^{2N+1} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 = S_i^+[N]. \tag{I.42}$$

- Third sub-integral:

$$\begin{aligned} & - \int_{k_1=0}^1 k_1^{1+2(m+n-l_p)} e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 \\ & = -S_i[m+n-l_p]. \end{aligned} \quad (\text{I.43})$$

- Fourth sub-integral:

$$\begin{aligned} & \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} (1+k_1)^{2i_p-1-2l_p} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 \\ & = \sum_{j=0}^{2+2(m+n-i_p)} \binom{2+2(m+n-i_p)}{j} (-1)^j \int_{k_1=0}^1 (1+k_1)^{j+2(i_p-l_p)-1} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 \\ & = \sum_{j_p=0}^{1+m+n-i_p} \binom{2+2(m+n-i_p)}{2j_p} \int_{k_1=0}^1 (1+k_1)^{2(j_p+i_p-l_p)-1} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 \\ & \quad - \sum_{j_i=0}^{m+n-i_p} \binom{2+2(m+n-i_p)}{2j_i+1} \int_{k_1=0}^1 (1+k_1)^{2(j_i+i_p-l_p)} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 \\ & = \sum_{j_p=0}^{1+m+n-i_p} \binom{2+2(m+n-i_p)}{2j_p} S_i^+[j_p+i_p-l_p-1] \\ & \quad - \sum_{j_i=0}^{m+n-i_p} \binom{2+2(m+n-i_p)}{2j_i+1} S_p^+[j_i+i_p-l_p]. \end{aligned} \quad (\text{I.44})$$

Sum over i_i : There are also four sub-integrals in the sum over i_i .

- First sub-integral:

$$\begin{aligned} & - \int_{k_1=0}^1 k_1^{1+2(m+n-i_i)} e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 \\ & = -S_i[m+n+i_i]. \end{aligned} \quad (\text{I.45})$$

- Second sub-integral:

$$\begin{aligned} & \int_{k_1=0}^1 k_1^{1+2(m+n-i_i)} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 \\ & = \sum_{j=0}^{1+2(m+n-i_i)} \binom{1+2(m+n-i_i)}{j} (-1)^{1-j} \int_{k_1=0}^1 (1+k_1)^j e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 \\ & = - \sum_{j_p=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_p} S_p^+[j_p] + \sum_{j_i=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_i+1} S_i^+[j_i]. \end{aligned} \quad (\text{I.46})$$

- Third sub-integral:

$$\begin{aligned} & - \int_{k_1=0}^1 k_1^{1+2(m+n-l_i)} e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 \\ & = -S_i[m+n-l_i]. \end{aligned} \quad (\text{I.47})$$

- Fourth sub-integral:

$$\begin{aligned} & \int_{k_1=0}^1 k_1^{1+2(m+n-i_i)} (1+k_1)^{2(i_i-l_i)} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 \\ & = \sum_{j=0}^{1+2(m+n-i_i)} \binom{1+2(m+n-i_i)}{j} (-1)^{1-j} \int_{k_1=0}^1 (1+k_1)^j e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 \\ & = - \sum_{j_p=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_p} S_p^+[j_p+i_i-l_i] + \sum_{j_i=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_i+1} S_i^+[j_i+i_i-l_i]. \end{aligned} \quad (\text{I.48})$$

Expression of integral I_2 : We have found each sub-integral of the second integral I_2 of the first part of the exchange energy. The expression of I_2 is thus

$$\begin{aligned} & I_2 \\ & = \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} e^{-\left(\frac{k_1+k_2}{2\mu}\right)^2} dk_2 dk_1 \\ & = - \sum_{i_p=0}^n \binom{1+2n}{2i_p} (2\mu)^{1+2i_p} \left\{ \frac{(2i_p-1)!!}{2^{i_p}} \frac{1}{3+2(m+n-i_p)} \left(\frac{\sqrt{\pi}}{2} \left[\operatorname{erf}\left(\frac{1}{\mu}\right) - \operatorname{erf}\left(\frac{1}{2\mu}\right) \right] \right. \right. \\ & \quad \left. \left. + \frac{1}{2\mu} \left[S_i[1+m+n-i_p] + \sum_{j_p=0}^{1+m+n-i_p} \binom{3+2(m+n-i_p)}{2j_p} S_p^+[j_p] - \sum_{j_i=0}^{1+m+n-i_p} \binom{3+2(m+n-i_p)}{2j_i+1} S_i^+[j_i] \right] \right) \right. \\ & \quad \left. - \sum_{l_p=0}^{i_p-1} \frac{1}{2^{l_p+1}} \frac{(2i_p-1)!!}{(2i_p-1-2l_p)!!} \frac{1}{(2\mu)^{2i_p-1-2l_p}} \left(-S_i[m+n-l_p] \right. \right. \\ & \quad \left. \left. + \sum_{j_p=0}^{1+m+n-i_p} \binom{2+2(m+n-i_p)}{2j_p} S_i^+[j_p+i_p-l_p-1] - \sum_{j_i=0}^{m+n-i_p} \binom{2+2(m+n-i_p)}{2j_i+1} S_p^+[j_i+i_p-l_p] \right) \right\} \\ & \quad + \sum_{i_i=0}^n \binom{1+2n}{2i_i+1} (2\mu)^{2+2i_i} \left\{ \frac{(2i_i)!!-1}{2^{i_i}} \frac{1}{2} \left(-S_i[m+n-i_i] \right. \right. \\ & \quad \left. \left. - \sum_{j_p=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_p} S_p^+[j_p] + \sum_{j_i=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_i+1} S_i^+[j_i] \right) \right. \\ & \quad \left. - \sum_{l_i=0}^{i_i-1} \frac{1}{2^{l_i+1}} \frac{(2i_i)!!}{(2i_i-2l_i)!!} \frac{1}{(2\mu)^{2i_i-2l_i}} \left(-S_i[m+n-l_i] \right. \right. \\ & \quad \left. \left. + \sum_{j_p=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_p} S_p^+[j_p+i_i-l_i] - \sum_{j_i=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_i+1} S_i^+[j_i+i_i-l_i] \right) \right\}. \end{aligned} \quad (\text{I.49})$$

Most of the following calculations use exactly the same steps. They are written now with less details.

Third integral of the first part (I_3)

$$\begin{aligned}
I_3 &= \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} e^{-\left(\frac{k_1-k_2}{2\mu}\right)^2} dk_2 dk_1 \\
&= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1+i} (2\mu)^{1+i} \int_{k_1=0}^1 k_1^{2+2(m+n)-i} \left(\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}} k^i e^{-k^2} dk \right) dk_1. \quad (I.50)
\end{aligned}$$

where we used the change of variable $k_2 = 2\mu k + k_1$.

Integration over k in I_3 : Once again, we can calculate the integral over k with repeated integrations by parts, with two different cases depending on the parity of i . If i is even we have

$$\begin{aligned}
&\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}} k^i e^{-k^2} dk \\
&= - \sum_{l_p=0}^{\frac{i}{2}-1} \frac{1}{2^{l_p+1}} \frac{(i-1)!!}{(i-1-2l_p)!!} \left[\left(\frac{k_1-1}{2\mu}\right)^{i-1-2l_p} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} - \left(\frac{k_1}{2\mu}\right)^{i-1-2l_p} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \\
&\quad + \frac{(i-1)!! \sqrt{\pi}}{2^{\frac{i}{2}}} \frac{1}{2} \left[\operatorname{erf}\left(\frac{k_1-1}{2\mu}\right) - \operatorname{erf}\left(\frac{k_1}{2\mu}\right) \right], \quad (I.51)
\end{aligned}$$

while if i is odd we have

$$\begin{aligned}
&\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1+1}{2\mu}} k^i e^{-k^2} dk \\
&= - \sum_{l_i=0}^{\frac{i-1}{2}-1} \frac{1}{2^{l_i+1}} \frac{(i-1)!!}{(i-1-2l_i)!!} \left[\left(\frac{k_1-1}{2\mu}\right)^{i-1-2l_i} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} - \left(\frac{k_1}{2\mu}\right)^{i-1-2l_i} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \\
&\quad + \frac{(i-1)!! - 1}{2^{\frac{i-1}{2}}} \frac{1}{2} \left[e^{-\left(\frac{k_1-1}{2\mu}\right)^2} - e^{-\left(\frac{k_1}{2\mu}\right)^2} \right]. \quad (I.52)
\end{aligned}$$

Integration over k_1 in I_3 : We write the integral I_3 as the sum of two sums over two indices, i_p and i_i with $i = 2i_p$ if i is even and $i = 2i_i + 1$ if i is odd, which both run between 0 and n so that we have indeed $2 + 2n$ terms. We have

$$\begin{aligned}
I_3 &= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1+i} (2\mu)^{1+i} \int_{k_1=0}^1 k_1^{2+2(m+n)-i} \left(\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}} k^i e^{-k^2} dk \right) dk_1 \\
&= - \sum_{i_p=0}^n \binom{1+2n}{2i_p} (2\mu)^{1+2i_p} \int_{k_1=0}^1 k_1^{2+2(m+n)-2i_p} \left(\frac{(2i_p-1)!!}{2^{i_p}} \frac{\sqrt{\pi}}{2} \left[\operatorname{erf}\left(\frac{k_1-1}{2\mu}\right) - \operatorname{erf}\left(\frac{k_1}{2\mu}\right) \right] \right. \\
&\quad \left. - \sum_{l_p=0}^{i_p-1} \frac{1}{2^{l_p+1}} \frac{(2i_p-1)!!}{(2i_p-1-2l_p)!!} \frac{1}{(2\mu)^{2i_p-1-2l_p}} \left[(k_1-1)^{2i_p-1-2l_p} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} - k_1^{2i_p-1-2l_p} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \right) dk_1 \\
&\quad + \sum_{i_i=0}^n \binom{1+2n}{2i_i+1} (2\mu)^{2+2i_i} \int_{k_1=0}^1 k_1^{1+2(m+n)-2i_i} \left(\frac{(2i_i)!!-1}{2^{i_i}} \frac{1}{2} \left[e^{-\left(\frac{k_1-1}{2\mu}\right)^2} - e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \right. \\
&\quad \left. - \sum_{l_i=0}^{i_i-1} \frac{1}{2^{l_i+1}} \frac{(2i_i)!!}{(2i_i-2l_i)!!} \frac{1}{(2\mu)^{2i_i-2l_i}} \left[(k_1-1)^{2i_i-2l_i} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} - k_1^{2i_i-2l_i} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \right) dk_1. \tag{I.53}
\end{aligned}$$

Sum over i_p : There are four sub-integrals in the sum over i_p .

- First sub-integral:

$$\begin{aligned}
& - \frac{\sqrt{\pi}}{2} \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} \operatorname{erf}\left(\frac{k_1}{2\mu}\right) dk_1 \\
&= \frac{1}{3+2(m+n-i_p)} \left(- \frac{\sqrt{\pi}}{2} \operatorname{erf}\left(\frac{1}{2\mu}\right) + \frac{1}{2\mu} S_i[1+m+n-i_p] \right). \tag{I.54}
\end{aligned}$$

- Second sub-integral:

$$\begin{aligned}
& \frac{\sqrt{\pi}}{2} \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} \operatorname{erf}\left(\frac{k_1-1}{2\mu}\right) dk_1 \\
&= \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} \int_{t=0}^{\frac{k_1-1}{2\mu}} e^{-t^2} dt dk_1 \\
&= \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} \int_{k=0}^{k_1} e^{-\left(\frac{k-1}{2\mu}\right)^2} \frac{1}{2\mu} dk dk_1 \\
&= \frac{1}{3+2(m+n-i_p)} \left(0 - \frac{1}{2\mu} \int_{k_1=0}^1 k_1^{3+2(m+n-i_p)} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 \right) \\
&= \frac{1}{3+2(m+n-i_p)} \left(0 - \frac{1}{2\mu} \sum_{j=0}^{3+2(m+n-i_p)} \binom{3+2(m+n-i_p)}{j} \int_{k_1=0}^1 (k_1-1)^j e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 \right) \\
&= \frac{1}{3+2(m+n-i_p)} \frac{-1}{2\mu} \left(\sum_{j_p=0}^{1+m+n-i_p} \binom{1+m+n-i_p}{2j_p} \left[(2\mu^2)^{j_p} (2j_p-1)!! \frac{\sqrt{\pi}}{2} \left[0 - \operatorname{erf}\left(\frac{-1}{2\mu}\right) \right] \right. \right. \\
&\quad \left. \left. - \sum_{\lambda_p=0}^{j_p-1} \left[(2\mu^2)^{\lambda_p+1} \frac{(2j_p-1)!!}{(2j_p-1-2\lambda_p)!!} \left[0 - (-1)^{2j_p-1-2\lambda_p} e^{-\left(\frac{-1}{2\mu}\right)^2} \right] \right] \right. \right. \\
&\quad \left. \left. + \sum_{j_i=0}^{1+m+n-i_p} \binom{3+2(m+n-i_p)}{2j_i+1} \left[(2\mu^2)^{j_i} (2j_i)!! (-2\mu^2) \left[1 - e^{-\left(\frac{-1}{2\mu}\right)^2} \right] \right. \right. \right. \\
&\quad \left. \left. \left. - \sum_{\lambda_i=0}^{j_i-1} \left[(2\mu^2)^{\lambda_i+1} \frac{(2j_i)!!}{(2j_i-2\lambda_i)!!} \left[0 - (-1)^{2j_i-2\lambda_i} e^{-\left(\frac{-1}{2\mu}\right)^2} \right] \right] \right] \right] \right) \\
&= \frac{1}{3+2(m+n-i_p)} \frac{-1}{2\mu} \left(\sum_{j_p=0}^{1+m+n-i_p} \binom{3+2(m+n-i_p)}{2j_p} \mathcal{S}_p^- [j_p] \right. \\
&\quad \left. + \sum_{j_i=0}^{1+m+n-i_p} \binom{3+2(m+n-i_p)}{2j_i+1} \mathcal{S}_i^- [j_i] \right), \tag{I.55}
\end{aligned}$$

where we used the binomial expansion

$$k_1^{3+2(m+n-i_p)} = \sum_{j=0}^{3+2(m+n-i_p)} \binom{3+2(m+n-i_p)}{j} (k_1-1)^j, \tag{I.56}$$

and split the sum over j into two sums over j_p and j_i . We also introduced the notations

$$\int_{k_1=0}^1 (k_1-1)^{2N} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 = \mathcal{S}_p^- [N] \quad \text{and} \quad \int_{k_1=0}^1 (k_1-1)^{2N+1} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 = \mathcal{S}_i^- [N]. \tag{I.57}$$

- Third sub-integral:

$$\begin{aligned}
& - \int_{k_1=0}^1 k_1^{1+2(m+n-l_p)} e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 \\
&= -\mathcal{S}_i [m+n-l_p]. \tag{I.58}
\end{aligned}$$

- Fourth sub-integral:

$$\begin{aligned}
& \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} (k_1-1)^{2i_p-1-2l_p} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 \\
&= \sum_{j=0}^{2+2(m+n-i_p)} \binom{2+2(m+n-i_p)}{j} \int_{k_1=0}^1 (k_1-1)^{j+2(i_p-l_p)-1} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 \\
&= \sum_{j_p=0}^{1+m+n-i_p} \binom{2+2(m+n-i_p)}{2j_p} S_i^- [j_p+i_p-l_p-1] \\
&+ \sum_{j_i=0}^{m+n-i_p} \binom{2+2(m+n-i_p)}{2j_i+1} S_p^- [j_i+i_p-l_p]. \tag{I.59}
\end{aligned}$$

Sum over i_i : There are four sub-integrals in the sum over i_i .

- First sub-integral:

$$\begin{aligned}
& - \int_{k_1=0}^1 k_1^{1+2(m+n-i_i)} e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 \\
&= -S_i [m+n+i_i]. \tag{I.60}
\end{aligned}$$

- Second sub-integral:

$$\begin{aligned}
& \int_{k_1=0}^1 k_1^{1+2(m+n-i_i)} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 \\
&= \sum_{j=0}^{1+2(m+n-i_i)} \binom{1+2(m+n-i_i)}{j} \int_{k_1=0}^1 (k_1-1)^j e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 \\
&= \sum_{j_p=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_p} S_p^- [j_p] + \sum_{j_i=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_i+1} S_i^- [j_i]. \tag{I.61}
\end{aligned}$$

- Third sub-integral:

$$\begin{aligned}
& - \int_{k_1=0}^1 k_1^{1+2(m+n-l_i)} e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 \\
&= -S_i [m+n-l_i]. \tag{I.62}
\end{aligned}$$

- Fourth sub-integral:

$$\begin{aligned}
& \int_{k_1=0}^1 k_1^{1+2(m+n-i_i)} (k_1-1)^{2(i_i-l_i)} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 \\
&= \sum_{j=0}^{1+2(m+n-i_i)} \binom{1+2(m+n-i_i)}{j} \int_{k_1=0}^1 (k_1-1)^j e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 \\
&= \sum_{j_p=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_p} S_p^- [j_p+i-l_i] \\
&+ \sum_{j_i=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_i+1} S_i^- [j_i+i-l_i]. \tag{I.63}
\end{aligned}$$

Expression of integral I_3 : We have found each sub-integral of the third integral I_3 of the first part of the exchange energy. The expression of I_3 is thus

$$\begin{aligned}
& I_3 \\
&= \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} e^{-\left(\frac{k_1-k_2}{2\mu}\right)^2} dk_2 dk_1 \\
&= - \sum_{i_p=0}^n \binom{1+2n}{2i_p} (2\mu)^{1+2i_p} \left\{ \frac{(2i_p-1)!!}{2^{i_p}} \frac{1}{3+2(m+n-i_p)} \left(\frac{\sqrt{\pi}}{2} \left[0 - \operatorname{erf}\left(\frac{1}{2\mu}\right) \right] \right. \right. \\
&\quad \left. \left. + \frac{1}{2\mu} \left[S_i[1+m+n-i_p] - \sum_{j_p=0}^{1+m+n-i_p} \binom{3+2(m+n-i_p)}{2j_p} S_p^- [j_p] - \sum_{j_i=0}^{1+m+n-i_p} \binom{3+2(m+n-i_p)}{2j_i+1} S_i^- [j_i] \right] \right) \right. \\
&\quad \left. - \sum_{l_p=0}^{i_p-1} \frac{1}{2^{l_p+1}} \frac{(2i_p-1)!!}{(2i_p-1-2l_p)!!} \frac{1}{(2\mu)^{2i_p-1-2l_p}} \left(-S_i[m+n-l_p] \right. \right. \\
&\quad \left. \left. + \sum_{j_p=0}^{1+m+n-i_p} \binom{2+2(m+n-i_p)}{2j_p} S_i^- [j_p+i_p-l_p-1] + \sum_{j_i=0}^{m+n-i_p} \binom{2+2(m+n-i_p)}{2j_i+1} S_p^- [j_i+i_p-l_p] \right) \right\} \\
&+ \sum_{i_i=0}^n \binom{1+2n}{2i_i+1} (2\mu)^{2+2i_i} \left\{ \frac{(2i_i)!!-1}{2^{i_i}} \frac{1}{2} \left(-S_i[m+n-i_i] \right. \right. \\
&\quad \left. \left. + \sum_{j_p=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_p} S_p^- [j_p] + \sum_{j_i=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_i+1} S_i^- [j_i] \right) \right. \\
&\quad \left. - \sum_{l_i=0}^{i_i-1} \frac{1}{2^{l_i+1}} \frac{(2i_i)!!}{(2i_i-2l_i)!!} \frac{1}{(2\mu)^{2i_i-2l_i}} \left(-S_i[m+n-l_i] \right. \right. \\
&\quad \left. \left. + \sum_{j_p=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_p} S_p^- [j_p+i-l_i] + \sum_{j_i=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_i+1} S_i^- [j_i+i-l_i] \right) \right\}. \tag{I.64}
\end{aligned}$$

This expression has to be subtracted from the one of the second integral I_2 , many terms in fact cancel each other.

I.2.2 Second part of the exchange energy (II)

$$II = \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \left[\text{Ei} \left(- \left(\frac{k_1+k_2}{2\mu} \right)^2 \right) - \text{Ei} \left(- \left(\frac{k_1-k_2}{2\mu} \right)^2 \right) + \ln((k_1-k_2)^2) - \ln((k_1+k_2)^2) \right] dk_2 dk_1. \quad (\text{I.65})$$

First integral of the second part (II_1)

$$\begin{aligned} II_1 &= \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \ln((k_1+k_2)^2) dk_2 dk_1 \\ &= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1-i} \int_{k_1=0}^1 k_1^{1+2(m+n)-i} \left(\int_{k=k_1}^{1+k_1} k^i 2 \ln(k) dk \right) dk_1, \end{aligned} \quad (\text{I.66})$$

where we used the change of variable $k_2 = k - k_1$.

Integration over k in II_1 :

$$\begin{aligned} &\int_{k=k_1}^{1+k_1} k^i 2 \ln(k) dk \\ &= 2 \frac{1}{(1+i)^2} \left(k_1^{1+i} - (1+k_1)^{1+i} - (1+i)k_1^{1+i} \ln(k_1) + (1+i)(1+k_1)^{1+i} \ln(1+k_1) \right). \end{aligned} \quad (\text{I.67})$$

Integration over k_1 in II_1 :

$$\begin{aligned} II_1 &= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1-i} \int_{k_1=0}^1 k_1^{1+2(m+n)-i} \left(\int_{k=k_1}^{1+k_1} k^i 2 \ln(k) dk \right) dk_1 \\ &= \sum_{i=0}^{1+2n} \binom{1+2n}{i} \frac{2(-1)^{1-i}}{(1+i)^2} \int_{k_1=0}^1 k_1^{1+2(m+n)-i} \left(k_1^{1+i} - (1+k_1)^{1+i} - (1+i)k_1^{1+i} \ln(k_1) \right. \\ &\quad \left. + (1+i)(1+k_1)^{1+i} \ln(1+k_1) \right) dk_1, \end{aligned} \quad (\text{I.68})$$

which we will integrate term by term over k_1 .

- First sub-integral:

$$\begin{aligned} &\int_{k_1=0}^1 k_1^{2+2(m+n)+1} dk_1 \\ &= \frac{1}{4+2(m+n)}. \end{aligned} \quad (\text{I.69})$$

- Second sub-integral:

$$\begin{aligned}
& - \int_{k_1=0}^1 k_1^{2+2(m+n)-i} (1+k_1)^{i+1} dk_1 \\
&= - \sum_{j=0}^{1+i} \binom{1+i}{j} \int_{k_1=0}^1 k_1^{2+2(m+n)-i+j} dk_1 \\
&= - \sum_{j=0}^{1+i} \binom{1+i}{j} \frac{1}{3+2(m+n)-i+j}. \tag{I.70}
\end{aligned}$$

- Third sub-integral:

$$\begin{aligned}
& -(1+i) \int_{k_1=0}^1 k_1^{2+2(m+n)+1} \ln(k_1) dk_1 \\
&= (1+i) \frac{1}{4(2+m+n)^2}. \tag{I.71}
\end{aligned}$$

- Fourth sub-integral:

$$\begin{aligned}
& (1+i) \int_{k_1=0}^1 k_1^{2+2(m+n)-i} (1+k_1)^{i+1} \ln(1+k_1) dk_1 \\
&= (1+i) \sum_{j=0}^{2+2(m+n)-i} \binom{2+2(m+n)-i}{j} (-1)^{-i-j} \int_{k_1=0}^1 (1+k_1)^{1+i+j} \ln(1+k_1) dk_1 \\
&= (1+i) \sum_{j=0}^{2+2(m+n)-i} \binom{2+2(m+n)-i}{j} \frac{(-1)^{-i-j}}{(2+i+j)^2} \left(1 + 2^{2+i+j} \left(-1 + (i+j) \ln(2) + \ln(4) \right) \right), \tag{I.72}
\end{aligned}$$

where we used the binomial relation in Eq. (I.41).

Expression of integral II_1 : We have found each sub-integral of the first integral II_1 of the second part of the exchange energy. The expression of II_1 is thus

$$\begin{aligned}
& II_1 \\
&= \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \ln((k_1+k_2)^2) dk_2 dk_1 \\
&= \sum_{i=0}^{1+2n} \binom{1+2n}{i} \frac{2(-1)^{1-i}}{(1+i)^2} \left\{ \frac{1}{4+2(m+n)} - \sum_{j=0}^{1+i} \binom{1+i}{j} \frac{1}{3+2(m+n)-i+j} + (1+i) \frac{1}{4(2+m+n)^2} \right. \\
&\quad \left. + (1+i) \sum_{j=0}^{2+2(m+n)-i} \binom{2+2(m+n)-i}{j} \frac{(-1)^{-i-j}}{(2+i+j)^2} \left(1 + 2^{2+i+j} \left(-1 + (i+j) \ln(2) + \ln(4) \right) \right) \right\}. \tag{I.73}
\end{aligned}$$

Second integral of the second part (II_2)

$$\begin{aligned}
II_2 &= \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \ln((k_1-k_2)^2) dk_2 dk_1 \\
&= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1+i} \int_{k_1=0}^1 k_1^{1+2(m+n)-i} \left(\int_{k=k_1}^{k_1-1} k^i 2 \ln(k) dk \right) dk_1, \tag{I.74}
\end{aligned}$$

where we used the change of variable $k_2 = k_1 - k$ and a binomial expansion.

Integration over k in I_2 :

$$\begin{aligned} & \int_{k=k_1}^{k_1-1} k^i 2 \ln(k) dk_1 \\ = & 2 \frac{1}{(1+i)^2} \left(k_1^{1+i} - (k_1-1)^{1+i} - (1+i)k_1^{1+i} \ln(k_1) + (1+i)(k_1-1)^{1+i} \ln(k_1-1) \right). \end{aligned} \quad (\text{I.75})$$

Integration over k_1 in I_2 :

$$\begin{aligned} I_2 &= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1+i} \int_{k_1=0}^1 k_1^{1+2(m+n)-i} \left(\int_{k=k_1}^{k_1-1} k^i 2 \ln(k) dk \right) dk_1 \\ &= \sum_{i=0}^{1+2n} \binom{1+2n}{i} \frac{2(-1)^{1-i}}{(1+i)^2} \int_{k_1=0}^1 k_1^{1+2(m+n)-i} \left(k_1^{1+i} - (k_1-1)^{1+i} - (1+i)k_1^{1+i} \ln(k_1) \right. \\ & \quad \left. + (1+i)(k_1-1)^{1+i} \ln(1-k_1) \right) dk_1, \end{aligned} \quad (\text{I.76})$$

which we integrate term by term over k_1 .

- First sub-integral:

$$\begin{aligned} & \int_{k_1=0}^1 k_1^{2+2(m+n)+1} dk_1 \\ = & \frac{1}{4+2(m+n)}. \end{aligned} \quad (\text{I.77})$$

- Second sub-integral:

$$\begin{aligned} & - \int_{k_1=0}^1 k_1^{2+2(m+n)-i} (k_1-1)^{i+1} dk_1 \\ = & - \sum_{j=0}^{1+i} \binom{1+i}{j} (-1)^{1+i-j} \int_{k_1=0}^1 k_1^{2+2(m+n)-i+j} dk_1 \\ = & - \sum_{j=0}^{1+i} \binom{1+i}{j} (-1)^{1+i-j} \frac{1}{3+2(m+n)-i+j}. \end{aligned} \quad (\text{I.78})$$

- Third sub-integral:

$$\begin{aligned} & -(1+i) \int_{k_1=0}^1 k_1^{2+2(m+n)+1} \ln(k_1) dk_1 \\ = & (1+i) \frac{1}{4(2+m+n)^2}. \end{aligned} \quad (\text{I.79})$$

- Fourth sub-integral:

$$\begin{aligned}
& (1+i) \int_{k_1=0}^1 k_1^{2+2(m+n)-i} (k_1-1)^{i+1} \ln(1-k_1) dk_1 \\
&= (1+i) \sum_{j=0}^{2+2(m+n)-i} \binom{2+2(m+n)-i}{j} \int_{k_1=0}^1 (k_1-1)^{1+i+j} \ln(1-k_1) dk_1 \\
&= (1+i) \sum_{j=0}^{2+2(m+n)-i} \binom{2+2(m+n)-i}{j} \frac{(-1)^{i+j}}{(2+i+j)^2}, \tag{I.80}
\end{aligned}$$

where we used the binomial relation in Eq. (I.56).

Expression of integral II_2 : We have found each sub-integral of the second integral II_2 of the second part of the exchange energy. The expression of II_2 is thus

$$\begin{aligned}
& II_2 \\
&= \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \ln((k_1-k_2)^2) dk_2 dk_1 \\
&= \sum_{i=0}^{1+2n} \binom{1+2n}{i} \frac{2(-1)^{1-i}}{(1+i)^2} \left\{ \frac{1}{4+2(m+n)} - \sum_{j=0}^{1+i} \binom{1+i}{j} (-1)^{1+i-j} \frac{1}{3+2(m+n)-i+j} \right. \\
&\quad \left. + (1+i) \frac{1}{4(2+m+n)^2} + (1+i) \sum_{j=0}^{2+2(m+n)-i} \binom{2+2(m+n)-i}{j} \frac{(-1)^{i+j}}{(2+i+j)^2} \right\}. \tag{I.81}
\end{aligned}$$

Third integral of the second part (II_3)

$$\begin{aligned}
II_3 &= \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \text{Ei} \left(- \left(\frac{k_1+k_2}{2\mu} \right)^2 \right) dk_1 dk_2 \\
&= \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \left(- \int_{\left(\frac{k_1+k_2}{2\mu}\right)^2}^{\infty} \frac{e^{-t}}{t} dt \right) dk_1 dk_2 \\
&= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1-i} (2\mu)^{1+i} \int_{k_1=0}^1 k_1^{2+2(m+n)-i} \left(\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i \left(- \int_{k^2}^{\infty} \frac{e^{-t}}{t} dt \right) dk \right) dk_1, \tag{I.82}
\end{aligned}$$

where we used the change of variable $k_2 = 2\mu k - k_1$.

Integration over k in II_3 : We calculate the integral over k with an integration by parts using

$$\frac{d}{dk} \text{Ei}(-k^2) = \frac{2e^{-k^2}}{k} \quad \text{and} \quad \int^k x^i dx = \frac{k^{i+1}}{i+1}, \tag{I.83}$$

so that we have

$$\begin{aligned}
& \int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i \left(- \int_{k^2}^{\infty} \frac{e^{-t}}{t} dt \right) dk \\
&= \frac{1}{i+1} \frac{1}{(2\mu)^{i+1}} \left[(1+k_1)^{i+1} \text{Ei} \left(- \left(\frac{1+k_1}{2\mu} \right)^2 \right) - (k_1)^{i+1} \text{Ei} \left(- \left(\frac{k_1}{2\mu} \right)^2 \right) \right] \\
&\quad - \frac{2}{i+1} \int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i e^{-k^2} dk. \tag{I.84}
\end{aligned}$$

We can observe that the integral over k is now exactly the integral that has been calculated for the second integral of the first part of the exchange energy but for a $-2/(1+i)$ factor. We introduce the notation

$$\binom{1+2n}{i} (-1)^{1-i} (2\mu)^{1+i} \int_{k_1=0}^1 k_1^{2+2(m+n)-i} \int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i e^{-k^2} dk dk_1 = \{I_{2,i}\}, \quad (\text{I.85})$$

for the following calculations.

Integration over k_1 in I_3 : We now can split the sum over i_p and i_i

$$\begin{aligned} I_3 &= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1-i} (2\mu)^{1+i} \int_{k_1=0}^1 k_1^{2+2(m+n)-i} \left(\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i \left(- \int_{k^2}^{\infty} \frac{e^{-t}}{t} dt \right) dk \right) dk_1 \\ &= \sum_{i_p=0}^n \left(\frac{-2}{2i_p+1} \{I_{2,2i_p}\} - \binom{1+2n}{2i_p} \int_{k_1=0}^1 \frac{k_1^{2+2(m+n)-2i_p}}{2i_p+1} \left[(1+k_1)^{2i_p+1} \text{Ei} \left(- \left(\frac{1+k_1}{2\mu} \right)^2 \right) \right. \right. \\ &\quad \left. \left. - (k_1)^{2i_p+1} \text{Ei} \left(- \left(\frac{k_1}{2\mu} \right)^2 \right) \right] dk_1 \right) \\ &\quad + \sum_{i_i=0}^n \left(\frac{-2}{2i_i+2} \{I_{2,2i_i+1}\} + \binom{1+2n}{2i_i+1} \int_{k_1=0}^1 \frac{k_1^{1+2(m+n)-2i_i}}{2i_i+2} \left[(1+k_1)^{2i_i+2} \text{Ei} \left(- \left(\frac{1+k_1}{2\mu} \right)^2 \right) \right. \right. \\ &\quad \left. \left. - (k_1)^{2i_i+2} \text{Ei} \left(- \left(\frac{k_1}{2\mu} \right)^2 \right) \right] dk_1 \right). \quad (\text{I.86}) \end{aligned}$$

Sum over i_p : There are two sub-integrals in the sum over i_p .

- First sub-integral:

We calculate this integral over k_1 with an integration by parts using

$$\frac{d}{dk} \text{Ei} \left(- \left(\frac{k_1}{2\mu} \right)^2 \right) = \frac{2 e^{-\left(\frac{k_1}{2\mu}\right)^2}}{k_1} \quad \text{and} \quad \int^k x^{3+2(m+n)} dx = \frac{k^{4+2(m+n)}}{4+2(m+n)}, \quad (\text{I.87})$$

so that we have

$$\begin{aligned} & - \int_{k_1=0}^1 k_1^{2+2(m+n)+1} \text{Ei} \left(- \left(\frac{k_1}{2\mu} \right)^2 \right) dk_1 \\ &= - \frac{\text{Ei} \left(- \left(\frac{1}{2\mu} \right)^2 \right)}{4+2(m+n)} + \frac{2}{4+2(m+n)} \int_{k_1=0}^1 k_1^{3+2(m+n)} e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 \\ &= - \frac{\text{Ei} \left(- \left(\frac{1}{2\mu} \right)^2 \right)}{4+2(m+n)} + \frac{2}{4+2(m+n)} \mathcal{S}_i[m+n+1]. \quad (\text{I.88}) \end{aligned}$$

- Second sub-integral:

$$\begin{aligned}
& \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} (1+k_1)^{2i_p+1} \text{Ei} \left(-\left(\frac{1+k_1}{2\mu}\right)^2 \right) dk_1 \\
&= \sum_{j=0}^{2+2(m+n-i_p)} \binom{2+2(m+n-i_p)}{j} (-1)^{-j} \int_{k_1=0}^1 (1+k_1)^{j+2i_p+1} \text{Ei} \left(-\left(\frac{1+k_1}{2\mu}\right)^2 \right) dk_1 \\
&= \sum_{j=0}^{2+2(m+n-i_p)} \binom{2+2(m+n-i_p)}{j} \frac{(-1)^{-j}}{j+2i_p+2} \left[2^{j+2i_p+2} \text{Ei} \left(-\left(\frac{1}{\mu}\right)^2 \right) - \text{Ei} \left(-\left(\frac{1}{2\mu}\right)^2 \right) \right] \\
&\quad - \sum_{j_p=0}^{1+m+n-i_p} \binom{2+2(m+n-i_p)}{2j_p} \frac{1}{2j_p+2i_p+2} S_i^+[j_p+i_p] \\
&\quad + \sum_{j_i=0}^{m+n-i_p} \binom{2+2(m+n-i_p)}{2j_i+1} \frac{1}{2j_i+2i_p+3} S_p^+[j_i+i_p+1], \tag{I.89}
\end{aligned}$$

where we used a binomial expansion, the same integration by parts as before, and then split the sum over j .

Sum over i_i : There are two sub-integrals in the sum over i_i .

- First sub-integral:

$$\begin{aligned}
& - \int_{k_1=0}^1 k_1^{2+2(m+n)+1} \text{Ei} \left(-\left(\frac{k_1}{2\mu}\right)^2 \right) dk_1 \\
&= - \frac{\text{Ei} \left(-\left(\frac{1}{2\mu}\right)^2 \right)}{4+2(m+n)} + \frac{2}{4+2(m+n)} S_i[m+n+1]. \tag{I.90}
\end{aligned}$$

- Second sub-integral:

$$\begin{aligned}
& \int_{k_1=0}^1 k_1^{1+2(m+n-i_i)} (1+k_1)^{2i_i+2} \text{Ei} \left(-\left(\frac{1+k_1}{2\mu}\right)^2 \right) dk_1 \\
&= \sum_{j=0}^{1+2(m+n-i_i)} \binom{1+2(m+n-i_i)}{j} (-1)^{-j} \int_{k_1=0}^1 (1+k_1)^{j+2i_i+2} \text{Ei} \left(-\left(\frac{1+k_1}{2\mu}\right)^2 \right) dk_1 \\
&= \sum_{j=0}^{1+2(m+n-i_i)} \binom{1+2(m+n-i_i)}{j} \frac{(-1)^{1-j}}{j+2i_i+3} \left[2^{j+2i_i+3} \text{Ei} \left(-\left(\frac{1}{\mu}\right)^2 \right) - \text{Ei} \left(-\left(\frac{1}{2\mu}\right)^2 \right) \right] \\
&\quad + \sum_{j_p=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_p} \frac{1}{2j_p+2i_i+3} S_p^+[j_p+i_i+1] \\
&\quad - \sum_{j_i=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_i+1} \frac{1}{2j_i+2i_i+4} S_i^+[j_i+i_i+1]. \tag{I.91}
\end{aligned}$$

Expression of integral II_3 : We have found each sub-integral of the third integral II_3 of the second part of the exchange energy. The expression of II_3 is thus

$$\begin{aligned}
& II_3 \\
&= \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \text{Ei} \left(- \left(\frac{k_1 + k_2}{2\mu} \right)^2 \right) dk_2 dk_1 \\
&= \sum_{i_p=0}^n \left\{ \frac{-2}{2i_p+1} \{I_{2,2i_p}\} - \frac{1}{2i_p+1} \binom{1+2n}{2i_p} \left[- \frac{\text{Ei} \left(- \left(\frac{1}{2\mu} \right)^2 \right)}{4+2(m+n)} + \frac{2}{4+2(m+n)} S_i[m+n+1] \right. \right. \\
&\quad + \sum_{j=0}^{2+2(m+n-i_p)} \binom{2+2(m+n-i_p)}{j} \frac{(-1)^{-j}}{j+2i_p+2} \left[2^{j+2i_p+2} \text{Ei} \left(- \left(\frac{1}{\mu} \right)^2 \right) - \text{Ei} \left(- \left(\frac{1}{2\mu} \right)^2 \right) \right] \\
&\quad + \sum_{j_p=0}^{m+n-i_p+1} \binom{2+2(m+n-i_p)}{2j_p} \frac{1}{2j_p+2i_p+2} S_i^+[j_p+i_p] \\
&\quad \left. \left. - \sum_{j_i=0}^{m+n-i_p} \binom{2+2(m+n-i_p)}{2j_i+1} \frac{1}{2j_i+2i_p+3} S_i^+[j_i+i_p+1] \right] \right\} \\
&+ \sum_{i_i=0}^n \left\{ \frac{-2}{2i_i+2} \{I_{2,2i_i+1}\} - \frac{1}{2i_i+2} \binom{1+2n}{2i_i+1} \left[- \frac{\text{Ei} \left(- \left(\frac{1}{2\mu} \right)^2 \right)}{4+2(m+n)} + \frac{2}{4+2(m+n)} S_i[m+n+1] \right. \right. \\
&\quad + \sum_{j=0}^{1+2(m+n-i_i)} \binom{1+2(m+n-i_i)}{j} \frac{(-1)^{1-j}}{j+2i_i+3} \left[2^{j+2i_i+3} \text{Ei} \left(- \left(\frac{1}{\mu} \right)^2 \right) - \text{Ei} \left(- \left(\frac{1}{2\mu} \right)^2 \right) \right] \\
&\quad + \sum_{j_p=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_p} \frac{1}{2j_p+2i_i+3} S_i^+[j_p+i_i+1] \\
&\quad \left. \left. - \sum_{j_i=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_i+1} \frac{1}{2j_i+2i_i+4} S_i^+[j_i+i_i+1] \right] \right\}. \tag{I.92}
\end{aligned}$$

Fourth integral of the second part (II_4)

$$\begin{aligned}
II_4 &= \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \text{Ei} \left(- \left(\frac{k_1 - k_2}{2\mu} \right)^2 \right) dk_2 dk_1 \\
&= \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \left(- \int_{\left(\frac{k_1-k_2}{2\mu}\right)^2}^{\infty} \frac{e^{-t}}{t} dt \right) dk_2 dk_1 \\
&= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1+i} (2\mu)^{1+i} \int_{k_1=0}^1 k_1^{2+2(m+n)-i} \left(\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}} k^i \left(- \int_{k^2}^{\infty} \frac{e^{-t}}{t} dt \right) dk \right) dk_1, \tag{I.93}
\end{aligned}$$

where we used the change of variable $k_2 = -2\mu k + k_1$.

Integration over k in II_4 : We calculate the integral over k using the usual integration by parts

$$\begin{aligned}
& \int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}} k^i \left(- \int_{k^2}^{\infty} \frac{e^{-t}}{t} dt \right) dk \\
&= \frac{1}{i+1} \frac{1}{(2\mu)^{i+1}} \left[(k_1-1)^{i+1} \text{Ei} \left(- \left(\frac{k_1-1}{2\mu} \right)^2 \right) - (k_1)^{i+1} \text{Ei} \left(- \left(\frac{k_1}{2\mu} \right)^2 \right) \right] \\
& \quad - \frac{2}{i+1} \int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}} k^i e^{-k^2} dk. \tag{I.94}
\end{aligned}$$

We observe that the integral on k is now exactly the integral that has been calculated for the third integral of the first part of the exchange energy but for a $-2/(1+i)$ factor. We introduce the notation

$$\binom{1+2n}{i} (-1)^{1-i} (2\mu)^{1+i} \int_{k_1=0}^1 k_1^{2+2(m+n)-i} \int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}} k^i e^{-k^2} dk dk_1 = \{I_{3,i}\}, \tag{I.95}$$

for the following calculations.

Integration over k_1 in II_4 : We split the sum over i_p and i_i

$$\begin{aligned}
II_4 &= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1+i} (2\mu)^{1+i} \int_{k_1=0}^1 k_1^{2+2(m+n)-i} \left(\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}} k^i \left(- \int_{k^2}^{\infty} \frac{e^{-t}}{t} dt \right) dk \right) dk_1 \\
&= \sum_{i_p=0}^n \left(\frac{-2}{2i_p+1} \{I_{3,2i_p}\} - \binom{1+2n}{2i_p} \int_{k_1=0}^1 \frac{k_1^{2+2(m+n)-2i_p}}{2i_p+1} \left[(k_1-1)^{2i_p+1} \text{Ei} \left(- \left(\frac{k_1-1}{2\mu} \right)^2 \right) \right. \right. \\
& \quad \left. \left. - (k_1)^{2i_p+1} \text{Ei} \left(- \left(\frac{k_1}{2\mu} \right)^2 \right) \right] dk_1 \right) \\
& \quad + \sum_{i_i=0}^n \left(\frac{-2}{2i_i+2} \{I_{3,2i_i+1}\} + \binom{1+2n}{2i_i+1} \int_{k_1=0}^1 \frac{k_1^{1+2(m+n)-2i_i}}{2i_i+2} \left[(k_1-1)^{2i_i+2} \text{Ei} \left(- \left(\frac{k_1-1}{2\mu} \right)^2 \right) \right. \right. \\
& \quad \left. \left. - (k_1)^{2i_i+2} \text{Ei} \left(- \left(\frac{k_1}{2\mu} \right)^2 \right) \right] dk_1 \right). \tag{I.96}
\end{aligned}$$

Sum over i_p : There are two sub-integrals in the sum over i_p .

- First sub-integral:

$$\begin{aligned}
& - \int_{k_1=0}^1 k_1^{2+2(m+n)+1} \text{Ei} \left(- \left(\frac{k_1}{2\mu} \right)^2 \right) dk_1 \\
&= - \frac{\text{Ei} \left(- \left(\frac{1}{2\mu} \right)^2 \right)}{4+2(m+n)} + \frac{2}{4+2(m+n)} S_i[m+n+1]. \tag{I.97}
\end{aligned}$$

- Second sub-integral:

$$\begin{aligned}
& \int_{k_1=0}^1 k_1^{2+2(m+n-i_p)} (k_1-1)^{2i_p+1} \text{Ei} \left(-\left(\frac{k_1-1}{2\mu}\right)^2 \right) dk_1 \\
&= \sum_{j=0}^{2+2(m+n-i_p)} \binom{2+2(m+n-i_p)}{j} \int_{k_1=0}^1 (k_1-1)^{j+2i_p+1} \text{Ei} \left(-\left(\frac{k_1-1}{2\mu}\right)^2 \right) dk_1 \\
&= \sum_{j=0}^{2+2(m+n-i_p)} \binom{2+2(m+n-i_p)}{j} \frac{1}{j+2i_p+2} \left[0 - (-1)^{j+2i_p+2} \text{Ei} \left(-\left(\frac{-1}{2\mu}\right)^2 \right) \right] \\
&\quad - \sum_{j_p=0}^{1+m+n-i_p} \binom{2+2(m+n-i_p)}{2j_p} \frac{1}{2j_p+2i_p+2} S_i^- [j_p+i_p] \\
&\quad - \sum_{j_i=0}^{m+n-i_p} \binom{2+2(m+n-i_p)}{2j_i+1} \frac{1}{2j_i+2i_p+3} S_p^- [j_i+i_p+1]. \tag{I.98}
\end{aligned}$$

Sum over i_i : There are two sub-integrals in the sum over i_i .

- First sub-integral:

$$\begin{aligned}
& - \int_{k_1=0}^1 k_1^{2+2(m+n)+1} \text{Ei} \left(-\left(\frac{k_1}{2\mu}\right)^2 \right) dk_1 \\
&= - \frac{\text{Ei} \left(-\left(\frac{1}{2\mu}\right)^2 \right)}{4+2(m+n)} + \frac{2}{4+2(m+n)} S_i [m+n+1]. \tag{I.99}
\end{aligned}$$

- second sub-integral:

$$\begin{aligned}
& \int_{k_1=0}^1 k_1^{1+2(m+n-i_i)} (k_1-1)^{2i_i+2} \text{Ei} \left(-\left(\frac{k_1-1}{2\mu}\right)^2 \right) dk_1 \\
&= \sum_{j=0}^{1+2(m+n-i_i)} \binom{1+2(m+n-i_i)}{j} \int_{k_1=0}^1 (k_1-1)^{j+2i_i+2} \text{Ei} \left(-\left(\frac{k_1-1}{2\mu}\right)^2 \right) dk_1 \\
&= \sum_{j=0}^{1+2(m+n-i_i)} \binom{1+2(m+n-i_i)}{j} \frac{1}{j+2i_i+3} \left[0 - (-1)^{j+i_i+3} \text{Ei} \left(-\left(\frac{-1}{2\mu}\right)^2 \right) \right] \\
&\quad - \sum_{j_p=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_p} \frac{1}{2j_p+2i_i+3} S_p^+ [j_p+i_i+1] \\
&\quad - \sum_{j_i=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_i+1} \frac{1}{2j_i+2i_i+4} S_i^+ [j_i+i_i+1]. \tag{I.100}
\end{aligned}$$

Expression of integral II_4 We have found each sub-integral of the fourth integral II_4 of the second part of the exchange energy. The expression of II_4 is thus

$$\begin{aligned}
& II_4 \\
&= \int_{k_1=0}^1 \int_{k_2=0}^1 k_1^{1+2m} k_2^{1+2n} \text{Ei} \left(- \left(\frac{k_1 - k_2}{2\mu} \right)^2 \right) dk_2 dk_1 \\
&= \sum_{i_p=0}^n \left\{ \frac{-2}{2i_p+1} \{I_{3,2i_p}\} - \frac{1}{2i_p+1} \binom{1+2n}{2i_p} \left[- \frac{\text{Ei} \left(- \left(\frac{1}{2\mu} \right)^2 \right)}{4+2(m+n)} + \frac{2}{4+2(m+n)} S_i[m+n+1] \right. \right. \\
&\quad + \sum_{j=0}^{2+2(m+n-i_p)} \binom{2+2(m+n-i_p)}{j} \frac{1}{j+2i_p+2} \left[0 - \text{Ei} \left(- \left(\frac{-1}{2\mu} \right)^2 \right) \right] \\
&\quad - \sum_{j_p=0}^{m+n-i_p+1} \binom{2+2(m+n-i_p)}{2j_p} \frac{1}{2j_p+2i_p+2} S_i^-[j_p+i_p] \\
&\quad \left. \left. - \sum_{j_i=0}^{m+n-i_p} \binom{2+2(m+n-i_p)}{2j_i+1} \frac{1}{2j_i+2i_p+3} S_p^-[j_i+i_p+1] \right] \right\} \\
&+ \sum_{i_i=0}^n \left\{ \frac{-2}{2i_i+2} \{I_{3,2i_i+1}\} - \frac{1}{2i_i+2} \binom{1+2n}{2i_i+1} \left[- \frac{\text{Ei} \left(- \left(\frac{1}{2\mu} \right)^2 \right)}{4+2(m+n)} + \frac{2}{4+2(m+n)} S_i[m+n+1] \right. \right. \\
&\quad + \sum_{j=0}^{1+2(m+n-i_i)} \binom{1+2(m+n-i_i)}{j} \frac{1}{j+2i_i+3} \left[0 - \text{Ei} \left(- \left(\frac{-1}{2\mu} \right)^2 \right) \right] \\
&\quad + \sum_{j_p=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_p} \frac{1}{2j_p+2i_i+3} S_p^-[j_p+i_i+1] \\
&\quad \left. \left. - \sum_{j_i=0}^{m+n-i_i} \binom{1+2(m+n-i_i)}{2j_i+1} \frac{1}{2j_i+2i_i+4} S_i^-[j_i+i_i+1] \right] \right\}. \tag{I.101}
\end{aligned}$$

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Appendix J

Uniform coordinate scaling relation for the relativistic no-pair short-range exchange density functional

Here, we generalize the uniform coordinate scaling relation of the non-relativistic exchange density functional [1] and of the non-relativistic no-pair short-range exchange density functional [2] to the case of the relativistic short-range exchange density functional of Eq. (4.16) that we used in Chapter 4. Since the scaling relation involves scaling the speed of light c , we will explicitly indicate in this section the dependence on c .

First, we introduce the non-interacting Dirac kinetic + rest mass energy density functional $T_s^c[n]$ defined by Eq. (4.9) in the special case of a vanishing range-separation parameter, $\mu = 0$,

$$T_s^c[n] = \min_{\Phi_+} \max_{\Phi_+} \langle \Phi_+ | \hat{T}_D^c | \Phi_+ \rangle = \langle \Phi_+^c[n] | \hat{T}_D^c | \Phi_+^c[n] \rangle, \quad (\text{J.1})$$

where $\Phi_+^c[n]$ is the relativistic Kohn-Sham single-determinant wave function. Let us now consider the scaled wave function $\Phi_{+,\gamma}^c[n]$ defined by, for N electrons,

$$\Phi_{+,\gamma}^c[n](\mathbf{r}_1, \dots, \mathbf{r}_N) = \gamma^{3N/2} \Phi_+^c[n](\gamma \mathbf{r}_1, \dots, \gamma \mathbf{r}_N), \quad (\text{J.2})$$

where $\gamma > 0$ is a scaling factor. The wave function $\Phi_{+,\gamma}^c[n]$ yields the scaled density $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma \mathbf{r})$ and is the minmax optimal wave function of $\langle \Phi_+ | \hat{T}_D^{c\gamma} | \Phi_+ \rangle$ since it can be checked that

$$\langle \Phi_{+,\gamma}^c[n] | \hat{T}_D^{c\gamma} | \Phi_{+,\gamma}^c[n] \rangle = \gamma^2 \langle \Phi_+^c[n] | \hat{T}_D^c | \Phi_+^c[n] \rangle, \quad (\text{J.3})$$

and the right-hand side is minmax optimal by definition of $\Phi_+^c[n]$. Therefore, we conclude that

$$\Phi_{+,\gamma}^c[n] = \Phi_+^{c\gamma}[n_\gamma]. \quad (\text{J.4})$$

From the definition of the relativistic short-range exchange energy density functional

$$E_x^{\text{sr},\mu,c}[n] = \langle \Phi_+^c[n] | \hat{W}_{\text{ee}}^{\text{sr},\mu} | \Phi_+^c[n] \rangle - E_{\text{H}}^{\text{sr},\mu}[n], \quad (\text{J.5})$$

we then arrive at the scaling relation

$$E_x^{\text{sr},\mu,c\gamma}[n_\gamma] = \gamma E_x^{\text{sr},\mu,c}[n], \quad (\text{J.6})$$

or, equivalently,

$$E_x^{\text{sr},\mu,c}[n_\gamma] = \gamma E_x^{\text{sr},\mu/\gamma,c/\gamma}[n]. \quad (\text{J.7})$$

This scaling relation is an important constraint which is satisfied by our approximate density functionals. Besides, it shows that the low-density limit ($\gamma \rightarrow 0$) corresponds to the non-relativistic limit ($c \rightarrow \infty$), while the high-density limit ($\gamma \rightarrow \infty$) corresponds to the ultra-relativistic limit ($c \rightarrow 0$). It also shows that, for a fixed value of the range-separation parameter μ , low-density regions explore the functional in the short-range limit ($\mu \rightarrow \infty$) and high-density regions explore the functional in the full-range limit ($\mu = 0$).

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Appendix K

Four-component on-top exchange pair-density

We wish to derive the expression of the four-component on-top exchange pair-density that we used in Chapter 4, in a no-pair relativistic framework. Using the four-component-spinor orbitals

$$\Psi_i(\mathbf{r}) = \begin{pmatrix} \Psi_i^{L\alpha}(\mathbf{r}) \\ \Psi_i^{L\beta}(\mathbf{r}) \\ \Psi_i^{S\alpha}(\mathbf{r}) \\ \Psi_i^{S\beta}(\mathbf{r}) \end{pmatrix}, \quad (\text{K.1})$$

the on-top value of the 4×4 one-electron density matrix has the expression

$$\begin{aligned} \gamma(\mathbf{r}, \mathbf{r}) &= \sum_{i=1}^N \Psi_i(\mathbf{r}) \Psi_i^\dagger(\mathbf{r}) \\ &= \begin{pmatrix} \Psi_i^{L\alpha}(\mathbf{r})\Psi_i^{L\alpha}(\mathbf{r})^* & \Psi_i^{L\alpha}(\mathbf{r})\Psi_i^{L\beta}(\mathbf{r})^* & \Psi_i^{L\alpha}(\mathbf{r})\Psi_i^{S\alpha}(\mathbf{r})^* & \Psi_i^{L\alpha}(\mathbf{r})\Psi_i^{S\beta}(\mathbf{r})^* \\ \Psi_i^{L\beta}(\mathbf{r})\Psi_i^{L\alpha}(\mathbf{r})^* & \Psi_i^{L\beta}(\mathbf{r})\Psi_i^{L\beta}(\mathbf{r})^* & \Psi_i^{L\beta}(\mathbf{r})\Psi_i^{S\alpha}(\mathbf{r})^* & \Psi_i^{L\beta}(\mathbf{r})\Psi_i^{S\beta}(\mathbf{r})^* \\ \Psi_i^{S\alpha}(\mathbf{r})\Psi_i^{L\alpha}(\mathbf{r})^* & \Psi_i^{S\alpha}(\mathbf{r})\Psi_i^{L\beta}(\mathbf{r})^* & \Psi_i^{S\alpha}(\mathbf{r})\Psi_i^{S\alpha}(\mathbf{r})^* & \Psi_i^{S\alpha}(\mathbf{r})\Psi_i^{S\beta}(\mathbf{r})^* \\ \Psi_i^{S\beta}(\mathbf{r})\Psi_i^{L\alpha}(\mathbf{r})^* & \Psi_i^{S\beta}(\mathbf{r})\Psi_i^{L\beta}(\mathbf{r})^* & \Psi_i^{S\beta}(\mathbf{r})\Psi_i^{S\alpha}(\mathbf{r})^* & \Psi_i^{S\beta}(\mathbf{r})\Psi_i^{S\beta}(\mathbf{r})^* \end{pmatrix}, \end{aligned} \quad (\text{K.2})$$

which leads to the density

$$n(\mathbf{r}) = \text{Tr}[\gamma(\mathbf{r}, \mathbf{r})] = \sum_{i=1}^N |\Psi_i^{L\alpha}(\mathbf{r})|^2 + |\Psi_i^{L\beta}(\mathbf{r})|^2 + |\Psi_i^{S\alpha}(\mathbf{r})|^2 + |\Psi_i^{S\beta}(\mathbf{r})|^2. \quad (\text{K.3})$$

The on-top exchange pair density has the expression

$$\begin{aligned} n_{2,x}(\mathbf{r}, \mathbf{r}) &= -\text{Tr}[\gamma(\mathbf{r}, \mathbf{r})^2] \\ &= -\sum_{i=1}^N \sum_{j=1}^N \left(|\Psi_i^{L\alpha}(\mathbf{r})|^2 |\Psi_j^{L\alpha}(\mathbf{r})|^2 + |\Psi_i^{L\beta}(\mathbf{r})|^2 |\Psi_j^{L\beta}(\mathbf{r})|^2 + 2\Psi_i^{L\alpha}(\mathbf{r})\Psi_i^{L\beta}(\mathbf{r})^* \Psi_j^{L\beta}(\mathbf{r})\Psi_j^{L\alpha}(\mathbf{r})^* \right. \\ &\quad + |\Psi_i^{S\alpha}(\mathbf{r})|^2 |\Psi_j^{S\alpha}(\mathbf{r})|^2 + |\Psi_i^{S\beta}(\mathbf{r})|^2 |\Psi_j^{S\beta}(\mathbf{r})|^2 + 2\Psi_i^{S\alpha}(\mathbf{r})\Psi_i^{S\beta}(\mathbf{r})^* \Psi_j^{S\beta}(\mathbf{r})\Psi_j^{S\alpha}(\mathbf{r})^* \\ &\quad + 2\Psi_i^{L\alpha}(\mathbf{r})\Psi_i^{S\alpha}(\mathbf{r})^* \Psi_j^{S\alpha}(\mathbf{r})\Psi_j^{L\alpha}(\mathbf{r})^* + 2\Psi_i^{L\beta}(\mathbf{r})\Psi_i^{S\beta}(\mathbf{r})^* \Psi_j^{S\beta}(\mathbf{r})\Psi_j^{L\beta}(\mathbf{r})^* \\ &\quad \left. + 2\Psi_i^{L\alpha}(\mathbf{r})\Psi_i^{S\beta}(\mathbf{r})^* \Psi_j^{S\beta}(\mathbf{r})\Psi_j^{L\alpha}(\mathbf{r})^* + 2\Psi_i^{L\beta}(\mathbf{r})\Psi_i^{S\alpha}(\mathbf{r})^* \Psi_j^{S\alpha}(\mathbf{r})\Psi_j^{L\beta}(\mathbf{r})^* \right). \end{aligned} \quad (\text{K.4})$$

In the non-relativistic limit, each orbital has a definite spin state, i.e. $\Psi_i(\mathbf{r}) = (\Psi_i^{L\alpha}(\mathbf{r}), 0, 0, 0)$ or $\Psi_i(\mathbf{r}) = (0, \Psi_i^{L\beta}(\mathbf{r}), 0, 0)$, and we recover the well-known expression of the on-top exchange pair density in terms

of the spin densities

$$\begin{aligned} n_{2,x}^{\text{NR}}(\mathbf{r}, \mathbf{r}) &= -\sum_{i=1}^N \sum_{j=1}^N \left(|\psi_i^{\text{L}\alpha}(\mathbf{r})|^2 |\psi_j^{\text{L}\alpha}(\mathbf{r})|^2 + |\psi_i^{\text{L}\beta}(\mathbf{r})|^2 |\psi_j^{\text{L}\beta}(\mathbf{r})|^2 \right) \\ &= -n_\alpha(\mathbf{r})^2 - n_\beta(\mathbf{r})^2, \end{aligned} \quad (\text{K.5})$$

or, for closed-shell systems, $n_{2,x}^{\text{NR}}(\mathbf{r}, \mathbf{r}) = -n(\mathbf{r})^2/2$. However, in the relativistic case, $n_{2,x}(\mathbf{r}, \mathbf{r})$ can no longer be generally expressed explicitly with the density, as seen from the presence of terms mixing different spinor components in Eq. (K.5). There are however two exceptions. The first exception is provided by one-electron systems for which it is easy to check that $n_{2,x}(\mathbf{r}, \mathbf{r}) = -n(\mathbf{r})^2$, as in the non-relativistic case. The second exception is provided by systems of two electrons in a unique Kramers pair, for which $n_{2,x}(\mathbf{r}, \mathbf{r}) = -n(\mathbf{r})^2/2$, as in the non-relativistic case. Indeed, for closed-shell systems, the one-electron density matrix can be decomposed into Kramers contributions

$$\gamma(\mathbf{r}, \mathbf{r}) = \gamma_+(\mathbf{r}, \mathbf{r}) + \gamma_-(\mathbf{r}, \mathbf{r}), \quad (\text{K.6})$$

where $\gamma_+(\mathbf{r}, \mathbf{r}) = \sum_{i=1}^{N/2} \psi_i(\mathbf{r}) \psi_i^\dagger(\mathbf{r})$ and $\gamma_-(\mathbf{r}, \mathbf{r}) = \sum_{i=1}^{N/2} \bar{\psi}_i(\mathbf{r}) \bar{\psi}_i^\dagger(\mathbf{r})$, and $\bar{\psi}_i(\mathbf{r})$ is the Kramers partner of $\psi_i(\mathbf{r})$

$$\bar{\psi}_i(\mathbf{r}) = \begin{pmatrix} -\psi_i^{\text{L}\beta}(\mathbf{r})^* \\ \psi_i^{\text{L}\alpha}(\mathbf{r})^* \\ -\psi_i^{\text{S}\beta}(\mathbf{r})^* \\ \psi_i^{\text{S}\alpha}(\mathbf{r})^* \end{pmatrix}. \quad (\text{K.7})$$

In this case, the density can then be expressed as $n(\mathbf{r}) = 2\text{Tr}[\gamma_+(\mathbf{r}, \mathbf{r})]$, and the on-top exchange pair density as

$$n_{2,x}(\mathbf{r}, \mathbf{r}) = -2 \left(\text{Tr}[\gamma_+(\mathbf{r}, \mathbf{r})^2] + \text{Tr}[\gamma_+(\mathbf{r}, \mathbf{r})\gamma_-(\mathbf{r}, \mathbf{r})] \right), \quad (\text{K.8})$$

where we have used $\text{Tr}[\gamma_+(\mathbf{r}, \mathbf{r})^2] = \text{Tr}[\gamma_-(\mathbf{r}, \mathbf{r})^2]$. For an unique Kramers pair (i.e. for $N = 2$), it is easy to check that $\text{Tr}[\gamma_+(\mathbf{r}, \mathbf{r})^2] = (\text{Tr}[\gamma_+(\mathbf{r}, \mathbf{r})])^2$ and $\text{Tr}[\gamma_+(\mathbf{r}, \mathbf{r})\gamma_-(\mathbf{r}, \mathbf{r})] = 0$, and thus

$$n_{2,x}(\mathbf{r}, \mathbf{r}) = -2(\text{Tr}[\gamma_+(\mathbf{r}, \mathbf{r})])^2 = -\frac{n(\mathbf{r})^2}{2} \text{ for } N = 2. \quad (\text{K.9})$$

The reason why systems with one electron or two electrons in a single Kramers pair constitute exceptions is that in these systems exchange only represents in fact a self-interaction correction, and we have $E_x^{\text{sr},\mu}[n] = -E_H^{\text{sr},\mu}[n]$ for one electron and $E_x^{\text{sr},\mu}[n] = -(1/2)E_H^{\text{sr},\mu}[n]$ for two electrons in a single Kramers pair, as for the non-relativistic theory.

Appendix L

Even-tempered basis sets parameters for the He, Be, Ne, and Ar isoelectronic series

We give the parameters of the even-tempered basis sets that we used for the calculations in chapter 4.

Table L.1: Parameters ζ_1 and q for generating all the exponents $\zeta_v = \zeta_1 q^{v-1}$ of our uncontracted even-tempered large-component basis functions for the Yb⁶⁸⁺ and U⁹⁰⁺ systems of the helium isoelectronic series. We use ten s basis functions, two sets of p basis functions, and one set of d basis functions. The small-component basis functions are generated from the unrestricted kinetic-balance scheme.

	Ten s basis functions		Two p basis functions		One d basis function
	ζ_1	q	ζ_1	q	ζ_1
Yb ⁶⁸⁺	1.39601904E+07	0.30	3.39128349E+06	0.25	4.75587491E+03
U ⁹⁰⁺	5.58567332E+07	0.295	2.64721605E+07	0.25	3.34172062E+04

Table L.2: Parameters ζ_1 and q for generating all the exponents $\zeta_v = \zeta_1 q^{v-1}$ of our uncontracted even-tempered large-component basis functions for the beryllium isoelectronic series. We use ten s basis functions, six sets of p basis functions, and one set of d basis functions. The small-component basis functions are generated from the unrestricted kinetic-balance scheme.

	Ten s basis functions		Six p basis functions		One d basis function
	ζ_1	q	ζ_1	q	ζ_1
Be	6.40943779E+03	0.25	1.31800101E+01	0.25	2.71217265E-01
Ne ⁶⁺	2.63937466E+04	0.30	1.01356529E+02	0.25	2.16640868E+00
Ar ¹⁴⁺	2.16279421E+05	0.26	4.94782136E+02	0.25	1.13941141E+01
Kr ³²⁺	4.14098736E+06	0.23	9.01590791E+03	0.25	2.25939509E+02
Xe ⁵⁰⁺	9.04292743E+06	0.23	2.81773747E+05	0.25	1.95959651E+03
Yb ⁶⁶⁺	1.39601904E+07	0.236	3.39128349E+06	0.25	4.75587491E+03
Rn ⁸²⁺	1.46794059E+07	0.25	1.72824122E+07	0.25	1.25385658E+03
U ⁸⁸⁺	1.46346866E+07	0.26	2.64721605E+07	0.25	3.34172062E+04

Table L.3: Parameters ζ_1 and q for generating all the exponents $\zeta_v = \zeta_1 q^{v-1}$ of our uncontracted even-tempered large-component basis functions for the neon isoelectronic series. We use ten s basis functions, six sets of p basis functions, and one set of d basis functions. The small-component basis functions are generated from the unrestricted kinetic-balance scheme.

	Ten s basis functions		Six p basis functions		One d basis function
	ζ_1	q	ζ_1	q	ζ_1
Ne	2.63937466E+04	0.30	1.01356529E+02	0.30	2.16640868E+00
Ar ⁸⁺	2.16279421E+05	0.29	4.94782136E+02	0.32	1.13941141E+01
Kr ²⁶⁺	4.14098736E+06	0.25	9.01590791E+03	0.25	2.25939509E+02
Xe ⁴⁴⁺	9.04292743E+06	0.255	9.36856349E+03	0.31	1.95959651E+03
Yb ⁶⁰⁺	1.39601904E+07	0.235	2.61264417E+04	0.32	4.75587491E+03
Rn ⁷⁶⁺	1.46794059E+07	0.25	5.70898829E+04	0.30	1.25385658E+03
U ⁸²⁺	1.46346866E+07	0.26	1.22880210E+05	0.28	3.34172062E+04

Table L.4: Parameters ζ_1 and q for generating all the exponents $\zeta_v = \zeta_1 q^{v-1}$ of our uncontracted even-tempered large-component basis functions for the argon isoelectronic series. We use twelve s basis functions, eight sets of p basis functions, and three set of d basis functions. The small-component basis functions are generated from the unrestricted kinetic-balance scheme.

	Twelve s basis functions		Eight p basis functions		Three d basis functions	
	ζ_1	q	ζ_1	q	ζ_1	q
Ar	2.16279421E+05	0.30	4.94782136E+02	0.325	1.13941141E+01	0.25
Kr ¹⁸⁺	4.14098736E+06	0.25	9.01590791E+03	0.30	2.25939509E+02	0.25
Xe ³⁶⁺	9.04292743E+06	0.25	9.36856349E+03	0.36	1.95959651E+03	0.25
Yb ⁵²⁺	1.39601904E+07	0.26	2.61264417E+04	0.33	4.75587491E+03	0.25
Rn ⁶⁸⁺	1.46794059E+07	0.30	1.92412503E+05	0.30	1.25385658E+03	0.25
U ⁷⁴⁺	1.46346866E+07	0.29	1.22880210E+05	0.29	4.95593590E+02	0.25

Appendix M

No-pair one-particle non-interacting Green's function of the RHEG

We derive the expression of the one-particle non-interacting Green's function of a RHEG, following the logic of the book from Fetter and Walecka [1] (Example:free fermions, page 70). We first define the positive energy plane-wave solution of the Dirac equation for the non-interacting relativistic homogeneous electron gas

$$\Psi_{\mathbf{k},\sigma}(\mathbf{x}t) = \frac{1}{\sqrt{V}} \sqrt{\frac{E_k + mc^2}{2E_k}} e^{i\mathbf{k}\cdot\mathbf{x}} e^{-i\omega_k t} \Phi_{\mathbf{k},\sigma} \quad (\text{M.1})$$

where $E_k = \sqrt{\hbar^2 k^2 c^2 + m^2 c^4}$ and $\omega_k = E_k/\hbar$. For the two possible values of σ for spin $-1/2$ fermions, we have

$$\Phi_{\mathbf{k},\uparrow} = \begin{pmatrix} \Phi_{\uparrow} \\ c \frac{\boldsymbol{\sigma}\cdot\mathbf{k}}{E_k + mc^2} \Phi_{\uparrow} \end{pmatrix} \quad \text{and} \quad \Phi_{\mathbf{k},\downarrow} = \begin{pmatrix} \Phi_{\downarrow} \\ c \frac{\boldsymbol{\sigma}\cdot\mathbf{k}}{E_k + mc^2} \Phi_{\downarrow} \end{pmatrix} \quad (\text{M.2})$$

with $\Phi_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\Phi_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$, and $\boldsymbol{\sigma}$ being the vector composed of the three Pauli matrices. For the no-pair one-particle non-interacting Green's function of the RHEG we have in matrix form

$$\begin{aligned} i G^0(\mathbf{x}t, \mathbf{x}'t') &= \sum_{\mathbf{k},\sigma} \Psi_{\mathbf{k},\sigma}(\mathbf{x}t) \Psi_{\mathbf{k},\sigma}^{\dagger}(\mathbf{x}'t') \\ &\quad \times [\theta(t-t')\theta(k-k_F) - \theta(t'-t)\theta(k_F-k)] \\ &= \frac{1}{V} \sum_{\mathbf{k}} \frac{E_k + mc^2}{2E_k} e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')} e^{-i\omega_k(t-t')} \sum_{\sigma} \Phi_{\mathbf{k},\sigma} \Phi_{\mathbf{k},\sigma}^{\dagger} \\ &\quad \times [\theta(t-t')\theta(k-k_F) - \theta(t'-t)\theta(k_F-k)] \end{aligned} \quad (\text{M.3})$$

where we have summed over all wave vectors \mathbf{k} for the positive energy solutions only, and where

$$\sum_{\sigma} \Phi_{\mathbf{k},\sigma} \Phi_{\mathbf{k},\sigma}^{\dagger} \quad (\text{M.4})$$

is a 4x4 matrix non-diagonal matrix. In the limit of an infinite volume, the summation over \mathbf{k} becomes an integration,

$$\sum_{\mathbf{k}} \rightarrow \frac{V}{(2\pi)^3} \int d^3k. \quad (\text{M.5})$$

We therefore express

$$i G^0(\mathbf{x}t, \mathbf{x}'t') = \frac{1}{(2\pi)^3} \int d^3k \frac{E_k + mc^2}{2E_k} \sum_{\sigma} \Phi_{\mathbf{k},\sigma} \Phi_{\mathbf{k},\sigma}^{\dagger} e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')} e^{-i\omega_{\mathbf{k}}(t-t')} \times [\theta(t-t')\theta(k-k_F) - \theta(t'-t)\theta(k_F-k)]. \quad (\text{M.6})$$

We introduce the following integral representation for the step function

$$\theta(t-t') = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \frac{e^{-i\omega(t-t')}}{\omega + i\eta} \quad \text{and} \quad \theta(t'-t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \frac{e^{-i\omega(t-t')}}{\omega - i\eta} \quad (\text{M.7})$$

with $\eta \rightarrow 0^+$, such that

$$G^0(\mathbf{x}t, \mathbf{x}'t') = \frac{1}{(2\pi)^4} \int d^3k \int_{-\infty}^{\infty} d\omega e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')} e^{-i\omega(t-t')} \times \frac{E_k + mc^2}{2E_k} \sum_{\sigma} \Phi_{\mathbf{k},\sigma} \Phi_{\mathbf{k},\sigma}^{\dagger} \left[\frac{\theta(k-k_F)}{\omega - \omega_k + i\eta} + \frac{\theta(k_F-k)}{\omega - \omega_k - i\eta} \right]. \quad (\text{M.8})$$

which immediately yields

$$G^0(\mathbf{k}, \omega) = \frac{E_k + mc^2}{2E_k} \sum_{\sigma} \Phi_{\mathbf{k},\sigma} \Phi_{\mathbf{k},\sigma}^{\dagger} \left[\frac{\theta(k-k_F)}{\omega - \omega_k + i\eta} + \frac{\theta(k_F-k)}{\omega - \omega_k - i\eta} \right]. \quad (\text{M.9})$$

In the non-relativistic limit, we have

$$\frac{E_k + mc^2}{2E_k} \xrightarrow{c \rightarrow \infty} 1 \quad \text{and} \quad \Phi_{\mathbf{k},\sigma} \xrightarrow{c \rightarrow \infty} \begin{pmatrix} \Phi_{\sigma} \\ 0 \end{pmatrix} \quad (\text{M.10})$$

such that the sum over spin is the sparse matrix

$$\sum_{\sigma} \Phi_{\mathbf{k},\sigma} \Phi_{\mathbf{k},\sigma}^{\dagger} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad (\text{M.11})$$

and the matrix elements of non-relativistic Green's function of the homogeneous electron gas are

$$G_{\alpha,\beta}^{0,\text{NR}}(\mathbf{k}, \omega) = \delta_{\alpha,\beta} \left[\frac{\theta(k-k_F)}{\omega - \omega_k + i\eta} + \frac{\theta(k_F-k)}{\omega - \omega_k - i\eta} \right]. \quad (\text{M.12})$$

We recover correctly the expression published in the book from Fetter and Walecka [1].

Bibliography

- [1] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (Dover, 2003).

Appendix N

Longitudinal no-pair non-interacting linear response function of the RHEG

We construct the non-interacting linear response function of the RHEG in the no-pair approximation, following the logic of the book from Fetter and Walecka [1] (Evaluation of Π^0 , page 158). For the non-interacting RHEG in the no-pair approximation, the linear response-function in momentum space can be calculated using Green's functions (see Appendix.M), such that

$$\begin{aligned}
& \chi^0(\mathbf{q}, q_0) \\
&= \frac{-i}{\hbar(2\pi)^4} \int d\mathbf{k} \int_{-\infty}^{+\infty} d\omega \text{Tr} [G^0(\mathbf{k}, \omega) G^0(\mathbf{k} + \mathbf{q}, \omega + q_0)] \\
&= \frac{1}{\hbar} \int \frac{d\mathbf{k}}{(2\pi)^3} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i} \left[\frac{\theta(k - k_F)}{\omega - \omega_k + i\eta} + \frac{\theta(k_F - k)}{\omega - \omega_k - i\eta} \right] \left[\frac{\theta(|\mathbf{k} + \mathbf{q}| - k_F)}{\omega + q_0 - \omega_{|\mathbf{k} + \mathbf{q}|} + i\eta} + \frac{\theta(k_F - |\mathbf{k} + \mathbf{q}|)}{\omega + q_0 - \omega_{|\mathbf{k} + \mathbf{q}|} - i\eta} \right] \\
&\quad \left\{ \frac{E_k + mc^2}{2E_k} \frac{E_{|\mathbf{k} + \mathbf{q}|} + mc^2}{2E_{|\mathbf{k} + \mathbf{q}|}} \sum_{\sigma, \sigma'} \text{Tr} \left[\Phi_{\mathbf{k}, \sigma} \Phi_{\mathbf{k}, \sigma}^\dagger \Phi_{\mathbf{k} + \mathbf{q}, \sigma} \Phi_{\mathbf{k} + \mathbf{q}, \sigma}^\dagger \right] \right\} \\
&= \frac{1}{\hbar} \int \frac{d\mathbf{k}}{(2\pi)^3} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i} \left[\frac{\theta(k - k_F)}{\omega - \omega_k + i\eta} + \frac{\theta(k_F - k)}{\omega - \omega_k - i\eta} \right] \left[\frac{\theta(|\mathbf{k} + \mathbf{q}| - k_F)}{\omega + q_0 - \omega_{|\mathbf{k} + \mathbf{q}|} + i\eta} + \frac{\theta(k_F - |\mathbf{k} + \mathbf{q}|)}{\omega + q_0 - \omega_{|\mathbf{k} + \mathbf{q}|} - i\eta} \right] \\
&\quad \left\{ \frac{E_k + mc^2}{2E_k} \frac{E_{|\mathbf{k} + \mathbf{q}|} + mc^2}{2E_{|\mathbf{k} + \mathbf{q}|}} \sum_{\sigma, \sigma'} \Phi_{\mathbf{k}, \sigma}^\dagger \Phi_{\mathbf{k} + \mathbf{q}, \sigma} \Phi_{\mathbf{k} + \mathbf{q}, \sigma}^\dagger \Phi_{\mathbf{k}, \sigma} \right\} \\
&= \frac{1}{\hbar} \int \frac{d\mathbf{k}}{(2\pi)^3} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i} \left[\frac{\theta(k - k_F)}{\omega - \omega_k + i\eta} + \frac{\theta(k_F - k)}{\omega - \omega_k - i\eta} \right] \left[\frac{\theta(|\mathbf{k} + \mathbf{q}| - k_F)}{\omega + q_0 - \omega_{|\mathbf{k} + \mathbf{q}|} + i\eta} + \frac{\theta(k_F - |\mathbf{k} + \mathbf{q}|)}{\omega + q_0 - \omega_{|\mathbf{k} + \mathbf{q}|} - i\eta} \right] \\
&\quad \left(1 + \frac{\hbar^2 \mathbf{k} \cdot (\mathbf{k} + \mathbf{q}) c^2 + m^2 c^4}{E_k E_{|\mathbf{k} + \mathbf{q}|}} \right) \tag{N.1}
\end{aligned}$$

where the equation between curly braces has been simplified through the same summation as developed in Appendix I.1. From this, we start by isolating the frequency integral and expand the integrand into

four terms before doing a contour integration

$$\begin{aligned}
& \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i} \left[\frac{\theta(k - k_F)}{\omega - \omega_k + i\eta} + \frac{\theta(k_F - k)}{\omega - \omega_k - i\eta} \right] \left[\frac{\theta(|\mathbf{k} + \mathbf{q}| - k_F)}{\omega + q_0 - \omega_{|\mathbf{k} + \mathbf{q}|} + i\eta} + \frac{\theta(k_F - |\mathbf{k} + \mathbf{q}|)}{\omega + q_0 - \omega_{|\mathbf{k} + \mathbf{q}|} - i\eta} \right] \\
&= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i} \left\{ \frac{\theta(k - k_F)}{\omega - \omega_k + i\eta} \frac{\theta(|\mathbf{k} + \mathbf{q}| - k_F)}{\omega + q_0 - \omega_{|\mathbf{k} + \mathbf{q}|} + i\eta} + \frac{\theta(k_F - k)}{\omega - \omega_k - i\eta} \frac{\theta(k_F - |\mathbf{k} + \mathbf{q}|)}{\omega + q_0 - \omega_{|\mathbf{k} + \mathbf{q}|} - i\eta} \right. \\
&\quad \left. + \frac{\theta(k - k_F)}{\omega - \omega_k + i\eta} \frac{\theta(k_F - |\mathbf{k} + \mathbf{q}|)}{\omega + q_0 - \omega_{|\mathbf{k} + \mathbf{q}|} - i\eta} + \frac{\theta(k_F - k)}{\omega - \omega_k - i\eta} \frac{\theta(|\mathbf{k} + \mathbf{q}| - k_F)}{\omega + q_0 - \omega_{|\mathbf{k} + \mathbf{q}|} + i\eta} \right\} \\
&= -\frac{\theta(k - k_F)\theta(k_F - |\mathbf{k} + \mathbf{q}|)}{q_0 + \omega_k - \omega_{|\mathbf{k} + \mathbf{q}|} - i\eta} + \frac{\theta(k_F - k)\theta(|\mathbf{k} + \mathbf{q}| - k_F)}{q_0 + \omega_k - \omega_{|\mathbf{k} + \mathbf{q}|} + i\eta} \tag{N.2}
\end{aligned}$$

where the first and second terms have vanishing contour integrals due to their poles being all on the same side of the real axis (respectively, all under and all above the real axis), and the third and fourth term yield non-vanishing contributions with residues at $\omega = \omega_k$ when closing the contour, respectively, from under and from above the real axis. After this contour integration we have the no-pair non-interacting linear response-function

$$\begin{aligned}
\chi^0(\mathbf{q}, q_0) &= \frac{1}{\hbar} \int \frac{d\mathbf{k}}{(2\pi)^3} \left(1 + \frac{\hbar^2 \mathbf{k} \cdot (\mathbf{k} + \mathbf{q}) c^2 + m^2 c^4}{E_k E_{|\mathbf{k} + \mathbf{q}|}} \right) \\
&\quad \left[-\frac{\theta(k - k_F)\theta(k_F - |\mathbf{k} + \mathbf{q}|)}{q_0 + \omega_k - \omega_{|\mathbf{k} + \mathbf{q}|} - i\eta} + \frac{\theta(k_F - k)\theta(|\mathbf{k} + \mathbf{q}| - k_F)}{q_0 + \omega_k - \omega_{|\mathbf{k} + \mathbf{q}|} + i\eta} \right] \\
&= \frac{1}{\hbar} \int \frac{d\mathbf{k}}{(2\pi)^3} \left(1 + \frac{\hbar^2 \mathbf{k} \cdot (\mathbf{k} + \mathbf{q}) c^2 + m^2 c^4}{E_k E_{|\mathbf{k} + \mathbf{q}|}} \right) \theta(|\mathbf{k} + \mathbf{q}| - k_F) \theta(k_F - k) \\
&\quad \left[\frac{-1}{q_0 + \omega_{|\mathbf{k} + \mathbf{q}|} - \omega_k - i\eta} + \frac{1}{q_0 + \omega_k - \omega_{|\mathbf{k} + \mathbf{q}|} + i\eta} \right] \tag{N.3}
\end{aligned}$$

where we used the change of variable $\mathbf{k}' = -(\mathbf{k} + \mathbf{q})$ in the first term and then, due to the infinite integration space, removed the superfluous prime. We use the identity of the step function $\theta(|\mathbf{k} + \mathbf{q}| - k_F) = 1 - \theta(k_F - |\mathbf{k} + \mathbf{q}|)$ and consider an analytical continuation to an imaginary frequency $q_0 = i u$ with $u > 0$ such that, as $\eta \rightarrow 0^+$ we can now neglect η in front of u and evaluate the linear no-pair non-interacting linear response-function as

$$\begin{aligned}
\chi^0(\mathbf{q}, i u) &= \frac{1}{\hbar} \int \frac{d\mathbf{k}}{(2\pi)^3} \left(1 + \frac{\hbar^2 \mathbf{k} \cdot (\mathbf{k} + \mathbf{q}) c^2 + m^2 c^4}{E_k E_{|\mathbf{k} + \mathbf{q}|}} \right) (1 - \theta(k_F - |\mathbf{k} + \mathbf{q}|)) \theta(k_F - k) \\
&\quad \left[\frac{-1}{i u + \omega_{|\mathbf{k} + \mathbf{q}|} - \omega_k} + \frac{1}{i u + \omega_k - \omega_{|\mathbf{k} + \mathbf{q}|}} \right] \\
&= \frac{1}{\hbar} \int \frac{d\mathbf{k}}{(2\pi)^3} \left(1 + \frac{\hbar^2 \mathbf{k} \cdot (\mathbf{k} + \mathbf{q}) c^2 + m^2 c^4}{E_k E_{|\mathbf{k} + \mathbf{q}|}} \right) (1 - \theta(k_F - |\mathbf{k} + \mathbf{q}|)) \theta(k_F - k) \\
&\quad 2 \frac{\omega_{|\mathbf{k} + \mathbf{q}|} - \omega_k}{(i u)^2 - (\omega_{|\mathbf{k} + \mathbf{q}|} - \omega_k)^2}. \tag{N.4}
\end{aligned}$$

As both the coefficient coming from the sum over states and the product of the two step functions are even under an interchange $\mathbf{k} \rightleftharpoons \mathbf{k} + \mathbf{q}$ while $\omega_{|\mathbf{k} + \mathbf{q}|} - \omega_k$ is obviously odd, the integral of the term featuring two step functions vanishes leaving only

$$\chi^0(\mathbf{q}, i u) = \frac{-1}{\hbar} \int \frac{d\mathbf{k}}{(2\pi)^3} \left(1 + \frac{\hbar^2 \mathbf{k} \cdot (\mathbf{k} + \mathbf{q}) c^2 + m^2 c^4}{E_k E_{|\mathbf{k} + \mathbf{q}|}} \right) \theta(k_F - k) 2 \frac{\omega_{|\mathbf{k} + \mathbf{q}|} - \omega_k}{u^2 + (\omega_{|\mathbf{k} + \mathbf{q}|} - \omega_k)^2}. \tag{N.5}$$

As the pulsation and energies are related through $E_k = \hbar\omega_k$, we have

$$\chi^0(\mathbf{q}, i u) = - \int \frac{d\mathbf{k}}{(2\pi)^3} \theta(k_F - k) 2 \left(1 + \frac{\hbar^2 \mathbf{k} \cdot (\mathbf{k} + \mathbf{q}) c^2 + m^2 c^4}{E_k E_{|\mathbf{k} + \mathbf{q}|}} \right) \frac{E_{|\mathbf{k} + \mathbf{q}|} - E_k}{\hbar^2 u^2 + (E_{|\mathbf{k} + \mathbf{q}|} - E_k)^2}, \quad (\text{N.6})$$

which, using

$$\begin{aligned} & 2E_k E_{|\mathbf{k} + \mathbf{q}|} + 2\hbar^2 \mathbf{k} \cdot (\mathbf{k} + \mathbf{q}) c^2 + 2m^2 c^4 \\ &= (\hbar^2 k^2 c^2 + m^2 c^4) + 2E_k E_{|\mathbf{k} + \mathbf{q}|} + (\hbar^2 k^2 c^2 + 2\hbar^2 \mathbf{k} \cdot \mathbf{q} c^2 + \hbar^2 q^2 c^2 + m^2 c^4) - \hbar^2 q^2 c^2 \\ &= (E_k + E_{|\mathbf{k} + \mathbf{q}|})^2 - \hbar^2 q^2 c^2 \end{aligned} \quad (\text{N.7})$$

can be rewritten as

$$\chi^0(\mathbf{q}, i u) = - \int \frac{d\mathbf{k}}{(2\pi)^3} \theta(k_F - k) \frac{\left[(E_k + E_{|\mathbf{k} + \mathbf{q}|})^2 - \hbar^2 q^2 c^2 \right] (E_{|\mathbf{k} + \mathbf{q}|} - E_k)}{E_k E_{|\mathbf{k} + \mathbf{q}|} \left[\hbar^2 u^2 + (E_{|\mathbf{k} + \mathbf{q}|} - E_k)^2 \right]}. \quad (\text{N.8})$$

This expression is equal, up to a trivial sign convention choice, to the first term of the longitudinal non-interacting linear response function of the RHEG $Q_{00}(\mathbf{q}, \omega)$ as written by M. V. Ramana and A. K. Rajagopal [2]. The expression determined in their work is not within the frame of the no-pair approximation, and their first term is thus counterbalanced by a second one due to the renormalization process. The longitudinal no-pair non-interacting linear-response function of the RHEG $\chi_{0,\text{np}}^{00}(q)$ as written by A. Facco Bonetti et al. [3] has been analytically integrated for real frequencies within the general framework of the QED full photon propagator and, to the best of our knowledge, the expression published in this article is not straightforwardly extended to imaginary frequencies. The longitudinal no-pair non-interacting linear response-function of the RHEG for imaginary frequencies of Eq N.8 is thus most easily evaluated through numerical integration. To simplify the numerical integration, we express wave vectors in units of k_F through the change of variables $\mathbf{k} = \mathbf{k}' k_F$ and $\mathbf{q} = \mathbf{q}' k_F$, such that

$$\begin{aligned} & \chi^0(\mathbf{q}, i u) \\ &= - \int \frac{d\mathbf{k}' k_F^3}{(2\pi)^3} \theta(k_F - k' k_F) \frac{\left(\sqrt{\hbar^2 k'^2 k_F^2 c^2 + m^2 c^4} + \sqrt{\hbar^2 |\mathbf{k}' + \mathbf{q}'|^2 k_F^2 c^2 + m^2 c^4} \right)^2 - \hbar^2 q'^2 k_F^2 c^2}{\sqrt{\hbar^2 k'^2 k_F^2 c^2 + m^2 c^4} \sqrt{\hbar^2 |\mathbf{k}' + \mathbf{q}'|^2 k_F^2 c^2 + m^2 c^4}} \\ & \quad \frac{\sqrt{\hbar^2 |\mathbf{k}' + \mathbf{q}'|^2 k_F^2 c^2 + m^2 c^4} - \sqrt{\hbar^2 k'^2 k_F^2 c^2 + m^2 c^4}}{\hbar^2 u^2 + \left(\sqrt{\hbar^2 |\mathbf{k}' + \mathbf{q}'|^2 k_F^2 c^2 + m^2 c^4} - \sqrt{\hbar^2 k'^2 k_F^2 c^2 + m^2 c^4} \right)^2} \\ &= - \int \frac{d\mathbf{k}' k_F^3}{(2\pi)^3} \theta(1 - k') \frac{\left(\sqrt{k'^2 + \tilde{c}^2} + \sqrt{|\mathbf{k}' + \mathbf{q}'|^2 + \tilde{c}^2} \right)^2 - q'^2}{\sqrt{k'^2 + \tilde{c}^2} \sqrt{|\mathbf{k}' + \mathbf{q}'|^2 + \tilde{c}^2}} \\ & \quad \frac{\hbar k_F c \left(\sqrt{|\mathbf{k}' + \mathbf{q}'|^2 + \tilde{c}^2} - \sqrt{k'^2 + \tilde{c}^2} \right)}{\hbar^2 u^2 + \hbar^2 k_F^2 c^2 \left(\sqrt{|\mathbf{k}' + \mathbf{q}'|^2 + \tilde{c}^2} - \sqrt{k'^2 + \tilde{c}^2} \right)^2} \\ &= - \frac{m k_F}{\hbar^2} \int \frac{d\mathbf{k}'}{(2\pi)^3} \theta(1 - k') \frac{\left(\sqrt{k'^2 + \tilde{c}^2} + \sqrt{|\mathbf{k}' + \mathbf{q}'|^2 + \tilde{c}^2} \right)^2 - q'^2}{\sqrt{k'^2 + \tilde{c}^2} \sqrt{|\mathbf{k}' + \mathbf{q}'|^2 + \tilde{c}^2}} \\ & \quad \frac{\tilde{c} \left(\sqrt{|\mathbf{k}' + \mathbf{q}'|^2 + \tilde{c}^2} - \sqrt{k'^2 + \tilde{c}^2} \right)}{v^2 + \tilde{c}^2 \left(\sqrt{|\mathbf{k}' + \mathbf{q}'|^2 + \tilde{c}^2} - \sqrt{k'^2 + \tilde{c}^2} \right)^2}, \end{aligned} \quad (\text{N.9})$$

where we have introduced the dimensionless variables

$$\tilde{c} = \frac{mc}{\hbar k_F} \quad \text{and} \quad v = \hbar u \frac{m}{\hbar^2 k_F^2}, \quad (\text{N.10})$$

and kept the primed quantities for clarity in order to avoid any confusion between the dimensional variable \mathbf{q} and the adimensional one \mathbf{q}' . In the non-relativistic limit, the non-interacting linear response function of the HEG reduces to

$$\begin{aligned} \chi^{0,\text{NR}}(q, i u) &= -\frac{m k_F}{\hbar^2} \int \frac{d\mathbf{k}'}{(2\pi)^3} \theta(1-k') 2 \frac{2\mathbf{q}' \cdot (\frac{1}{2}\mathbf{q}' + \mathbf{k}')}{(\mathbf{q}' \cdot (\frac{1}{2}\mathbf{q}' + \mathbf{k}'))^2 + v^2} \\ &= -\frac{m k_F}{2\hbar^2 \pi^2} \left(1 + \frac{1}{2q'} \left(\left(\frac{q'}{2} \right)^2 - 1 - \left(\frac{v}{q'} \right)^2 \right) \log \left(\frac{\left(1 - \frac{q'}{2} \right)^2 + \left(\frac{v}{q'} \right)^2}{\left(1 + \frac{q'}{2} \right)^2 + \left(\frac{v}{q'} \right)^2} \right) \right. \\ &\quad \left. - \frac{v}{q'} \arctan \left(\frac{q'}{v} \left(1 - \frac{q'}{2} \right) \right) - \frac{v}{q'} \arctan \left(\frac{q'}{v} \left(1 + \frac{q'}{2} \right) \right) \right), \quad (\text{N.11}) \end{aligned}$$

which is the Lindhard function at imaginary frequency [4], written here using the dimensionless variables defined previously.

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