



Quantum computational methodologies for the study of molecular crystals

Davide Presti

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Quantum computational methodologies for the study of molecular crystals

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Notice

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Introduction

In the last decades, the development of increasingly powerful technologies for computation allowed a broad range of chemical applications to be investigated, and even predicted, through the use of methods spanning different scales of space and time.

A particular field of research, that in the last years enormously grew, spreading throughout a great number of disciplines such as pharmaceuticals, optoelectronics, dye chemistry, etc... is the computational investigation of molecular crystalline compounds – some of these, organic and inorganic molecular crystals, are the subject of the present work of thesis. Since *crystal engineering* is becoming important for the design of new materials, a detailed theoretical understanding of polymorphism and related effects at the atomistic level is of primary concern.

The study of *polymorphism* – strictly related to the behaviour of solid crystalline materials – plays a leading role for a successful production, for example, of *active pharmaceutical ingredients* (API) for efficient health therapies.

It is well-known, in fact, that polymorphism affects key properties such as solubility, morphology and thermal stability [1, 2]. Authoritative works and reviews were published in recent years on theory, protocols and methods for modelling and predicting polymorphic forms of APIs [3–7] and, more in general, of molecular crystals [3, 8–11].

Though the structure of molecular compounds can, usually, be predicted with confidence, crystals still represent an ambitious frontier: more than twenty years ago, the unpredictability of crystal structures was even defined “a scandal in physical sciences” [12].

In the last years, notable advancements in computational chemistry methods gave rise to the *Crystal Structure Prediction* (CSP) [3]. This consists of an energy-landscape approach devised to find all possible polymorphs of a given molecule – which is particularly important for organic molecular crystals, due to the variety of factors which determine their stability (e.g. numerous long-range interactions are usually present). The CSP adopts molecular mechanics (MM) and force fields to rank the lattice energies of all possible structures generated from the input molecule through some *screening* method (such as random sampling). To find the most probable polymorph structures, however, lattice energies of the most stable structures are successively computed at higher level (quantum mechanics, QM) – usually, Density Functional Theory (DFT). CSP proved to be reliable for crystals containing small organic molecules – as testified by the ‘blind-tests’ that took place recently [13, 14]. Lacks of CSP on particular systems [15] have recently been solved by the use of dispersion-corrected DFT.

Nevertheless, the study of relevant properties depending primarily by the electronic structure needs a full QM treatment, sometimes also in the case of simple but challenging systems – as the benzene crystal [16, 17].

The aim of this work of thesis is to unravel the relationship between physico-chemical and structural properties of molecular crystals with known structure, by means of quantum chemistry methods. The results show that here is shown that, even though structures and properties are experimentally known, theoretical calculations are needed to develop accurate prediction protocols [18] and to investigate structures and phenomena that cannot be explained satisfactorily by experiment [19].

Molecular crystals are built over an infinite molecular framework which is governed by noncovalent *intermolecular* interactions: dispersive forces (ubiquitous and always present) and, in case, by intermolecular hydrogen or halogen bonds. Notwithstanding such interactions are weaker than the *intramolecular* ones, they are fundamental in determining all the properties of the crystal.

The thesis contents are divided into two major parts (‘Theoretical Background’ and ‘Applications’) outlined as follows:

The long story of QM methods is summarized in Chapters 1 and 2. **Chapter 1** deals with atomistic theories such as the Hartree-Fock theory, that brought computational chemistry from a pioneering idea to reality. This led to post-HF techniques (briefly discussed in **Chapter 1**) and Density Functional Theory (discussed in **Chapter 2**). The latter methods still represent the apex of quantum theories, for different reasons: while the first ones are computationally more expensive, they yield to a quite complete description of the complex physics underlying atomic interactions – especially because of the natural inclusion of electron correlation.

On the contrary, the success of DFT is due to its applicability to large systems, being computationally less expensive – though also less accurate – with respect to post-HF methods, and the possibility of determine all the (ground-state) properties from the ground-state density.

The true electron correlation is not described by DFT, as standard density functionals are not able to catch dispersive interactions. The inclusion of such effects into DFT is then necessary – so that different correction schemes (described in **Chapter 2**) were devised in the last decade (see, for example, [20–23]). Many of these schemes are almost inexpensive, and they can seamlessly be associated – besides molecules – with a full periodic description (PBC, periodic boundary conditions) of crystalline solids (calculations in PBC are revised in **Chapter 3**).

The extension of such methods to the time-dependent (TD) formalism (e.g., see TD-DFT in **Chapter 4**) yielded to the study of dynamic phenomena that span from kinetic reactions to charge transfer and, notably, to determine optical properties and the related simulation of many diverse spectroscopy techniques [24, 25].

Finally, the combination between QM and MM or semiempirical methods lead to achieve a large, even quite accurate, sight of complex phenomena that take place in manifold, extended systems (e.g. biological macromolecules). This can be done by combining two different methods in the same calculation – as in the case of ONIOM [26] (see **Chapter 5**), where different parts of the system are treated at different levels of accuracy.

Though the present project of thesis was initially focused on the study of structure and energetics of molecular crystals that find applications in pharmaceuticals/pharmaceutical processes – e.g. para-diiodobenzene [27] – we decided to generalize our investigations to different kinds of molecular crystals and to go beyond the prediction of basic electronic properties, as energetics could be.

This was done in a methodological way, in the sense that we got insights on properties by exploring different methods (though always using DFT) at the same time, to determine:

(i) structure, polymorphism and stability – adopting various combinations of density functionals and different dispersion-correction schemes – on the molecular crystals of para-diiodobenzene and oxalyl dihydrazide [27, 28]. This aimed not only at describing the target properties, but also to assess the performance of a variety of available computational methods (these are discussed in **Chapter 6**);

(ii) the structures and the solid-state $^{13}\text{C}/^1\text{H}$ NMR parameters – of the four crystal forms of a challenging Ru(II)-complex solid system, that works as host-guest compound – discussed in **Chapter 7**. The inclusion of water molecules within the crystal makes it an hygroscopic material. This leads such class of compounds to have diverse applications: catalysis, “green” chemistry and gas storage [29, 30]. Moreover, one potential application, that can be thought by substituting the guest water molecules, is *drug release*.

(iii) structures (DFT) and optical properties (TD-DFT) of cutting-edge technological materials: thermochromic and photochromic molecular crystals. These families of compounds undergo to a structural and color transformation when irradiated with heat or light, respectively. They are largely used for their versatile applicability as sensors, displays and storage devices [31, 32]. In particular, in **Chapter 8** we focused on the UV-Visible spectroscopic properties of the thermochromic polymorph of salicylidene aniline. We set up a protocol – based both on periodic and cluster calculations – that can help to study such properties in the solid-state within a QM/QM’ fashion, enhanced by the introduction of electronic charge embedding effects.

In **Appendix A** the computational details for points i) and iii) are reported, whereas for point ii) are discussed within the text.

Finally, we mention that the implementation of some recent schemes for dispersion-correction in the CRYSTAL suite of programs [33, 34] was also part of the present project. However, since still ongoing, this is not commented here.

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Theoretical background

*Theory, sooner or later,
is killed by experience.*

Albert Einstein

– Part I –

**Quantum theories for
ground-state chemistry**

Chapter 1

Wave function theory

*We are perhaps not far removed
from the time when
we shall be able to submit
the bulk of chemical phenomena to calculation.*

Joseph Louis Gay-Lussac – 1809

Dealing with the electronic properties of a N -body system is a complex problem that needs to be solved in terms of quantum mechanics. Though the basic tools which are necessary to describe real systems at the atomic scale are available since the early 20th century, when the “standard” Hamiltonian formulation of quantum mechanics was complete, we still have to deal with intrinsic, natural issues.

Briefly, even when theories furnish analytical solutions, these usually need to be *approximated* or truncated, to deal with the essentially finite size of computational resources. In general, due to different kinds of approximations, nontrivial issues arise even for the most physically consistent and elegant theories.

Anyway, the outstanding progresses in computational and theoretical chemistry are nowadays allowing researchers to reach a great accuracy in modeling and predicting almost every aspect of experimental observations.

1.1 The Hartree-Fock Method

The first, simplest approximation a quantum chemist would think about to solve the (time-independent) N -electron problem is the Hartree-Fock (HF) method.

It is aimed at finding a solution for the Schrödinger equation:

$$\hat{H}_e \Psi = E \Psi \quad (1.1.1)$$

of the ground-state N -electron problem expressed, in the Born-Oppenheimer non-relativistic approximation, by the quantum Hamiltonian operator:

$$\begin{aligned} \hat{H}_e &= \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nuclep} \\ &= - \sum_{i=1}^N \frac{\nabla_i^2}{2} - \sum_{i=1}^N \sum_A^I \frac{Z_A}{\mathbf{r}_{iA}} + \frac{1}{2} \sum_{i \neq j}^N \frac{1}{r_{ij}} + \frac{1}{2} \sum_{A \neq B}^I \frac{Z_A Z_B}{R_{AB}} \\ &= \sum_{i=1}^N \hat{h}_i + \frac{1}{2} \sum_{i \neq j}^N \frac{1}{r_{ij}} + \text{const.} \end{aligned} \quad (1.1.2)$$

that is mathematically defined in a N -dimensional Hilbert space, $\mathcal{H}$.

$\hat{h}_i$ is the core Hamiltonian which includes all the monoelectronic terms (kinetic energy operator and electron-nuclear potential operator), and $\frac{1}{2} \sum_{i \neq j}^N \frac{1}{r_{ij}}$ is the bi-electronic Coulomb operator.

$\hat{V}_{en}$ can be defined as:

$$\hat{V}_{en} = \sum_{i=1}^N v(\mathbf{r}_i) \quad \text{with} \quad v(\mathbf{r}_i) = - \sum_A^I \frac{Z_A}{\mathbf{r}_{iA}} \quad (1.1.3)$$

where $v(\mathbf{r})$ is the *external potential* for a given i -th electron.

Since it is constant for a fixed nuclei configuration, the nucleus-nucleus repulsion term is included in $\hat{H}_e$.

When taking into account for nuclear motion, the total Hamiltonian can be subsequently defined as:

$$\hat{H}_{tot} \Psi_{tot} = (\hat{T}_N + \hat{H}_e) \Psi_{tot} = E_{tot} \Psi_{tot} \quad (1.1.4)$$

given $\hat{T}_N$ as the kinetic energy term for nuclei. Within the Born-Oppenheimer approximation, the total wave function can be written in the following way:

$$\Psi_{tot}(\mathbf{r}_i; \mathbf{R}_I) = \Psi(\mathbf{r}_i; \mathbf{R}_I) \Psi_{nuc}(\mathbf{R}_I) \quad (1.1.5)$$

Notice that the electronic part (Ψ) depends explicitly on the electron coordinates ($\mathbf{r}_I$) and only *parametrically* on the nuclear coordinates ($\mathbf{R}_I$). Analogue expressions for the Hamiltonian operator and the total energy can be derived straightforwardly. The solutions of eq. 1.1.1 can be thought as a product of monoelectronic functions, called *spin-orbitals* (SOs), having the form:

$$\chi(\mathbf{x}) = \chi(\mathbf{r}; \omega) = \psi(\mathbf{r})\sigma(\omega) \quad (1.1.6)$$

where $\mathbf{r}$ is the position vector and ω is the spin variable. A set of N indexes, which refer to N spin-orbitals taken from an orthonormal and complete set (ONC), is chosen – they are labeled with $\mathbf{t}$ ($t_1, t_2, \dots, t_N$) – and a N -electron function $\Pi_{\mathbf{t}}$ is defined as the product of the corresponding SOs:

$$|\Pi_{\mathbf{t}}\rangle = \Pi_{\mathbf{t}}(\mathbf{x}_1 \cdots \mathbf{x}_N) = \chi_{t_1}(\mathbf{x}_1) \cdots \chi_{t_N}(\mathbf{x}_N) \quad (1.1.7)$$

The product obtained above is called *Hartree-Product*. A function of this form would describe a system of boson particles, but in the case of electrons (fermions) the wave function is antisymmetric, that is when the coordinates of two particles are exchanged the sign of the wave function must change, i.e.:

$$\chi_{t_1}(\mathbf{x}_1) \cdots \chi_{t_k}(\mathbf{x}_k) \chi_{t_l}(\mathbf{x}_l) \cdots \chi_{t_N}(\mathbf{x}_N) = -\chi_{t_1}(\mathbf{x}_1) \cdots \chi_{t_k}(\mathbf{x}_l) \chi_{t_l}(\mathbf{x}_k) \cdots \chi_{t_N}(\mathbf{x}_N) \quad (1.1.8)$$

The simplest way to antisymmetrize the Hartree-Product is to rewrite it as a determinant $|T\rangle$:

$$|T\rangle = \frac{1}{\sqrt{N!}} \begin{bmatrix} \chi_{t_1}(\mathbf{x}_1) & \chi_{t_1}(\mathbf{x}_2) & \cdots & \chi_{t_1}(\mathbf{x}_N) \\ \chi_{t_2}(\mathbf{x}_1) & \chi_{t_2}(\mathbf{x}_2) & \cdots & \chi_{t_2}(\mathbf{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_{t_N}(\mathbf{x}_1) & \chi_{t_N}(\mathbf{x}_2) & \cdots & \chi_{t_N}(\mathbf{x}_N) \end{bmatrix} \quad (1.1.9)$$

Such determinant, called Slater determinant or *detor*, forms an ONC set built from N -electronic antisymmetric functions, and it represents a prototypical ensemble of solutions for equation 1.1.1.

In general, it is possible to expand the ground-state wave function Ψ_0 as:

$$|\Psi_0\rangle = \sum_T c_T |T\rangle \quad (1.1.10)$$

i.e. as a linear combination of Slater determinants. According to eq. 1.1.10, the Hartree-Fock method approximates the expansion of the wave function with a single determinant.

Therefore, it aims at finding the best monodeterminantal approximation to the N -electronic wave function, the so-called Hartree-Fock solution $|\Psi^{HF}\rangle$. This is possible thanks to the application of the *Variational Principle*, which states that every approximation to the exact ground-state wave function has an expectation value larger or, at best, equal to the energy of the exact ground-state ($\hat{H}_e$ will be indicated simply as $\hat{H}$ from now on):

$$\tilde{E} = \langle \Psi^{HF} | \hat{H} | \Psi^{HF} \rangle \longrightarrow \tilde{E} \geq \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E_0 \quad (1.1.11)$$

This principle gives a reliable and unambiguous way to search the best approximation to the wave function by searching the minimum of the energy $\tilde{E}$.

1.1.1 The Hartree-Fock equations

We define N spin-orbitals $(\cdots \chi_i(\mathbf{x}) \cdots)$, each one orthonormal to the others. These give rise to the detor $|K\rangle$ that minimizes $\tilde{E}$. Given the expression 1.1.2 for the Hamiltonian, and the Slater-Condon rules (see, e.g. [1, 2]), we can write:

$$\tilde{E} = E^{HF} = \langle K | \hat{H} | K \rangle = \langle \Psi^{HF} | \hat{H} | \Psi^{HF} \rangle = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle \quad (1.1.12)$$

where i and j are spin-orbitals, the first right term is the core part integral and the second right term is a compact notation for the integrals of the electron part (bielectronic coulomb and exchange integrals):

$$\begin{aligned} \langle ij || ij \rangle &= \langle ij | ij \rangle - \langle ij | ji \rangle = \\ &= \int d\mathbf{x} d\mathbf{x}' \chi_i^*(\mathbf{x}) \chi_j^*(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \chi_i(\mathbf{x}) \chi_j(\mathbf{x}') + \\ &- \int d\mathbf{x} d\mathbf{x}' \chi_i^*(\mathbf{x}) \chi_j^*(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \chi_j(\mathbf{x}) \chi_i(\mathbf{x}') \end{aligned} \quad (1.1.13)$$

The detor $|K\rangle$ is labeled $|\Psi^{HF}\rangle$ and the corresponding energy value ($\tilde{E}$) Hartree-Fock energy E^{HF} . It can be demonstrated, by minimizing expression 1.1.12 (see next section) and by imposing orthogonality to the spin-orbitals, that the SOs are

obtained from the solution of the following coupled system of one-electron integral-differential equations, the **Hartree-Fock equations**:

$$\hat{f}|\chi_i\rangle = (\hat{h} + \hat{B})|\chi_i\rangle \equiv \left[\hat{h} + \sum_j (\bullet j || \bullet j) \right] |\chi_i\rangle = \varepsilon_i |\chi_i\rangle \quad (1.1.14)$$

The one-electron operator $\hat{f}$ is named *Fock operator*; it is made up by a core part $\hat{h}$ and by an electronic part $\hat{B}$ which describes the average interaction between the electron of the selected SOs and all the others. The symbol $(\bullet j || \bullet j)$ represents a hermitian operator $\hat{B}_j$ acting in the following way (a and b being two SOs):

$$\langle a | \hat{B}_j | b \rangle = \langle a | (\bullet j || \bullet j) | b \rangle = \langle a j || b j \rangle \quad (1.1.15)$$

We showed an important result, since the solution of an N-electronic problem is reduced to a set of N coupled one-electron differential equations, by solving the problem for each electron interacting with the resulting charge distribution (say electrostatic potential) of the whole system.

Solving such equations corresponds to apply a Self Consistent Field (SCF) procedure (see Figure 1.1): the SOs obtained as solution determine a new potential which is used to calculate a new operator $\hat{B}$, and the new set of differential equations 1.1.14 is used to determine a new and better set of SOs. The SCF procedure must be reiterated until certain tolerances are satisfied (mainly, on the energy difference between the last cycle and the previous one). Such procedure needs an initial guess for the wave function, in order to calculate the $\hat{B}$ operator for the first cycle.

1.1.2 How to derive the HF equations

The minimum of $\tilde{E}$, with the $N(N+1)/2$ orthonormality constraints $\langle \chi_i | \chi_j \rangle \equiv \langle i | j \rangle = \delta_{ij}$, is obtained by minimizing with respect to χ_i , *without constraints*, the following expression:

$$\mathcal{L}[\dots, \chi_i, \dots] = \tilde{E}[\dots, \chi_i, \dots] - \sum_{i \geq j} \epsilon_{ij} \langle i | j \rangle \quad (1.1.16)$$

where ϵ_{ij} are the $N(N+1)/2$ Lagrangian multipliers. We can take into account that the detor $|\Psi^{HF}\rangle$ can be determined for a unitary transformation that involves N spin-orbitals: such a transformation multiplies the detor for a phase factor. Since the corresponding unitary matrix is defined by $N(N-1)/2$ constants (that

represent the rotations for every i, j pair), an arbitrary condition – which makes the $N(N - 1)/2$ off-diagonal Lagrangian multipliers equal to zero – can be imposed.

The problem is then reduced to search the minimum for:

$$\mathcal{L}'[..., \chi_i, ...] = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | | ij \rangle - \sum_i \epsilon_i \langle i | i \rangle \quad (1.1.17)$$

By differentiating the expression above with respect to χ_i , neglecting $\delta\chi_i$ terms beyond the second-order and imposing the minimum condition, one obtains:

$$\begin{aligned} \delta\mathcal{L}' &\equiv \mathcal{L}'[..., \chi_i + \delta\chi_i, ..., \chi_j + \delta\chi_j, ...] - \mathcal{L}'[..., \chi_i, ..., \chi_j, ...] = \\ &\sum_i \langle \delta i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} (\langle \delta ij | | ij \rangle + \langle i \delta j | | ij \rangle) - \sum_i \epsilon_i \langle \delta i | i \rangle + \text{complex conj.} = \\ &\sum_i \langle \delta i | \left(\left[\hat{h} + \sum_j (\bullet j | | \bullet j) - \epsilon_i \right] | i \rangle \right) + \text{complex conj.} = 0 \end{aligned} \quad (1.1.18)$$

Since $\delta\mathcal{L}'$ must be zero for every variation of each χ_i , it follows that the term included within the big round parentheses must be null. Eq. 1.1.14 are then obtained. The resulting SOs are called *canonical HF spin-orbitals*, whereas the ϵ_i are labeled *energy levels* of the corresponding SOs.

It has to be noted that the sum of the energy eigenvalues, i.e. the sum of energy levels **is not** equal to the Hartree-Fock energy (*vide infra*, Section 1.1.9).

1.1.3 Spinless HF equations

To better highlight how the $\hat{B}$ operator acts, let us consider:

$$\begin{aligned} \hat{B}\xi(\mathbf{x}) &= \sum_j (\bullet j | | \bullet j) |\xi\rangle = \\ &= \int d\mathbf{x}' \sum_j \frac{|\chi_j(\mathbf{x}')|^2}{|\mathbf{r} - \mathbf{r}'|} \xi(\mathbf{x}) - \int d\mathbf{x}' \sum_j \frac{\chi_j^*(\mathbf{x}') \xi(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \chi_j(\mathbf{x}) \end{aligned} \quad (1.1.19)$$

where the sum over j runs over every SOs of the detor (occupied SOs). When $\xi = \chi_j$ the two integrals cancel each other out: this fact ensures that an electron does not interact with itself. Since the spin-orbitals (according to eq. 1.1.14) are the eigenfunctions of the hermitian Fock operator $\hat{f}$, they must be orthogonal; and we will consider them also normalized.

According to the definition provided in equation 1.1.6 it is possible to express each SO as the product of an orbital part times a spin part. There will be $N^\alpha + N^\beta = N$ electrons in the system. In a *closed-shell* system $N^\alpha = N^\beta = N/2$.

Let us consider a spin-orbital $\chi_i(\mathbf{x}) = \psi_i^\alpha(\mathbf{r})\alpha(\omega)$. Given equation 1.1.14, it follows:

$$(\hat{h} + \hat{B})[\psi_i^\alpha(\mathbf{r})\alpha(\omega)] = \varepsilon_i^\alpha[\psi_i^\alpha(\mathbf{r})\alpha(\omega)] \quad (1.1.20)$$

where:

$$\begin{aligned} \hat{B}[\psi_i^\alpha(\mathbf{r})\alpha(\omega)] = & \int d\mathbf{r}' d\omega' \left[\sum_j^{N^\alpha} \frac{[\psi_j^\alpha(\mathbf{r}')\alpha(\omega')]^* \psi_j^\alpha(\mathbf{r}')\alpha(\omega')}{|\mathbf{r} - \mathbf{r}'|} + \right. \\ & \left. + \sum_j^{N^\beta} \frac{[\psi_j^\beta(\mathbf{r}')\beta(\omega')]^* \psi_j^\beta(\mathbf{r}')\beta(\omega')}{|\mathbf{r} - \mathbf{r}'|} \right] [\psi_i^\alpha(\mathbf{r})\alpha(\omega)] + \\ & - \int d\mathbf{r}' d\omega' \sum_j^{N^\alpha} \frac{[\psi_j^\alpha(\mathbf{r}')\alpha(\omega')]^* \psi_i^\alpha(\mathbf{r}')\alpha(\omega')}{|\mathbf{r} - \mathbf{r}'|} [\psi_j^\alpha(\mathbf{r})\alpha(\omega)] + \\ & - \int d\mathbf{r}' d\omega' \sum_j^{N^\beta} \frac{[\psi_j^\beta(\mathbf{r}')\beta(\omega')]^* \psi_i^\alpha(\mathbf{r}')\alpha(\omega')}{|\mathbf{r} - \mathbf{r}'|} [\psi_j^\beta(\mathbf{r})\beta(\omega)] \end{aligned} \quad (1.1.21)$$

The integration over the spin coordinate ω' gives 0 for the last integral while it gives 1 for the previous three. By eliminating also $\alpha(\omega)$ from both sides of equation 1.1.20 one gets the *Hartree-Fock spinless equations*:

$$\hat{f}^\sigma \psi_i^\sigma = \varepsilon_i^\sigma \psi_i^\sigma \quad \text{with} \quad \sigma = \alpha \text{ or } \beta \quad \text{and} \quad \hat{f}^\sigma = \hat{h} + \hat{J} - \hat{K}^\sigma \quad (1.1.22)$$

where:

$$\begin{aligned} \hat{h} &= \hat{T}_e + \hat{V}_{en} \\ \hat{J}(\mathbf{r})\psi(\mathbf{r}) &= \left[\int d\mathbf{r}' \frac{\sum_j^{N^\alpha} |\psi_j^\alpha(\mathbf{r}')|^2 + \sum_j^{N^\beta} |\psi_j^\beta(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \right] \psi(\mathbf{r}) \\ \hat{K}^\sigma(\mathbf{r})\psi(\mathbf{r}) &= \sum_j^{N^\sigma} \left[\left(\int d\mathbf{r}' \frac{\psi_j^{\sigma*}(\mathbf{r}')\psi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right) \psi_j^\sigma(\mathbf{r}) \right] \end{aligned} \quad (1.1.23)$$

with $\hat{J}(\mathbf{r})$ and $\hat{K}^\sigma(\mathbf{r})$ that correspond to the spinless *Coulomb operator* and the spinless *Fermi operator*, respectively.

1.1.4 Coulomb operator

The Coulomb operator $\hat{J}(\mathbf{r})$, which is the first term of eq. 1.1.19 :

$$\hat{J}(\mathbf{r})\xi(\mathbf{r}) = \int d\mathbf{r}' \sum_j \frac{|\chi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \xi(\mathbf{r}) \quad (1.1.24)$$

represents the potential that an electron at position $\mathbf{r}$ experiences due to the average charge distribution of another electron in a spin orbital χ_j , being $|\chi_j(\mathbf{r}')|^2$ the probability that the latter is within the volume element $d\mathbf{r}'$.

Thus, the Coulomb repulsion for a particular distance between the reference electron at $\mathbf{r}$ and another one at position $\mathbf{r}'$ is weighted by the probability that the second one is located in that portion of space. Since the result of the application of $\hat{J}(\mathbf{r})$ on $\xi(\mathbf{r})$ depends by the value of ξ *only* at position $\mathbf{r}$, this operator and the corresponding potential are called *local*.

1.1.5 Fermi or Exchange operator

The second term in eq. 1.1.19 is the Fermi (exchange) contribution to the HF potential. The exchange operator $\hat{K}(\mathbf{r})$ has no classical interpretation and it can only be defined through its effect when operating on a spin-orbital:

$$\hat{K}(\mathbf{r})\xi(\mathbf{r}) = \int d\mathbf{r}' \sum_j \frac{\chi_j^*(\mathbf{r}')\xi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \chi_j(\mathbf{r}) \quad (1.1.25)$$

As evident from eq. 1.1.25, $\hat{K}(\mathbf{r})$ leads to an *exchange* of the variables in the two SOs. The result of acting with $\hat{K}(\mathbf{r})$ on $\xi(\mathbf{r})$ depends on the value of $\xi(\mathbf{r})$ on all points in space, since $\xi(\mathbf{r})$ is now related to $\mathbf{r}'$, the variable over which it is integrated. Consequently, the exchange operator and the corresponding potential are called *non-local*.

Notice that the occurrence of the exchange term is entirely due to the anti-symmetry of detors which describe fermion particles. As we have seen, the $1/r_{12}$ operator is spin-independent and it can be written as product of two different spin orbitals which both depend on the same coordinate $\mathbf{r}'$ (see HF spinless equations 1.1.21). Because spin functions are orthonormal, it follows that exchange contributions exist only for electrons of parallel spin, because in the case of opposite spins, the integrand would contain a factor $\langle \alpha | \beta \rangle$ (or $\langle \beta | \alpha \rangle$) which is zero, thus making the whole integral vanish (see e.g. the last term of eq. 1.1.21).

1.1.6 The Self-Interaction (SI) Error and Why the HF scheme is SI-free

An important thing to emphasize is that in the double summation of eq. 1.1.12 the term $i = j$ is allowed. This means that if we compute the energy of a one-electron system, such as the hydrogen atom, where there is definitely no electron-electron repulsion, the first term (coulomb term) of eq. 1.1.13 would nevertheless give a non-zero result. This *self-interaction* (SI) is a physical nonsense. However, the exchange term takes perfect care of this: for $i = j$ the Coulomb and the exchange integrals are identical. Since they enter in eq. 1.1.12 with opposite signs, the SI is exactly cancelled. The *self-interaction problem*, which is elegantly solved in the HF scheme, constitutes one of the lacks of Density Functional Theory (DFT).

1.1.7 RPN linearization of the HF equations

Looking for the solution of the multielectronic problem in the form of a detor of one-electron SOs, is a great reduction of complexity. The set of equations 1.1.14 is still rather hard to solve, since these are coupled integral-differential equations. A further linearization step is thus necessary.

It is possible to express each molecular orbital (MO) $\psi_i^\sigma(\mathbf{r})$ as a linear combination of functions (the atomic orbitals, AO) belonging to a given *basis set** $\{\phi_\mu(\mathbf{r})\}$ – where μ is an index running from 1 to M , with $2M \geq N$:

$$\psi_i^\sigma(\mathbf{r}) = \sum_{\mu} c_{\mu i}^\sigma \phi_\mu(\mathbf{r}) \quad (1.1.26)$$

The problem thus becomes the determination of the two unknown coefficients matrices C^σ ($\sigma = \alpha$ or β) of elements $c_{\mu i}^\sigma$. Multiplying to the left both sides of equation 1.1.22 by $\phi_\nu^*(\mathbf{r})$ and integrating over space, we obtain:

$$\begin{aligned} \int d\mathbf{r} \phi_\nu^*(\mathbf{r}) [\hat{f}^\sigma \psi_i^\sigma(\mathbf{r})] &= \varepsilon_i^\sigma \int d\mathbf{r} \phi_\nu^*(\mathbf{r}) \psi_i^\sigma(\mathbf{r}) \\ \sum_{\mu} \left[\int d\mathbf{r} \phi_\nu^*(\mathbf{r}) \hat{f}^\sigma \phi_\mu(\mathbf{r}) \right] c_{\mu i}^\sigma &= \varepsilon_i^\sigma \sum_{\mu} \left[\int d\mathbf{r} \phi_\nu^*(\mathbf{r}) \phi_\mu(\mathbf{r}) \right] c_{\mu i}^\sigma \\ \sum_{\mu} F_{\nu\mu}^\sigma c_{\mu i}^\sigma &= \sum_{\mu} S_{\nu\mu} c_{\mu i}^\sigma \varepsilon_i^\sigma \end{aligned} \quad (1.1.27)$$

*: basis-sets are not discussed here. The two most common forms of basis-set functions used in quantum chemistry are the Gaussian Type Orbitals (GTO), and the Plane-Waves (PW).

From eq.1.1.22:

$$\begin{aligned}
F_{\nu\mu}^\sigma &= h_{\nu\mu} + J_{\nu\mu} - K_{\nu\mu}^\sigma \quad , \text{ with} \\
J_{\nu\mu} &= \int d\mathbf{r} \phi_\nu^*(\mathbf{r}) \left(\hat{J} \phi_\mu(\mathbf{r}) \right) = \\
&= \int d\mathbf{r} \phi_\nu^*(\mathbf{r}) \left(\sum_{\rho,\tau} \sum_i^\alpha c_{\rho i}^{\alpha*} c_{\tau i}^\alpha \int d\mathbf{r}' \frac{\phi_\rho^*(\mathbf{r}') \phi_\tau(\mathbf{r}')}{\mathbf{r} - \mathbf{r}'} \phi_\mu(\mathbf{r}) \right) + \\
&+ \int d\mathbf{r} \phi_\nu^*(\mathbf{r}) \left(\sum_{\rho,\tau} \sum_j^\beta c_{\rho j}^{\beta*} c_{\tau j}^\beta \int d\mathbf{r}' \frac{\phi_\rho^*(\mathbf{r}') \phi_\tau(\mathbf{r}')}{\mathbf{r} - \mathbf{r}'} \phi_\mu(\mathbf{r}) \right) = \\
&= \sum_{\rho,\tau} \left(P_{\rho\tau}^\alpha + P_{\rho\tau}^\beta \right) (\nu\mu|\rho\tau) \\
K_{\nu\mu}^\sigma &= \int d\mathbf{r} \phi_\nu^*(\mathbf{r}) \left(\hat{K}^\sigma \phi_\mu(\mathbf{r}) \right) = \\
&= \int d\mathbf{r} \phi_\nu^*(\mathbf{r}) \left(\sum_{\rho,\tau} \sum_i^\sigma c_{\rho i}^{\sigma*} c_{\tau i}^\sigma \int d\mathbf{r}' \frac{\phi_\rho^*(\mathbf{r}') \phi_\mu(\mathbf{r}')}{\mathbf{r} - \mathbf{r}'} \phi_\tau(\mathbf{r}) \right) = \\
&= \sum_{\rho,\tau} P_{\rho\tau}^\sigma (\nu\tau|\rho\mu) \tag{1.1.28}
\end{aligned}$$

where the *density matrix* $P_{\rho\tau}^\sigma$ and the bielectronic Coulomb integral $(\nu\mu|\rho\tau)$ (the chemists' notation for bielectronic integrals is used here) were defined, respectively:

$$\begin{aligned}
P_{\rho\tau}^\sigma &= \sum_i^{N^\sigma} c_{\rho i}^{\sigma*} c_{\tau i}^\sigma \\
(\nu\mu|\rho\tau) &= \int d\mathbf{r} d\mathbf{r}' \left(\phi_\nu^*(\mathbf{r}) \phi_\mu(\mathbf{r}) \frac{1}{\mathbf{r} - \mathbf{r}'} \phi_\rho^*(\mathbf{r}') \phi_\tau(\mathbf{r}') \right) \tag{1.1.29}
\end{aligned}$$

the exchange integral $(\nu\tau|\rho\mu)$ can be derived in the same way.

The **Roothan-Pople-Nesbet (RPN) matricial equations** are then expressed as:

$$F^\sigma C^\sigma = S C^\sigma E^\sigma \tag{1.1.30}$$

F^σ is the *Fock matrix*, S is the *overlap matrix*, C^σ is the matrix of the $c_{\mu i}^\sigma$ coefficients for the i -th σ molecular orbital, and E^σ is a diagonal matrix containing the

MO energy eigenvalues.

Considering the case of a closed-shell system, the problem is unique for the set of α and β electrons so that equation 1.1.30 reduces to:

$$FC = SCE \quad (1.1.31)$$

where the density matrix is redefined as:

$$P_{\rho\tau} = 2 \sum_i^{N_{occ}} c_{\rho i}^* c_{\tau i} \quad (1.1.32)$$

The Fock matrix F can be written in the form:

$$F = F_{\nu\mu} = h_{\nu\mu} + \sum_{\rho\tau} P_{\rho\tau} \left[(\nu\mu|\rho\tau) - \frac{1}{2}(\nu\tau|\rho\mu) \right] \quad (1.1.33)$$

The HF energy in the closed-shell case (restricted Hartree-Fock, RHF) is thus calculated as in the following:

$$E^{RHF} = \sum_{\mu\nu} P_{\mu\nu} h_{\nu\mu} + \frac{1}{2} \sum_{\mu\nu} \sum_{\rho\tau} P_{\mu\nu} P_{\rho\tau} \left[(\nu\mu|\rho\tau) - \frac{1}{2}(\nu\tau|\rho\mu) \right] \quad (1.1.34)$$

By solving the RPN equations one gets two sets of spin-orbitals: N **occupied** SOs $\chi_1\chi_2\cdots\chi_N$ (the lowest in energy – *Aufbau principle*) which define the fundamental configuration $|\Psi^{HF}\rangle$ (the HF approximation of $|\Psi_0\rangle$) and $2M - N$ **virtual** SOs $\chi_{N+1}\chi_{N+2}\cdots\chi_{2M}$. The *active space* (occupied orbitals) is important in the description of the ground state, while the *virtual space* (unoccupied orbitals) becomes important if one needs to compute properties that derive from excited configurations, using post-HF techniques.

Such techniques have been developed to take into account the effects of the true electron correlation, that is neglected by the standard HF theory.

At this point, we have the ingredients to make a simple scheme for the HF self-consistent procedure (SCF), which is depicted below.

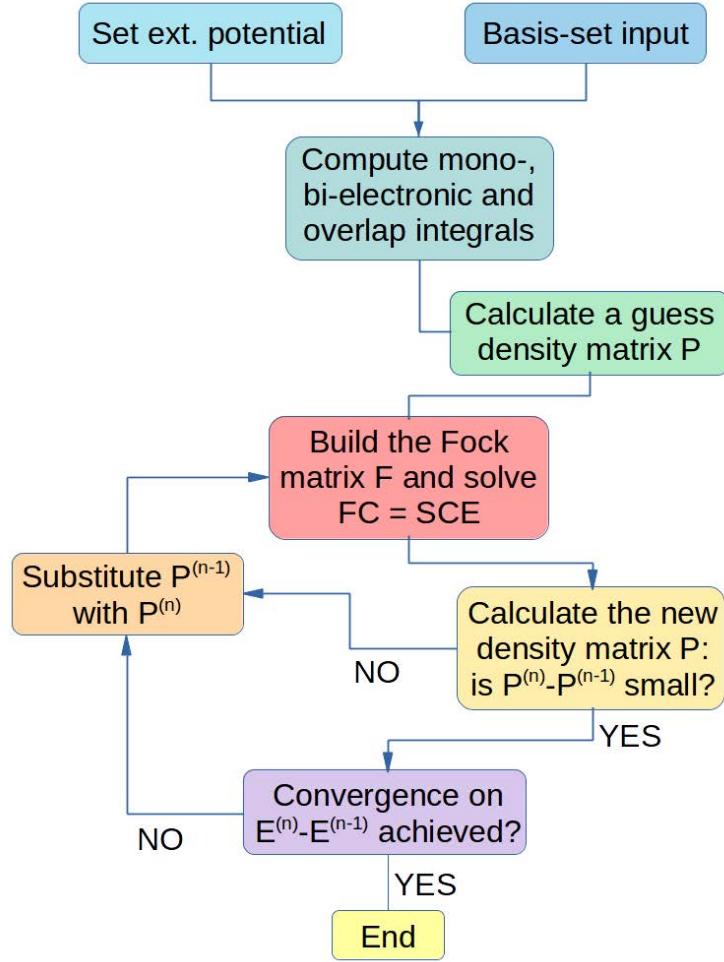


Figure 1.1: A scheme for the Hartree-Fock self-consistent procedure – SCF.

1.1.8 Switching to the standard form

The presence of the overlap matrix, S , complicates the solution of eq. 1.1.31. A smart procedure – proposed by Löwdin – can be used to bypass this problem.

When the hermitian matrix S is diagonalized by a unitary transformation ($S = U\Sigma U^\dagger$), it can be demonstrated that S is *positive definite*. In fact we can write:

$$\sum_{\mu\nu} U_{i\mu}^\dagger S_{\mu\nu} U_{\nu i} = \int d\mathbf{r} \left[\sum_{\mu} u_{\mu i} \phi_{\mu}(d\mathbf{r}) \right]^* \left[\sum_{\nu} u_{\nu i} \phi_{\nu}(d\mathbf{r}) \right] \equiv \int d\mathbf{r} |\xi_i(\mathbf{r})|^2 > 0 \quad (1.1.35)$$

When a $T = U\Sigma^{-\frac{1}{2}}$ matrix is defined, one may notice that:

$$TT^\dagger = U\Sigma^{-\frac{1}{2}}\Sigma^{-\frac{1}{2}}U^\dagger = S^{-1}, \text{ i.e. } T^\dagger S = T^{-1}$$

Multiplying to the left both members of eq. 1.1.31 by $T^\dagger$ we obtain:

$$T^\dagger FTT^{-1}C = T^\dagger SCE \quad (1.1.36)$$

and finally:

$$F'C' = C'E \quad (1.1.37)$$

with $F' = T^\dagger FT$ and $C' = T^{-1}C$.

Thus, eq. 1.1.37 can be easily solved by diagonalization of the F' matrix.

1.1.9 Orbital energies

Let us consider the orbital energies, as defined before (see Section 1.1.2). From equation 1.1.14, it is easy to demonstrate that the Fock operator acts on two different spin-orbitals in the following way:

$$\langle \chi_j | \hat{f} | \chi_i \rangle = \epsilon_i \langle \chi_j | \chi_i \rangle = \epsilon_i \delta_{ji} \quad (1.1.38)$$

so that, in terms of matrices, the orbital energies are the diagonal elements of the Fock matrix, defined in the basis of SO eigenfunctions.

Thus, taking into account of the definition of the Fock operator and of eq. 1.1.38, we can write:

$$\begin{aligned} \langle \chi_i | \hat{f} | \chi_i \rangle &= \langle \chi_i | (\hat{h} + \hat{B}) | \chi_i \rangle = \langle \chi_i | \left[\hat{h} + \sum_j (\bullet j || \bullet j) \right] | \chi_i \rangle = \\ &= \langle i | \hat{h} | i \rangle + \langle i | \sum_j (\bullet j || \bullet j) | i \rangle = \langle i | \hat{h} | i \rangle + \sum_j \langle ij || ij \rangle = \epsilon_i \end{aligned} \quad (1.1.39)$$

Summing up the ϵ_i over N electrons, one gets:

$$\sum_i \epsilon_i = \sum_i \langle i | \hat{h} | i \rangle + \sum_{i,j} \langle ij || ij \rangle \quad (1.1.40)$$

which differs from the HF energy expectation value (eq. 1.1.12):

$$\begin{aligned} E^{HF} &= \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{i,j} \langle ij || ij \rangle \neq \sum_i \epsilon_i \quad ; \\ &= \sum_i \epsilon_i - \frac{1}{2} \sum_{i,j} \langle ij || ij \rangle \end{aligned} \quad (1.1.41)$$

Hence, at this point a concrete meaning for ϵ_i , beyond the fact they are eigenvalues of the Fock operator, is still lacking – it is unveiled in the following Section.

1.1.10 Koopman's theorem

The physical role of the HF orbital energies is explained through the Koopman's theorem.

If one takes the HF ground-state wave function $|\Psi\rangle = |\Psi^{HF}\rangle$, a new wave function with $N - 1$ electrons can be written as $|\Psi_a^{N-1}\rangle$. This indicates that one electron was extracted from the spin-orbital “ a ”. The expectation value of the Hamiltonian for this system is:

$$E_a^{N-1} = \langle \Psi_a^{N-1} | \hat{H} | \Psi_a^{N-1} \rangle = \sum_{i \neq a} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{i \neq a} \sum_{j \neq a} \langle ij || ij \rangle \quad (1.1.42)$$

We define *Ionization Potential* (IP) the difference between such energy and the HF energy, i.e. the potential needed to extract one electron from the N -electron system defined by $|\Psi^{HF}\rangle$:

$$\begin{aligned} IP &= E_a^{N-1} - E^{HF} = \sum_{i \neq a} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{i \neq a} \sum_{j \neq a} \langle ij || ij \rangle - \sum_i \langle i | \hat{h} | i \rangle - \frac{1}{2} \sum_{i,j} \langle ij || ij \rangle \\ &= -\langle a | \hat{h} | a \rangle + \frac{1}{2} \left[\sum_{i \neq a} \sum_{j \neq a} \langle ij || ij \rangle - \sum_{i,j} \langle ij || ij \rangle \right] = \\ &= -\langle a | \hat{h} | a \rangle - \frac{1}{2} \left[\sum_j \langle aj || aj \rangle + \sum_i \langle ia || ia \rangle \right] = \\ &= -\langle a | \hat{h} | a \rangle - \sum_j \langle aj || aj \rangle = -\epsilon_a \end{aligned} \quad (1.1.43)$$

This result, explained by the Koopman's theorem, tells that “*The ionization potential corresponds to the opposite of the eigenvalue ϵ_a* ”. In the same way, the *Electron Affinity* (EA) can be defined as:

$$EA = E^{HF} - E_a^{N-1} = E_a^{N+1} - E^{HF} = \langle a | \hat{h} | a \rangle + \sum_j \langle aj || aj \rangle = +\epsilon_a \quad (1.1.44)$$

This consists of a notable approximation, since HF does not take into account for electron correlation. Moreover, after the extraction (or addition) of one electron from (to) the system, one should proceed to carry out an orbital relaxation. However, since these two effects almost compensate, the HF estimate of IPs and EAs is usually quite accurate.

1.2 The correlation energy problem

A single determinant, taken as an approximate wave function, is able to describe a significant portion of the physics of a many-electron system. However, it never corresponds to the exact wave function. Thus, owing to the variational principle, E^{HF} is necessarily always higher (i.e., less negative) than the exact ground-state energy E_0 . The difference between these two energies[†] is called **correlation energy** (see Ref. [3]):

$$E_{HF}^{corr} = E_0 - E^{HF} \quad (1.2.1)$$

E_{HF}^{corr} is a negative quantity because $E_0 < 0$, $E^{HF} < 0$ and $|E_0| > |E^{HF}|$.

It is a measure for the error introduced through the HF scheme and it leads to the so-called *correlation energy problem*.

The electron correlation is mainly caused by instantaneous repulsion among electrons, which is not covered by the effective HF potential because the electrostatic interaction is treated in an average manner (mean-field approximation).

Consequently, the electron-electron repulsion term is too large, resulting in E^{HF} being above E_0 . This part of the correlation energy is usually called *dynamical correlation* because it is related to the instantaneous motion of individual electrons and it is known to be a short range effect. It is directly connected to the $1/r_{12}$ operator and it obviously increases when the distance r_{12} between two electrons becomes close.

[†]: E^{HF} here is intended to be the HF limit, i.e. the extrapolation of the HF energy to the complete basis-set (CBS).

The second main contribution to E^{HF} is the *non-dynamical* or *static correlation*. It is related to the fact that a single-determinant wave function is not sufficient to reach a correct description of the true ground-state.

A typical example that shows the effect of the missing correlation contribution is provided by the dissociation of the H_2 molecule (Fig. 1.2). At the equilibrium distance the restricted HF scheme provides a good approximation to the H_2 molecule. The correlation error, which is almost exclusively due to dynamical correlation, is small. However, as the bond is stretched the correlation gets larger and larger. In the limit of very broad distances, the energy converges to a positive value, instead of zero. This cannot be due to the dynamical correlation because at $r_{HH} \rightarrow \infty$ there are two independent hydrogen atoms with only one electron at each center and no electron-electron interaction: the static correlation becomes the main contribution. While the RHF completely fails the long-range description of the dissociation (i.e. it is not *size-consistent*), the unrestricted HF scheme (UHF), which treats separately the average potential experienced by the α -electron and the β -electron, leads to a nearly exact behavior.

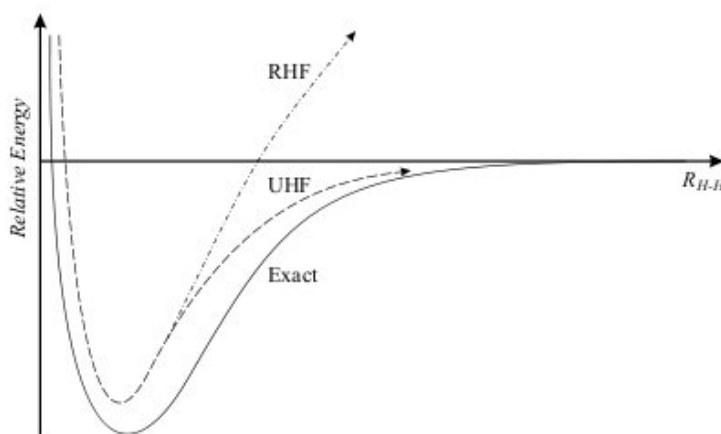


Figure 1.2: H_2 homonuclear dissociation: the potential behavior vs. distance of H nuclei is shown for RHF, UHF and the exact calculation. Image adapted from Ref. [4], ©Wiley-VCH 2001, all rights reserved.

1.3 Accurate electron correlation: hints on post-HF methods

A precise quantification of the electron correlation can be exploited by using post-HF methods. These are, together with Quantum Monte Carlo (QMC), the most accurate computational techniques available nowadays, because they are able to include electron correlation by considering excited-states configurations within the solid framework of wave function theory.

In this section, only basic concepts for the most popular post-HF techniques are given, since they were not mainly used to carry out calculations in the present work of thesis because of the large size of the investigated systems. However, we were able to run local-MP2 calculations assuming them as a benchmarking reference for the study of the relative stability of oxalyl dihydrazide (see Chapter 6.2).

Since a finite basis-set expansion is used, the HF method yields to a finite set of M spatial wave functions – this constitutes the HF basis-set truncation error. Moreover, an infinite number of detors can (in theory) be used to describe the N occupied SOs of the ground-state wave function; the HF method, instead, uses only one determinant. We also recall that $2M - N$ virtual SOs can be defined from M spatial wave functions.

Hence, multiple detors can describe both occupied and virtual SOs. These last can be classified taking as reference the single determinantal HF wave function, only by highlighting the promotion of electrons from ground state to excited configurations.

Defining the ground state HF detor as $|\Psi_0\rangle$, one can express a *singly-excited determinant* as $|\Psi_a^r\rangle$, where one electron is promoted from the occupied orbital a to the virtual orbital r . A *doubly-excited determinant* can be similarly defined as $|\Psi_{ab}^{rs}\rangle$, whereas detors for higher order excitations can be derived in the same way – these are called *configuration state functions* (CSFs). When the expressions for the wave function and the Hamiltonian operator are defined, every post-HF method can be solved self-consistently by applying the Variational Principle as in the case of HF.

1.3.1 Configuration Interaction

As suggested above, we can write the exact electronic wave function for any state of the N -electron system considering a linear combination of an infinite number of detors which represent an ONC set of spin-orbitals.

Assuming that the HF wave function is a good approximation for a ground state closed-shell detor, we can thus write the exact wave function in the following form:

$$|\Phi_{fullCI}\rangle = C_0|\Psi_0\rangle + \sum_{a<r} C_a^r |\Psi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} C_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c \\ r<s<t}} C_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \dots \quad (1.3.1)$$

which is the **full CI** wave function. If we had an infinite set of detors, we would obtain the exact E_0 ground state energy of equation 1.2.1. Adopting a finite basis-set, a “full CI calculation” indicates the use of all possible detors for such given basis-set. This yields, however, to a huge number of detors, even for relatively small systems: for example, a system with 20 electrons described by 40 spatial wave functions ($2M = 80$ spin-orbitals) gives rise to $\binom{2M}{N} \simeq 3.54 \cdot 10^{18}$ detors.

Usually, it is difficult to employ more than about 10^4 detors; the full CI method thus needs to be truncated at some order.

Typical formulations are, for example, CI *singles*, (CIS) CI *doubles* (CID) and CI singles and doubles (CISD). In such methods, only singly excited configurations, doubly excited configurations or both singly and doubly excited configurations are added to the ground-state HF detor, respectively.

As demonstrated by the Brillouin’s theorem (1934, see e.g. [2]), through the use of Slater’s rules, singly excited determinants do not affect the ground-state (the mixed matrix elements vanish). The CIS method is then useless to improve the HF description of the ground-state energy, but it is adopted when studying excited states.

Oppositely, the effects of double excitations affect the ground-state. Hence, the CID method provides a reasonable improvement on the HF ground-state energy. The contribution of single excitations, however, affects *indirectly* the ground-state, by mixing with doubly excited configurations (e.g. in CISD). The main limit of truncated CI is the lack of size-consistency, though the *size-extensivity* (which is the correct linear scaling in function of the increasing number of electrons) is respected.

1.3.2 Coupled Cluster

The Coupled Cluster (CC) expression for the total wave function of an N -electron system is written as an exponential ansatz:

$$|\Phi_{CC}\rangle = e^{\hat{T}}|\Psi_0\rangle \quad (1.3.2)$$

where $|\Psi_0\rangle$ is the HF wave function for the ground state. $\hat{T}$ is the *cluster operator*, which represents a linear combination of $\hat{T}_i$ operators. Each $\hat{T}_i$ originates all possible determinants including i excitations with respect to the ground-state:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \dots \quad (1.3.3)$$

$$\hat{T}_1 = \sum_{\substack{a \\ r}} t_a^r \hat{a}_a \hat{a}_r^\dagger \quad \hat{T}_2 = \sum_{\substack{a < b \\ r < s}} t_{ab}^{rs} \hat{a}_a \hat{a}_b \hat{a}_r^\dagger \hat{a}_s^\dagger \quad \hat{T}_3 = \sum_{\substack{a < b < c \\ r < s < t}} t_{abc}^{rst} \hat{a}_a \hat{a}_b \hat{a}_c \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_t^\dagger \quad \dots \quad (1.3.4)$$

where $\hat{T}_i$ are expressed in term of *annihilation* and *creation* operators from the formalism of second quantization.

For simplicity, let us neglect configurations with an odd number of excitations, thus the operator $e^{\hat{T}}$ corresponds to a Taylor series expansion with $\hat{T} = \hat{T}_2$ (all the even excitations are expressed as powers of the biexcitation operator, $\hat{T}_2$):

$$\begin{aligned} e^{\hat{T}} &= 1 + \hat{T}_2 + \frac{\hat{T}_2^2}{2!} + \frac{\hat{T}_2^3}{3!} + \dots \\ &= 1 + C_{ab}^{rs} + C_{abcd}^{rstu} + C_{abcdef}^{rstuvw} + \dots \end{aligned} \quad (1.3.5)$$

It follows that the total wave function expansion is written as:

$$|\Phi_{CC}\rangle = |\Psi_0\rangle + \sum_{\substack{a < b \\ r < s}} C_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a < b < c < d \\ r < s < t < u}} C_{abcd}^{rstu} |\Psi_{abcd}^{rstu}\rangle + \sum_{\substack{a < b < c < d < e < f \\ r < s < t < u < v < w}} C_{abcdef}^{rstuvw} |\Psi_{abcdef}^{rstuvw}\rangle + \dots \quad (1.3.6)$$

All the C coefficients are seen as products of biexcited configurations (those originated by $\hat{T}_2$), assuming that $a, b, \dots, r, s$ and $c, d, \dots, t, u$ molecular orbitals are “far” from each other (i.e. weakly interacting):

$$C_{abcd}^{rstu} \simeq C_{ab}^{rs} \star C_{cd}^{tu} \quad (1.3.7)$$

and so on. The CC wave function finally assumes the following form:

$$|\Phi_{CC}\rangle = |\Psi_0\rangle + \sum_{\substack{a < b \\ r < s}} C_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a < b < c < d \\ r < s < t < u}} C_{ab}^{rs} \star C_{cd}^{tu} |\Psi_{abcd}^{rstu}\rangle + \dots \quad (1.3.8)$$

Within this approximation, the size consistency condition is maintained.

A popular formulation of Coupled Cluster theory, often indicated as the “gold standard” benchmarking method for a wide range of molecular properties, is the CCSD(T) – where *singles* and *doubles* are considered. In addition, triple excitations are treated approximately with Many-Body Perturbation Theory (MBPT) arguments.

Since CC, similarly to CI, treats a large number of configurations, it scales as N^6 - N^7 : the benefit of obtaining really accurate predictions with the inclusion of a nearly-true correlation contribution is paid with the fact that only systems composed by a small number of atoms can be treated. The MP2 method (*vide infra*), instead, provides a better balance between computational demanding and accuracy, so that is more and more frequently becoming an alternative choice to the popular DFT.

1.3.3 Møller-Plesset Perturbation Theory

The Møller-Plesset (MP) perturbation theory is a particular case of the Rayleigh-Schrödinger (RS) perturbation theory. The latter defines the total electronic Hamiltonian as the sum of an unperturbed Hamiltonian operator $\hat{H}_0$ and a small perturbation $\hat{H}'$:

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}' \quad (1.3.9)$$

where λ is a small, arbitrary real parameter that weights the perturbation. This last corresponds to the electron correlation potential. λ regulates the order of perturbation, entering in the power series that express the form of the energy and the wave function.

If we consider also a second order perturbation term, we can write:

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}' + \lambda^2 \hat{H}'' \quad (1.3.10)$$

When using the *shifted* Fock operator (see eq. 1.3.11 below) as the unperturbed Hamiltonian operator $\hat{H}_0$, the MP perturbation theory can be derived. It follows that $\hat{H}_0$ – the zeroth order MP Hamiltonian operator – is given by:

$$\hat{H}_0 = \hat{F} + \langle \Psi_0 | \hat{H} - \hat{F} | \Psi_0 \rangle \quad (1.3.11)$$

Here, $\hat{F}$ is the sum over N electrons of all the i monoelectronic Fock operators, as already defined in HF theory (see eq. 1.1.14):

$$\hat{F} \equiv \hat{f} = \sum_i^N \hat{f}_i \quad (1.3.12)$$

Thus, the perturbed operator (i.e. the correlation operator) – with simple substitution of eq. 1.3.11 into eq. 1.3.9 – is expressed as:

$$\hat{H}' = \hat{H} - \left(\hat{F} + \langle \Psi_0 | \hat{H} - \hat{F} | \Psi_0 \rangle \right) \quad (1.3.13)$$

The application of the Fock operator to Ψ_0 gives the lowest orbitals eigenvalues. Moreover, being Ψ_0 an eigenstate of $\hat{F}$, we can write:

$$\hat{F}\Psi_0 = \sum_i^N \hat{f}_i \Psi_0 = 2 \sum_i^{N/2} \epsilon_i \Psi_0 = \langle \Psi_0 | \hat{F} | \Psi_0 \rangle \Psi_0 \quad (1.3.14)$$

so that:

$$\hat{F}\Psi_0 - \langle \Psi_0 | \hat{F} | \Psi_0 \rangle \Psi_0 = 0 \quad (1.3.15)$$

The previous equation is put into eq. 1.3.11, to obtain:

$$\hat{H}_0 \Psi_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \Psi_0 = E_{MP0} \Psi_0 \equiv E_{HF} \Psi_0 \quad (1.3.16)$$

i.e. the 0-th order MP energy corresponds to the HF energy.

The first order MP energy can be consequently derived from eq. 1.3.13, and it is equal to zero:

$$E_{MP1} = \langle \Psi_0 | \hat{H}' | \Psi_0 \rangle = 0 \quad (1.3.17)$$

The first – and major – contribution to the electron correlation is that given by the 2nd-order MP energy (MP2), for which (from the Slater rules) only biexcited configurations are considered:

$$E_{MP2} = \sum_{\substack{a < b \\ r < s}} \frac{\langle \Psi_0 | \hat{H} | \Psi_{ab}^{rs} \rangle \langle \Psi_{ab}^{rs} | \hat{H} | \Psi_0 \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} = \sum_{\substack{a < b \\ r < s}} \frac{|\langle ab || rs \rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \quad (1.3.18)$$

where the right-hand side term is written in compact notation (see e.g. eq. 1.1.12).

Usually, calculations involving perturbation theory are done at MP2 level, but also contributions of higher order correlation are sometimes considered, typically up to the fourth order (MP4).

Since Density Fitting (df) techniques can be exploited to accelerate computations, the nominal scaling of MP2 (N^4 or N^5) decreases to the HF scaling, or even better (N^3).

Moreover, a *local* formulation of MP2 (LMP2),[‡] as the one implemented in the software CRYSCOR [5] for periodic systems, yields to a quasi-linear scaling – the modeling of extended systems that are normally treated by DFT functionals is thus feasible.

[‡]the local method relies on the fact that electron correlation decays more rapidly than coulomb interactions. Thus, instead of molecular or crystalline orbitals, localized functions (e.g. Wannier functions) can be adopted to describe occupied states. On the other hand, localized virtual states are obtained by projecting the virtual part of atomic orbitals (projected atomic orbitals, PAO).

1.3.4 Multireference Ansätze

In many cases – which include, e.g., a ground-state which is quasi-degenerate with excited states, complex dynamical (time-dependent) processes in photochemistry, etc. – the monodeterminantal expression of the wave function is not sufficient to correctly describe such kind of phenomena.

Hence, a multideterminantal expression can be given for $|\Psi\rangle$ (see also eq. 1.1.10):

$$|\Psi\rangle = \sum_T^{N'} C_t |T\rangle \quad (1.3.19)$$

where the linear combination of N' detors $|T\rangle$ – built on N spin-orbitals – is weighted by the expansion coefficients C_t . The expectation value for the total energy is minimized both with respect to the C_t and to the $c_{\mu,i}$ spin-orbital coefficients – $\psi_i = \sum_{\mu}^N c_{\mu,i} \chi_{\mu}$.

Such method derives in a natural way from wave function theory, applying the expansion and developing the same principles exposed for HF theory, in a self-consistent formulation. However, the equations obtained are really much more complex. The discussed approach is called **multiconfigurational SCF** (MCSCF) and, when all the possible linear combinations deriving from a certain number of SOs are used, it is called *complete-active-space* SCF (CASSCF).

The configuration state functions originated by eq. 1.3.19 can be used to build reference states also for a CI expansion or for perturbation theory, thus yielding to the multireference CI (MRCI) or to the complete-active-space perturbation theory (CASPT) ansätze, respectively.

Amongst other similar techniques available, one can also find the multireference treatment of coupled-cluster theory (MRCC).

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Chapter 2

Density Functional Theory

*Density-functional theory is a subtle, seductive, provocative business.
Its basic premise, that all the intricate motions
and pair correlations in a many-electron system
are somehow contained in the total electron density alone,
is so compelling it can drive one mad.*

[J. Chem. Phys. 140, 18A301, 2014]

Axel D. Becke

Density Functional Theory (DFT) is an extremely successful theoretical approach for the description of ground-state quantum properties of the matter (from atoms to extended solids).

Its success in computational chemistry is due to the fact that the energy of any N -electron system can be expressed as a functional of the ground-state electronic density ρ – from which any other ground-state property can be derived – and that ρ is uniquely determined by a given external potential.

Some proper modifications to standard DFT (e.g. hybrid HF/DFT functionals, or additive terms that partly take into account for the true electron correlation) brought it to gain a degree of accuracy sometime comparable with that of post-HF methods. This reasons, coupled with the relatively low computational demand, contributed to increase its popularity – in the last years – as never before.

In the following sections is explained how the DFT is formulated, through the Hohenberg-Kohn theorems [1, 2], and how this approximation was made useful for its application to computational chemistry thanks to the Kohn-Sham approach.

2.1 Density operators, reduced and spinless density matrices

In general, the description of a *pure*[†] quantum state can be given by the following definition of probability:

$$\Psi_N(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N)\Psi_N^*(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N) \quad (2.1.1)$$

which is associated with the solutions of the Schrödinger equation for an N -electron system. The set $\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N$ includes all the space and spin coordinates for each electron. We define a *density operator* as:

$$\hat{\gamma}_N = |\Psi_N\rangle\langle\Psi_N| \quad (2.1.2)$$

that – for two distinct sets of coordinates $\{\mathbf{x}_i\}$, $\{\mathbf{x}'_i\}$ – acts in the following way:

$$\begin{aligned} \langle\mathbf{x}'_1\mathbf{x}'_2\cdots\mathbf{x}'_N|\hat{\gamma}_N|\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N\rangle &= \langle\mathbf{x}'_1\mathbf{x}'_2\cdots\mathbf{x}'_N|\Psi_N\rangle\langle\Psi_N|\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N\rangle = \\ &= \Psi_N(\mathbf{x}'_1\mathbf{x}'_2\cdots\mathbf{x}'_N)\Psi_N^*(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N) \end{aligned} \quad (2.1.3)$$

Thus, it corresponds to a projection operator. For a normalized set of Ψ_N , we have:

$$tr(\hat{\gamma}_N) = \int \Psi_N(\mathbf{x}^N)\Psi_N^*(\mathbf{x}^N)d\mathbf{x}^N = 1 \quad (2.1.4)$$

this means that, in the matrix form, the trace (sum of diagonal elements) is normalized to the total number of electrons in the system.

Eq. 2.1.1 represents the *density matrix* of p -th order for a pure quantum state. Since in the standard form of the Hamiltonian operator (see eq. 1.1.2), only mono-electronic and bielectronic operators are defined, we can make use only of the *reduced density matrices* of order 1 and 2. The latter, in particular, can be written as:

$$\gamma_2(\mathbf{x}'_1\mathbf{x}'_2, \mathbf{x}_1\mathbf{x}_2) = \frac{N(N-1)}{2} \int \cdots \int \Psi_N(\mathbf{x}'_1\mathbf{x}'_2\cdots\mathbf{x}'_N)\Psi_N^*(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N)d\mathbf{x}_3\cdots d\mathbf{x}_N \quad (2.1.5)$$

[†]a *pure* state can be described by a wave function. A *mixed* state is a more general situation for which a wave function cannot be defined, i.e. the system of interest is part of a larger closed system. This means that the latter cannot be described by an Hamiltonian mapped with the same degrees of freedom of the one belonging to the smaller system.

where the term that comes before integrals – the binomial coefficient – is always present, and it is defined as $\binom{N}{p}$ for a p -th order density matrix on N electrons. For the 2nd order density matrix, the binomial coefficient normalizes γ_2 to the number of electron pairs:

$$\text{tr } \gamma_2(\mathbf{x}'_1 \mathbf{x}'_2, \mathbf{x}_1 \mathbf{x}_2) = \iint \gamma_2(\mathbf{x}_1 \mathbf{x}_2, \mathbf{x}_1 \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 = \frac{N(N-1)}{2} \quad (2.1.6)$$

whereas γ_1 – the first order density matrix – is normalized to the total number of electrons:

$$\begin{aligned} \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) &= N \int \cdots \int \Psi_N(\mathbf{x}'_1 \mathbf{x}'_2 \cdots \mathbf{x}'_N) \Psi_N^*(\mathbf{x}_1 \mathbf{x}_2 \cdots \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N \\ \text{tr } \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) &= \int \gamma_1(\mathbf{x}_1, \mathbf{x}_1) d\mathbf{x}_1 = N \end{aligned} \quad (2.1.7)$$

γ_1 and γ_2 are positive semidefinite, Hermitian and – as required for a fermion wave function – antisymmetric.

Since most of the one-electron operators – for the Hamiltonian of eq. 1.1.2 – are local, they act only on diagonal elements. Thus, we can define, generally:

$$\hat{O}_1 = \sum_i^N O_1(\mathbf{x}'_i, \mathbf{x}_i) = \sum_i^N O_1(\mathbf{x}_i) \quad (2.1.8)$$

and the form of its expectation value:

$$\langle \hat{O}_1 \rangle = \int [O_1(\mathbf{x}_1) \gamma_1(\mathbf{x}'_1, \mathbf{x}_1)]_{\mathbf{x}'_1=\mathbf{x}_1} d\mathbf{x}_1 \quad (2.1.9)$$

In a similar way, the two-electron operators in DFT are local*, so that they are expressed as:

$$\begin{aligned} \hat{O}_2 &= \sum_{i < j}^N O_2(\mathbf{x}_i, \mathbf{x}_j) \quad ; \\ \langle \hat{O}_2 \rangle &= \iint [O_2(\mathbf{x}_1, \mathbf{x}_2) \gamma_2(\mathbf{x}'_1 \mathbf{x}'_2, \mathbf{x}_1 \mathbf{x}_2)]_{\mathbf{x}'_1=\mathbf{x}_1, \mathbf{x}'_2=\mathbf{x}_2} d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \quad (2.1.10)$$

*: it is worth recalling that in HF theory, instead, the bielectronic exchange operator is – correctly – non-local.

Combining such definitions, one gets the expectation value for the Hamiltonian 1.1.2 in terms of first and second order reduced density matrices:

$$\begin{aligned}
 E &= \text{tr}(\hat{H}\hat{\gamma}_N) = E[\gamma_1, \gamma_2] = \\
 &= \int \left[\left(-\frac{\nabla_1^2}{2} + v(\mathbf{r}_1) \right) \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) \right]_{\mathbf{x}'_1=\mathbf{x}_1} d\mathbf{x}_1 + \iint \frac{1}{r_{12}} \gamma_2(\mathbf{x}_1\mathbf{x}_2, \mathbf{x}_1\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2
 \end{aligned} \tag{2.1.11}$$

Notice, in the equation above, the dependence by space-only coordinates of the *external potential* $v(\mathbf{r}_1)$, i.e. the nucleus-electron interaction.

As similarly done for spin-orbitals in Hartree-Fock equations (see Sec. 1.1.3), one can separate space and spin coordinates of the electron density.

By integrating over spin ($\sigma(\omega) = \sigma = \alpha$ or β), it is possible to further simplify the reduced density matrices to the *spinless density matrices*:

$$\begin{aligned}
 \rho_1(\mathbf{r}'_1, \mathbf{r}_1) &= N \int \cdots \int \Psi_N(\mathbf{r}'_1\sigma_1\mathbf{x}'_2 \cdots \mathbf{x}'_N) \Psi_N^*(\mathbf{r}_1\sigma_1\mathbf{x}_2 \cdots \mathbf{x}_N) d\sigma_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \\
 &= \int \gamma_1(\mathbf{r}'_1\sigma_1, \mathbf{r}_1\sigma_1) d\sigma_1
 \end{aligned} \tag{2.1.12}$$

and for the second order:

$$\begin{aligned}
 \rho_2(\mathbf{r}'_1\mathbf{r}'_2, \mathbf{r}_1\mathbf{r}_2) &= \frac{N(N-1)}{2} \int \cdots \\
 &\cdots \int \Psi_N(\mathbf{r}'_1\sigma_1\mathbf{r}'_2\sigma_2\mathbf{x}'_3 \cdots \mathbf{x}'_N) \Psi_N^*(\mathbf{r}_1\sigma_1\mathbf{r}_2\sigma_2\mathbf{x}_3 \cdots \mathbf{x}_N) d\sigma_1 d\sigma_2 d\mathbf{x}_3 \cdots d\mathbf{x}_N = \\
 &= \iint \gamma_2(\mathbf{r}'_1\sigma_1\mathbf{r}'_2\sigma_2, \mathbf{r}_1\sigma_1\mathbf{r}_2\sigma_2) d\sigma_1 d\sigma_2
 \end{aligned} \tag{2.1.13}$$

The traces of this two matrices correspond to:

$$\begin{aligned}
 \rho_1(\mathbf{r}_1, \mathbf{r}_1) &= N \int \cdots \int |\Psi|^2(\mathbf{r}_1\sigma_1\mathbf{x}_2 \cdots \mathbf{x}_N) d\sigma_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N = \\
 &= \rho_1(\mathbf{r}_1) \\
 \rho_2(\mathbf{r}_1\mathbf{r}_2, \mathbf{r}_1\mathbf{r}_2) &= \frac{N(N-1)}{2} \int \cdots \int |\Psi|^2(\mathbf{r}_1\sigma_1\mathbf{r}_2\sigma_2\mathbf{x}_3 \cdots \mathbf{x}_N) d\sigma_1 d\sigma_2 d\mathbf{x}_3 \cdots d\mathbf{x}_N = \\
 &= \rho_2(\mathbf{r}_1, \mathbf{r}_2)
 \end{aligned} \tag{2.1.14}$$

where shorthand notations $\rho_1(\mathbf{r}_1)$ and $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ – have been introduced.

We can finally rewrite the energy expression of eq. 2.1.11 *as a functional* of the electron density (which, in turns, depends on space coordinates only):

$$\begin{aligned} E &= E[\rho_1(\mathbf{r}', \mathbf{r}), \rho_2(\mathbf{r}_1, \mathbf{r}_2)] = \\ &= \int \left[-\frac{\nabla_{\mathbf{r}}^2}{2} \rho_1(\mathbf{r}', \mathbf{r}) \right]_{\mathbf{r}'=\mathbf{r}} d\mathbf{r} + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \iint \frac{1}{r_{12}} \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (2.1.15)$$

In this expression, we have the kinetic energy, the external potential and, at last, a term that includes all kinds of electron-electron interactions (classical Coulomb and quantum Coulomb and Fermi contributions).

2.2 The Hohenberg-Kohn theorems

The Hohenberg-Kohn (HK) theorems [1] (1964) recall that – for any N -electron system – the external potential $v(\mathbf{r})$ of the Hamiltonian (equation 1.1.3) defines the whole nuclear frame, and together with the number of electrons N , it determines all the ground-state properties.

Instead of using N and $v(\mathbf{r})$, the first HK theorem assumes the electron density $\rho(\mathbf{r})$ to be used as the fundamental variable:

Theorem 1

“The external potential $v(\mathbf{r})$ is (to within a constant) a unique functional of $\rho(\mathbf{r})$; since, in turn $v(\mathbf{r})$ fixes $\hat{H}$, we see that the full many particle ground state is a unique functional of $\rho(\mathbf{r})$.”

This means that, since $\rho(\mathbf{r})$ determines the number of electrons, it also determines the ground-state wave function and all the related electronic properties. The proof for the first HK theorem is given by using the minimum-energy principle for the ground-state.

Let us consider, *ad absurdum*, that two external potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$, differing by more than a constant, give exactly the same $\rho(\mathbf{r})$ for the nondegenerate[†]

ground-state of some N -electron system. There would be two Hamiltonians $\hat{H}$ and $\hat{H}'$ whose ground-state densities were the same, though the normalized wave functions Ψ and Ψ' would be different. Taking Ψ' as a trial wave function for $\hat{H}$, we obtain:

$$E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle = E'_0 + \int \rho(\mathbf{r}) [v(\mathbf{r}) - v'(\mathbf{r})] d\mathbf{r} \quad (2.2.1)$$

with E_0 and E'_0 the energies for $\hat{H}$ and $\hat{H}'$, respectively. In the same way, using Ψ as a trial wave function for $\hat{H}'$, we can write:

$$E'_0 < \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle = E_0 - \int \rho(\mathbf{r}) [v(\mathbf{r}) - v'(\mathbf{r})] d\mathbf{r} \quad (2.2.2)$$

When summing equations 2.2.1 and 2.2.2 we obtain a contradiction:

$$E_0 + E'_0 < E'_0 + E_0 \quad (2.2.3)$$

hence, two different $v(\mathbf{r})$ that furnish the same $\rho(\mathbf{r})$ for their ground-state cannot exist. It follows that $\rho(\mathbf{r})$ determines N and, for a given $v(\mathbf{r})$, also the other properties (terms) of the Hamiltonian – which can be written in the form 2.1.15.

Thus, the different terms for the total energy $E_v[\rho(\mathbf{r})]$ – where the dependence from $v(\mathbf{r})$ is explicitly underlined – can be expressed as:

$$E = E_v[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + V_{ne}[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] = F_{HK}[\rho(\mathbf{r})] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \quad (2.2.4)$$

with $F_{HK}[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})]$

where F_{HK} is the *universal functional*, since it is defined independently from $v(\mathbf{r})$. The electron-electron potential energy, in turn, is constituted by two terms:

$$V_{ee}[\rho(\mathbf{r})] = J[\rho(\mathbf{r})] + J_{nc}[\rho(\mathbf{r})] \quad (2.2.5)$$

being $J[\rho(\mathbf{r})]$ the classical Coulomb repulsion. The *nonclassical term* ($J_{nc} \equiv E_{xc}$) is called **exchange-correlation energy** (see Section 2.4) and it contains all the

[†]nondegeneracy of the ground-state is required for HK theorems to be valid. However, in Sec. 2.3 it is proved that such condition can be eliminated.

nonclassical (quantum) effects of interelectronic interactions. The exact form of the corresponding functional is, unfortunately, unknown.

The second HK theorem [1] (1964) provides in DFT – analogously to wave function theory – for the energy variational principle.

Theorem 2

“For a trial density $\tilde{\rho}(\mathbf{r})$, such that $\tilde{\rho}(\mathbf{r}) \geq 0$ and $\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = N$,

$$E_v[\tilde{\rho}(\mathbf{r})] \geq E_0 \quad ” \quad (2.2.6)$$

where the left-hand term is the *energy functional* defined in eq. 2.2.4.

Since it is assured that $\tilde{\rho}(\mathbf{r})$ determines a $\tilde{v}(\mathbf{r})$, the hamiltonian $\hat{H}(\mathbf{r})$ and the trial wave function $\tilde{\Psi}(\mathbf{r})$, the latter can be used for the problem defined by an external potential $v(\mathbf{r})$, thus yielding to the proof for the second theorem:

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F_{HK}[\tilde{\rho}(\mathbf{r})] = E_v[\tilde{\rho}(\mathbf{r})] \geq E_v[\rho(\mathbf{r})] \quad (2.2.7)$$

Assuming differentiable $E_v[\rho(\mathbf{r})]$, the stationary principle can be applied, leading to the Euler-Lagrange equation that defines the *chemical potential*, μ :

$$\mu = \frac{\delta E_v[\delta \rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = v(\mathbf{r}) + \frac{F_{HK}[\delta \rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \quad (2.2.8)$$

2.2.1 v- and N-representability of the electron density

Being the electron density minimized, it must satisfy two conditions, namely the *v-representability* and *N-representability*. The first one requests that such density truly corresponds to the ground-state density of a potential $v(\mathbf{r})$ – which is not necessarily a Coulomb potential – associated with the antisymmetric ground-state wave function of the Hamiltonian defined in eq. 1.1.2. The first HK theorem can be stated, in other words, as the fact that there is a unique mapping between a *v-representable* density and the ground-state wave function.

This leads to the determination of all the other ground-state properties. The universal functional – F_{HK} – in particular has to be *v-representable*. Since it enters in the definition of the variational principle, it is clear that both the HK theorems,

so the DFT itself, request a trial density to be v -representable. Unfortunately, the conditions for a density to be v -representable are still unknown. On the other hand, some reasonable expressions for trial densities have been demonstrated to be non v -representable.

However, DFT can be formulated in a way – vide infra, Sec. 2.3 – that the density only requires to satisfy the N-representability condition, i.e. to be obtained from an antisymmetric wave function. This constitutes a weaker condition with respect to the v -representability, because it is a necessary condition for the latter. Mathematically, the properties to be satisfied are:

$$\rho(\mathbf{r}) \geq 0 \quad ; \quad \int \rho(\mathbf{r}) d(\mathbf{r}) = N \quad ; \quad \int |\nabla \rho(\mathbf{r})^{1/2}|^2 d(\mathbf{r}) < \infty \quad (2.2.9)$$

2.3 The Levy-Lieb constrained-search

We have established the univocal correspondence between the ground state electron density and the ground-state wave function but still not the vice versa. In fact, the problem is that an infinite number of antisymmetric wave functions – not only from the ground-state – can yield to the same density.

If one chooses a proper trial wave function that integrates to the ground-state $\rho_0(\mathbf{r})$, e.g. $|\tilde{\Psi}_0\rangle$, he does have to distinguish it from the true ground-state $|\Psi_0\rangle$. This can be achieved by the procedure of Levy [3, 4], which makes use of the minimum energy principle for the ground-state:

$$\langle \tilde{\Psi}_0 | \hat{H} | \tilde{\Psi}_0 \rangle \geq \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E_0 \quad (2.3.1)$$

that yields to:

$$\begin{aligned} \langle \tilde{\Psi}_0 | \hat{T} + \hat{V}_{ee} | \tilde{\Psi}_0 \rangle + \int v(\mathbf{r}) \rho_0(\mathbf{r}) d\mathbf{r} &\geq \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle + \int v(\mathbf{r}) \rho_0(\mathbf{r}) d\mathbf{r} \\ \longrightarrow \quad \langle \tilde{\Psi}_0 | \hat{T} + \hat{V}_{ee} | \tilde{\Psi}_0 \rangle &\geq \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle \end{aligned} \quad (2.3.2)$$

We thus obtain that, amongst all the possible wave functions giving ρ_0 , only $|\Psi_0\rangle$ furnishes the lowest limit for the expectation value $\langle \hat{T} + \hat{V}_{ee} \rangle$, i.e. the true ground state density.

Since the right-hand side of eq. 2.3.2 corresponds to the universal functional $F_{HK}[\rho_0(\mathbf{r})]$, it is possible to write that:

$$F_{HK}[\rho_0(\mathbf{r})] = \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle = \min_{\Psi \rightarrow \rho_0} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \quad (2.3.3)$$

for any N-representable $\rho_0(\mathbf{r})$. Eq. 2.3.3 is the *constrained-search* definition for $F_{HK}[\rho_0(\mathbf{r})]$. This is a notable result, because the minimization of the expectation value of all the wave functions that lead to $\rho_0(\mathbf{r})$ is mapped into $F_{HK}[\rho_0(\mathbf{r})]$, which is defined, in turn, for the true ground-state wave function $|\Psi_0\rangle$.

The term “constrained” arises from the fact that the space chosen to search for the trial wave function comprises only those Ψ which give $\rho_0(\mathbf{r})$. This approach constitutes a further proof of the first HK theorem. Since in the latter a non-degeneracy condition is required for ground-state wave functions, the constrained-search even provides to remove it – because the trial wave functions are a subset of the $|\Psi\rangle$ belonging to the N -particles Hilbert space wherein the quantum Hamiltonian is defined.

A consequence of having defined the ground-state $F_{HK}[\rho_0(\mathbf{r})]$ for trial antisymmetric wave functions is that the N-representability condition holds instead of the v -representability, thus leading to the fact that the definition of $F_{HK}[\rho_0(\mathbf{r})]$ is extended to any v -representable $\rho_0(\mathbf{r})$.

Such property is useful since the whole Hamiltonian cannot be expressed for a subset of N-representable wave functions. In fact, it contains the external potential term, for which the summation over N implies a search for all the possible wave functions that furnish a v -representable $\rho_0(\mathbf{r})$.

In this context, Lieb demonstrated [5], more generally, the existence of the minimum:

$$F_{HK}[\rho(\mathbf{r})] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \quad (2.3.4)$$

valid for any N-representable $\rho(\mathbf{r})$.

This allows to extend the search of Levy for all the densities which minimize to $\rho_0(\mathbf{r})$ from a trial wave function that does not necessarily correspond to the true ground-state one ($|\Psi_0\rangle$).

Thus, putting all together, the total energy minimization is wisely carried out in a two-steps procedure:

$$\begin{aligned}
 E_0 &= \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_i^N v(\mathbf{r}_i) | \Psi \rangle \\
 &= \min_{\rho} \left\{ \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_i^N v(\mathbf{r}_i) | \Psi \rangle \right\} \\
 &= \min_{\rho} \left\{ \min_{\Psi \rightarrow \rho} \left[\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right] \right\} \quad (2.3.5)
 \end{aligned}$$

where the external minimization proceeds on searching the wave functions giving all the $\rho(\mathbf{r})$, whereas the internal one is constrained on the subset of $|\Psi\rangle$ that furnish only $\rho_0(\mathbf{r})$.

Expressing the equations above in terms of the universal functional, we finally get:

$$\begin{aligned}
 E[\rho(\mathbf{r})] &= F_{HK}[\rho(\mathbf{r})] + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \quad ; \\
 E_0 &= \min_{\rho} \left\{ F_{HK}[\rho(\mathbf{r})] + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right\} \\
 &= \min_{\rho} E[\rho(\mathbf{r})] \quad (2.3.6)
 \end{aligned}$$

2.4 The Kohn-Sham formulation of DFT

Kohn and Sham [2] (1965) introduced the concept of a *noninteracting reference system* built from a set of orbitals such that the major part of the kinetic energy can be computed to good accuracy. The remaining terms are merged with the nonclassical contributions to the electron-electron repulsion – which are unknown – but usually small.

Using this method, as much information as possible is computed exactly, leaving only a small part of the total energy to be determined by an approximate functional.

The exact formula for the ground state kinetic energy and for the density are, respectively:

$$T = \sum_i^N n_i \langle \psi_i | -\frac{\nabla^2}{2} | \psi_i \rangle \quad \rho(\mathbf{r}) = \sum_i^N n_i \sum_s |\psi_i(\mathbf{r}, s)|^2 \quad (2.4.1)$$

where ψ_i are the natural spin-orbitals and n_i their occupation numbers.

KS demonstrated that simpler expressions can be used, for that eq. 2.4.1 are substituted by their special cases for $n_i = 1$ for the N orbitals and $n_i = 0$ for the rest, as showed below:

$$T_s[\rho(\mathbf{r})] = \sum_i^N \langle \psi_i | -\frac{\nabla^2}{2} | \psi_i \rangle \quad \rho(\mathbf{r}) = \sum_i^N \sum_s |\psi_i(\mathbf{r}, s)|^2 \quad (2.4.2)$$

Such representation of kinetic energy and electron density is valid for a wave function that describes a system in a pure state, composed by N noninteracting electrons. Since any well-defined, reasonable density is N-representable – and it can be expressed in the form of eq. 2.4.2 – it can be *uniquely decomposed* in terms of orbitals, yielding to the definition of $T_s[\rho(\mathbf{r})]$ through eq. 2.4.2.

Analogously to the HK definition of the universal functional $F_{HK}[\rho(\mathbf{r})]$, KS formulated the corresponding noninteracting reference system by using the Hamiltonian:

$$\hat{H}_s = \sum_i^N \left(-\frac{\nabla_i^2}{2} \right) + \sum_i^N v_s(\mathbf{r}) \quad (2.4.3)$$

i.e. the portion of $\hat{H}$ where interelectron repulsion terms are not present, and for that the ground-state electron density is exactly determined by an antisymmetric detor (wave function), $|\Psi_s\rangle = \{\psi_i\}$. The latter is built on the set of N lowest eigenstates – ψ_i – of the one-electron Hamiltonian $\hat{h}_s$, that is given by:

$$\hat{h}_s \psi_i = \left[-\frac{\nabla^2}{2} + v_s(\mathbf{r}) \right] \psi_i = \epsilon_i \psi_i \quad (2.4.4)$$

so that the kinetic energy $T_s[\rho(\mathbf{r})]$ of eq. 2.4.2 corresponds to:

$$T_s[\rho(\mathbf{r})] = \langle \Psi_s | \sum_i^N \left(-\frac{\nabla_i^2}{2} \right) | \Psi_s \rangle \quad (2.4.5)$$

Thus, the universal functional $F_{HK}[\rho(\mathbf{r})] = F[\rho(\mathbf{r})]$ can be expressed in terms of $T_s[\rho(\mathbf{r})]$:

$$F[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + J[\rho(\mathbf{r})] + E_{xc}[\rho(\mathbf{r})] \quad (2.4.6)$$

whereas the exchange-correlation energy (E_{xc} , see also eq. 2.2.5) term includes, beyond the electron-electron nonclassical effects, the kinetic energy component that

leads to the exact kinetic energy of an interacting system – starting from a noninteracting one:

$$E_{xc}[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] - T_s[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] - J[\rho(\mathbf{r})] \quad (2.4.7)$$

The Euler-Lagrange equation for the chemical potential of eq. 2.2.8 becomes:

$$\mu = v_{eff}(\mathbf{r}) + \frac{\delta T_s[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \quad (2.4.8)$$

in which the *KS effective potential* is defined as:

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta J[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \quad (2.4.9)$$

In the above equation, the last term is the *exchange-correlation potential* – i.e. simply the partial derivative of E_{xc} with respect to the electron density.

These are the **Kohn-Sham equations**, that are treated as a system of noninteracting electrons moving inside an external potential $v_s(\mathbf{r}) = v_{eff}(\mathbf{r})$.

For a given $v_{eff}(\mathbf{r})$, the density $\rho(\mathbf{r})$ is determined by solving self-consistently the N one-electron (KS) Schrödinger equations:

$$\left[-\frac{\nabla^2}{2} + v_{eff}(\mathbf{r}) \right] \psi_i = \epsilon_i \psi_i \quad (2.4.10)$$

Following the previous equations, the **total KS-DFT energy** is thus given by:

$$\begin{aligned} E^{KS-DFT}[\rho(\mathbf{r})] &= T_s[\rho(\mathbf{r})] + J[\rho(\mathbf{r})] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{xc}[\rho] = \\ &= \sum_i^N \epsilon_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \end{aligned} \quad (2.4.11)$$

Equation 2.4.11 includes the definition of KS orbital eigenvalues, for which their summation – as in Hartree-Fock theory – does not correspond to the total energy:

$$\begin{aligned} \sum_i^N \epsilon_i &= T_s[\rho(\mathbf{r})] + \int v_{eff}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} = \\ &= E^{KS-DFT}[\rho(\mathbf{r})] + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \end{aligned} \quad (2.4.12)$$

2.5 The adiabatic connection and the XC hole

The definition of the *exchange-correlation hole* (XC hole), through the *adiabatic connection* method, consists of a powerful approach to link a noninteracting system to the interacting one in the framework of KS-DFT – and a first step to build approximations for the exchange-correlation functional.

The universal functional defined in Sec. 2.2 for the constrained search of the electron density $\rho(\mathbf{r})$ can be rewritten as:

$$F_\lambda[\rho(\mathbf{r})] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle = \langle \Psi_\rho^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_\rho^\lambda \rangle \quad (2.5.1)$$

where λ is a parameter that controls the strength of the interelectronic interactions – the *coupling strength parameter* – and Ψ_ρ^λ represents the wave function which minimizes $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$. Given that λ *connects* the noninteracting system ($\lambda = 0$) to the fully interacting one ($\lambda = 1$), we may express the corresponding two forms of $F[\rho]$ as:

$$\begin{aligned} F_1[\rho(\mathbf{r})] &= T[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] \\ F_0[\rho(\mathbf{r})] &= \tilde{T}_s[\rho(\mathbf{r})] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} | \Psi \rangle \end{aligned} \quad (2.5.2)$$

that, in turn, allow to define the exchange-correlation energy as in the following:

$$\begin{aligned} E_{xc}[\rho(\mathbf{r})] &= T[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] - \tilde{T}_s[\rho(\mathbf{r})] - J[\rho(\mathbf{r})] = \\ &= F_1[\rho(\mathbf{r})] - F_0[\rho(\mathbf{r})] - J[\rho(\mathbf{r})] = \int_0^1 \frac{\partial F_\lambda[\rho(\mathbf{r})]}{\partial \lambda} d\lambda - J[\rho(\mathbf{r})] \end{aligned} \quad (2.5.3)$$

thus, the difference between $F_1[\rho(\mathbf{r})]$ and $F_0[\rho(\mathbf{r})]$ gives rise to the adiabatic connection.

The variational search of eq. 2.5.1 can be carried out by making stationary the functional:

$$\langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle + \int (v_\lambda(\mathbf{r}) - E_\lambda/N) d\mathbf{r} |\Psi\rangle \quad (2.5.4)$$

The equation above obeys to the constraint for $\Psi \rightarrow \rho(\mathbf{r})$:

$$\rho(\mathbf{r}) = \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle = \langle \Psi | \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle \quad (2.5.5)$$

through the term $v_\lambda(\mathbf{r}) - E_\lambda/N$.

The Hamiltonian $\hat{H}_\lambda$ is thus written in the form:

$$\left(\hat{T} + \lambda \hat{V}_{ee} + \sum_i^N v_\lambda(\mathbf{r}_i) \right) |\Psi_\rho^\lambda\rangle = E_\lambda |\Psi_\rho^\lambda\rangle \quad (2.5.6)$$

Through the derivation of $\hat{E}_\lambda$ from the previous equation, we obtain that:

$$\frac{\partial F_\lambda[\rho(\mathbf{r})]}{\partial \lambda} = \langle \Psi_\rho^\lambda | \hat{V}_{ee} | \Psi_\rho^\lambda \rangle \quad (2.5.7)$$

which finally gives, for $E_{xc}[\rho(\mathbf{r})]$ (eq. 2.5.3):

$$E_{xc}[\rho(\mathbf{r})] = \int_0^1 \langle \Psi_\rho^\lambda | \hat{V}_{ee} | \Psi_\rho^\lambda \rangle d\lambda - J[\rho(\mathbf{r})] = \frac{1}{2} \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1) \bar{\rho}_{xc}(\mathbf{r}_{1,2}) \quad (2.5.8)$$

Above, we expressed $E_{xc}[\rho(\mathbf{r})]$ in terms of the classical Coulomb interaction between the density and a charge $\bar{\rho}_{xc}$ averaged over the parameter λ – leading to the adiabatic connection.

In fact, $\bar{\rho}_{xc}$ is the *average exchange-correlation hole*, built on the *average pair correlation function* $\bar{h}$:

$$\bar{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_2) \bar{h}(\mathbf{r}_1, \mathbf{r}_2) \quad (2.5.9)$$

The latter, in turn, is defined from the diagonal elements of the second-order density matrix for the interacting system, determined by Ψ_ρ^λ :

$$\int_0^1 d\lambda \rho_2^\lambda(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) [1 + \bar{h}(\mathbf{r}_1, \mathbf{r}_2)] \quad (2.5.10)$$

This allows to rewrite the exchange-correlation energy as:

$$E_{xc}[\rho] = \frac{1}{2} \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \bar{h}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.5.11)$$

The introduction of the average exchange-correlation hole yields to the sum-rule, for that the integrated charge of $\bar{\rho}_{xc}$ is normalized to -1, for a reference electron in $\mathbf{r}_1$:

$$\int \bar{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \int \rho(\mathbf{r}_2) \bar{h}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1 \quad (2.5.12)$$

this means that $\bar{\rho}_{xc}$ represents a hole around $\mathbf{r}_1$ with a positive unitary charge experienced by $\mathbf{r}_2$.

The average exchange-correlation hole can be split into two contributions, namely the *exchange hole* and the *correlation hole*, as in the following:

$$\bar{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \rho_x(\mathbf{r}_1, \mathbf{r}_2) + \rho_c(\mathbf{r}_1, \mathbf{r}_2) \quad (2.5.13)$$

where the two terms are constrained to satisfy eq. 2.5.12-2.5.13, by the relationships:

$$\int \rho_x(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1 \quad \text{and} \quad \int \rho_c(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0 \quad (2.5.14)$$

As for the average exchange-correlation hole, the total exchange-correlation energy is given by the sum of the exchange energy and the correlation energy:

$$\begin{aligned} E_{xc}[\rho(\mathbf{r})] &= E_x[\rho(\mathbf{r})] + E_c[\rho(\mathbf{r})] = \\ &= \frac{1}{2} \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1) \rho_x(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{2} \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1) \rho_c(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (2.5.15)$$

2.6 The Self-Interaction error and the HF/KS method

Even though standard KS-DFT contains an exchange term, it is affected by the *self-interaction error*, SIE (which is not present in HF, as discussed in 1.1.6). It is caused by the *local* form of the exchange interaction, which should be *nonlocal*, as the HF exact exchange is.

The SIE disappears only in one-electron systems, where the self-Coulomb repulsion is exactly canceled by the self-exchange term. This corresponds to an intrinsic *self-interaction correction* (SIC).

In many-electron systems, the one-electron SIE leads to an artificial stabilization of delocalized states, whereas the many-electron SIE (*N-SIE* – that is due to the nonlinear dependence of energy with respect of the particle number, for fractionally charged systems) leads to an incorrect description of band gaps, ionization potentials, electron affinities and other important properties.

The SIE issue could be partially solved by substituting the local KS-DFT exchange with a percentage of – or the full – HF nonlocal exchange. This gives rise to the hybrid HF/KS method (see also Sec. 3.3): the standard HF scheme can be thought as a DFT method without correlation, with an exact, nonlocal description

of the exchange potential. Thus, a full inclusion of the latter in DFT leads to a more rigorous physics – and only the correlation potential needs to be approximated. However, notice that since the KS-DFT requires the exchange potential to be local, the nonlocal HF one *is not the exact exchange contribution within the framework of DFT*. This means that the KS and HF/KS exchange must be related in some way (see e.g. [6]).

2.7 Exchange-correlation functional approximations

DFT is formally exact, but in practice approximations are needed to define the unknown exchange-correlation functional – $E_{xc}[\rho(\mathbf{r})]$. Many approximated expressions have been proposed in the past – and still now they are the main matter of development in DFT.

$E_{xc}[\rho(\mathbf{r})]$ approximations can be classified hierarchically following the so-called Jacob’s Ladder, proposed by Perdew [7] (Fig. 2.1), from the oldest and simplest ones to more recent and complex ones.



Figure 2.1: A “French version” of the Jacob’s Ladder for XC functionals: climbing the five rungs of DFT methods from the Hartree World to the Chemical Accuracy.

The ladder connects the HF approximation, where correlation is not taken into account, to the “Chemical Accuracy” of an ideal exact description of quantum properties that includes the true electron correlation by the inclusion of the description of virtual orbitals.

Starting by the lowest rung, we have:

- **LDA:** the Local Density Approximation (LDA) – also a spin-polarized variant (LSDA) exists – is the simplest expression for $E_{xc}[\rho(\mathbf{r})]$, based on the idea that exchange-correlation energy depends point by point only on the absolute value of the electron density:

$$E_{xc}[\rho(\mathbf{r})] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r})) \quad (2.7.1)$$

where $\epsilon_{xc}[\rho(\mathbf{r})]$ is the exchange-correlation energy for one electron.

Since it is based on the idea of the uniform electron gas (UEG), such approximation is still utilized to describe homogeneous, non-defective systems with a uniform distribution of charge density, for example bulk metals. However, the more inhomogeneous a system is, the more unreliable is the use of LDA approximations.

Functionals like the Dirac-Slater’s one (S) [8, 9] for exchange and the Vosko-Wilk-Nusair (VWN) [10] for correlation, or the von Barth-Hedin (VBH) one [11] for both exchange and correlation belong to the LDA family of functionals.

- **GGA:** the Generalized Gradient (or gradient corrected) Approximation (GGA) is a more accurate approximation of $E_{xc}[\rho(\mathbf{r})]$ and – as the successive rungs of the Jacob’s ladder – consists of an amelioration over LDA. Its expression for the exchange-correlation energy can be written as:

$$E_{xc}[\rho(\mathbf{r})] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})) \quad (2.7.2)$$

In this case, the gradient (first derivative with respect to spatial coordinates) of the electron density is also taken into account.

In particular, the exchange term contains an *enhancement factor* (F_x^{en}) that improves the local density. This allows to better describe inhomogeneous systems:

$$E_x[\rho(\mathbf{r})] = \int d\mathbf{r} \rho_x(\mathbf{r}) \epsilon_x(\rho(\mathbf{r})) F_x^{en}(s(\nabla \rho(\mathbf{r}))) \quad s(\nabla \rho(\mathbf{r})) = \frac{|\nabla \rho(\mathbf{r})|}{\rho^{\frac{4}{3}}(\mathbf{r})} \quad (2.7.3)$$

where $s(\nabla\rho(\mathbf{r}))$ is the *reduced density gradient*. The form of the enhancement factor of the Perdew-Burke-Ernzerhof (PBE) exchange term [12], for example, is given by:

$$F_x^{en}(s(\nabla\rho(\mathbf{r}))) = 1 + k - \frac{k}{1 + \frac{\mu}{k}s^2} \quad (2.7.4)$$

with the parameters $\mu = 0.22$ and $k = 0.804$ tuned on the Lieb-Oxford bound condition [13] and the asymptotic behavior of the uniform electron gas. Other popular GGA functionals are, e.g. the Perdew-Wang 91 (PW91 – exchange and correlation) [14], B88 (Becke 88 exchange) [15] and LYP (Lee-Yang-Parr correlation) [16].

- **meta-GGA:** this family of functionals (mGGA), beyond the density gradient, even takes into account of the Laplacian of density $\nabla^2\rho(\mathbf{r})$. However, more typically, nowadays mGGA indicates the inclusion of the Laplacian of occupied orbitals (τ):

$$E_{xc}[\rho(\mathbf{r})] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \tau(\mathbf{r})) \quad (2.7.5)$$

where τ , called *kinetic energy density* is:

$$\tau(\mathbf{r}) = \sum_i^{occ.} \frac{1}{2} |\nabla\psi_i(\mathbf{r})|^2 \quad (2.7.6)$$

Functionals like TPSS [17], VSXC [18] and PKZB [19] are among these.

- **hyper-GGA:** such functionals are devised to contain a fraction, or the full, HF exact exchange, beyond the DFT exchange correlation terms – based on the HF/KS method sketched before (Section 2.6). Common hybrid functionals are considered as semiempirical approximations to this 4th rung.

They can be broadly classified into three classes – briefly discussed in the next section – depending on the way the amount of the HF exchange is included in the expression of the total exchange-correlation energy:

- *global hybrids* (GH) – discussed more in detail in the next Section – in which the quantity of HF exchange is weighted by a constant parameter a ;
- *local hybrids* (LH), where the weighting parameter is function of the spatial position $a = a(\vec{r})$;

- *range-separated hybrids* (RSHs), in which the Coulomb potential $1/r_{ij}$ is subdivided, in general, in a long-range (LR) and in a short-range (SR) contribution – even triple subdivisions of $1/r_{ij}$ are made (LR, SR and middle range – MR). The HF exchange is then adopted in either the LR or SR part of the range separated exchange term.

A peculiar family of hybrid functionals – excepted for some purely local ones [20–22] – is constituted by the Minnesota functionals [23–27], which is a comprehensive collection of functionals based on the τ -mGGA approximation, and which are parametrized on very large benchmark sets for different properties.

- **5th rung**: the last rung, which does not have a particular name, includes functionals that have, in addition to the exact-exchange, also a partial contribution to the exact correlation. This is obtained by considering unoccupied (virtual) orbitals.

Post-HF-like techniques can be mixed with HF/DFT hybrids in a semiempirical way to obtain such correlation term.

This is the case of *double-hybrid* functionals like the B2PLYP method proposed by Grimme [28], which includes a weighted PT2 (second-order perturbation theory) correction to the DFT exchange-correlation energy obtained in a hybrid fashion. Many other double-hybrid functionals – devised on existing GGA/hyper-GGA ones – were proposed, e.g. 1DH-BLYP [29] and PBE0-DH [30] are only two of them.

2.8 Global hybrid functionals

In this section, the most popular HF/DFT hybrid functionals are briefly presented, since they are widely utilized as approximation for $E_{xc}[\rho(\mathbf{r})]$.[‡]In particular, global hybrids were mainly adopted for calculations in the present work of thesis.

A general definition for global hybrids can be expressed as:

$$E_{xc}^{GH} = aE_x^{HF} + (1 - a)E_x^{DFT} + E_c^{DFT} \quad (2.8.1)$$

The parameter a , that weights the HF exact exchange admixture, is the constant throughout the space of coordinates. For this reason, they are called *global*.

The difference between various methods depends on the choice of DFT exchange and correlation functionals and on the value of a . It can be reasonably tuned, taking account of physical implications and experimental data, in order to obtain best results.

One of the most popular hybrid functionals is the B3LYP [16, 31, 32]:

$$E_{xc}^{B3LYP} = (1 - a)E_{xc}^{LDA} + aE_{xc}^{\lambda=0} + b\Delta E_x^{B88} + c\Delta E_c^{LYP} + (1 - c)E_c^{LDA} \quad (2.8.2)$$

in which the parameters $a = 0.20$, $b = 0.72$ and $c = 0.81$ are based on the empirically fitted data (experimental atomizations, ionization energies and proton affinities) used originally to devise the B93 functional [32].

In the late 90s, Perdew and colleagues had the idea to try to remove the dependence from empirical parameters in favor of a more theoretical-based formulations. In this context, Adamo and Barone proposed another very popular hybrid functional: the PBE0 [33].

$$E_{xc}^{PBE0} = 0.25E_x^{HF} + 0.75E_x^{PBE} + E_c^{PBE} \quad (2.8.3)$$

where the amount of 25% of HF exact exchange was derived from theoretical reasonings through perturbation theory arguments. Such functional obtained great success thanks to the consistency with the most reliable semiempirical hybrids (e.g. B3LYP). Many other hybrid HF/GGA functionals were proposed using the same definition as in eq. 2.8.3, the general form is:

$$E_{xc}^{hyb} = 0.25E_x^{HF} + 0.75E_x^{GGA} + E_c^{GGA} \quad (2.8.4)$$

The outcome of global hybrids is that the exchange-correlation mixing parameter is supposed to balance the partial elimination of self-interaction (SI), by using the

[‡]for simplicity, in the present Section we do not write explicitly the dependence by $[\rho(\mathbf{r})]$.

exact-exchange, and the inclusion of non-dynamical correlation. However, there are noticeable limits to this approximation that are evidenced, e.g., by calculations of reaction barriers and spectroscopic data.

2.9 Including electron correlation into DFT

*Ye living ones, ye are fools indeed
Who do not know the ways of the wind
And the unseen forces
That govern the processes of life.*

*[Serepta Mason - Spoon River's Anthology]
Edgar Lee Masters*

As explained before, standard HF and DFT methods cannot recover the long-range electronic effects that originate the London dispersive forces.

This happens simply because such techniques do not include the true electron correlation, which is due both to statical and dynamical phenomena; in particular, the statical ones become important at long distances. However, even the dynamical fluctuation of charges due to the particles motion (which dominate at short distances) cannot be neglected, because correlation phenomena are ubiquitous and always present.

London forces – often wrongly addressed as van der Waals forces (vdW) – constitute only the long-range attractive contribution to vdW, not the repulsive one. Being of a coulombian electrostatic nature, the repulsive contribution is implicitly accounted for, by the classical Coulomb potential in either HF or DFT.

Though dispersion arises between quantum systems, it can be derived by a Taylor series expansion applied to the classical $1/R_{AB}$ Coulomb potential, which approximately describes vdW interactions between two atoms A and B (R is the interatomic distance): the attractive term – which represents the London dispersion – is given mostly by $-C_6/R_{AB}^6$, whereas terms of higher order contribute less.

$$E_{disp} = -\frac{C_6}{R_{AB}^6} - \frac{C_8}{R_{AB}^8} - \frac{C_{10}}{R_{AB}^{10}} - \dots \quad (2.9.1)$$

where the C_n coefficients depend on the nature of the system under investigation. This results by considering the attraction of A and B, due to an instantaneous dipole moment interaction induced by A on B, and vice versa, at long-range – hence, this kind of interaction owns a nonlocal character.

Since two (or more) atoms A and B interact in such a way, being in the electronic ground-state of one or two different systems, their correlation is influenced also by virtual orbitals – those representing, when occupied, the excited configurations. The use of a monodeterminantal basis-set to describe the wave function – as in HF and DFT – thus becomes inadequate. Nevertheless, the adoption of techniques which include a description of virtual orbitals, such as the post-HF ones (vide Sec. 1.3), could result impracticable for applicative purposes: e.g. the study of extended crystalline/amorphous systems.

To overcome such limitations, numerous schemes to describe dispersive interactions have been devised in the last years. They allow to combine the good computational scaling of DFT or hybrid HF/DFT methods with, in most cases, costless additive terms that take into account for dispersion in a more or less empirical way. More elaborate (and computationally demanding) schemes are nowadays demonstrating an accuracy often comparable with that of pure post-HF methods for many properties.

However, approximations always depend on the exchange correlation functional adopted, so that – like a density functional approximation – a universal expression for describing dispersive interactions in DFT cannot exist.

2.9.1 The Stairway to Heaven of dispersion

It should be reasonable to think that, besides the well-established Jacobs’s ladder classification, Klimeš and Michaelides (2012) [34] thought about a famous rock song of the ’70s (see figure below), when giving the name to their ladder for dispersion correction schemes.

Here, in a similar way, we summarize these approaches by starting from the zero-rung to the 4th-rung, where the considered criteria are the increasing accuracy (and, possibly, the physical rigour) and the computational cost.

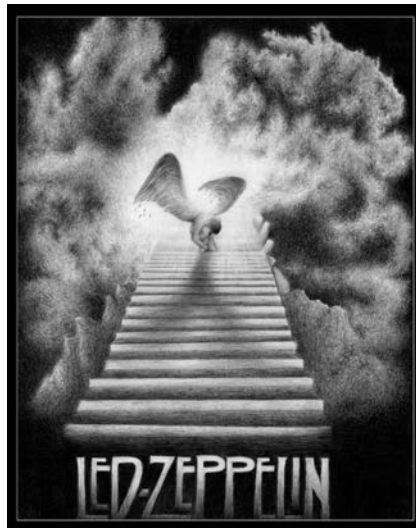


Figure 2.2: Led Zeppelin’s “Stairway to Heaven” is a nice way to imagine a classification ladder for dispersion correction schemes. (Source: Google Images for “Stairway to Heaven”, ©Atlantic Records, 1971, all rights reserved.)

The classification of dispersion-correction schemes includes:

Rung 0 – DCACP [35], LAP [36] and DCP [37]. Actually, these are not schemes but consist of one-electron, atom-centered pseudopotential basis-sets of empirical nature – fitted on binding energies – that partly recover the dispersive interactions. The three labels correspond to Dispersion-Corrected Atom-Centered Potential, Local Atomic Potential and Dispersion-Correcting Potential, respectively.

Rung 1 – Empirically fitted C_n – from the $-C_6/R^6$ expansion. Typically, only the first term of such expansion is considered. Long-range correlation is thus represented as a pairwise harmonic potential that is scaled by a *damping function*. The latter allows to recover the correct behavior of the potential at short-medium distances, i.e. it avoids singularity problems and the double-counting of correlation at such distances. This is the scheme proposed by Grimme (-D, -D2) [38, 39], for that the so-obtained dispersion contribution is

added *a posteriori* to the total KS-DFT energy:

$$E_{DFT-D} = E_{KS-DFT} + E_{disp} \quad (2.9.2)$$

$$E_{disp} = -s_6 \sum_A^{N_{At}-1} \sum_{B>A}^{N_{At}} f_{damp}(R_{AB}) \frac{C_6^{AB}}{R_{AB}^6} \quad (2.9.3)$$

$$\text{with} \quad f_{damp} = \frac{1}{1 + e^{-d\left(\frac{R_{AB}}{R_{vdW}} - 1\right)}} \quad (2.9.4)$$

where R_{AB} is the interatomic distance, C_6^{AB} are the dispersion coefficients for atoms A and B, R_{vdW} is the sum of vdW radii of the atoms A and B. In this case, the f_{damp} is that proposed by Wu-Yang [40].

d – the damping coefficient – and s_6 – the scaling factor – are tuned depending on the exchange-correlation functional used.

Different alternatives exist, according to the damping function adopted, or due to a different value of d and s_6 from the Grimme parametrization. For example, the -D* [41] is a variant of -D2, devised for B3LYP calculations on molecular crystals – where only d and s_6 change with respect to -D2.

Rung 2 – Structure- or electron density- dependent C_n . One scheme is the evolution of the Grimme -D2 scheme [39], the -D3 [42]: it considers (i) parameters derived *a priori* from KS-TDDFT (ii) two-body interactions as in the -D2 scheme, but also a higher order term of the expansion is taken into account (C_8) (iii) a three-body dispersion term which arises from geometrical considerations of perturbation theory on triplets of atoms (i.e. Axilrod-Teller-Muto [43, 44]) – that allows to define an atomic coordination-dependence of the C_9^{ABC} parameters. This method can be thus coupled with the Zero-damping function [45] or the Becke-Johnson damping function [46].

The total dispersion energy is thus calculated as the sum of the two-body and the three-body contributions: $E_{disp-D3} = E_{disp}^{(2)} + E_{disp}^{(3)}$.

Another *a posteriori* method consists of the Tkatchenko-Scheffler (TS) one [47]. In this case, the dependence of C_n is given by their dependence on atomic polarizabilities, whereas the interatomic distances depend on the atomic volumes. These last, in turn, are obtained from the Hirshfeld partitioning of the

electronic density [48].

The scheme of Becke and Johnson [46, 49–51], instead, is based on the eXchange-hole Dipole Moment (XDM) – that, from perturbation theory, defines an analytical form of the C_6 , C_8 and C_{10} pairwise coefficients and related vdW atomic radii. The physical argumentation is based on the dependence of such coefficients by the dipole-moment fluctuations of a (electron-density dependent) spherically behaved GGA-type exchange hole.

The alternative methods dDXDM [52] and dDsC [53] of Corminbeuf and co-workers evolve from the XDM model by including a density-dependence through different kinds of Hirshfeld partitioning and the use of the Tang-Toennies (TT) damping function [54].

Rung 3 – Long-range, non local density functionals. In this case, the whole vdW interactions are intrinsically included within the exchange-correlation functional approximation. Generally, the latter can be expressed as:

$$E_{vdW-DF} = E_x^{GGA} + E_c^{LDA} + E_c^{nl} \quad (2.9.5)$$

where the non-local correlation (E_c^{nl}) is somehow dependent by the C_6 dispersion coefficients, Diverse functionals were proposed following such approach (vdW-DF) [55], e.g. the VV10 non-local correlation [56]. A similar scheme is constituted by the vdW-DF2 [57], in which also a non-local exchange term is included.

Many of the Minnesota family of functionals[23–25] can be addressed to the present rung, as they are designed to include the description of noncovalent interactions. However, their parametrization is empirically obtained by fitting properties on large sets of training systems.

Rung 4 – Many-body dispersion terms, Random-Phase Approximation (RPA)/RPA derived methods, double-hybrid density functionals. All the mentioned approaches, in most cases, furnish an excellent degree of accuracy – comparable to that of post-HF methods – in predicting dispersive interactions. However, their computational cost is, in general, expensive.

As regards the inclusion of many-body dispersion terms, the above mentioned DFT-D3 scheme [42] can also be included at this level.

The MBD (Many-Body Dispersion) approach of Tkatchenko and colleagues [58–60] is a self-consistent implementation of the screening equation of classical electrodynamics, which includes the TS scheme (*vide supra*), for the description of polarization molecules and solids. Successively, the long-range many-body vdW energy is thus obtained by solving the Schrödinger equations for a system of coupled oscillators. This approach combines physical accuracy and a quite low computational demand.

The already mentioned double-hybrid density functionals (see above, Sec. 2.7) recover the major part of true correlation by the adopting a post-HF – usually a perturbative-type (as the second-order Perturbation Theory, PT2) – term to describe the long-range correlation, i.e. by describing also virtual orbitals. Such methods are in general quite accurate but, obviously, this depends on the bounty of the choosen DFT functional to predict the target properties and its mixing with the non-local correlation term. The main lacks of such methods are constituted by (i) the not totally consistent physical justification of including a post-wavefunction-virtual-orbitals-correlation term in the more rigorous frame of a ground-state (hybrid or not) density functional theory – such as KS or HF/KS-DFT – and (ii) the computational cost, which is comparable or often more expensive than that of pure post-HF methods.

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Chapter 3

Periodic quantum calculations

*This crystal can change you
into anything you want to be.
Quickly tell it your wish,
before it is too late.
Swiftly, speak your command,
before the stone vanishes.*

*[Piktor's Metamorphosis]
Hermann Hesse*

Since the applications of the present work of thesis concerned about solid crystalline materials, we report here the basic notions needed to practically solve the many-electron problem in periodic boundary conditions (PBC).

In particular, these equations hold for periodic LCAO codes – see, e.g. [1, 2] – which make use of localized functions such as gaussian-type orbitals (GTOs). This approach, when combined with a full exploitation of symmetry, constitutes a powerful instrument to deal with large, periodic compounds that often present a manifold structure – but that have some symmetry within the unit cell. This is especially the case of numerous molecular crystals with technological applications.

3.1 Reciprocal lattice and first Brillouin Zone

A *direct lattice* is constituted by an infinite group of points repeated at intervals of length a_1, a_2, a_3 along three non-coplanar directions. The three constants are called lattice parameters, and the corresponding a_1, a_2 , and a_3 vectors are the basis vectors that define the unit cell. Lattice parameters and angles between the basis vectors are called *cell parameters*.

A general vector $\mathbf{g}$ is a lattice vector defined as:

$$\mathbf{g} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (3.1.1)$$

that means, as a linear combination of the lattice parameters, where the $\{n_i\}$ are integers. A general position $\mathbf{r}$ in the unit cell is usually expressed in terms of fractional coordinates x_i , so that:

$$\mathbf{r} = x_1 \mathbf{a}_1 + x_2 \mathbf{a}_2 + x_3 \mathbf{a}_3 \quad (3.1.2)$$

If one considers two different positions – $\mathbf{r}$ and $\mathbf{r}'$ – for that $\mathbf{r}' = \mathbf{r} + \mathbf{g}$, they are equivalent, i.e. *translationally invariant*.

For any direct lattice a **reciprocal lattice** exists, defined through the following relationship:

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \quad (3.1.3)$$

where $\{\mathbf{b}_j\}$ are the basis vectors. Any reciprocal lattice vector can be written as a linear combination of the basis vectors, as shown for the direct lattice in eq. 3.1.1 – and a general position in the reciprocal lattice as a linear combination of the basis vectors with real coefficients:

$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3 \quad (3.1.4)$$

From equations 3.1.1 and 3.1.3, one finds that $\mathbf{g}$ and $\mathbf{K}$ are related by:

$$\mathbf{g} \cdot \mathbf{K} = 2\pi n \quad \exp(i\mathbf{g} \cdot \mathbf{K}) = 1 \quad (3.1.5)$$

Of particular importance for the reciprocal lattice is the Wigner-Seitz unit cell, which is obtained by connecting one point of the reciprocal lattice to all its nearest neighbors and letting orthogonal planes pass through their midpoints. The volume defined within these planes is the *first Brillouin Zone* (FBZ) and its value can be calculated as:

$$V_{FBZ} = (\mathbf{b}_1 \times \mathbf{b}_2) \cdot \mathbf{b}_3 = (\mathbf{b}_3 \times \mathbf{b}_1) \cdot \mathbf{b}_2 = (\mathbf{b}_3 \times \mathbf{b}_2) \cdot \mathbf{b}_1 \quad (3.1.6)$$

3.2 From local GTFs Basis-Set to Bloch Functions

A basis-set of local Gaussian-type functions (GTFs), that can be adopted to describe the atomic orbitals in cartesian coordinates, is defined as:

$$\gamma_\mu(\mathbf{r} - \mathbf{g}) = N Y_{\ell m}(\mathbf{r} - \mathbf{R}_\mu - \mathbf{g}) \exp[-\alpha(\mathbf{r} - \mathbf{R}_\mu - \mathbf{g})^2] \quad (3.2.1)$$

where μ labels the AOs, R_μ is the centroid of the Gaussian, for which the exponent is α , in the zero/reference cell, N is a normalization factor and $Y_{\ell m}$ is a real solid spherical harmonic. The variational basis-set usually consists of contractions of GTFs:

$$\chi_\mu(\mathbf{r} - \mathbf{g}) = \sum_j^{n_G} d_{\mu,j} \gamma_{\mu j}(\alpha_j; \mathbf{r} - \mathbf{R}_\mu - \mathbf{g}) \quad (3.2.2)$$

with n_G being the number of GTFs in the contraction and $d_{\mu,j}$ the coefficients of the GTF with the α_j exponent.

For an infinite lattice – made of an infinite number of atoms – the Hamiltonian matrix has infinite size. Thus, in order to solve the Schrödinger equation in periodic systems, a Bloch Function (BF) basis-set of AOs can be used, being defined from a given GTF basis-set. The advantage of adopting BFs is that the problem in PBC is reduced to the origin cell, i.e. more precisely to be solved for the k -points of the first Brillouin Zone.

BFs are expressed as a function of both the position $\mathbf{r}$ in the direct lattice and the wave vector $\mathbf{k}$, and are obtained by the Fourier Transform (FT) of AOs:

$$\phi_\mu(\mathbf{r}; \mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{g}} \exp(i\mathbf{k}\mathbf{g}) \chi_\mu^{\mathbf{g}}(\mathbf{r} - \mathbf{R}_\mu) \quad (3.2.3)$$

where $\mathbf{g}$ is a direct lattice translation vector and $\chi_\mu^{\mathbf{g}}$ is the μ AO in the $\mathbf{g}$ cell. BFs verify the *Bloch's theorem*, that can be written as:

$$\phi_n(\mathbf{r} + \mathbf{g}; \mathbf{k}) = \exp(i\mathbf{k}\mathbf{g}) \phi_n(\mathbf{r}; \mathbf{k}) \quad (3.2.4)$$

It provides a relationship among the values of an eigenfunction at equivalent points in the lattice, that is the starting function times a phase factor. If we consider a new point $\mathbf{k}' = \mathbf{k} + \mathbf{K}$, with $\mathbf{K}$ being a reciprocal lattice vector, from Bloch theorem it follows that:

$$\begin{aligned} \phi_n(\mathbf{r} + \mathbf{g}; \mathbf{k}') &= \exp(i\mathbf{k}'\mathbf{g}) \phi_n(\mathbf{r}; \mathbf{k}') = \exp(i(\mathbf{k} + \mathbf{K})\mathbf{g}) \phi_n(\mathbf{r}; \mathbf{k}') = \\ &= \exp(i\mathbf{k}\mathbf{g}) \exp(i\mathbf{K}\mathbf{g}) \phi_n(\mathbf{r}; \mathbf{k}') = \exp(i\mathbf{k}\mathbf{g}) \phi_n(\mathbf{r}; \mathbf{k}') \end{aligned} \quad (3.2.5)$$

for that we finally obtain:

$$\phi_n(\mathbf{r}; \mathbf{k}) = \phi_n(\mathbf{r}; \mathbf{k}') \quad (3.2.6)$$

that is a consequence of translation invariance: BFs are periodic functions with respect to $\mathbf{k}$, and have the same value when equivalent $\mathbf{k}$ points are considered. This very useful property allows to solve the problem of an infinite number of cells in periodic systems, because it allows to restrict the analysis of the k -points to the FBZ, as hinted before.

Moreover, BFs are eigenfunctions of translation operators and of all operators commuting with them, as the Hamiltonian one. This property again derives from the translation invariance.

3.3 Crystalline Orbitals

As Molecular Orbitals (MO) are linear combinations of AOs, Crystalline Orbitals (CO) can be defined by linear combinations of BFs, as in the following:

$$\psi_n(\mathbf{r}; \mathbf{k}) = \sum_j c_{jn}(\mathbf{k}) \phi_j(\mathbf{r}; \mathbf{k}) \quad (3.3.1)$$

The Schrödinger equation takes the form:

$$\hat{H} \psi_n(\mathbf{r}; \mathbf{k}) = E_n(\mathbf{k}) \psi_n(\mathbf{r}; \mathbf{k}) \quad (3.3.2)$$

where $\hat{H}$ is the Hamiltonian operator which corresponds either to the Fock operator (HF scheme) or to the Kohn-Sham operator (DFT scheme).

It would be nice to compare, at this point, the different expressions given by the HF and DFT schemes for the above equation:

$$\left[\underbrace{-\frac{1}{2}\nabla^2 + V(\mathbf{r})}_{\hat{h}_i} + \underbrace{\int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{\hat{j}} - \hat{K} \right] \psi_n^{HF}(\mathbf{r}; \mathbf{k}) = E_n^{HF}(\mathbf{k}) \psi_n^{HF}(\mathbf{r}; \mathbf{k})$$

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + \underbrace{\int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r})}_{V_{eff}(\mathbf{r})} \right] \psi_n^{KS}(\mathbf{r}; \mathbf{k}) = E_n^{KS}(\mathbf{k}) \psi_n^{KS}(\mathbf{r}; \mathbf{k}) \quad (3.3.3)$$

where the Hamiltonian operator changes only in the last term inside the square brackets (the Fock exchange operator becomes the Kohn-Sham exchange-correlation potential).

Before the crucial step of diagonalization, the AOs can be transformed to BFs and, in the BFs basis, the matrix equations for electronic problem can be solved for each k -point of the reciprocal space:

$$\begin{aligned} H(\mathbf{k}) C(\mathbf{k}) &= S(\mathbf{k}) C(\mathbf{k}) E(\mathbf{k}) \\ C(\mathbf{k}) S(\mathbf{k}) C^\dagger(\mathbf{k}) &= I \end{aligned} \quad (3.3.4)$$

where all matrices have equal size n_f , $S(\mathbf{k})$ is the overlap matrix, and $C(\mathbf{k})$ the eigenvector matrix. The $H(\mathbf{k})$ matrix corresponds either to the Fock matrix or to the Kohn-Sham matrix.

Importantly, the infinite Hamiltonian matrix in the AOs basis-set becomes an infinite block-diagonal matrix in the BFs basis-set (see Figure 3.1). Each block refers to each different k -point, and the infinite number of $n_f \times n_f$ blocks, where n_f is the number of BFs, are independent from each other and can be treated separately.

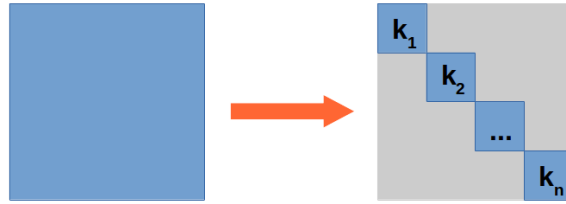


Figure 3.1: Transformation of the H-matrix from the AOs basis-set (left) to the block-diagonal BF basis-set (right). The problem of an infinite size turns to an infinite number of problems of finite size.

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– Part II –

Excited-state properties and multiscale methods

Chapter 4

Time-Dependent Density Functional Theory

*Avec le temps...
avec le temps tout s'en va...
[...] alors vraiment,
avec le temps on n'aime plus.*

*[Avec le temps]
Leo Ferré*

In this chapter we briefly expose the principles of time-dependent DFT (TD-DFT), since we adopted such level of theory for the QM study of optical (excited-state) properties of organic molecular crystals (see Chapter 8).

As mentioned in the previous chapters, the use of post-HF methods is required when the contribution of correlation has to be very finely balanced – in the present case between ground- and excited- states; moreover, the use of multideterminantal theories is required in order to correctly describe challenging properties, e.g. photochemical processes involving quasi-degenerate states.

However such methods are very costly for small-sized systems: their use for extended systems (hundreds of atoms) is generally prohibitive.

In the last years, TD-DFT reached a certain level of reliability, thanks to the efforts that brought to safely transpose the KS theorems into a time-dependent fashion, even that some formal problems on its domain of application remain: the (time-independent) DFT was devised on the electronic ground-state.

Thus, even including some lacks, TD-DFT is becoming widely used in computational chemistry because provides, in general, good estimations of many different time-dependent properties. Of course, its accuracy depends by the complexity of the studied processes, and by the density functional approximation used. Indeed, another issue is due to the fact that most of the DFs are devised for time-independent calculations.

However, some recent approaches to the design of density functionals – as, for example, long-range separation/coulomb-attenuated methods [1] – have demonstrated to lead to reliable results – beyond the more typical prediction of UV-Visible optical properties – in the study of dynamical electronic processes that include Rydberg excitations, charge-transfer, etc. [2, 3]

In the following, basic notions concerning TD-DFT are thus presented – other time-dependent theories are not discussed here.

4.1 Time-dependent KS equations: RG theorems

For our purpose, we firstly consider the Schrödinger equation, for a N -electron system within the Born-Oppenheimer approximation, in its time-dependent fashion:

$$\hat{H}(t)\Psi(t) = i\frac{\partial}{\partial t}\Psi(t) \quad (4.1.1)$$

where the Hamiltonian operator corresponds to:

$$\hat{H}(t) = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en}(t) \quad (4.1.2)$$

The first and second term correspond, respectively, to the kinetic energy and to the electron-electron repulsion of the time-independent case (see Chapter 1), whereas the third term – the time-dependent external potential – is given by:

$$\hat{V}_{en}(t) = \hat{V}_{ext}(t) = \sum_{i=1}^N v(\mathbf{r}_i, t) \quad (4.1.3)$$

which is assumed constant for $t < t_0$. This describes an interacting system for that a time-dependent (electric) field is switched-on at t_0 (t_0 denotes the initial condition). The first issue is to obtain the expectation values as functionals of the time-dependent charge density.

Runge and Gross (RG), with their theorem [4], showed that the time-dependent charge density determines the wave function up to a time-dependent phase factor, i.e.:

$$\Psi(t) = e^{-i\phi(t)} \Psi[\rho, \Psi_0](t) \quad (4.1.4)$$

where Ψ_0 represents the wave function at $t = t_0$. The external potential $v(\mathbf{r}, t)$ is determined by the electronic density, up to a spatially constant time-dependent function, namely $c(t)$ – the current density. This definition works if the external potential is represented by an electric potential due to a normalized charge density, and if its time-dependent behavior can be expressed through a Taylor's series about $t = t_0$.

The proof of the RG theorem, in particular, first shows the dependence of $v(\mathbf{r}, t)$ by the current density and, successively, provides to eliminate such dependence in favor of the charge density alone.

It is assumed that Ψ_0 is determined by the stationary ground-state initial charge density, $\rho_0 = \rho(t_0)$. As a consequence, equation 4.1.4 can be simplified by eliminating Ψ_0 :

$$\Psi(t) = e^{-i\phi(t)} \Psi[\rho] \quad (4.1.5)$$

where Ψ is determined only by ρ .

The second KS theorem [5] (see Chapter 2) was transposed by Runge and Gross to the time-dependent theory [4], by applying the variational principle to a new concept, represented by the *action* A:

$$A = \int_{t_0}^{t_1} \langle \Psi(t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi(t) \rangle dt \quad (4.1.6)$$

The action is made stationary by the true TD density, i.e. the variational principle is given by:

$$\frac{\delta A}{\delta \rho(\mathbf{r}, t)} = 0 = \int_{t_0}^{t_1} \langle \frac{\delta \Psi(t)}{\delta \rho(\mathbf{r}, t)} | i \frac{\partial}{\partial t'} - \hat{H}(t') | \Psi(t') \rangle dt' + \text{compl. conj.} \quad (4.1.7)$$

Using eq. 4.1.5, and the expression for the action, we can rewrite A, up to a constant phase factor ϕ , as:

$$A = \int_{t_0}^{t_1} \langle \Psi[\rho](t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi[\rho](t) \rangle dt + \phi(t_1) - \phi(t_0) = A[\rho] + \text{const.} \quad (4.1.8)$$

When the variational condition is utilized, an analogue of the second HK theorem is therefore provided in time-dependent theory.

The action functional A can also be rewritten as in the following:

$$A[\rho] = B[\rho] - \int_{t_0}^{t_1} \int v(\mathbf{r}, t) \rho(\mathbf{r}, t) d\mathbf{r} dt \quad \rho(\mathbf{r}, t) = \sum_i f_i |\psi_i(\mathbf{r}, t)|^2 \quad (4.1.9)$$

where the B functional is independent by the external potential (it is universal) and where – as in DFT – a noninteracting reference system is considered. This is done by introducing the effective potential ($v_{eff}(\mathbf{r}, t)$) for a noninteracting system, whose orbitals yield the same charge density of the interacting ones (see above, the second term of eq. 4.1.9).

The existence or not of such kind of $v_{eff}(\mathbf{r}, t)$ constitutes the “time-dependent v-representability problem”.

In terms of the definitions given before, the universal functional B – which corresponds to the universal functional F_{HK} in DFT – can be finally defined as:

$$B[\rho] = \sum_i f_i \int_{t_0}^{t_1} \langle \psi_i(t) | i \frac{\partial}{\partial t} - \frac{1}{2} \nabla^2 | \psi_i(t) \rangle dt + \\ - \frac{1}{2} \int_{t_0}^{t_1} \iint \frac{\rho(\mathbf{r}_1, t) \rho(\mathbf{r}_2, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 dt - A_{xc}[\rho] \quad (4.1.10)$$

where the functional A_{xc} is analogous to the exchange-correlation energy (E_{xc}) of DFT.

The minimization of the action leads to the **time-dependent Kohn-Sham equations**:

$$\left[-\frac{\nabla^2}{2} + v_{eff}(\mathbf{r}, t) \right] \psi_i(\mathbf{r}, t) = i \frac{\partial}{\partial t} \psi_i(\mathbf{r}, t) \quad (4.1.11)$$

with:

$$v_{eff}(\mathbf{r}, t) = v(\mathbf{r}, t) + \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}, t) \quad (4.1.12)$$

The exchange-correlation potential is thus formulated in terms of the exchange-correlation action functional [6]:

$$v_{xc}(\mathbf{r}, t) = \frac{\delta A_{xc}[\rho]}{\delta \rho(\mathbf{r}, t)} \quad (4.1.13)$$

Even if unknown, within the context of the adiabatic approximation – i.e. in the limit of a slowly varying (in time) $v_{eff}(\mathbf{r}, t) - A_{xc}$ can be expressed in function of the stationary ground-state exchange-correlation energy:

$$A_{xc} = \int_{t_0}^{t_1} E_{xc}[\rho_t] dt \quad (4.1.14)$$

where ρ_t is a density evaluated at a certain fixed time t . The time-dependence of A_{xc} is then exploited by integrating over t the only spatially-dependent E_{xc} . This constitutes a local approximation (beside space) also in the time domain.

From the previous equation, a relationship connecting DFT and TD-DFT can be given for the TD exchange-correlation potential within the adiabatic approximation:

$$v_{xc}[\rho](\mathbf{r}, t) = \frac{\delta A_{xc}[\rho]}{\delta \rho(\mathbf{r}, t)} \cong \frac{\delta E_{xc}[\rho_t]}{\delta \rho_t(\mathbf{r})} = v_{xc}[\rho_t](\mathbf{r}) \quad (4.1.15)$$

The above expression, however, implies a neglect of retardation effects, since an instantaneous reaction of the self-consistent field to the perturbed density takes place.

4.2 Linear response theory in TD-DFT

TD-DFT alone is not sufficient to get excited-states properties, i.e. it has to be combined with a perturbation from which a change in the charge density arises and brings the system out of a steady unperturbed state.

For brevity, we give here only some hints on linear response theory (within the context of TD-DFT), just those necessary to obtain some interesting properties for applications (e.g. optical absorption and emission spectra), that can be derived from the calculation of vertical excitation energies and oscillator strengths.

The perturbation is introduced in the KS Hamiltonian by switching on an applied field – $\delta v_{appl}(\mathbf{r}, t)$:

$$\delta v_{eff}^\sigma(\mathbf{r}, t) = \delta v_{appl}(\mathbf{r}, t) + \delta v_{SCF}^\sigma(\mathbf{r}, t) \quad (4.2.1)$$

where, for convenience, the spin-unrestricted formalism is made explicit. The $\delta v_{SCF}^\sigma(\mathbf{r}, t)$ corresponds to the linear response of the self-consistent field to the applied field, that results in a change of the charge density.

$\delta v_{appl}(\mathbf{r}, t)$ is assumed to be turned on slowly (adiabatic approximation in time) at $t = t_0$ in a distant past.

Thus, the linear response of the density matrix (δP) in the frequency domain, is expressed as:

$$\delta P_{ij\sigma}(\omega) = \frac{f_{j\sigma} - f_{i\sigma}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} \delta v_{ij\sigma}^{eff}(\omega) \quad (4.2.2)$$

which is written in term of the unperturbed molecular orbitals (ϵ_{xx}) and their occupation numbers (f_{xx}). Here the linear response of the true density is given, but not that of the true density matrix. A complication is given by the fact that, in turn, also $\delta v_{SCF}^\sigma(\mathbf{r}, t)$ depends by δP :

$$\delta v_{ij\sigma}^{SCF}(\omega) = \sum_{kl\tau} K_{ij\sigma,kl\tau}(\omega) \delta P_{kl\tau}(\omega) \quad (4.2.3)$$

where $K_{ij\sigma,kl\tau}(\omega)$ is the *coupling matrix*.

The adiabatic approximation furnishes real values for MOs, and consequently the coupling matrix loses its dependency by ω .

All these elements can be combined to get a step-back and finally derive the **Casida's equations** – that yield to a suitable matrix relationship between the linear response density matrix and the applied field:

$$\left\{ \begin{bmatrix} \mathcal{A}(\omega) & \mathcal{B}(\omega) \\ \mathcal{B}(\omega) & \mathcal{A}(\omega) \end{bmatrix} - \omega \begin{bmatrix} \mathcal{C} & 0 \\ 0 & \mathcal{C} \end{bmatrix} \right\} \begin{bmatrix} \delta \vec{P}(\omega) \\ \delta \vec{P}^*(\omega) \end{bmatrix} = \begin{bmatrix} \delta \vec{v}_{appl}(\omega) \\ \delta \vec{v}_{appl}^*(\omega) \end{bmatrix} \quad (4.2.4)$$

with:

$$\begin{aligned} \mathcal{A}_{ij\sigma,kl\tau}(\omega) &= \delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l} \frac{\epsilon_{k\tau} - \epsilon_{l\tau}}{f_{k\tau} - f_{l\tau}} - K_{ij\sigma,kl\tau}(\omega) \\ \mathcal{B}_{ij\sigma,kl\tau}(\omega) &= -K_{ij\sigma,lk\tau}(\omega) \quad \mathcal{C}_{ij\sigma,kl\tau} = \frac{\delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l}}{f_{k\tau} - f_{l\tau}} \end{aligned}$$

4.3 Excitation energies and oscillator strengths

Excitation energies and oscillator strengths can be derived from the poles and residues of the dynamic polarizability. The latter, in turn, is subject – in the case of an interaction of matter with light – to an electric field that varies sinusoidally in time.

Considering a real perturbation, only the real part of $\delta\vec{P}$ is necessary to be computed:

$$\left(\text{Re } \delta\vec{P}\right)(\omega) = \mathcal{S}^{-1/2} \left\{ \omega^2 \mathbf{1} - \mathbf{\Omega}(\omega) \right\}^{-1} \mathcal{S}^{-1/2} \delta\vec{v}_{apl}^*(\omega)$$

where:

$$\mathbf{\Omega}(\omega) = -\mathcal{S}^{-1/2}(\mathcal{A} + \mathcal{B})\mathcal{S}^{-1/2} \quad (4.3.1)$$

The excitation energies correspond to the solutions of the pseudoeigenvalue problem defined as:

$$\mathbf{\Omega}(\omega)\vec{F}_I = \omega^2\vec{F}_I \quad (4.3.2)$$

whereas the eigenvectors $\vec{F}_I$ correspond to the oscillator strengths.

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Chapter 5

Multiscale methods

Often, pursuing the quest of modelling accurately large systems becomes a very challenging task. In fact, the computational demand of atomistic methods scales unfavorably while increasing the system size, N .

This is true especially for amorphous compounds, for example proteins, glasses and macromolecules in general, with low- or no-symmetry. Furthermore, even accurate calculations on molecules, clusters and crystalline solids – characterized, in their ideal state, by a certain level of symmetry – become challenging because of a subsequent symmetry breaking that can be due to many different reasons (addition/modification of functional groups, conformational changes, insertion of defects).

Multiscale methods, such as ONIOM (Our N-layered Integrated molecular Orbital molecular Mechanics) [1] can provide to solve this issue. ONIOM is a multiscale method that allows to assign different degrees of accuracy (in terms of levels of theory) to the different layers of an onion-like sphere model that contains the whole system. Thus, the different regions of the system are modeled with diverse methods within a unique procedure.

The basic idea is to predict with accuracy (quantum mechanical level, QM) the processes (and related properties) that take place within the core region (high-level layer) – i.e. wherein the most interesting physico-chemical events are happening – and to model with a minor accuracy (molecular mechanics level, MM) the effects

given by the surrounding environment (low-level layer) to the region where the investigation is mainly focused.

In particular, to achieve a reliable estimation of the total energy, three calculations (or one, in the case of an automated procedure) are done:

- the total energy of the whole system (real system) is computed adopting the low level method, that gives $E_{(low,real)}$.
- the total energy of the high-level layer (model system) is computed with the high level method, that gives $E_{(high,model)}$.
- the total energy of the high-level layer (model system) is computed with the low level method, that gives $E_{(low,model)}$.

$E_{(high,model)} - E_{(low,model)}$ furnishes an estimation of the energy correction that must be applied to the model system. This difference is additive with the correction for the real system: $E_{(low,real)} - E_{(low,model)}$, from which the total ONIOM energy can be extrapolated as:

$$E_{real}(ONIOM) = E_{(high,model)} + E_{(low,real)} - E_{(low,model)} \quad (5.0.1)$$

The ONIOM method involves, typically, a QM/MM calculation. The system can be subdivided, if needed, also in three layers (high/medium/low).

Lots of combinations are possible when choosing the level of theory: the high layer is, generally, a DFT or a post-HF method, whereas the lower one(s) can be MM or semiempirical methods (e.g. PM3, NDO, etc.).

It is even possible to use QM methods for all layers, but always keeping the difference of accuracy between layers: in this case, the method is called QM/QM' (for example DFT (high level)/HF (low level)).

As regards the layers, their boundaries can deliberately be chosen according to the purpose of the investigations: the borders can virtually 'cut' covalent bonds, or the space between two molecules where only vdW interactions are present. In the case of a solute-solvent system, the choice can be easier than in other cases: usually, the central molecule (solute) is treated as high-level, whereas the solvent molecules are treated at low level.

5.1 Environmental effects

When one has to deal with properties of the model system that are non-negligibly affected even by small changes in the environment, a consistent *embedding* between the high- and low- level layers should be exploited.

In fact, when the interaction between the two regions is treated entirely by the low level of theory to derive the ONIOM extrapolated energy (see equation 5.0.1 above), this constitutes only a *mechanical embedding* (ME).

In ONIOM-ME calculations there is no real coupling between the wave function of the high-level layer and the surrounding low-level-layer for the model system. This means that the electronic effects between layers are included only at the low level of theory, when the real system calculation (low level) is performed.

An improvement on the ONIOM-ME model is given by the inclusion of the charge distribution of the low-level layer into the model system calculation, procedure which is called *electronic embedding* (EE) [2].

The ONIOM-EE approach allows the charge distribution of the low-level layer to polarize the wave function of the model system, thus leading to include the electrostatic interaction between the regions by integrating over the charge density of the high-level layer.

In the case of QM/QM' + EE calculations [3, 4] as, for example, those discussed in Chapter 8, the Mulliken charges obtained from the low-level QM' calculation polarize the model system, which is treated at high-level (QM).

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Applications

*We did everything adults would do.
What went wrong?*

*[Lord of the flies]
William Golding*

*Physical chemistry is all very well,
but it does not apply to organic substances.*

Sir William Perkins

Conspectus

The structures of crystalline polymorphs can be investigated within the context of Crystal Structure Prediction (CSP), a successful computational methodology that helps to predict the most probable stable/metastable crystal packing arrangements. This model is based on the generation of all the possible packing arrangements of a given atom or molecule – in terms of space groups – to find the three-dimensional structures that furnish the lowest lattice energies [1].

An accurate computational characterization of molecular crystals, however, represents a great challenge for solid-state chemistry, because of the difficulty in describing noncovalent forces, such as dispersive interactions, that can only be accounted for by correlated wave function methods [2–4] or by the Quantum Monte Carlo (QMC) method [5]. Recently, post-Hartree Fock methods became available also for crystalline systems [3, 6–9], and molecular crystals have been used as to benchmark them [10–16]. These methods furnish accurate predictions, but they are computationally very expensive.

On the other hand, DFT is powerful and less demanding, and allow us to model quite accurately the structural and electronic properties of molecular crystals, though a certain degree of approximation is implied.

In fact, standard DFT cannot correctly describe the long-range attractive ($1/R^6$) interaction tail for separated molecules [17], but it constitutes, nonetheless, a fertile environment for the development of methods that can take into account for dispersion [18]. Numerous schemes have been proposed, in the last years, to take into account dispersive forces (see Section 2.9.1). Briefly, some of them involve the *a posteriori* formulation of a London-type pairwise potential, in different flavours [19–25] based on either empirical parameters (as the DFT-D2 scheme [19] and its enhanced D3 version [26]) or non-empirical parameters (like the exchange-dipole

moment model [27], the Tkatchenko-Scheffler (TS) scheme [24]). More complex but rigorous approaches are constituted by the TS scheme with the inclusion of many-body electrodynamic dispersion (MBD) effects [28]) and non-local DFT functionals (e.g. vdw-DF [29] and VV10 [30]).

When this project of thesis started, some of the schemes mentioned above were still under development or they were still not implemented in the most common quantum chemistry packages.

Schemes like D* [25] or TS [24], however, previously demonstrated to provide a good balance between results – in terms of structures and energetics – and computational efficiency, for compounds governed by noncovalent interactions.

Therefore, we decided to adopt such schemes – combined with GGA or hybrid HF/GGA functionals – in order to investigate and characterize different challenging molecular crystals.

Our research strategy led to significant advancements:

1) in the understanding of polymorphism and relative stability between polymorphs.

- Para-diiodobenzene (p-DIB) is a simple apolar organic molecule; however, its computational characterization is nontrivial. This is due to the difficulty of common DFT techniques to recover the contribution of dispersive forces to the energy of the system, leading to a wrong description of the crystal structure. This lack affects severely the prediction of all the ground-state properties, e.g. the relative stability between its two polymorphs – α and β .

In particular, the adoption of DFT methods without dispersion-correction leads, usually, to a reversed stability between α and β (the correct one is, experimentally, α more stable than β). As noted before, the use of schemes for dispersion-correction, when carrying out DFT geometry optimizations on molecular crystals, should be mandatory.

However, in a previous study [31] it was shown that high-level diffusion Monte Carlo (DMC) succeeds in the prediction of relative stability, whereas the failure of DFT in general was even highlighted. On the contrary, we demonstrated that – if a proper correction for dispersive forces is used – DFT

can safely be employed to predict the energy ordering of p-DIB polymorphs with an accuracy comparable to that yielded by DMC calculations.

- The energetic features of the five known polymorphs of oxalyl dihydrazide (ODH) are characterized by the competition between different types of hydrogen bond (HB) and vdW forces between π -stacked molecules: this makes ODH another challenging system for computational DFT investigations. Indeed, also the incompleteness of experimental data [32], as regards the stability of the different polymorphs, encouraged our theoretical study.

We adopted different DFT/hybrid-DFT methods [33–35] – and we coupled them with different corrections for dispersive interactions [19, 24, 26], and the B3LYP [35] with the geometrical-CounterPoise (gCP) correction [36].

The benchmark between dispersion-corrected DFT and the high-level Local-MP2 (LMP2) post-HF method allowed us to assess the accuracy of the mentioned schemes in relation to energetics and to the stability ordering of the ODH polymorphs.

We showed that, in spite of a larger stability range, also in this case dispersion-corrected DFT results are comparable to those of higher-level methods.

2) in the study of polymorphism and the structural characterization of a host-guest system, the [(p-cymene)Ru(*k*N-INA)Cl₂]. This Ru(II) complex (host) constitutes, within its solid polymorphs, a complicated framework of hydrogen-bond interactions. Its main feature is the inclusion (in the **1·H₂O** hydrate form) of water molecules (guests), that make the crystal hygroscopic – the inclusion/extraction of water is a thermally-regulated reversible process. By modifying host and guest molecules, this class of compounds can find applications in numerous fields, such as drug delivery.

The metastability of different phases of [(p-cymene)Ru(*k*N-INA)Cl₂] made the analysis of experimental measures difficult [37]. Since we also noticed some lacks in the interpretation of structural data [37, 38], we made use of advanced tools, such as the DFT calculation (PBE-GIPAW [39, 40]) of solid-state ¹³C/¹H NMR chemical shifts (δ_{iso}) of the four crystalline forms (**1 α** ,

$1\cdot\text{H}_2\text{O}$, 1β and 1γ).

The comparison with experiment, both in terms of δ_{iso} and simulated NMR spectra highlighted the reliability of DFT in predicting such properties, provided that dispersion-correction DFT is used in the preliminary phase of geometry optimization of the experimental structures.

3) in the study of basic photophysical/photochemical properties of a thermochromic molecular crystal, the β polymorph of salicylidene aniline (SA). Though numerous experimental works are present in literature for the SA molecule, its optical features in solid-state are still lacking. In fact, after the structural revision of known polymorphs made by Arod et al. [41], no experimental studies of SA in solid-state were available, and the mechanism of the thermochromic processes is still unknown, as well as the crystal structure of the excited-states intramolecular proton transfer (ESIPT) products (cis-keto or trans-keto tautomers). This process however, is similar to the molecular one, where the enol form of SA, upon thermal- (or photo-) irradiation undergoes to electronic excitation and successively, to the ESIPT process that brings the enol form to the cis-keto form. The latter can also give cis-trans tautomerization.

We thus studied SA computationally, in its solid form, for the first time. Our study was carried out by establishing a protocol which combines the ground-state periodic dispersion-corrected DFT optimization of experimental structures and the use of cluster of molecules cut out from the optimized solid. These last were investigated by time-dependent QM/QM' ONIOM techniques to obtain UV-Visible absorption features of the crystalline material. The introduction of a charge embedding model [42] in QM/QM' calculations, was needed to reproduce the influence of the surrounding environment – always in the enol form – to the optical properties of the central molecule – in the enol-, cis-keto and trans-keto forms.

Overall, we showed that the results encourage the application of our protocol to similar molecular crystals with interesting optical features.

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Chapter 6

Polymorphism and stability of p-diiodobenzene and oxalyl dihydrazide

6.1 p-diiodobenzene (p-DIB)

In a quite recent work [1], different exchange-correlation functionals (that is, the LDA approximation of Ceperley and Alder [2] parametrized by Perdew and Zunger [3], pure GGA functionals PW91 [4] and PBE [5], and the popular B3LYP [6]) were benchmarked against diffusion MonteCarlo (DMC) calculations in order to predict the relative stability of the α and β forms of para-diiodobenzene (p-DIB) molecular crystal (displayed in Figure 6.1).

Such a compound, in its solid form, is widely used in chemical and pharmaceutical industry as precursor for other chemical substances, e.g. the production of polymers and elemental iodine [7], and it is studied, as well, because it shows high-pressure-induced dissociation processes [8]. Its crystalline molecular forms are characterized by a relatively simple structure which, however, represents a challenging target for the theoretical determination of the polymorphism and relative stability by quantum methods.

In the work mentioned before [1], Hongo and co-workers showed that DMC succeeds in reproducing the relative stability of the two polymorphs at zero tem-

perature, while the conventional DFT functionals fail, and the B3LYP functional augmented with a dispersion-correction term proposed by Grimme [9] markedly overestimates the stability magnitude of the α -phase in comparison with the β one, leading to a strong contraction of the cell volume.

On the contrary, here [10] it is shown that, if a proper correction for dispersive forces is used, DFT can be reliably employed to predict the energy ordering of the α and β forms of *p*-DIB molecular crystal with an accuracy comparable to that furnished by DMC calculations.

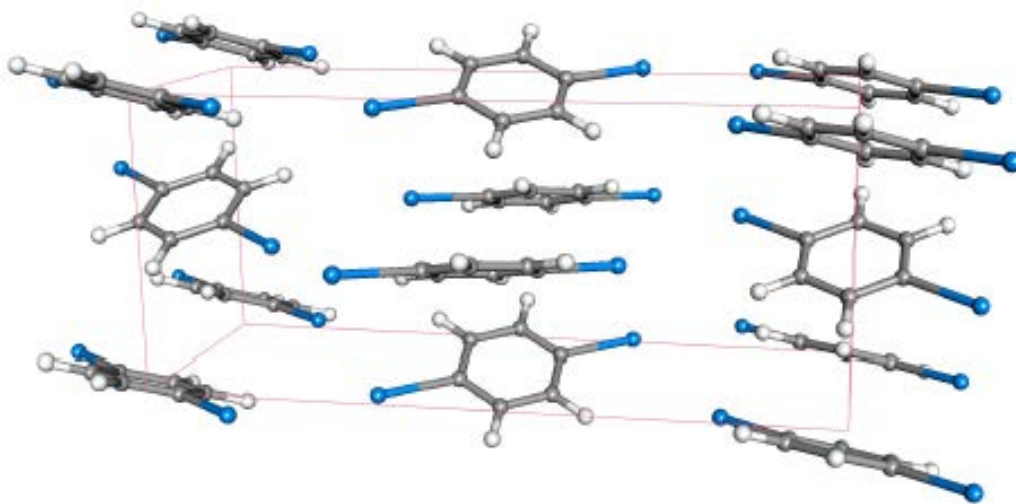


Figure 6.1: Perspective view of the α -polymorph of para-diiodobenzene (*p*-DIB). The unit cell, in violet, contains only four molecules.

6.1.1 Relative stability of *p*-DIB

As a first step, single point calculations (all the computational details are given in Appendix A) on the experimental structures have been performed to evaluate the relative energy stability between the two phases. The energy differences – $\Delta E = E(\alpha) - E(\beta)$ – computed with the conventional and TS and D empirical dispersion-corrected PBE, PBE0 and B3LYP functionals, are displayed in Figure 6.2. The results obtained previously by means of DMC [1] are also reported for comparison.

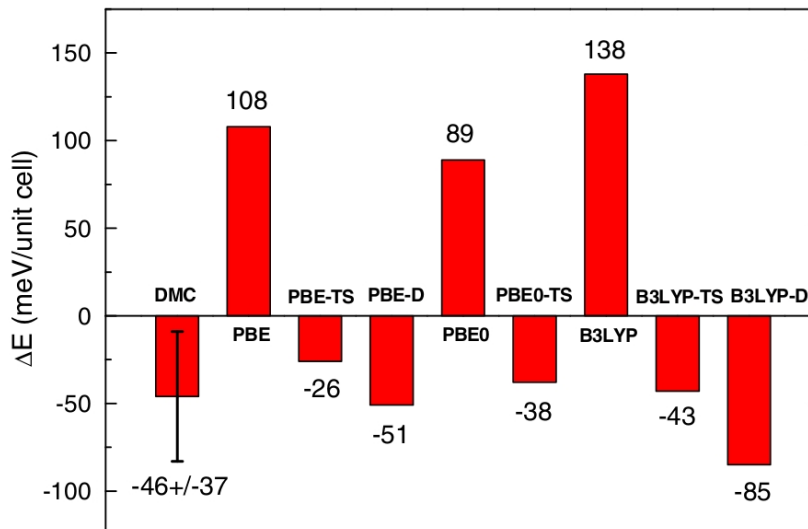


Figure 6.2: Energy differences between the α and β of p-DIB computed with the PBE, PBE0 and B3LYP functionals with and without the TS and D empirical dispersion corrections. The result obtained by means of DMC [1] (the error bar is also shown) is reported for comparative purposes.

The experimental measurements of enthalpy of transition between the two phases were performed by van Miltenburg et al. [11], and showed that the α -phase is more stable than the β one of 2.3 meV at 320 K. Nonetheless, it is quite difficult to extrapolate an experimental value at 0 K, that is, the temperature at which our calculations were performed and, thus, only a qualitative comparison can be done. The DMC results, including the finite-size correction, predict $\Delta E = -46$ meV per unit cell, although a very large error bar (± 37 meV) is associated to such calculations. In a recent paper, instead, Taylor and co-workers [12] employed a fragment based two-body correction scheme (using the spin-scaled variant of second-order Møller-Plesset perturbation theory) to the cohesive energies obtained by periodic DFT calculations on the p-DIB at the experimental geometry. The results, consistently with DMC calculations, showed a relative stability of the α -phase of ca. -50 meV.

On the other hand, all the energy differences computed by conventional functionals in the present work (PBE, PBE0 and B3LYP), gave the wrong relative stability

for the two polymorphs at the experimental geometries, ranging from 89 meV for PBE0 to 138 meV for B3LYP. However, when including empirical correction terms for dispersion, negative energy differences are predicted within the range of the DMC error bar – excepted for B3LYP-D, which is the only method that yields the α -phase at being more stable than the β one of 85 meV.

Even though such (absolute) value is much smaller than that reported by Hongo and co-workers [1], (-155 meV, obtained with a different basis-set) it still leads to overestimate the magnitude of ΔE with respect to DMC.

The comparison between the -TS and -D -corrected energy differences – obtained with the PBE and B3LYP functionals – shows that the Grimme scheme provides values which are almost twice than those predicted by the TS scheme. The PBE-TS and PBE-D functionals, in conjunction with normconserving pseudopotentials (NCPs), were also tested and they yielded the α -phase at being more stable than the β one of 38 and 63 meV, respectively. These data alone confirms that all the corrected functionals tested could be employed to predict the most stable form of an apolar molecular crystal, such as p-DIB.

6.1.2 Structural parameters

A better discrimination on which one of the two dispersion-corrections provides the best results was obtained by testing them in predicting the structural parameters of the two crystalline phases. This was done by optimizing both the atomic positions and lattice constants to the fully relaxed structures.

An important limitation of using non-local functionals – in the framework of planewave calculations – is that the potential depends, beyond the electron density, on the k -points. This makes all the DFT calculations with non-local functionals significantly more expensive in terms of memory usage and CPU time with respect to the local ones. For these reason, only the cell parameters optimized at the PBE, PBE-TS and PBE-D levels were compared with the experimental values, reported in Table 6.1.

Although it was not possible to compare the results of the different functionals within the pseudopotential and planewave approach, it was still possible to compare how the TS and D corrections performed in predicting the molecular structure of

the two *p*-DIB polymorphs. This gave an interesting insight into the problem, since the homonuclear dispersion coefficients are generated in the two schemes through different approximations.

Method	α -phase				ΔE (meV)
	a	b	c	V	
PBE	17.842 (5.0)	8.816 (20.4)	6.194 (0.4)	974 (26.8)	+49.7
PBE-TS	17.020 (0.1)	7.140 (-2.5)	6.164 (-0.1)	749 (-2.5)	-47.7
PBE-D	16.924 (-0.4)	6.856 (-6.3)	5.957 (-3.4)	691 (-10.0)	-49.2
Expt.	17.000	7.323	6.168	768	-
	β -phase				
	a	b	c	V	
PBE	17.333 (1.4)	8.958 (20.1)	6.189 (0.1)	961 (22.4)	
PBE-TS	17.136 (0.3)	7.289 (-2.3)	6.110 (-0.7)	763 (-2.8)	
PBE-D	17.145 (0.3)	6.966 (-6.2)	5.902 (-4.1)	705 (-10.2)	
Expt.	17.092	7.461	6.154	785	

Table 6.1: Optimized lattice parameters Å and unit cell volume Å³ for the two polymorphs of *p*-DIB evaluated using the PBE, PBE-TS and PBE-D functionals and compared with experimental values. The latter have been obtained at 298 and 333 K for the α and β forms, respectively [13]. Relative errors are reported in parenthesis. Computed energy differences in (meV) are given in the last column.

The original scheme introduced by Grimme [9] (see eq. 2.9.2 in Section 2.9.1), and implemented into the CASTEP code, as well as in several other periodic DFT packages [14–18], ignores the substantial variation in properties between effective atoms of the same species in the molecule, for example the influence of hybridization states on effective polarizability is neglected – and the same dispersion parameters are employed for atoms embedded in different environments. Thus, such parameters do not depend on the electronic structure of the molecule.

Instead, the TS correction employs the electron density to compute the Hirshfeld volumes of an atom, both isolated and within its bonding environment. Then, it exploits the relationship between polarizability and volume to compute the effective

dispersion coefficient for an atom in a molecule, thus accounting to some degree for the relative variation in dispersion coefficients of differently bonded atoms [19].

The results reported in Table 6.1 show that, after full geometry relaxation, the PBE functional gives the incorrect sign for ΔE (opt.) and too large unit cell volumes, certainly due to the lack of attractive vdW interactions.

Interestingly, the PBE-TS predictions are in very nice agreement with the experimental data, showing a relative error on the unit cell volume below 2.8%, while the PBE-D functional markedly reduces the cell parameters. It leads to a very compact structure, with relative errors greater than 10% on the cell volume, because of a severe contraction along the *b* and *c* axis. This can be observed in Figure 6.3, where the optimized PBE-D and PBE-TS crystal structures of the α -polymorph are superimposed to the experimental ones.

Figure 6.3 shows that the packing of the *p*-DIB molecules along the *b* axis is governed by the interactions between the π -electron density on the benzene rings and the hydrogen atoms of a benzene molecule in an overlying molecular layer. The PBE-TS functional reproduces these interactions better than the PBE-D functional. Moreover, it should be noted that the experimental data have been collected at 298 and 333 K for the α and β forms, respectively [13] while our calculations refer to 0 K. A proper account of thermal effects would probably further improve the agreement between calculations and experiments, since the population of excited vibrational states would lead to a less compact structure.

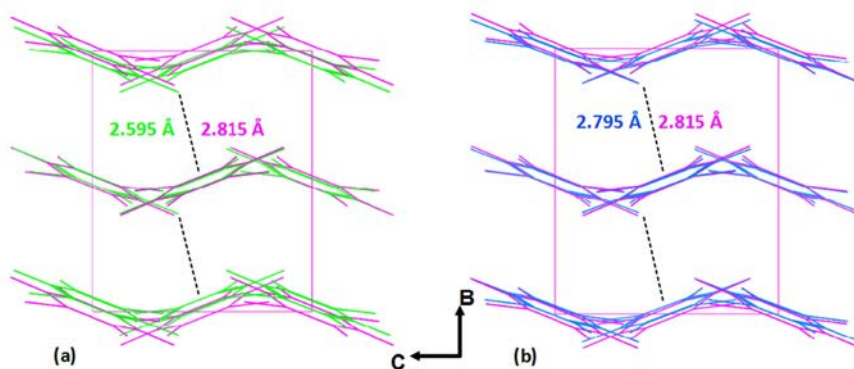


Figure 6.3: View of the *bc* plane of the optimized (a) PBE-D (light green sticks) and (b) PBE-TS (blue sticks) α -polymorph superimposed to the experimental structure (purple sticks). The H- π interaction is shown by the black dashed line.

6.2 Oxalyl dihydrazide (ODH)

As shown in the previous Section, we demonstrated [10] that – amongst the various models available to correct DFT for a dispersion-interaction inclusive term – the Tkatchenko-Scheffler (TS) model [19] is a simple, costless approach that accurately recovers vdW-type weak interactions, in a nearly non-empirical way. It was, of course, already applied before to the study of diverse systems [20–26], but its good results on the *p*-DIB system led us to adopt it – in the present work – for the computational investigation of another challenging system: the oxalyl dihydrazide (ODH) molecular crystal.

ODH exploits a peculiar kind of conformational polymorphism with five known polymorphs (*i.e.* α , β , γ , δ and ϵ) whose stabilities are determined by the competition between different types of hydrogen bond (HB) and vdW forces between π -stacked molecules. The α phase is experimentally the denser one (1.76 g/cm³) and involves only the intermolecular hydrogen bonds. The other phases ($\beta, \gamma, \delta, \epsilon$), instead, present mixtures of *inter*- and *intra*- molecular hydrogen bonds and are less dense than the α one.

According to density measurements, the α phase was proposed to be the most stable even if there are still no certain proofs, due to the incompleteness of the experimental data.[27] In fact, the authors only point out that the stability ordering is α , δ , $\epsilon > \gamma > \beta$ (without specifying the relative stability between α , δ and ϵ). Such ordering is justified by the endothermic phase transition of α , δ , ϵ into γ that occurs at different temperatures under 250° C, and the great difficulty to obtain the receding metastable β phase.

Many theoretical works have been carried out to shed light on the ODH polymorphs, in particular:

- Karamertzanis et al. [28] used a dispersion-corrected (plane-wave) D2-PW91 functional to predict the relative stability of the ODH, with reasonably good results. The energies span in a range of about 15 kJ/mol, that is slightly wider than the usually accepted one (10 kJ/mol) for experimentally observed polymorphs [29].
- Wen et al. [30] showed that the energy ranking of the five polymorphs is

markedly sensitive to different functionals and basis sets [30], and compared B3LYP-D* results with their fragment-based Hybrid Many-Body Interaction method (HMBI) [30–33] – that combines MP2 level short-range one- and two-body terms with MM two- and many-body long-range terms. They obtained structures in good agreement with the experimental ones, but underlined the inefficacy of DFT-D in predicting the energetics, specially if compared to HMBI. In fact, HMBI single-point energies (SPEs) – which were, however, performed on the B3LYP-D* optimized structures – yielded to the correct stability ordering of the five ODH polymorphs within an energy span of 5 kJ/mol.

In the present study, we combined the well-known PBE [5] functional with the TS dispersion correction and we compared it with the PBE, PBE0 [34] and B3LYP [35–37] functionals combined with the D2 approach [9].

As a further assessment of the TS and D2 schemes – and for comparison with HMBI results – high-level periodic Local second order Møller-Plesset Perturbation theory (LMP2) calculations have also been carried out, for the first time, and presented here. Furthermore, besides D2, the B3LYP functional was combined with the D3(BJ) correction [38]. Also, we investigated the combination of B3LYP-D3(BJ) with the geometrical-CounterPoise (gCP) correction [39] – this last recently applied for the study of cohesive energy of molecular crystals [40]. More details on the computational methods adopted here are given in Appendix A.

6.2.1 Crystal structure optimizations

Cell parameters. Firstly, we tested the accuracy of PBE-TS and PBE-D2 functionals in predicting the cell parameters of the five polymorphs of oxalyl dihydrazide. The relative deviation % of the optimized cell parameters and volume computed at 0 K, with respect to the experimental ones, are reported in Table 6.2. B3LYP-D* results from the recent paper of Wen et al. [30] and D2-PW91 plane-waves calculation [28] are also reported for comparison.

The overall accuracy given by PBE-TS is remarkable: the error in predicting cell volumes is notably smaller with respect to those of other methods and less than 0.6% for all phases but β , whose deviation is around 4%. Furthermore, in most cases, PBE-TS functional yields to small deviations on cell parameters.

Table 6.2: PBE-D2 and PBE-TS optimized cell parameters of crystalline oxalyl dihydrazide. The results are reported in % relative deviation from experimental data.

Method/Basis-set	a (Å)	b (Å)	c (Å)	γ (deg)	Volume (Å ³)
α polymorph					
experiment ^a	3.622	6.832	9.129	99.30	223.0
B3LYP-D*/6-31G(d,p) ^b	-3.66%	-1.24%	-1.44%	-1.81%	-5.80%
B3LYP-D*/TZP ^b	-1.33%	-0.26%	-1.73%	-1.58%	-2.90%
D2-PW91/PW ^c	-0.80%	-2.28%	-1.14%	-0.61%	-4.04%
PBE-D2/NCPP	-4.14 %	-1.86 %	-0.54 %	-1.44 %	-6.11 %
PBE-TS/NCPP	0.67 %	-1.24 %	0.53 %	-0.32 %	0.01 %
β polymorph					
experiment ^a	3.762	11.652	5.619	92.79	246.0
B3LYP-D*/6-31G(d,p) ^b	2.83%	-4.05%	-8.96%	-4.08%	-10.08%
B3LYP-D*/TZP ^b	2.60%	-3.60%	-6.19%	-2.68%	-7.11%
D2-PW91/PW ^c	7.95%	-6.39%	-8.84%	-1.19%	-7.81%
PBE-D2/NCPP	-0.01 %	-3.28 %	-4.95 %	-1.25 %	-8.00 %
PBE-TS/NCPP	7.26 %	-4.60 %	-6.89 %	-1.38 %	-4.63 %
γ polymorph					
experiment ^a	5.080	14.668	7.035	114.16	478.2
B3LYP-D*/6-31G(d,p) ^b	0.52%	-1.27%	-3.69%	2.42%	-6.58%
B3LYP-D*/TZP ^b	0.55%	-0.88%	-1.43%	1.68%	-3.26%
D2-PW91/PW ^c	-1.14%	-1.70%	0.00%	0.53%	-3.31%
PBE-D2/NCPP	-0.76 %	-0.92 %	-1.93 %	0.88 %	-4.32 %
PBE-TS/NCPP	-0.05 %	-0.60 %	0.60 %	0.57 %	-0.56 %
δ polymorph					
experiment ^a	3.661	14.550	5.065	119.01	235.9
B3LYP-D*/6-31G(d,p) ^b	4.26%	-3.15%	-0.05%	4.51%	-4.74%
B3LYP-D*/TZP ^b	6.32%	-2.79%	0.05%	3.55%	-1.09%
D2-PW91/PW ^c	1.86%	-3.90%	-0.89%	0.81%	-3.93%
PBE-D2/NCPP	-2.52 %	-2.29 %	-0.19 %	0.35 %	-5.30 %
PBE-TS/NCPP	3.74 %	-2.31 %	0.05 %	1.21 %	-0.03 %
ϵ polymorph					
experiment ^a	5.364	3.841	12.319	109.00	240.0
B3LYP-D*/6-31G(d,p) ^b	2.52%	-4.91%	0.23%	3.19%	-4.52%
B3LYP-D*/TZP ^b	3.86%	-3.56%	1.36%	3.76%	-1.25%
D2-PW91/PW ^c	-0.39%	0.57%	-1.44%	3.01%	-3.43%
PBE-D2/NCPP	2.78 %	-2.02 %	-0.68 %	3.83 %	-2.76 %
PBE-TS/NCPP	-0.62 %	1.96 %	-0.82 %	1.59 %	-0.60 %

a: Experiment from Ref. [27]; *b*: Ref. [30]; *c*: Ref. [28]

On the contrary, the Grimme dispersion scheme (D2) tends to overestimate the long-range interaction and consequently to give rise to more compact cells.

For the β polymorph – which is the less stable phase, and was experimentally obtained and characterized only once [27] – the agreement of computational methods with experiments, as expected, is rather poor. Though the a parameter is considerably overestimated by the PBE-TS ($\sim 7\%$), b and c compensate with an opposite trend, furnishing the smallest volume deviation (about 4.5%). The PBE-D2 leads, instead, to a better agreement with experiment of single cell parameters but a larger discrepancy in the cell volume.

All the PBE-TS fully optimized structures are reported in Figure 6.4–6.7, where also the complex intermolecular hydrogen bond networks constituting the three dimensional structures is shown.

Intermolecular distances.

The PBE-TS and PBE-D2 optimized hydrogen bond distances are reported in Table 6.3. The experimental distances are also reported for comparison. It can be observed that they show the same trend of the PBE-TS ones, but with larger deviations. Due to the uncertainty in the experimental positions of hydrogen atoms (which are not detected by XRD), the comparison is done on the $N\cdots N$ and $N\cdots O$ distances rather than the $N-H\cdots N$ and $N-H\cdots O$ ones.

α polymorph. ODH molecules belonging to the α polymorph are connected by two types of HBs: $N-H\cdots N$ and $N-H\cdots O$ in-plane (see Figure 6.4-top) – the out-of-plane HB, which is another $N-H\cdots O$, lies between planes and is a little longer than the other two. The mentioned planes are stacked along $[1\ 0\ -2]$.

The PBE-TS results are in good agreement with experimental data. Distances are mildly underestimated (absolute deviation less than 0.08 Å) and the cell is more compact along the stacking direction. In this case, the PBE-TS slightly overestimates both the vdW π -stacking interactions and the $N-H\cdots O$ between planes (this is clearly observable in Table 6.3), that dominate over the in-plane HBs.

β polymorph. β is characterized by long and nonplanar hydrogen bonds (see Figure 6.4-bottom), that probably explain its low stability. The only planar HBs are the $\text{N-H}\cdots\text{N}$ from the $-\text{NH}$ groups, that link the synthons to form molecular ‘ribbons’ while two types of $\text{N-H}\cdots\text{O}$ HBs lie out-of-plane, between adjacent ribbons. As shown for cell parameters, the structure prediction furnished by PBE-TS is not completely satisfactory: the $\text{N-H}\cdots\text{O}$ formed by $-\text{NH}$ groups split into two different HBs, in disagreement with experimental measures that provide two equal HBs. However, the absolute deviations given by PBE-TS are always less than 0.08 Å.

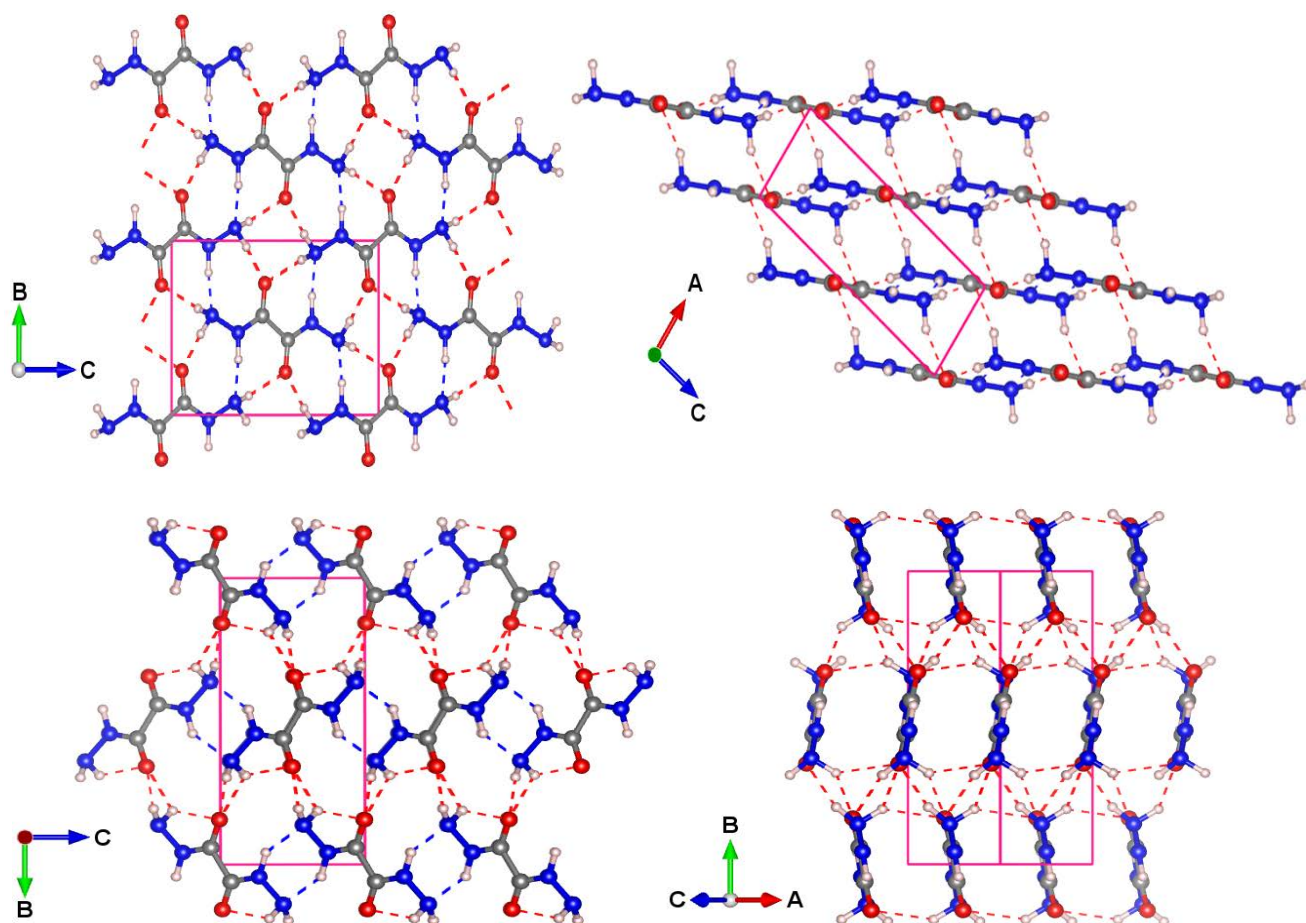


Figure 6.4: (Top) α polymorph and (bottom) β polymorph of crystalline oxalyl dihydrazide, from PBE-TS/NCPP full structure relaxations. Only intermolecular hydrogen bonds are displayed. The red dashed lines indicate $\text{N-H}\cdots\text{O}$ hydrogen bonds, while the blue dashed lines indicate $\text{N-H}\cdots\text{N}$ hydrogen bonds.

Table 6.3: Optimized structures at the PBE-TS and PBE-D2 level: HB distances and deviations are reported as N $\cdots$ O and N $\cdots$ N distances for the N-H $\cdots$ O and N-H $\cdots$ N interactions, respectively.

H-Bond	Type	PBE-TS ($\text{\AA}$)	Dev. ($\text{\AA}$)	PBE-D2 ($\text{\AA}$)	Dev. ($\text{\AA}$)	Exp. ^a ($\text{\AA}$)
α polymorph						
in-plane	N – H $\cdots$ N	2.882	-0.037	2.833	-0.086	2.919
	N – H $\cdots$ O	2.953	-0.059	2.937	-0.075	3.012
out-of-plane	N – H $\cdots$ O	3.094	-0.082	3.037	-0.139	3.176
β polymorph						
in-plane	N – H $\cdots$ N	2.927	-0.083	2.884	-0.126	3.010
out-of-plane	N – H $\cdots$ O	3.128	-0.081	3.088	-0.121	3.209
	N – H $\cdots$ O	3.150 ^b	0.084	3.083 ^b	0.017	3.066
		2.987 ^b	-0.079	2.945 ^b	-0.121	3.066
γ polymorph						
in-plane	N – H $\cdots$ O	2.851	-0.002	2.798	-0.055	2.853
	N – H $\cdots$ O	2.834	-0.036	2.807	-0.063	2.870
	N – H $\cdots$ N	3.141	-0.078	3.121	-0.098	3.219
	N – H $\cdots$ N	3.105	-0.043	3.092	-0.063	3.184
out-of-plane	N – H $\cdots$ O	3.045	-0.074	3.019	-0.100	3.119
	N – H $\cdots$ O	3.029	-0.079	2.986	-0.122	3.108
δ polymorph						
in-plane	N – H $\cdots$ O	2.821	-0.027	2.801	-0.047	2.848
	N – H $\cdots$ N	3.086	-0.076	3.060	-0.102	3.162
out-of-plane	N – H $\cdots$ O	3.072	-0.075	3.046	-0.101	3.147
ϵ polymorph						
in-plane	N – H $\cdots$ O	2.948	-0.051	2.940	-0.059	2.999
// ribbons	N – H $\cdots$ N	2.873	-0.069	2.845	-0.097	2.942
out-of-plane	N – H $\cdots$ O	3.019	-0.065	2.987	-0.097	3.084
($\perp$ ribbons)						

^a: Experiment from Ref. [27]; ^b: two different distances for the same hydrogen bond.

γ polymorph. The γ polymorph is characterized by four different HBs within the *ab* molecular plane: two N–H $\cdots$ N and two N–H $\cdots$ O (see Figure 6.5), whereas two N–H $\cdots$ O are located out of the molecular plane. Even in such case, distances are mildly underestimated (Max Abs Dev. < 0.08 Å). Cell parameters show such behavior only along the *a* and the *b* axis, probably because the in-plane interactions (intramolecular HBs are also present here) dominate the crystal packing over the out-of-plane interaction. This could be the result of a marked rearrangement of molecular synthons from the most stable phases (α , δ and ϵ). In fact, the γ one contains four molecules per unit cell – whereas the others contain only two molecules.

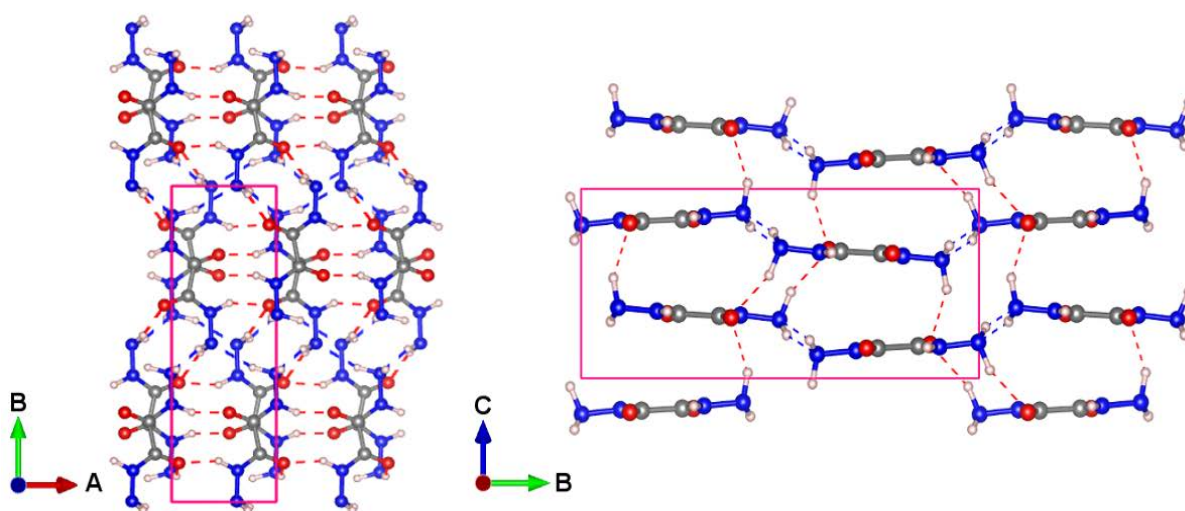


Figure 6.5: Fully optimized (PBE-TS/NCPP) γ polymorph of crystalline oxalyl dihydrazide. The intermolecular hydrogen bonds are colored as in Fig. 6.4

δ polymorph. The δ polymorph is structurally similar to γ , but it contains only two (N–H $\cdots$ N and the N–H $\cdots$ O) HBs within the *ab* molecular plane and an N–H $\cdots$ O bond out-of- the *ab* plane (see Figure 6.6). All such distances are mildly underestimated, especially the in-plane N–H $\cdots$ N and the out-of-plane N–H $\cdots$ O whose deviation with respect to the experimental measurements are around 0.075 Å. The distances between the -NH₂ groups found experimentally are shorter, but less directional than in γ . Consequently the *a* parameter and the γ ($\widehat{ab}$) angle are slightly overestimated (see Table 6.2).

This molecular arrangement – the planes are not perfectly flat – leads also to the overestimation of c , though $\text{N-H}\cdots\text{O}$ is underestimated.

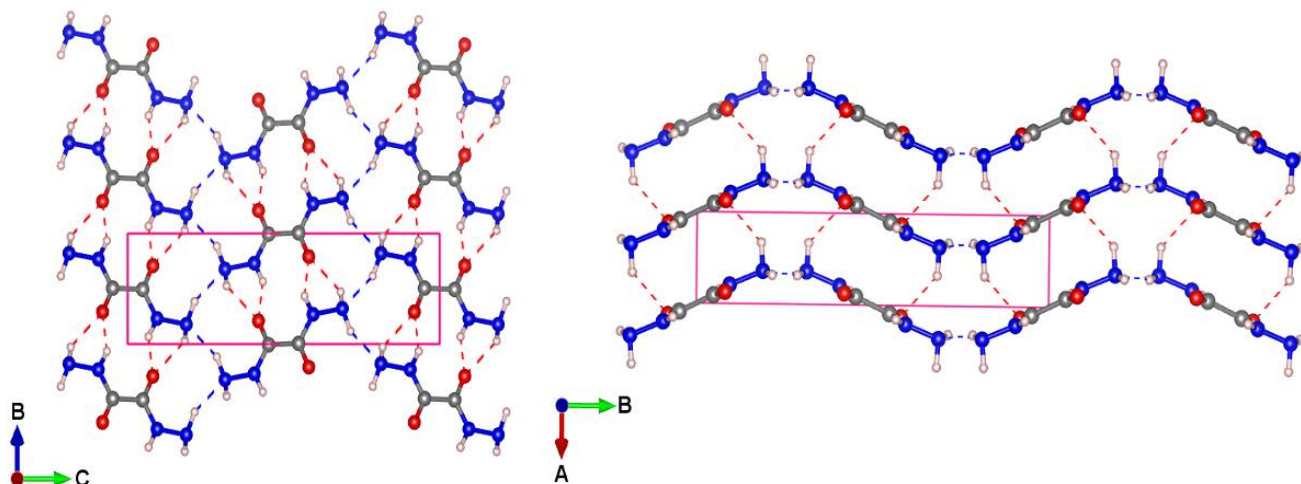


Figure 6.6: Fully optimized (PBE-TS/NCPP) δ polymorph of crystalline oxalyl dihydrazide. The intermolecular hydrogen bonds are colored as in Fig. 6.4

ϵ polymorph. This polymorph is quite different from the others: it is characterized by a ‘grid-like’ shape, in the ab plane, that arises from the alternate arrangement of molecular ribbons perpendicular to each other (see Figure 6.7).

There are two different intermolecular $\text{N-H}\cdots\text{O}$ HBs for each ribbon – one in-plane and one out-of-plane (the latter between parallel ribbons). The $\text{N-H}\cdots\text{N}$ hydrogen bonds from the $-\text{NH}$ groups and from the nitrogen of $-\text{NH}_2$ groups link adjacent ribbons along c . As in the other cases, the PBE-TS gives shorter HB distances – which are in agreement with the cell compacting along a and c . Thus indicates an overestimation of the interactions present between adjacent perpendicular ribbons.

In summary, the overall accuracy of PBE-TS in predicting cell parameters and hydrogen bond distances (Mean Abs. Dev. = 0.06 Å and Max Abs. Dev. = 0.08 Å) appears to be better than that obtained with PBE-D2 (Mean Abs. Dev. = 0.11 Å and Max Abs. Dev. = 0.14 Å).

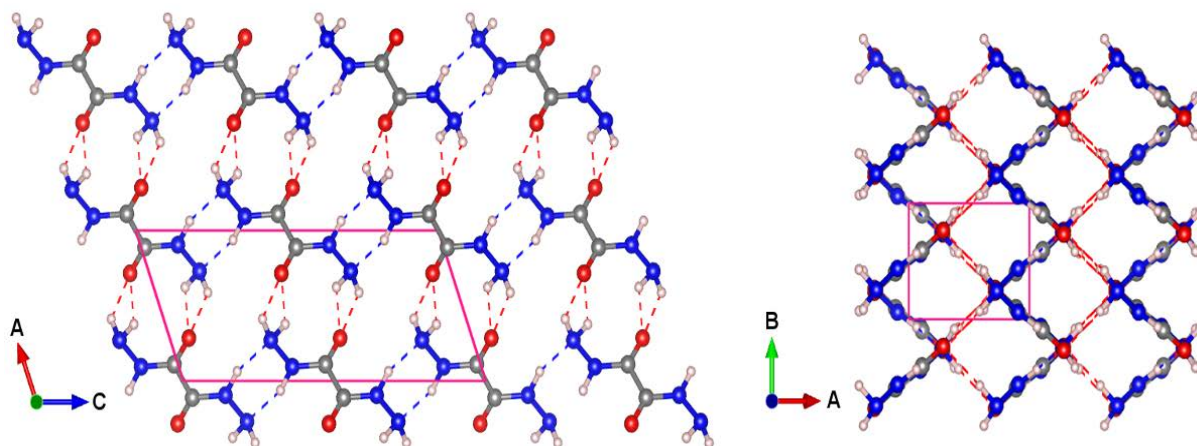


Figure 6.7: Fully optimized (PBE-TS/NCPP) ϵ polymorph of crystalline oxalyl dihydrazide. The intermolecular hydrogen bonds are colored as in Fig. 6.4

6.2.2 Relative Stability of ODH

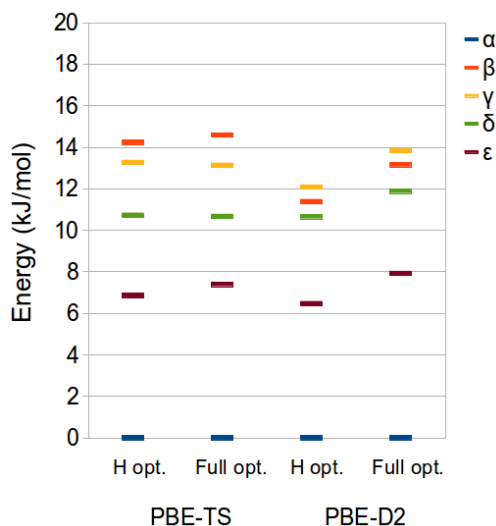
The relative stabilities of the five polymorphs of ODH were calculated at the PBE-TS and PBE-D2 level on the hydrogen- (revised experimental) and fully-optimized structures at the same level of theory (PBE-TS/PBE-TS and PBE-D2/PBE-D2), as the energy difference of each polymorph with respect to the α phase.

The obtained energy rankings are consistent with those given by D2-PW91 calculations [28] – see Figure 6.8. The difference between the most and the less stable phases corresponds to 12-15 kJ/mol per molecule, in accord with the commonly accepted value (10-15 kJ/mol per molecule). [29, 30]

PBE-TS led to the expected experimental stability [27]: $\alpha, \delta, \epsilon > \gamma > \beta$, that is in agreement with the density ordering of the five polymorphs (α is the most dense – 1.76 g/cm³, β is the less dense – 1.59/1.66 g/cm³) and the experimentally observed endothermic transformations of α, δ, ϵ into γ while heated below 250° C – temperature at which ODH decomposes to N,N'- dioxalylhydrazidylhydrazine (DOHH) and gaseous hydrazine through a solid state chemical reaction.

The PBE-D2 method, on the other hand, reverses the stability of the two less stable phases, giving $\beta > \gamma$. The relative stability of the ODH polymorphs as computed for the revised experimental structure (i.e. optimized hydrogen atoms) and the fully relaxed ones is only slightly different, thus indicating that – excepted for the positions of H atoms – the potential energy surface of this system is very flat.

Figure 6.8: Relative stability of crystalline ODH: PBE-TS (left) and PBE-D2 (right). For each method both the results from the optimizations of H atoms and full optimizations are shown. The α phase was taken as reference.



Also, the evaluation of the zero-point energy (ZPE) contribution to the total energy is shown in Figure 6.9. It is possible to see that the inclusion of the ZPE correction does not change the energy ranking, and the range is only slightly broadened (differently from what observed by Wen et al. [30]).

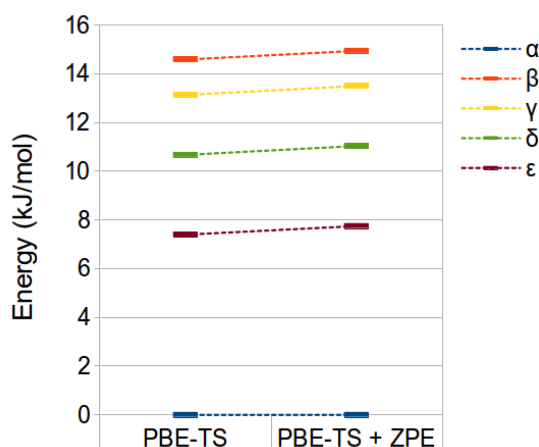


Figure 6.9: Relative stabilities of ODH (fully optimized structures): PBE-TS vs. PBE-TS+ZPE correction.

Comparing dispersion-corrected DFT and LMP2

We discuss here our main objective, which was the comparison of different calculation approaches applied to the prediction of relative stabilities of ODH polymorphs. In particular, the results given by periodic-Local MP2 represent, to our knowledge, the highest-quality calculations available up to now on ODH, and can be considered as a reference to the aims of this study. We carried out single-point energies (SPE) calculations by using different dispersion-corrected GGA and hybrid functionals (PBE-TS/D2, PBE0-D2, B3LYP-D2, B3LYP-D3(BJ), B3LYP-D3(BJ)+E⁽³⁾ and B3LYP-D3(BJ)+gCP) and LMP2 on the PBE-TS revised experimental structures. Since energy gradients are not currently available for all methods under investigation, this allowed us to make a consistent comparison among the chosen methods.

Table 6.4 reports a summary of the relative stabilities furnished by the above-mentioned approaches, which are even depicted, together with LMP2 results, in Figure 6.10.

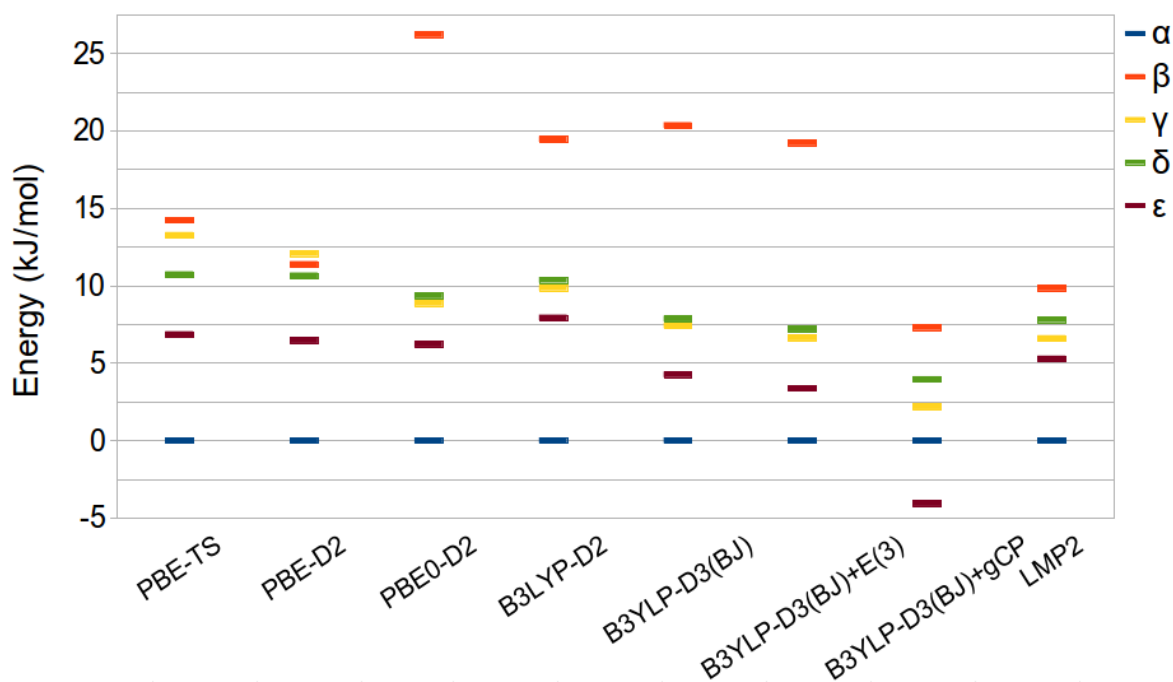
Table 6.4: Dispersion-corrected DFT and LMP2 single-point energy differences, computed with respect to the α -phase (kJ/mol per molecule).

Relative Stability, ΔE - kJ/mol per molecule				
<i>Method</i>	β	γ	δ	ϵ
PBE-TS	14.23	13.26	10.72	6.85
PBE-D2	11.38	12.08	10.65	6.46
PBE0 ^a -D2	26.21	8.86	9.35	6.21
B3LYP ^a -D2	19.45	9.85	10.36	7.93
B3LYP ^a -D3(BJ)	20.35	7.42	7.86	4.25
B3LYP ^a -D3(BJ)+E ⁽³⁾	19.22	6.63	7.20	3.37
B3LYP ^b -D3(BJ)+gCP	7.30	2.18	3.95	-4.07
LMP2 ^c	9.84	6.60	7.80	5.28

a: Basis set: QZVP; *b*: Basis set: 6-31G(d); *c*: Basis set: p-aug-6-31G(d,p).

The energy ranking predicted by LMP2 calculations is $\alpha > \epsilon > \gamma > \delta > \beta$ within an energy range below 10 kJ/mol. These results are slightly different with respect to those reported by Wen et al. [30]. In fact, their HMBI calculations without including the three body correction provided the δ phase to be more stable than the γ one whereas the inclusion of the three-body dispersion terms reversed the stability order of the α and ϵ polymorphs. In both cases, the energy range for the five polymorphs was below 5 kJ/mol. The difference between this value and our LMP2 result can be ascribed to the different approximations inherent to the HMBI and LMP2 approaches, different basis-sets adopted, and the treatment of BSSE effects.

Figure 6.10: Relative stabilities of ODH at the PBE-TS revised experimental (hydrogen optimized) geometry.



The energy differences obtained at DFT level highlight a marked dependence by the exchange-correlation functional form. In particular, the PBE-TS provides a stability ordering more similar to the one obtained by Wen [30] since the γ and δ stability is reversed with respect to the LMP2 calculations. However, the difference between the two phases is very small and the whole energy range is wider and more

similar to that computed at the LMP2 level. On the other hand, PBE0-D2 and B3LYP-D2 provide a stability ordering similar to LMP2 but with a much wider stability range of about 26 and 20 kJ/mol, respectively.

B3LYP-D3(BJ)/QZVP gives relative stabilities similar to B3LYP-D2, whereas the inclusion of the three-body contribution ($E^{(3)}$) stabilizes all the other phases with respect to α without changing the order. In fact, the $E^{(3)}$ contribution is very small, being about 1.0 kJ/mol, in agreement with the results reported by Wen et al. in Ref. [30].

It has to be observed, however, that the Axilrod-Teller-Muto term [41, 42] – which is present in the B3LYP-D3 scheme – cannot totally account for the many-body contribution to dispersion interactions in solids. The polarizability of molecules in solids, in fact, is significantly influenced by the environment through a collective electrodynamic response.[43] Very recently, Tkatchenko et al. [43–45] have demonstrated that these many-body effects cannot be neglected if one aims at an accurate prediction of solid-state properties and thus further studies including such terms should be carried out in the future.

Since Wen et al. [30] computed the relative stability of the five polymorphs by employing BSSE corrected total energies we decided to investigate the recently proposed gCP correction [39], which mimics the Boys-Bernardi [46] counterpoise correction, in the prediction of the energy ranking of ODH. The gCP correction, as fitted for the 6-31G(d) basis-set, is added to the B3LYP-D3(BJ) results. Oddly, the ϵ phase becomes the most stable one while all other polymorphs are stabilized with respect to α . When compared with other methods, this suggests that the gCP is probably not well balanced, at least for ODH.

In spite of the larger stability range, the PBE-TS and B3LYP-D2 functionals seem to be, amongst the considered functionals, the most compatible with LMP2 and HMBI results. Interestingly, the B3LYP-D3(BJ)+ $E^{(3)}$ /QZVP method gives results very similar to LMP2 for all polymorphs but the β phase.

Finally, the energy ranking that can be deduced from the different methods adopted here is: $\alpha > \epsilon > \gamma \sim \delta > \beta$.

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Chapter 7

Unveiling the polymorphism of [(p-cymene)Ru(*k*N-INA)Cl₂]

7.1 Introduction

Quite recently, Bacchi and co-workers [1] reported the design of a crystalline molecular wheel-and-axle (WAA) compound – the “half-sandwich” Ru(II)-complex [(p-cymene)Ru(*k*N-INA)Cl₂] (INA= isonicotinic acid) with the aim of obtaining a supramolecular synthon by cyclic supramolecular dimerization of the INA carboxylic groups.

Wheel-and-axle (WAA) compounds are a class of organic/inorganic molecules that are characterized by a long, usually linear spacer (axle – in the present case, INA) and two bulky groups (wheels – in the present case, the Ru(II)-complex attached to INA) at both ends. Their shape and irregularity promote the formation of a widespread supramolecular organization governed by hydrogen bonds and/or dispersive interactions. Therefore, WAAs present well-known host-guest properties and a high tendency to form clathrates with different solvents [2], thus attracting the interest of many fields of research to devise WAAs for applications in heterogeneous catalysis, solid-state “green” chemistry, sensing and storage of gases.[1, 3–5]

The solid [(p-cymene)Ru(*k*N-INA)Cl₂] was obtained in four different crystalline forms: **1α**, **1·H₂O**, **1β** and **1γ** (see Figure 7.1). The isolation of the metastable **1γ** polymorph and its XRPD/NMR characterization was achieved in a subsequent work by the same authors [6] who, in addition, realized that the **1β** form is also

metastable and some of its structural peculiarities were also reconsidered[6]. Different techniques (X-ray single crystal and powder diffraction - XRD, ATR-FTIR, solid-state NMR) revealed that, interestingly, the main intermolecular interactions governing the supramolecular architecture of the three anhydrous crystalline forms was not the expected cyclic supramolecular dimer involving the -COOH functions, but rather the hydrogen bonds between the chloride ligands (acceptor) bonded to Ru(II) and the carboxylic OH moiety (donor). Moreover, for the **1**·H₂O form the cyclic supramolecular dimerization of the COOH groups of INA is prevented by the inclusion of water.

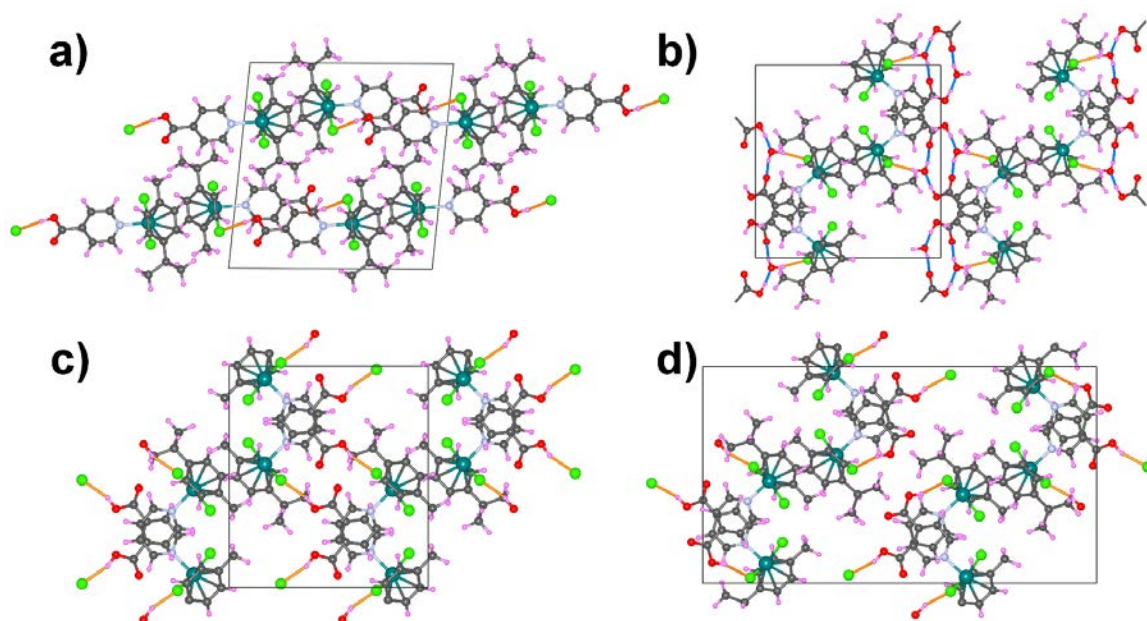
Such observations give an idea of the complexity of the [(p-cymene)Ru(kN-INA)Cl₂] polymorphism, knowledge of which represents an important challenge from both an experimental and a theoretical point of view, since it implies the characterization of the weak non-covalent interactions determining one molecular packing with respect to the others. Solid-state chemists exploit powerful tools – such as NMR crystallography – to address the structural properties of materials which are difficult to obtain as large single crystals.[7] This consists if the combination of solid-state NMR spectroscopy with X-ray powder diffraction (XRPD) methods.

However, the assignment of the observed ¹³C and ¹H solid-state NMR resonances to the atoms belonging to distinct molecules in the asymmetric unit cell is a considerable challenge that can only be met by the help of computational NMR.

This reason, and the fact that some structural peculiarities of [(p-cymene)-Ru(kN-INA)Cl₂] mentioned above were not fully disclosed, induced us to perform simulations in order to support and revise the experimental evidences about structures, polymorphism and ssNMR behavior of such system.

In the present study [8], the solid-state ¹³C/¹H NMR δ_{iso} parameters and ¹³C MAS ssNMR spectra of the **1** α , **1**·H₂O, **1** β and **1** γ crystal forms of [(p-cymene)Ru(kN-INA)Cl₂] were calculated by means of the PBE-GIPAW method and the results are compared with the experimental data. The correct treatment of dispersive interactions in the refinement of the crystal structure of the crystal forms is also discussed.

Figure 7.1: Fully optimized (B3LYP-D*) three dimensional structures of the four crystalline forms of $[(p\text{-cymene})\text{Ru}(k\text{N-INA})\text{Cl}_2]$: a) 1α form, b) $1\cdot\text{H}_2\text{O}$ form, c) 1β form and d) 1γ form (two unit cells are reported for a), b) and c)). The views are shown from the ab plane, excepted for a), which is depicted on the ac plane. The $\text{COOH}\cdots\text{Cl}$ interactions are displayed with orange lines, whereas the $\text{COOH}\cdots\text{H}_2\text{O}$ interactions (hydrated form) are displayed with blue lines.



7.2 Computational Methodologies

Geometry optimizations. The starting geometries of the 1α and $1\cdot\text{H}_2\text{O}$ crystal forms were taken from Ref. [1] whereas that of the 1β and 1γ crystal forms correspond to the non-refined ones of Ref. [6].

DFT calculations in the framework of gaussian-type orbitals were carried out by using a parallel version of the CRYSTAL09 package [9, 10], imposing periodic boundary conditions (PBC). Full geometry optimizations of the four crystalline forms were performed by using the hybrid B3LYP functional [11, 12], its combination with the empirical Grimme dispersion correction (B3LYP-D2) [13] and the alternative re-parametrization of the Grimme D2 term especially devised for molecular crystals

(B3LYP-D*) [14]. Moreover, for the **1 β** and **1 γ** crystal forms, B3LYP-D* geometry optimizations with allowance for the relaxation of the positions of the hydrogen atoms only were also carried out.

The basis-set was chosen in order to provide an optimal characterization of the electronic configuration of the Ru(II) metal-organic synthons and their arrangement within the manifold crystalline framework. The 6-31G(d) basis-set was used for H, C, N and O atoms; a p-type polarization was added on H atoms and sp-type diffuse functions (consistent with the 6-31+G(d) basis-set) were used for N and O atoms. The use of diffuse functions is justified by the fact that N atoms are directly involved in the Ru(II) complex, whereas O atoms can form, depending on case, the hydrogen bond.

Chlorine and ruthenium atoms were described by modified fully relativistic pseudopotentials on core electrons (MDF28 ECP for Ru [15], SDF10 ECP for Cl [16] – primitive Gaussians with exponents lower than 0.06 have been excluded to avoid basis-set linear dependence), and associated double- ζ quality basis-sets on valence electrons, taken from the Stuttgart pseudo-potential library [17].

The Monkhorst-Pack grid of k -points was generated with 8 k -points inside the Irreducible Brillouin Zone (IBZ), whereas the DFT integration grid consisted in 75 radial and 974 angular points. The five thresholds for Coulomb and Exchange series accuracy (see Ref. [9]) were set to tight values: 10^{-8} , 10^{-8} , 10^{-8} , 10^{-10} and 10^{-25} .

NMR calculations. Calculations of NMR parameters were carried out on the crystal structures previously optimized at the B3LYP, B3LYP-D2 and B3LYP-D* level of theory. The ¹H and ¹³C shielding tensors were computed by means of the GIPAW approach [18, 19] implemented in the CASTEP software [20, 21] which uses plane waves as basis-set and the pseudopotential approach to describe the core-valence interactions. All calculations were performed using the PBE exchange-correlation functional [22] in combination with ultrasoft pseudopotentials (USPPs) – included in the CASTEP library. The plane wave basis-set was cut at 610 eV. Dispersion-correction terms were not included: in fact, being a posteriori empirical corrections to the DFT energy and forces, they do not directly affect the computation of the NMR parameters. A Monkhorst-Pack grid of minimum sample spacing of 0.04 Å⁻¹ in the reciprocal lattice was used.

In order to compare the isotropic shielding directly with experimentally measured isotropic chemical shifts, the following relations were used for ¹³C and ¹H respectively:

$$\delta_{iso}({}^{13}\text{C}) = -0.960\sigma_{iso} + 166.6 \quad (7.2.1)$$

$$\delta_{iso}({}^1\text{H}) = -0.944\sigma_{iso} + 29.6 \quad (7.2.2)$$

which were fitted on the measured isotropic chemical shift of the **1α** crystal phase, that was taken as reference.

The linear regression – displayed in Figure 7.2 – yielded R² of 0.999 and 0.978 for ¹³C and ¹H, respectively. Computed ¹³C isotropic chemical shifts were thus employed to simulate the corresponding MAS NMR spectra of all the crystal forms, by means of a home-made code [23] based on the resolution of spin effective Hamiltonians. The ¹H MAS NMR spectra were not simulated because the broadening effects due to the homonuclear dipole-dipole interactions, which are not averaged out in the experimental spectra reported in literature [6], are not included in the present version of our code.

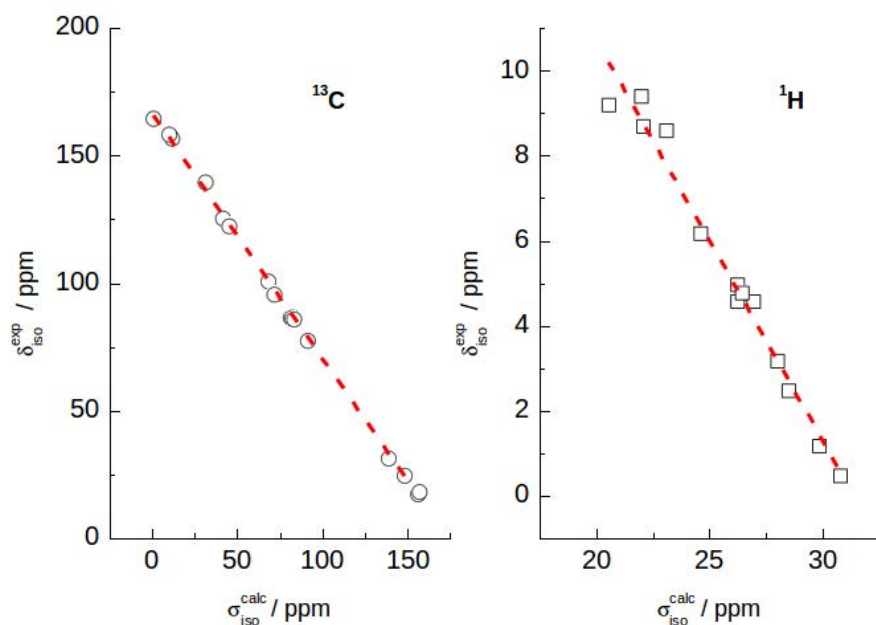


Figure 7.2: Correlations between the experimental isotropic chemical shifts and the computed isotropic shieldings for the ¹³C and ¹H of **1α**.

7.3 1 α and 1 $\cdot$ H₂O crystal forms

The **1 α** phase belongs to a monoclinic system (*P*2₁/*n*), it contains four molecules of [(p-cymene)Ru(*k*N-INA)Cl₂] per unit cell (164 atoms) and it is characterized by intermolecular interactions represented by the -COOH $\cdots$ Cl- hydrogen bond along the 2₁ axis, which involve two consecutive molecules arranged in two alternate zig-zag chains (see Figure 7.3 below).

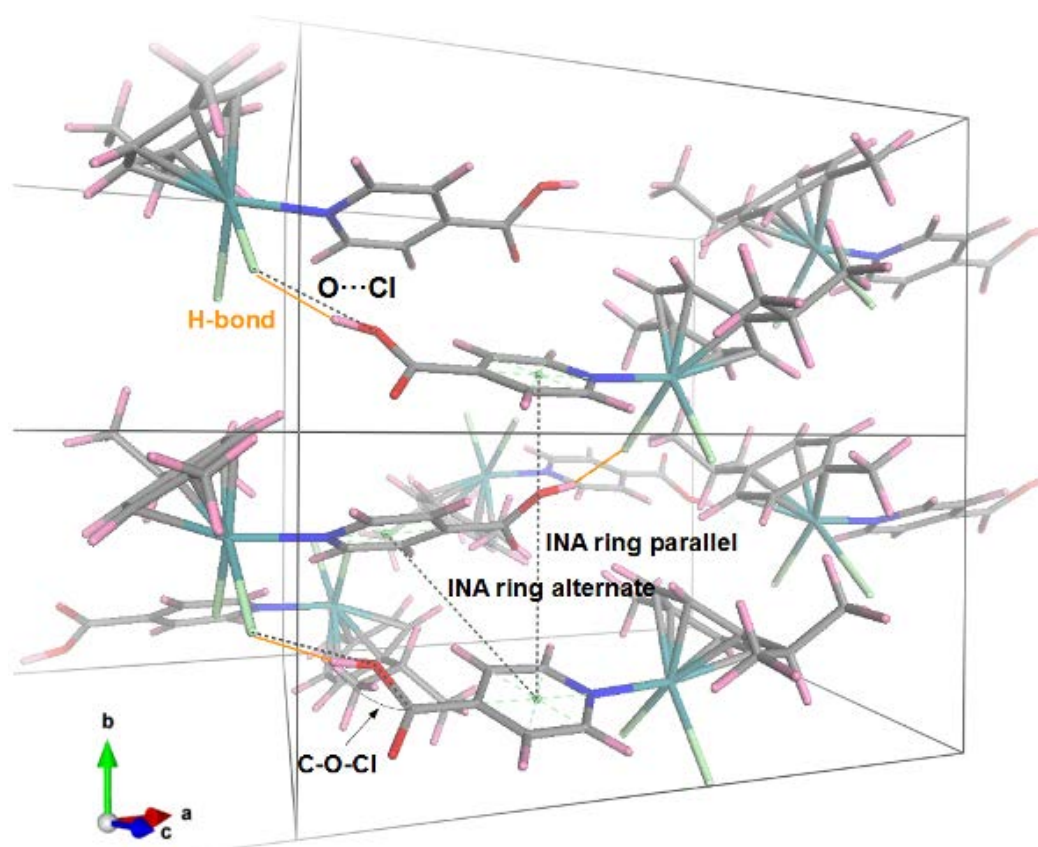


Figure 7.3: Perspective view of the **1 α** polymorph (B3LYP-D*) – the continuous black line is the unit cell. The Cl $\cdots$ O distance and the C–O–Cl angle are displayed, and hydrogen bonds are highlighted in orange. The distance between two INA rings belonging to two parallel equal layers (along *b*) or to two alternate neighbor layers (along *c*) is denoted by ‘INA ring parallel’, and ‘INA ring alternate’, respectively.

The inclusion of water (four molecules per unit cell) has a strong structural role in the packing of $1\cdot\text{H}_2\text{O}$, since it organizes the half-sandwich units in water-assisted centrosymmetric supramolecular dimers. The water molecules bridge pairs of carboxylic groups by the $\text{OH}\cdots\text{O}$ and $\text{OH}\cdots\text{Cl}$ interactions: the metal-arene wheels interact together, forming the “inverted piano-stool” supramolecular motif [1], which is clearly shown in Figure 7.4.

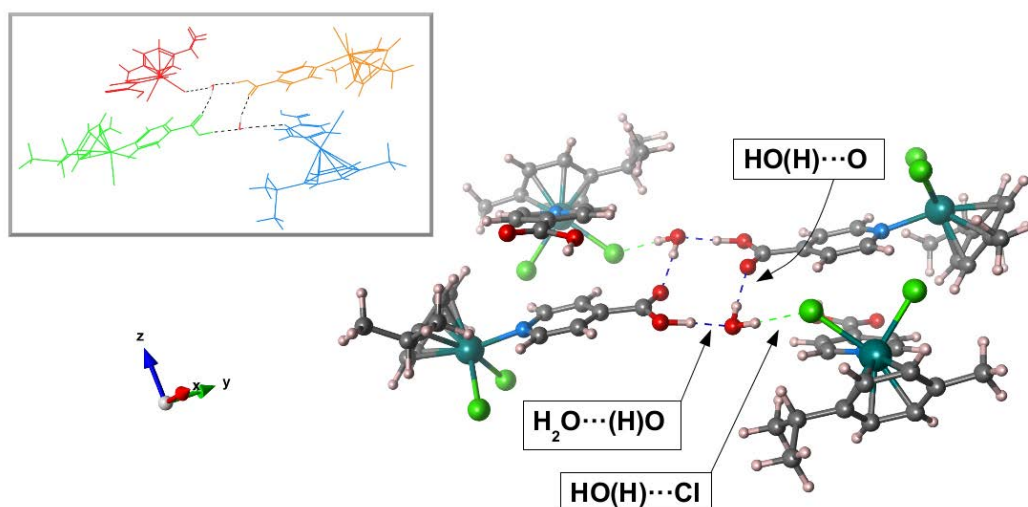


Figure 7.4: Inverted piano-stool of the $1\cdot\text{H}_2\text{O}$ form (B3LYP-D*) – with four water molecules per unit cell. The H_2O oxygen-chlorine distance ($\text{HO(H)}\cdots\text{Cl}$), and two oxygen-oxygen distances ($\text{H}_2\text{O}\cdots(\text{H})\text{O}$; $\text{HO(H)}\cdots\text{O}$) are displayed. The four molecules of $[(p\text{-cymene})\text{Ru}(kN\text{-INA})\text{Cl}_2]$ are also evidenced with differently colored sticks.

7.3.1 Structural parameters: cell constants.

An extensive analysis of the full optimized geometry of the 1α , and $1\cdot\text{H}_2\text{O}$ crystal forms, performed by using the hybrid B3LYP functional [11, 12, 24] its combination with the ‘classical’ Grimme dispersion correction (B3LYP-D2) [13], and the alternative reparametrization of the Grimme D2 term devised for crystals (B3LYP-D*) [14], was carried out.

The cell parameters obtained by full geometry optimizations and their % relative deviations from experimental data are listed in Table 7.1. As expected, the B3LYP functional yields the worst predictions of the 1α polymorph, largely overestimating

the parameter a , i.e. where both hydrogen bonds and vdW interactions lie. Such error affects also the cell volume that is overestimated by 30%. The dispersion-corrected B3LYP-D2 functional predicts a smaller cell, in particular along c , where the alternating chains are interconnected by means of dispersion forces only (no H-bonds lie along this direction), thus confirming the well-known overestimation effect of dispersion interactions of the D2 scheme. B3LYP-D* leads to the best predictions, with absolute errors on cell parameters less than 2.4%.

For the **1·H₂O** phase, the optimized cell parameters show two main trends depending on the functional used. B3LYP leads to good predictions of the a and b parameters, whereas c (along with both vdW forces and the weak H-bond that involves Cl atoms are present) is largely overestimated. On the contrary, the angle β is markedly underestimated (error > 21%). The introduction of the dispersion-correction leads to minor deviations (underestimations within 5%) along the three directions. Also in this case, the B3LYP-D* functional furnishes the best result with respect to the experimental structure, notwithstanding the angle β presents considerable deviations. The volume of the unit cell for the structure optimized by both B3LYP-D2 and B3LYP-D* functionals is smaller than the experimental one; this is probably due to a wrong inclusion of the long-range tail of the electrostatic part of H-bond interactions as dispersive interactions. The opposite effect, i.e. a lacking in description of long-range forces, is evident from the severe deviations (about 10% to 25%) on cell parameters given by the pure B3LYP functional.

Summarizing, the B3LYP-D* functional provided the best predictions for cell parameters – and even for intra- and inter- molecular ones (see Figure 7.5). Thus, for brevity, only the results obtained with such approximation are commented in the following.

Table 7.1: Cell parameters of the **1 α** and **1·H₂O** forms obtained from full geometry optimizations. % relative deviations in parentheses.

1α form				
	B3LYP	B3LYP-D2	B3LYP-D*	Exp. ^a
<i>a</i> (Å)	19.161 (27.572)	14.669 (-2.335)	14.890 (-0.867)	15.02
<i>b</i> (Å)	7.173 (-1.387)	7.067 (-2.848)	7.200 (-1.013)	7.274
<i>c</i> (Å)	15.973 (3.056)	14.840 (-4.256)	15.123 (-2.433)	15.5
β (deg)	93.213 (-2.345)	95.296 (-0.164)	95.726 (0.287)	95.452
Volume (Å ³)	2192.00 (30.03)	1531.81 (-9.13)	1613.20 (-4.30)	1685.75
1·H₂O form				
<i>a</i> (Å)	16.222 (3.157)	15.124 (-3.822)	15.146 (-3.684)	15.725
<i>b</i> (Å)	15.977 (0.871)	15.391 (-2.830)	15.753 (-0.544)	15.839
<i>c</i> (Å)	9.031 (21.707)	7.133 (-3.867)	7.257 (-2.204)	7.42
β (deg)	76.006 (-9.759)	87.981 (4.460)	87.830 (4.280)	84.225
Volume (Å ³)	2271.11 (23.51)	1659.40 (-9.76)	1730.14 (-5.91)	1838.78

a: from Ref. [1].

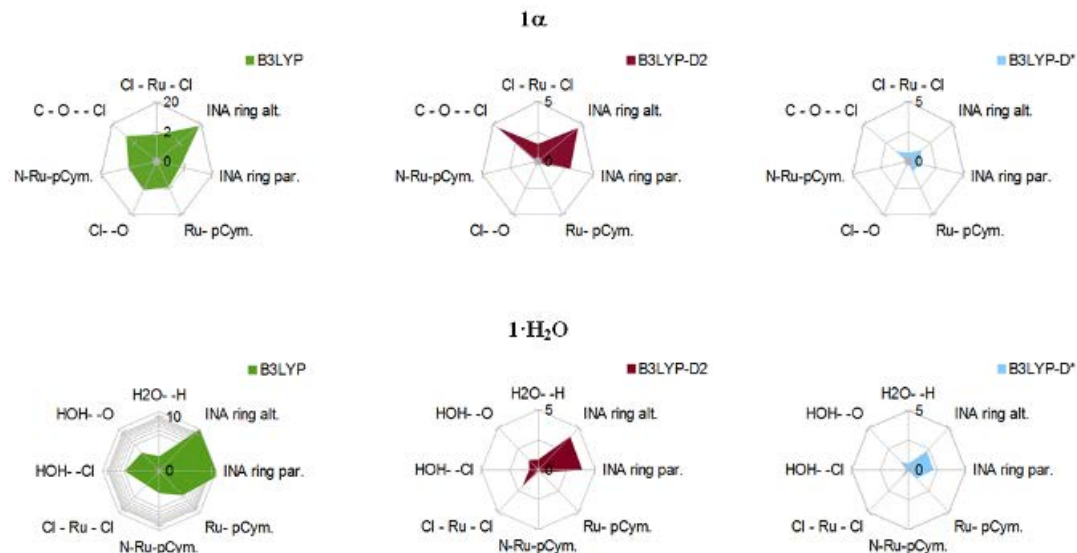
7.3.2 Intra- and inter- molecular parameters.

Some relevant **1 α** polymorph distances (B3LYP-D*) and angles are given in Table 7.2, together with their absolute deviation from the experimental data. The -Cl $\cdots$ (H)O distance (from now on referred as Cl $\cdots$ O) and the C-O(-H) $\cdots$ Cl- angle (from now on referred as C-O-Cl) are used to characterize the hydrogen bond length and angle of the **1 α** phase, respectively (Figure 7.3). In the same way, for **1·H₂O**, the H₂O oxygen-chlorine distance (HO(H) $\cdots$ Cl), and two oxygen-oxygen distances (H₂O $\cdots$ (H)O; HO(H) $\cdots$ O) are considered (both the water molecule and the carboxyl moieties give rise to H-bonds by using both their H and O atoms – vide supra, Figure 7.4). Moreover, two intermolecular parameters, which represent the INA arene-stacking distances depicted in Figure 7.3, are also reported in Table 7.2. Both the “parallel” and the “alternate” configurations are measured. If it is considered that long distances (3-4 Å to 7-9 Å) are involved, these parameters may give an idea of the structural impact of long-range dispersive effects.

Table 7.2: Important angles and distances of the **1 α** and **1·H₂O** forms obtained from full geometry optimizations. Absolute deviations in parentheses.

1α form			1·H₂O form		
	B3LYP-D*	Exp. ^a		B3LYP-D*	Exp. ^a
Cl...O (Å)	3.037 (0.004)	3.033	H ₂ O... (H)O (Å) ^b	2.542 (0.014)	2.556
C–O–Cl (deg)	112.435 (1.538)	113.973	HO(H)...O (Å) ^c	2.781 (0.027)	2.808
N–Ru–p-Cym. (deg)	127.166 (0.188)	127.354	HO(H)...Cl (Å) ^d	3.103 (0.007)	3.11
Ru–p-Cym. (Å)	1.685 (0.016)	1.669	N–Ru–p-Cym. (deg)	129.061 (0.115)	128.946
Cl–Ru–Cl (deg)	86.770 (0.629)	86.141	Ru–p-Cym. (Å)	1.685 (0.017)	1.668
INA ring parall. (Å)	7.200 (0.074)	7.274	Cl–Ru–Cl (deg)	86.873 (0.856)	86.017
INA ring altern. (Å)	5.030 (0.075)	5.105	INA ring parall. (Å)	7.257 (0.163)	7.42
			INA ring altern. (Å)	3.880 (0.089)	3.969

a: from Ref. [1]. *b:* H-bond between water oxygen and -COOH oxygen (hydrogen). *c:* H bond between water oxygen (hydrogen) and -COOH oxygen. *d:* H bond between water oxygen (hydrogen) and chlorine.

**Figure 7.5:** Net-charts for B3LYP, B3LYP-D2 and B3LYP-D* absolute % relative distances and angles deviations of the **1 α** and **1·H₂O** crystal forms: since showing a minor colored area, the B3LYP-D* parameters agree better with expt. data.

The **1 α** /B3LYP values are reported in a 0% - 20% logarithmic scale and the **1·H₂O**/B3LYP values are reported in a 0% - 16% logarithmic scale, for convenience.

7.3.3 ¹³C and ¹H NMR calculations.

The molecular labeling scheme adopted for the calculated ¹³C isotropic chemical shifts is shown in Figure 7.6. The corresponding ¹³C MAS-NMR spectra of **1α** and **1·H₂O** simulated by using the mentioned isotropic chemical shifts – computed on B3LYP-D* optimized geometries – are shown in Figure 7.7, together with their respective experimental spectra [1].

Overall, a satisfactory agreement is found, notwithstanding the perceivable peak shifts at 150÷160 and at ~138 ppm in the ¹³C MAS-NMR theoretical spectrum of the **1α** structure, and the marked peak splitting at ~120 ppm, ~100 ppm and ~80 ppm in the ¹³C MAS-NMR spectrum of the **1·H₂O** form, not detectable by the experiment (Figure 7.7). This can be addressed to the omission of thermal effects (calculations refer to 0K) which are intrinsically present in the experiments.

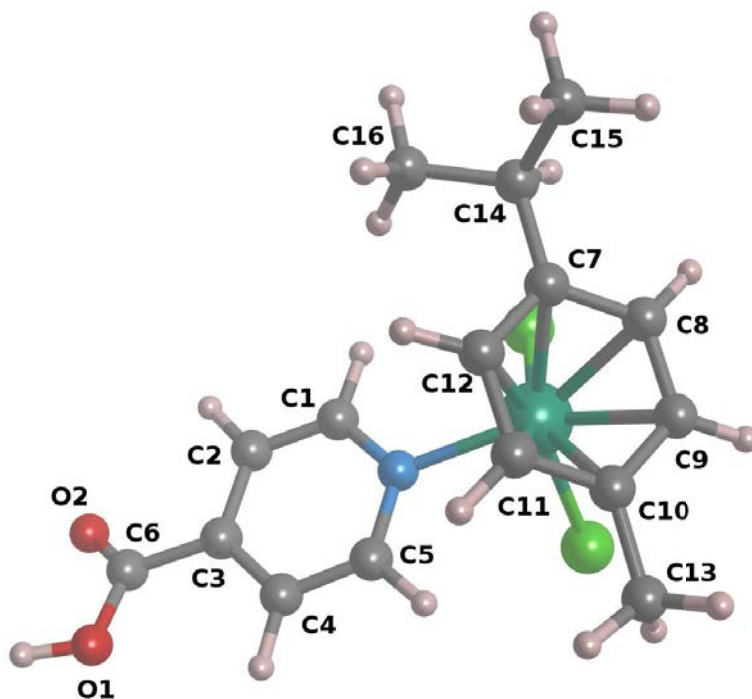


Figure 7.6: Molecular structure and labeling scheme of [(p-cymene)Ru(*k*N-INA)Cl₂]. The original NMR labeling from Ref. [1] on carbon and oxygen atoms of the **1α** polymorph is shown. The **1·H₂O**, **1β** and the two molecules of the **1γ** polymorphs are labeled accordingly, independent of the mutual position of the -COOH and iso-propyl groups (Figure 7.8).

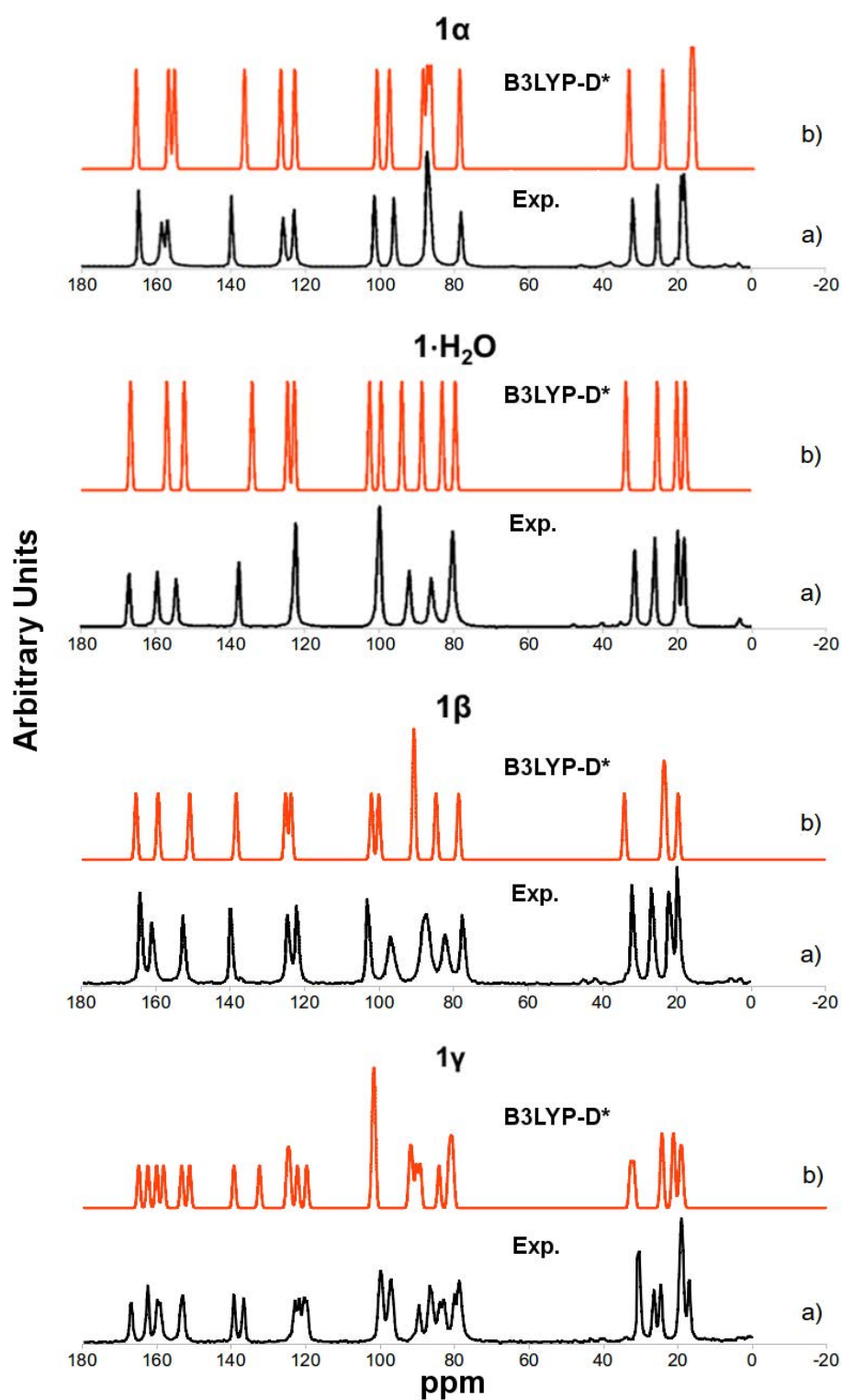


Figure 7.7: Simulated and experimental ^{13}C solid-state NMR spectra of the 1α , $1\cdot\text{H}_2\text{O}$, 1β and 1γ forms.

Further insights can be obtained by the analysis of the Mean Absolute Deviations (MAD) between the computed and experimental ¹³C chemical shifts (δ_{iso}) data values of the **1 α** and **1·H₂O** crystal forms.

MADs are computed as $(\sum_n |(\delta_{iso,n} \text{ (computed)} - \delta_{iso,n} \text{ (experimental)})|) / n$ and given in Table 7.3 for the B3LYP-D* optimized geometries. Overall, a good agreement is detected, the MAD being 1.3 ppm for **1 α** and 1.9 ppm for **1·H₂O**.

Table 7.3: Computed (from B3LYP-D* fully optimized structures) and experimental ¹³C δ_{iso} of the four crystalline forms of [(p-cymene)Ru(kN-INA)Cl₂]. Units in ppm.

	1α form		1·H₂O form		1β form		1γ form	
	B3LYP-D*	Exp. ^a	B3LYP-D*	Exp. ^a	B3LYP-D*	Exp. ^a	B3LYP-D*	Exp. ^b
C1	155.4	156.9	152.4	159.6^d	151.1	152.9	151.4/153.5	160.3/159.5^d
C2	126.8	125.8	124.5	122.6	123.9	122.2	122.4/125.1	120.8/120.0^d
C3	136.6	139.7	134.2	137.7	138.7	140.1	139.4/132.5	139.7/137.1
C4	123.1	122.8	122.7	122.6	125.2	124.8	124.4/119.8	123.3/122.2^d
C5	157	158.4	157	154.5^d	159.6	161.4	158.5/160.3	153.8/153.3^d
C6	165.8	164.6	166.7	167.2	165.7	164.5	165.2/162.7	167.3/162.9
C7	101.1	101.2	99.4	100.1	102.2	103.1	101.6/101.9	100.5/99.9
C8	88.7	86.9	93.9	92.1	90.7	77.6^d	92.2/91.6	79.2
C9	87.7	86.9	88.5	86.1	90.7	82.4^d	89.3/90.3	89.9/87.0
C10	97.8	96	102.5	100.1	100.1	97.1	102.2/101.5	97.4
C11	86.7	86.3	83.1	80.5	84.8	87.8^d	81.1/84.3	86.5/84.3
C12	79	77.9	79.6	80.5	78.7	87.3^d	81.7/80.5	83.2/80.5
C13	16.8	17.7	19.9	20.2	19.6	19.4	20.9/19.3	19.2/17.3
C14	33.5	31.7	33.6	31.7	34	31.8	31.8/32.7	30.8
C15	24.4	25	25.1	26.3	23.6	21.9	23.9/24.4	26.8/24.9
C16	16	18.6	17.6	18.4	23	26.5	18.8/21.2	19.2
MAD^c	1.3		1.9(1.6)^d		3.3(1.8)^d		3.1(2.3)^d	

a: from Ref. [1]. *b*: from Ref. [6]. *c*: Mean absolute deviations (reported in boldface). For **1 γ** , MADs are calculated on the mean of δ_{iso} data values of molecules (1) and (2). *d*: The exchange of C1/C5 δ_{iso} values for **1·H₂O**, C8/C12 and C9/C11 δ_{iso} values for **1 β** , and C1/C5 and C2/C4 δ_{iso} values for **1 γ** (reported in boldface) yields the MADs reported in parentheses.

A mildly larger deviation was expected for the **1**·H₂O chemical shifts since the δ_{iso} scale was set by using the **1** α structure. However, it is worth stressing that a major difference is noted between the computed and experimental ¹³C δ_{iso} assignments of the C1 and C5 atoms of **1**·H₂O. This implies a rotation of the whole INA moiety (C2 and C4 δ_{iso} , are experimentally equivalent). In fact, as it is clearly shown in Figure 7.8a and 7.8b, the mutual positions of the -COOH and p-cymene isopropyl group in the **1**·H₂O phase (C4-C3-C6-O1(H) -169.20°) are almost opposite with respect to those of the **1** α polymorph (C4-C3-C6-O1(H) dihedral angle being 17.92°). Figure 7.8 shows the fully optimized structures, however, this situation is present also in the experimental non-refined structures, but it has not been highlighted in previous works [1, 6]. The recalculated MADs are reported in parentheses in Table 7.3 and result in 1.6 ppm.

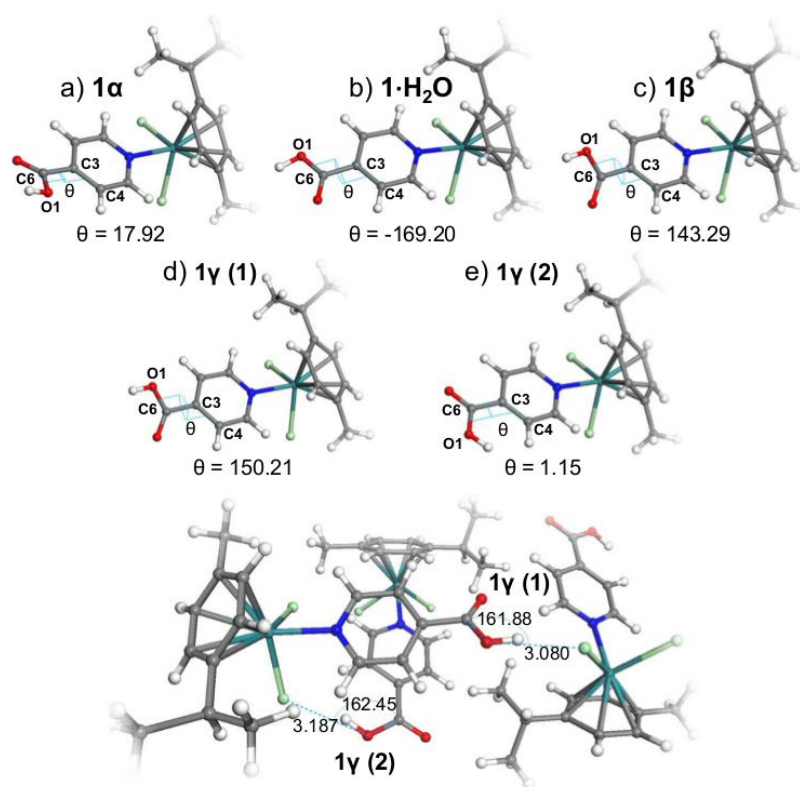


Figure 7.8: (Top) Comparison between the -COOH group structural positions of the different polymorphs (fully optimized geometries): (a) **1** α ; (b) **1**·H₂O; (c) **1** β ; (d, e) the two molecules (1) and (2), respectively, of **1** γ . (Bottom) The two H bonds in the **1** γ form (fully optimized geometry), highlighted with dotted lines.

For the ¹H NMR isotropic chemical shifts given in Table 7.4, the MADs computed after the exchange of H1 and H5 δ_{iso} data are almost invariant. However, a notable deviation of about 7 ppm of the signal of H(OH), that corresponds to the hydrogen atom belonging to the carboxyl group in **1**·H₂O should be highlighted. This discrepancy is probably due to a possible proton exchange with the water molecules that can occur during experiments and that is not taken into proper account by means of static calculations. A deeper investigation of the proton-exchange and of its effects on the ¹H chemical shifts should be based on molecular dynamics simulations that intrinsically include thermal effects [25–27].

Table 7.4: Computed (from B3LYP-D* fully optimized structures) and experimental ¹H δ_{iso} of the four crystalline forms of [(p-cymene)Ru(kN-INA)Cl₂]. Units in ppm.

	1 α form		1 ·H ₂ O form		1 β form		1 γ form	
	B3LYP-D*	Exp. ^a	B3LYP-D*	Exp. ^a	B3LYP-D*	Exp. ^a	B3LYP-D*	Exp. ^b
H1	8.8	9.4	8	8.6 ^d	7.7	8.5	8.2/8.3	9.1 ^d
H2	8.8	8.7	7.2	6.3 ^d	7	7.1	7.1/7.1	7.1 ^d
H4	6.4	6.2	6.4	6.7 ^d	7.2	-	7.1/7.4	6.6/6.5 ^d
H5	7.8	8.6	8.3	8.9 ^d	8.4	9.1	8.4/8.9	8.8/8.9 ^d
H(OH)	10.2	9.9 ^b	15.6	8.7	10.8	10.1	11.0/10.6	10.5
H8	4.8	4.6	5.7	5.8	5.4	5.3 ^d	5.6/5.9	5
H9	4.2	4.6	5.4	5.9	5.5	4.8 ^d	5.7/5.5	5.5
H11	4.9	5	4.5	5.1	4.6	6.0 ^d	4.7/4.8	5.6/5.4
H12	4.7	4.8	5.2	5.1	5.5	5.5 ^d	5.1/5.3	5.0/5.4
H13 ^e	2.7	2.5	2.3	1.8	2.5	1.8	2.6/2.6	1.7/1.4
H14	3.2	3.2	3.3	3.1	3.3	3.2	4.2/3.4	3.2
H15 ^e	1.5	1.2	2	1.4	2.3	1.2	2.3/2.3	1.8/1.6
H16 ^e	0.6	0.5	1.7	1.3	1.3	1.6	1.6/1.2	1.4
MAD ^c	0.3		0.9(0.9) ^d		0.6(0.5) ^d		0.5(0.5) ^d	

a: from Ref. [1]. *b*: from Ref. [6]. *c*: Mean absolute deviations (reported in boldface). For **1** γ , MADs are calculated on the mean of δ_{iso} data values of molecules (1) and (2). *d*: The exchange of H1/H5 and H2/H4 δ_{iso} values for **1**·H₂O, H8/H12 and H9/H11 δ_{iso} values for **1** β , and H1/H5 and H2/H4 δ_{iso} values for **1** γ (reported in boldface) yields the MADs reported in parentheses. *e*: Only one experimental δ_{iso} data value is given for the three H atoms of CH₃ groups (H13, H15, and H16); the mean value is reported for the computed data.

7.4 1 β polymorph

7.4.1 Structural parameters.

The 1 β polymorph ($P21/c - 164$ atoms per cell) is characterized by two layers containing an intermolecular $-\text{COOH} \cdots \text{Cl}$ interaction, which lies in the ab plane (vide supra, Figure 7.1). Although its structure is similar to the 1 $\cdot\text{H}_2\text{O}$ one, the 1 β phase presents the same kind of H-bond ($-\text{COOH} \cdots \text{Cl}$) that belongs to the 1 α polymorph.

The cell parameters obtained by B3LYP-D* full geometry optimizations and their % relative deviations from experimental data are given in Table 7.5. The final cell is more compact than the experimental one, since the overestimation of the b and β parameters compensates for the symmetry change due to a and c . The H-bond pattern along a prevails over the b direction. In the same way, the superposition of aromatic groups provides a strong directionality to long-range correlation effects, consequently giving an underestimation of c .

Table 7.5: Fully optimized 1 β polymorph: (Top) cell parameters (% relative deviations in parentheses), and (Bottom) and important angles and distances (absolute deviations in parentheses).

	B3LYP-D*	Exp. ^a
a (Å)	14.103 (-4.092)	14.705
b (Å)	15.444 (2.375)	15.086
c (Å)	7.410 (-4.054)	7.723
β (deg)	99.936 (1.928)	98.046
Volume (Å ³)	1589.91 (-6.28)	1696.54
Cl $\cdots$ O (Å)	3.130 (0.294)	3.424
C–O–Cl (deg)	124.006 (0.712)	123.294
N–Ru–p-Cymene (deg)	129.081 (0.846)	128.235
Ru–p-Cymene (Å)	1.687 (0.019)	1.668
Cl–Ru–Cl (deg)	87.943 (7.395)	80.548
INA ring parallel (Å)	7.410 (0.313)	7.723
INA ring alternate (Å)	3.792 (0.158)	3.95

a: from Ref. [6].

The results for inter- and intra- molecular parameters (Table 7.5) underline a slight change of the N-Ru-*p*-Cymene and C-O-Cl angles (0.7° and 0.8°, respectively), whereas the Cl-Ru-Cl angle is wider than the experimental one of about 7°. The Cl-Ru-Cl moiety lies perpendicular to the *c* direction, along which the interplay of the H-bond network and vdW forces results in an overestimation of the cell packing. Though the errors in all the distance parameters are small and fall within ~0.3 Å, it is worth to highlight the large absolute % relative deviations of the Cl...O distance (involving the hydrogen bond) displayed in Figure 7.9, which is comparable to the absolute % relative deviations of the Cl-Ru-Cl angle.

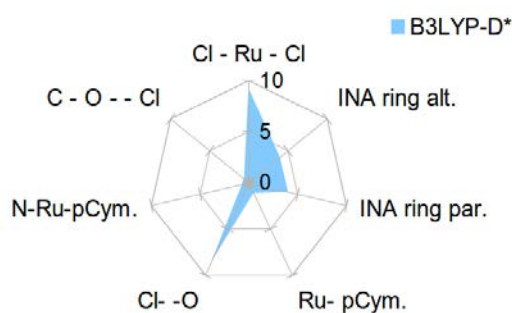


Figure 7.9: Graphical representation of the B3LYP-D* absolute % relative distances and angles deviations from the experimental structures of the **1β** form.

7.4.2 ¹³C and ¹H NMR calculations.

Figure 7.7 (vide supra) allows the comparison of the ¹³C MAS NMR experimental spectrum of the **1β** polymorph with the computed one. Moreover, the computed ¹³C and ¹H chemical shifts (δ_{iso}) are listed in Tables 7.3 and 7.4, together with the experimental values [1]. The impact of geometry optimization of the XRPD **1β** structure on the agreement between theoretical and experimental spectra is notable.

Briefly, the agreement between the δ_{iso} data values calculated on the non-refined XRPD experimental structure and the experimental one is poor. The optimization of H atoms ameliorates significantly the ¹³C and ¹H δ_{iso} data values and the ¹³C spectrum with respect to the non-refined values, while only minor differences are observed when the hydrogen-optimized and the fully-optimized spectra are compared.

Importantly, the computed δ_{iso} data values of the aromatic -CH- groups (Tables 7.3 and 7.4) seem to be in better agreement with the experiment if the δ_{iso} assignments of the C9 and C8 carbon atoms (which belong to the INA p-cymene ring) are interchanged with that of C11 and C12, respectively. In fact, the MAD values for the $^{13}\text{C}/^1\text{H}$ NMR signals after the 8/12 and 9/11 atom exchanging are: MAD ^{13}C = 1.8 ppm MAD ^1H = 0.5 ppm. These figures underline a significant improvement with respect to the assignment furnished by Chierotti et al. [6], which yields a MAD of ^{13}C = 3.3 ppm and MAD of ^1H = 0.6 ppm (see Tables 7.3 and 7.4).

To support this hypothesis, it is worth recalling that Chierotti et al. [6] detected some uncertainties on the aromatic hydrogens and labeled the assignments of ^1H δ_{iso} as H9/H11, H11/H9, H8/H12 and H12/H8. However, here, the first original atoms labeling from Ref. [1] has been retained (Figure 7.6).

7.5 1 γ polymorph

7.5.1 Comparison with the other forms

The phase **1 γ** belongs to the *P*21/a space group, a non-standard setting of *P*21/c for which the polymorph contains two molecules of [(p-cymene)Ru(kN-INA)Cl₂] in the asymmetric unit (8 molecules/328 atoms per cell). Substantial differences in the spatial position of the -COOH group in the two molecular units are observed.

A description of their fully optimized structure is given in Figure 7.10, where a comparison with the non-refined XRPD experimental structure, used as input, is also reported. A comparison among the four crystal forms furnishes interesting information (Figure 7.8): the -COOH moiety of the **1 α** polymorph is almost planar with respect to the INA ring, the C4-C3-C6-O1(H) dihedral angle being 17.92 ° (Figure 7.8a). As explained before, in the **1 $\cdot\text{H}_2\text{O}$** phase a substantial rotation of the -COOH is observed (C4-C3-C6-O1(H) -169.20 ° (Figure 7.8b); whereas the C4-C3-C6-O1(H) dihedral angle of the **1 β** polymorph is 143.29 ° (Figure 7.8c). The first molecule in the fully optimized structure of the **1 γ** polymorph, (also referred as (1) in the following) (Figure 7.8d), being characterized by the -COOH dihedral skewed of 150.21 ° with respect to the INA ring, is similar to the **1 β** form (Figure 7.8c). The second molecule (also referred as (2) in the following) (Figure 7.8e) presents a dihedral of 1.15 ° (almost planar) which is comparable to that of **1 α** (Figure 7.8a), although the acidic hydrogen points in a different direction with respect to **1 α** .

In both molecules of the 1γ polymorph, the acidic hydrogen establishes an $\text{H}\cdots\text{Cl}$ bond with similar geometry, as highlighted in Figure 7.10: the $\text{O}\cdots\text{Cl}$ distances are 3.080 and 3.187 Å for molecule (1) and (2) respectively), and the $\text{O-H}\cdots\text{Cl}$ angles are 161.88° and 162.45° for molecule (1) and (2) respectively. This is reflected also by the electron charge density of the H and Cl atoms involved in the $\text{COOH}\cdots\text{Cl}$ interaction.

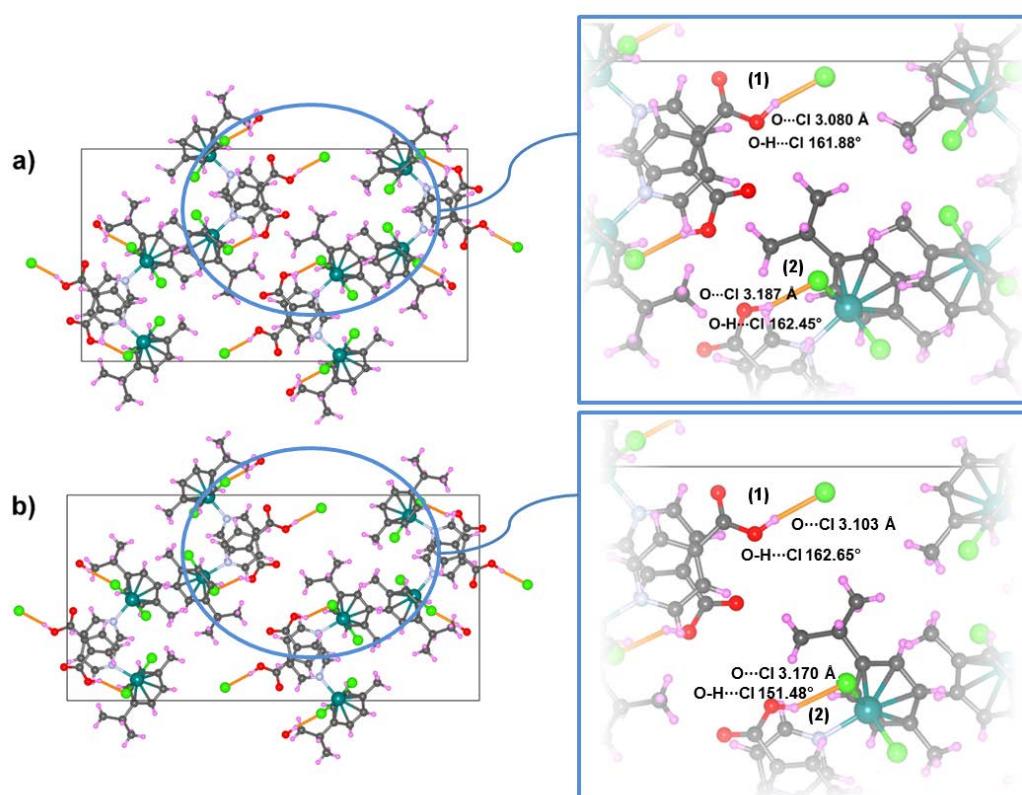


Figure 7.10: ab plane view of a) the fully optimized structure (B3LYP-D*) of the 1γ form, and of b) the non-refined XRPD experimental structure used as input for calculation.

A qualitative pictorial analysis for the three fully optimized (B3LYP-D*) anhydrous polymorphs is given in Figure 7.11. The Bader atomic volumes of the charge density around H and Cl atoms, partitioned according to the Bader's Quantum Theory of Atom in Molecules (QTAIM – [28]), are depicted with an isosurface density value of 0.02 a_0^{-3} . The figure shows that the partial charge on H atoms tends to delocal-

ize in the direction of acceptors (Cl atoms) and the charge density for the H···Cl interaction are similarly shaped for the four molecules, supporting the hypothesis that the two H-bonds present in the **1** γ phase have a similar strength.

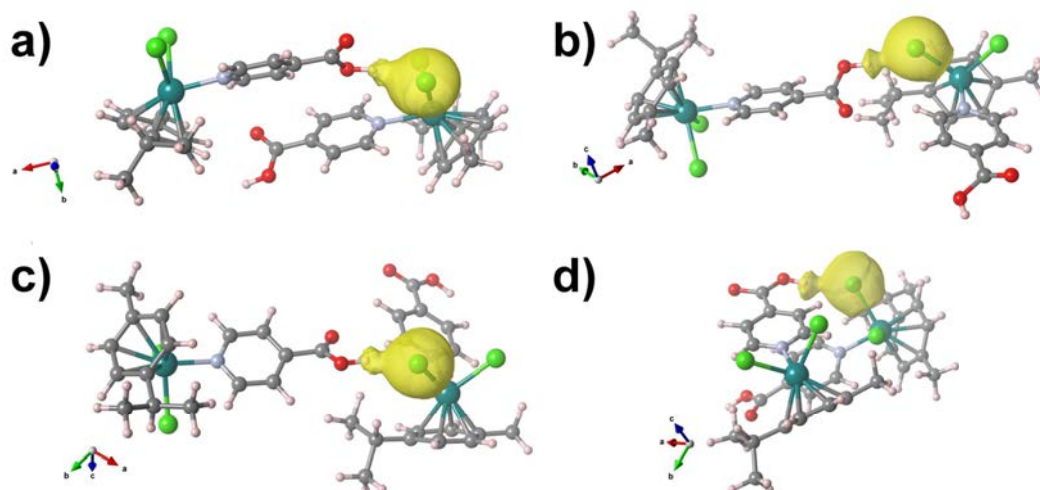


Figure 7.11: Atomic volume partitioning of the Bader charge around the atoms involved in the COOH···Cl interaction for the (a) **1** α , (b) **1** β , (c) **1** γ (1), and (d) **1** γ (2) crystal forms. The yellow surface around the H and Cl atoms is represented with an isosurface density value of $0.02\ a_0^{-3}$. The original charge density has been partitioned through the software ‘Bader’ [29].

Indeed, both the non-refined XRPD experimental structure (Figure 7.10) and the results of the refined XRPD/NMR/DFT structural characterization [6] furnish a detectable difference in the geometry of the O–H···Cl moiety. In fact, the O···Cl distances are 3.103/3.170 Å (Figure 7.10) and 3.085/3.183 Å, and the O–H···Cl angles are 162.65/151.48 (Figure 7.10) and 156.2°/166.2° for the molecules (1) and (2) of the non-refined XRPD experimental and refined XRPD/NMR/DFT structures [6], respectively. This evidence led Chierotti et al. [6] to hypothesize the presence of one strong H···Cl bond and a weaker H···Cl contact in the **1** γ polymorph. Nonetheless, the structure and labeling of molecule (2) in the asymmetric unit, was not reported in Ref. [6].

7.5.2 Structural parameters

The full geometry optimization leads to minor changes in cell parameters. The direction a , along which both H-bonds and dispersive interactions are present, constitutes an exception, being underestimated by 2.4 Å (Table 6). As for **1β**, the INA-rings of alternate layers are aligned along c . Marked absolute % relative deviations on intermolecular parameters are related to the C–O–Cl angle (C–O–Cl (1) 3.6°, and C–O–Cl (2) 9.9°), which involves the hydrogen bonds. Moreover, a considerable discrepancy with the experimental structure is observed for the optimized Cl–Ru–Cl intramolecular angle (overestimated of ~3°). Such rearrangement competes with ring-stacking dispersive interactions to the slight shortening of the c direction. Substantial differences are observed also for the N–Ru–p-Cymene angle (+2.4°/-4.3° for molecule (1) and (2), respectively).

Table 7.6: Fully optimized **1γ** polymorph: (Top) cell parameters (% relative deviations in parentheses), and (Bottom) and important angles and distances (absolute deviations in parentheses).

		B3LYP-D*	Exp. ^a
a (Å)		28.557 (-7.630)	30.916
b (Å)		15.613 (1.773)	15.341
c (Å)		7.309 (-0.791)	7.368
β (deg)		95.980 (0.740)	95.275
Volume (Å ³)		3241.32 (-6.85)	3479.64
Cl...O (Å)	(1)	3.080 (0.023)	3.103
	(2)	3.187 (0.017)	3.17
C–O–Cl (deg)	(1)	124.802 (3.604)	128.406
	(2)	130.037 (9.957)	139.994
N–Ru–p-Cymene (deg)	(1)	128.440 (2.388)	126.052
	(2)	128.286 (4.337)	132.623
Ru–p-Cymene (Å)	(1)	1.685 (0.017)	1.668
	(2)	1.690 (0.022)	1.668
Cl–Ru–Cl (deg)	(1)	88.756 (3.213)	85.543
	(2)	87.368 (3.708)	83.66
INA ring parallel (Å)		7.309 (0.059)	7.368
INA ring alternate (Å)		3.798 (0.037)	3.835

a: from Ref. [6].

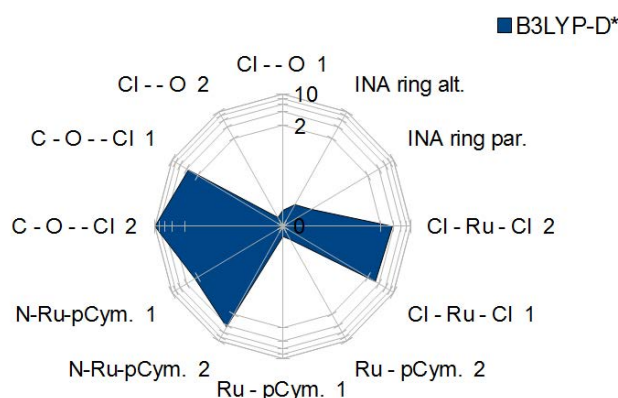


Figure 7.12: Graphical representation of the B3LYP-D* absolute % relative distances and angles deviations from the experimental structures of the 1γ form. Deviations are reported in a 0% - 10% logarithmic scale, for convenience.

7.5.3 ^{13}C and ^1H NMR calculations

The simulated ^{13}C MAS NMR spectra of the 1γ polymorph computed on the refined structure is shown in Figure 7.7, and the calculated ^{13}C and ^1H chemical shifts (δ_{iso}) are listed in 7.3 and 7.4.

The presence of two molecules of $[(p\text{-cymene})\text{Ru}(k\text{N-INA})\text{Cl}_2]$ in the asymmetric unit, almost indistinguishable in the experimental spectra, yields at two different sets of δ_{iso} data values for the calculated parameters and a manifold ^{13}C spectrum, where many peaks are overlapped. Therefore, the agreement between the experimental and simulated spectra can be considered only qualitative. Importantly, more accuracy in the peaks position of the carbon atoms belonging to the ring carrying the -COOH group of the two molecules (Table 7.3) is achieved when the δ_{iso} data value assignments of the aromatic C1 is exchanged with its equivalent atom C5, and C2 with C4. This is highlighted by the values of the MADs calculated by considering the mean δ_{iso} data values of molecule (1) and (2), both with the original assignment and after the exchange.

The comparison between the computed and experimental ^1H δ_{iso} data values (Table 7.4) is difficult, since the broad experimental signals impede the discrimination and assignments of most of the ^1H resonances for the symmetry non-equivalent molecules. However, in general, the same considerations done for the ^{13}C δ_{iso} data

values hold also in this case. Interestingly, a broad signal centered at 10.5 ppm was detected for the -COOH hydrogen (H6) in the experimental MAS spectrum recorded by Chierotti et al. [6].

This signal presents a reduced intensity with respect to the corresponding one in the **1 β** polymorph. Thus, the authors hypothesized the presence of a second weak hydrogen bond, whose signal is supposed to fall in the region characteristic of the pyridine protons. This hypothesis was supported by the results of a NMR-GIAO DFT calculation, which yielded ¹H δ_{iso} data values of 12.2 and 9.6 ppm for the strong and weak interaction, respectively. However, no signal is present at 12.2 ppm in the experimental spectrum.

Furthermore, the more accurate NMR-GIPAW DFT calculations carried out in this work, on the non-refined experimental geometry, yields to a very different result: a ¹H δ_{iso} of 9.5 and 9.4 ppm for the acidic hydrogen of the two molecules. These discrepancies suggest that, as pointed out previously, the experimental geometry might require further refinement. In fact, it is worth recalling that the experimental structure was obtained by an iterative XRPD-DFT calculation procedure and no correction for dispersion effects was included in the periodic lattice DFT calculations [6]. Moreover, NMR-GIPAW DFT calculations on the refined XRPD/NMR/DFT structure reported by Chierotti et al. [6] provide ¹H δ_{iso} data values of 11.0 and 10.9 ppm, for the strong and weak H bonds and are in disagreement with the DFT-GIAO results.

These results reflect the differences in the accuracy of the two theoretical approaches and suggest that the peaks of both the hydrogen atoms engaged in the formation of the H-bonds lie in the same spectral regions. That is, the peak of the second hydrogen does not fall overlapped under the signals of aromatic hydrogen atoms in ortho position, with respect to the pyridine nitrogen atoms as hypothesized by Chierotti et al. [6].

The NMR-GIPAW DFT calculations carried out in this work on the structures optimized by including the dispersion corrections furnish results more comparable with the experimental data, as testified by the impressive agreement with the ¹H-¹³C FSLG-HETCOR spectrum shown in Figure 7.13. In particular, the ¹H δ_{iso} data values computed for the -COOH hydrogen (H6) after hydrogen relaxation are 10.4/10.6 ppm for molecule (1)/(2), respectively. Slightly different values (11.0/10.6

ppm for molecule (1)/(2), respectively) are obtained also in the case of the fully relaxed structure (Table 7.4), once again endorsing the hypothesis of two distinct $\text{COOH}\cdots\text{Cl}$ bonds of comparable strength.

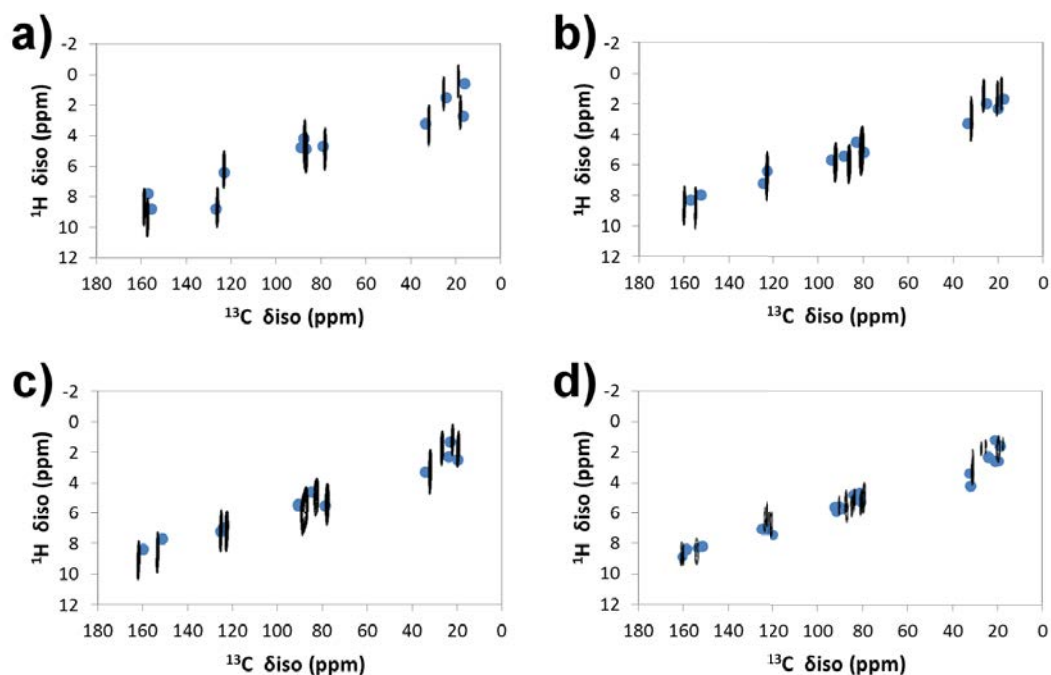


Figure 7.13: Superposition of the ^1H - ^{13}C FSLG-HETCOR experimental spectra (in black) obtained for the a) 1α form [1], b) $1\cdot\text{H}_2\text{O}$ form [1], c) 1γ form [1] and 1γ form (Ref. [6]) and the correlated ^1H - ^{13}C NMR parameters (blue dots) obtained by means of the NMR-GIPAW DFT calculations on B3LYP-D* fully optimized structures.

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Chapter 8

Investigating the optical features of thermochromic salicylidene aniline

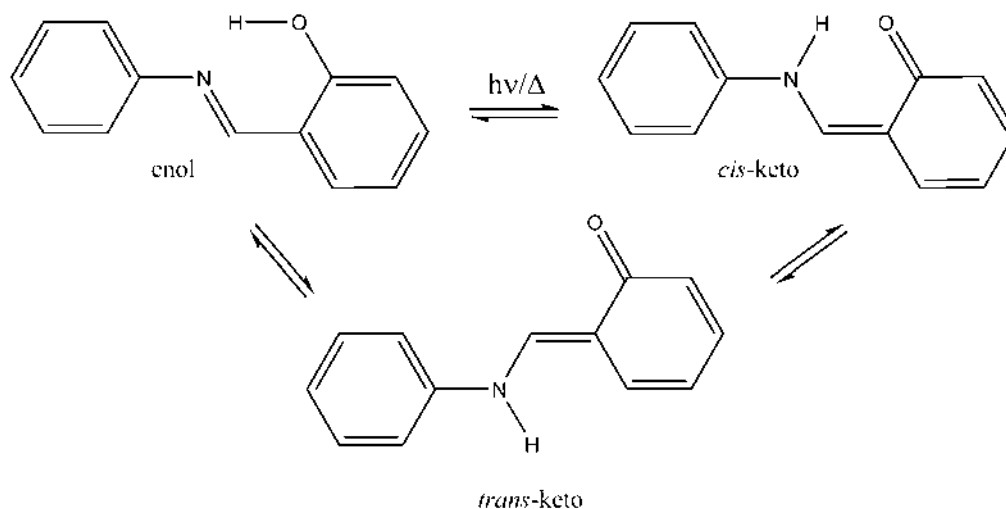
8.1 Introduction

Recently, thermochromic (TC) and photochromic (PC) organic molecular crystals, i.e. systems that change their colour under thermo- or photo- irradiation, have received a great attention in research fields like nanotechnology and optoelectronics, because of their applications as data storage, electronic display systems, optical switching devices and actuators [1–5].

In this context, the molecular and solid forms of salicylidene aniline (SA, see Figures 8.1 and 8.2) and its derivatives have been extensively investigated, through the use of spectroscopic techniques (such as UV-Visible absorption and emission spectroscopies [6–16]).

SA shows a simple structure, but it presents manifold PC/TC mechanisms. Briefly explained, SA is a compound that shows an excited-state intramolecular proton transfer (ESIPT) of the hydroxyl proton, switching from the colourless cis-enol form to the corresponding coloured cis-keto tautomer. Such reaction can be photo- or thermally induced [11, 16, 17]. After the proton transfer (PT), a cis-trans isomerization of the keto form takes place, yielding to the final orange-red coloured photoproduct.

Figure 8.1: Scheme of the molecular ESIPT process of SA: the ground-state enol-form, when excited by photo- or thermo- irradiation, undergoes to ESIPT, leading to the cis-keto form. The latter can give a cis-trans photoisomerization to the metastable trans-keto form or relax back.



From experimental studies, it was established that i) the pale-yellow colour firstly attributed to the stable enol form of molecular SA within all the solid phases is related, indeed, to the presence of traces of the unstable cis- keto form at RT (room temperature). 14 Hence, at present, it is accepted that ideal, stable and pure crystals of any phase of SA in the enol form are colorless. ii) Two PC structures, namely α_1 [18, 19] and α_1 [19, 20] and one TC (β - [19]) polymorph were obtained.

However, after the structural revision of Arod et al. [19], no experimental investigations of the PC/TC properties of SA in solid state are available, with the mechanisms of such PC/TC induced processes still unexplained. The crystal structure of the ESIPT products (i.e. the cis-keto or trans-keto tautomers) is, as well, still unknown.

Recent efforts from the theoretical point of view (see, for example, Refs. [17, 21, 22]), were focused only on the molecular isomerization and photoisomerization of SA, that were deeply investigated by using different approaches. Computational studies of the processes mentioned above are still lacking for the solid forms of SA.

With the aim of defining a general computational protocol that enables the theoretical description of photo- and thermo- chromic molecular crystals from a geometrical, electronic and spectroscopic point of view, SA can be considered as an excellent test case, in view of the detailed experimental characterization mentioned above. Due to the complexity of PC/TC mechanisms of crystalline SA we decided, here, to focus on the computational investigation of the β thermochromic polymorph.

In particular, with the present work, we aimed to define a Density Functional Theory (DFT)-based computational approach to describe the structural and optical (UV-Vis absorption) features of such molecular crystal.

The protocol relies on a periodic dispersion-corrected DFT description of the structural and electronic features of the molecular crystal at the ground-state. It makes also use of a Time-Dependent DFT (TD-DFT) QM/QM' ONIOM embedding model [23, 24] to reproduce the influence of the surroundings on the UV-Visible properties of the system. More details are given in the next Section, where the computational strategy is better explained.

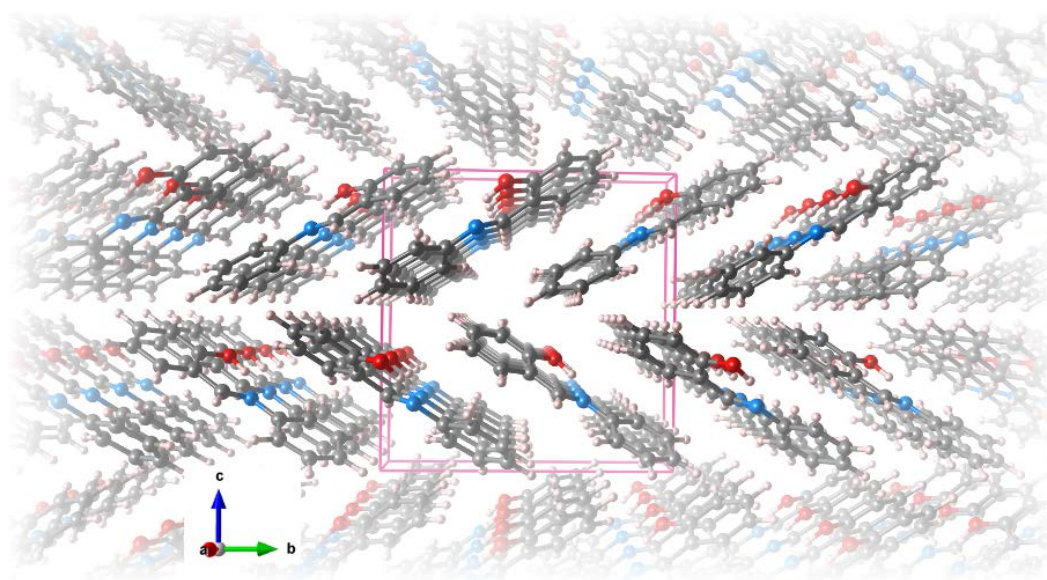


Figure 8.2: β thermochromic polymorph of SA: perspective view from the bc plane.

8.2 Computational protocol

It was recently shown that, in general, it is possible to describe the ESPT phenomena – at the molecular level – quite accurately, using both post-Hartree Fock and DFT based approaches [25–27]. Nonetheless, situations dealing with this kind of properties in molecular crystals are much more involved [10, 19].

In the present case, assuming that the enol-to-cis-keto PT process and, in the same way, the cis-trans (keto) isomerization do not take place *simultaneously* for all the molecules inside the crystal, but that these processes take place locally first, it is possible to spectroscopically characterize the photo- or thermally- induced proton transfer using a cluster model.

In particular, by cutting out from the molecular bulk crystal representative clusters containing all the relevant surrounding molecules, the ground- and excited- state properties of all the species involved in the PT reaction can be computed, and the properties of the molecular material simulated.

A previous theoretical study focused on the investigation of excited-state geometries of molecular crystals, using a QM/MM approach [28]. However, such a study did not consider periodic DFT calculations for the solid-state phase – and the MM level can be considered as insufficient for mimicking the surrounding effects on the local excited-state, especially when electronic embedding is missing.

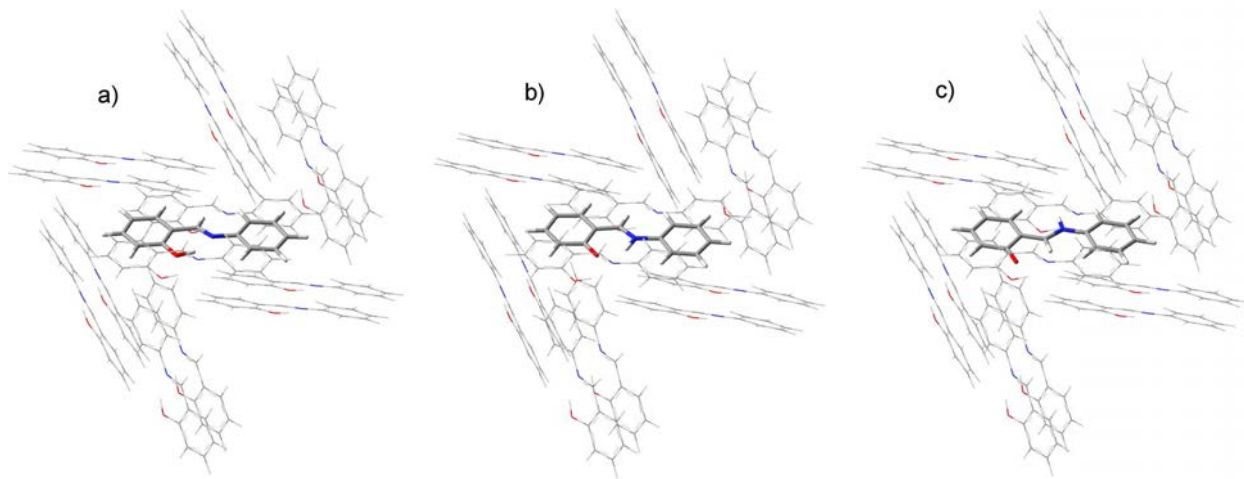
The considerations made above motivated us for the setup of a mixed periodic/cluster approach to study the proton transfer mechanism, provided that the same DFT computational level can be applied. DFT – especially in conjunction with the use of hybrid functionals – has proven to be a powerful tool for the description of electronic and structural features of bulk materials [29–32]; furthermore, its accuracy [33] have been further strengthened thanks to the recent implementation of corrections to take dispersive interactions into account. At the same time, the efficient implementation of embedding techniques in an ONIOM formalism – by allowing the simulation of the effect of the surroundings on ground- (DFT) and excited- (TD-DFT) states at molecular level – furnishes all the necessary building blocks for the setup of an efficient and accurate computational protocol for the description of ground- and excited-state properties of photo- and thermo- chromic molecular crystals.

Details regarding the computational methods used for calculations are given in Appendix A. Here, we give an idea of the protocol adopted to model ground- and excited-state properties of the crystalline SA, in particular:

- ground-state DFT calculations in periodic boundary conditions (PBC) were carried out in order to optimize the experimental input structure – the enol form of the β thermochromic polymorph of SA. The B3LYP [34] hybrid functional was used alone, and in combination with the Grimme D2 [35] and the alternative D* [36] schemes for dispersion correction – adopting the 6-311G(d) basis-set.
- As expected, the results given by dispersion-corrected DFT, especially those of B3LYP-D* are better in agreement with the experimental structure. After a careful analysis of the intermolecular interactions framework, a cluster of 15 enol molecules of SA was individuated and extracted from the optimized bulk, to be used for ONIOM QM/QM' calculations.
- One SA molecule was treated at high-level (QM layer), while fourteen molecules were kept at low-level (QM' layer). The innermost SA molecule (high-level) was fully optimized (B3LYP-D*/6-311G(d)), keeping fixed the coordinates of surrounding molecules. The same optimization procedure was pursued, maintaining fixed the low-level layer in the enol form, but while fully relaxing the central molecule in its cis-keto or trans- keto forms. The clusters obtained are labelled, for convenience, in the following as: **C-enol**, **C-cis-keto** and **C-trans-keto**, respectively. The three clusters are represented below in Figure 8.3.

Vertical excited states of the optimized clusters were computed at ONIOM QM/QM' level, with charge embedding (Mulliken charges), adopting the hybrid B3LYP/6-31+G(d) functional – as high-level method – and the HF/3-21+G(d) model, which was used as low-level approximation.

Previous works have demonstrated that the embedding potential obtained at this level of theory is able to accurately simulate the effects related to surrounding environment [37, 38].

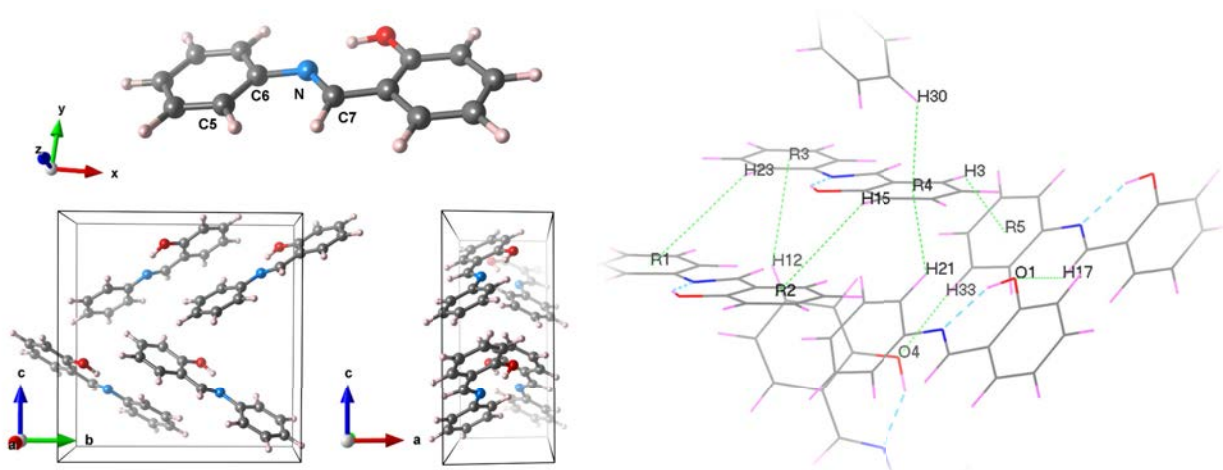
Figure 8.3: (a) C-enol, (b) C-cis-keto and, (c) C-trans-keto clusters.

8.3 β polymorph: structural and electronic behaviour

The β polymorph of crystalline SA (Figures 8.2 and 8.4) contains 104 atoms in the unit cell ($Z = 4$). Each molecule inside the crystal – at the ground state – is present in its colourless and stable enol-form, which is characterized by an intramolecular H-bond (see Figure 8.4). The enol-form is found to be almost planar, within the crystal, and leads to a solid structure that belongs to the $Pbc2_1$ space group (orthorhombic system), where the SA molecules lie along the b lattice vector. SA molecules are stacked along the c lattice vector, giving rise to a ‘fishbone’-like pattern that is depicted from the bc plane view in Figures 8.2 and 8.4.

Starting from the experimental structure, full geometry optimizations were performed at the B3LYP, B3YLP-D2 and B3LYP-D* levels of theory – utilizing the 6-311G(d) basis-set. Table 8.1 shows the predicted cell parameters and volumes. It can be noted that the largest differences between the three methods are due to the addition of dispersion-correction terms (either -D2 or -D*). Between them, the B3LYP-D* demonstrates a remarkable accuracy with small deviations from the experimental values, except for the c lattice vector, that is significantly underestimated at B3LYP-D* level (-0.5 Å). This is related to the well-known tendency of Grimme’s correction to overestimate dispersive interactions [32, 36]: not surprisingly, along the c axis a greater number of such interactions are present, with respect to the other two directions.

Figure 8.4: Molecular form of SA: Left (top) – the SA molecule in its almost-planar configuration within the crystal; (bottom): view of the unit cell from the bc and ac planes. Right: Intermolecular parameters (green lines) of the β polymorph (a labelling for involved atoms is given). Intramolecular H-bonds are also highlighted (blue lines).



The underestimation mentioned above can also be due to a spurious ‘attractive’ effect that arises from the Basis-Set Superposition Error (BSSE), which could be sizeable with the adopted basis-set (6-311G(d)). As a consequence, the cell volume is underestimated at the B3LYP-D* level of about -6%, which is, indeed, less than half of the error associated to B3LYP-D2 (ca. -14%).

Table 8.1: Cell parameters ($\text{\AA}$), volume ($\text{\AA}^3$), and percentage relative volume deviations with respect to the experimental data of the fully optimized SA β polymorph. Deviations in parentheses.

	B3LYP	B3LYP-D2	B3LYP-D*	Exp. ^a
a ($\text{\AA}$)	6.846 (1.052)	5.589 (-0.205)	5.755 (-0.039)	5.794
b ($\text{\AA}$)	11.855 (-1.163)	12.476 (-0.542)	12.781 (-0.237)	13.018
c ($\text{\AA}$)	18.111 (4.494)	12.720 (-0.897)	13.141 (-0.476)	13.617
Volume ($\text{\AA}^3$)	1469.829	886.934	966.651	1027.077
% Rel. Vol. Dev.	+43.11	-13.65	-5.88	-

a: from Ref. [19] – measured at $T = 120$ K.

Clearly, in absence of dispersion-corrections (i.e. B3LYP result) a large deviation on cell parameters is given, leading to a marked overestimation of the cell volume (more than 43%). Based on these results, only the B3LYP-D* seems to provide a reasonable description of the geometrical features of SA molecular crystals.

8.3.1 Intra- and inter- molecular properties

In Table 8.2, the most relevant computed intramolecular structural parameters are reported and compared with the experimental ones, for a better understanding of the SA molecular arrangement within the crystal.

Overall, small deviations from the experimental values are observed for all parameters computed by either the -D2 or -D* corrections. Bonds with non-covalent behaviour – i.e. $N\cdots O$ and $N\cdots H$ – seem to be described quite accurately.

The largest differences are related to the structural parameters affected by the crystal packing. These are the C5-C6-N-C7 dihedral angle and the C-O-H angle (*vide supra* Figure 8.4 for atom labelling), for which deviations of -0.3° and -1.8° were computed, respectively, at the B3LYP-D* level. B3LYP-D2 provides a larger deviation for C5-C6-N-C7 ($+1.9^\circ$), angle that is severely overestimated by B3LYP ($+24.5^\circ$). This provides further evidences for the need of accounting for dispersive interactions. A C5-C6-N-C7 dihedral angle of nearly 7° (at B3LYP-D* level) imposes an almost planar conformation to the SA molecule. This spatial arrangement of SA molecules in the β polymorph is due to the presence of many $H\cdots\pi$ interactions. These have been monitored to better investigate the manifold intermolecular interactions, together with two relevant $H\cdots O$ distances.

The values reported in Table 8.2 show that the optimized structural parameters are reasonably predicted at the B3LYP-D* level, since differences with available experimental data span from about 0.10 Å to 0.26 Å. All the monitored distances are mildly underestimated, due to the $H\cdots\pi$ interactions: the weak polar character – typical of such kind of interactions – is, probably, not correctly accounted for by the use of the -D* correction term. The overestimation of medium/long range effects could be the main cause for a compact packing: the molecules are more constricted than experimentally observed (as analogously explained before for calculated cell parameters). This affects also the $H\cdots O$ distances.

Table 8.2: Intra- and inter- molecular parameters (Å and degrees) of the fully optimized β structure of SA and for the isolated molecule in the enol form (see labels in Figure 8.2).

Gas-phase (intramolecular parameters)					
Bond		B3LYP	B3LYP-D2	B3LYP-D*	MP2/6-31G(d,p) ^a
N⋯H		1.780	1.795	1.779	-
N⋯O		2.656	2.666	2.655	2.641
C-O-H		108.2	108.4	108.1	-
C5-C6-N-C7		40.2	37.6	42.10	-
C8-C7-N-C6		(177.3)	(177.3)	(177.6)	177.9
O-H		0.988	0.987	0.988	0.990
C-O		1.340	1.341	1.341	1.350
C7-N		1.287	1.287	1.287	1.299
Solid-state (intramolecular parameters)					
		B3LYP	B3LYP-D2	B3LYP-D*	Exp. ^b
N⋯H		1.769	1.758	1.757	1.796
N⋯O		2.652	2.641	2.646	2.639
C-O-H		107.9	107.7	107.4	109.2
C5-C6-N-C7		31.116	8.542	6.955	6.637
O-H		0.991	0.995	0.994	0.963
C-O		1.346	1.348	1.348	1.365
C7-N		1.288	1.289	1.289	1.294
Solid-state (intermolecular parameters)					
H⋯O	H17⋯O1	3.388	2.550	2.699	2.909
	H33⋯O4	5.166	2.463	2.677	2.904
H⋯π	H23⋯R1	5.135	3.627	3.786	3.961
	H12⋯R3	4.288	2.926	3.061	3.323
	H30⋯R4	3.283	2.419	2.568	2.667
	H21⋯R4	3.334	2.400	2.532	2.773
	H3⋯R5	4.234	2.428	2.562	2.774
	H15⋯R2	4.594	3.546	3.715	3.884

a: from Ref. [21]; *b*: from Ref. [19].

As expected, the gas-phase intramolecular parameters provided by the three approaches are very similar, except for the C5-C6-N-C7 dihedral angle, which presents variations of only ca. 5°. Indeed, in this case, long-range effects are minimal and the contribution of dispersion-corrections is negligible. This is also proven by the small deviations furnished by the three methods with respect to previously published

high-level MP2/6-31G(d,p) calculations [21]. Notice that the non-planar conformation obtained for the isolated SA molecule in gas-phase (with a predicted dihedral angle of about 40°) was somehow expected due to intramolecular steric effects.

Nonetheless, the B3LYP-D* approach appears to be very accurate for the determination of the structural features of SA for all the three kinds of structural parameters that were considered, namely: i) the cell parameters, ii) the main intramolecular parameters and iii) the intermolecular parameters responsible for the crystal packing.

To get more insights on the electronic structure of solid SA, the total Density of States (DOS) of the β polymorph was computed – it is displayed in Figure 8.5. Here, the population of the highest valence bands (VB) and the bottom conduction bands (CB) are also given.

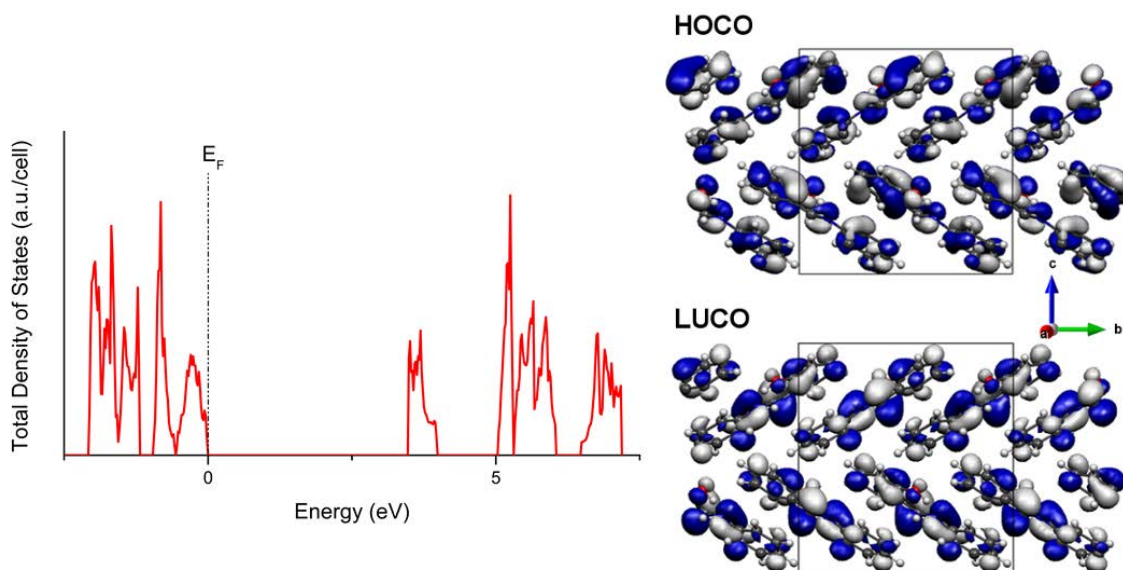


Figure 8.5: Fully optimized SA β polymorph – enol structure: computed total density of states (DOS). The top of B3LYP-D* valence bands was set as reference Fermi Energy ($E_F = 0$). The corresponding Γ -point frontier orbitals (HOCO-LUCO) are also reported (isocontour value of 0.02 a.u.).

The β polymorph in the enol-form presents a band gap of 3.50 eV at the B3LYP-D* level. This value can be compared with the HOMO-LUMO gap of 4.17 eV obtained from the relaxed SA molecule in gas-phase. This difference derives both

from structural and electronic factors. In order to decouple them, the HOMO-LUMO gap for the isolated SA molecule – kept fixed at the PBC optimized geometry – was also calculated. The value obtained (3.97 eV) shows that purely electronic effects, related to the presence of the surrounding molecules, account largely for the gap modification (0.47 eV over a total difference of 0.67 eV).

This fact clearly underlines the necessity of including the closest interacting molecules when aiming at reproducing the ground- or excited- electronic features of this molecular material via finite-cluster approach, and the necessity of explicitly including not only their geometrical effects but also the electronic ones.

As expected for molecular systems undergoing to ESIPT, the HOMO-LUMO transition (with $\pi - \pi^*$ character) that is responsible for the PT reaction gives rise to a density depletion of the hydroxyl-enolic oxygen atom, thus justifying its increase of acidity at the excited-state and, overall, the possibility of an energetically favorable proton transfer reaction.

On the other hand, the gain in density at the excited-state on the acceptor group (N atoms) seems, in the present case, to be quite limited. As clearly highlighted by the crystalline and molecular orbitals computed for SA in the enol-form (Figure 8.6), the nature of the MOs involved in the ESIPT process is not affected by the presence of the surrounding molecules. Thus, the main influence of the environment appears to be on the energetics of the process, but not on its mechanism.

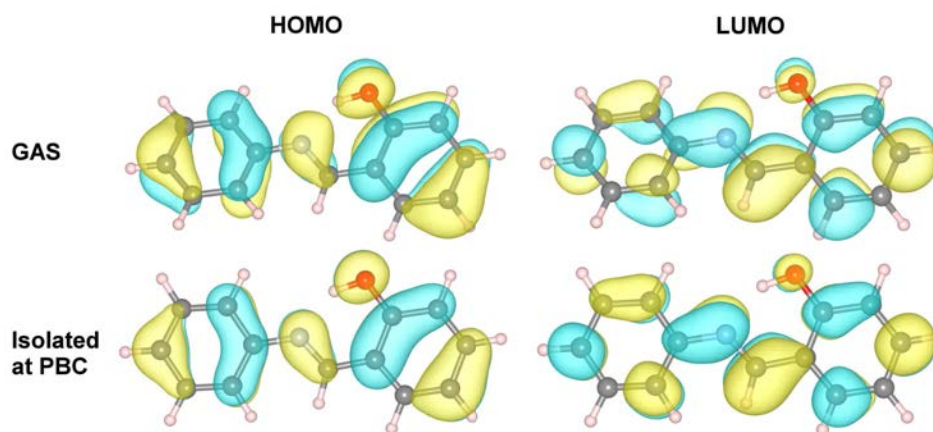


Figure 8.6: HOMO and LUMO orbitals displayed for the SA enol molecule: gas-phase and isolated molecule from PBC are shown.

8.4 Optical features: UV-Visible absorption

The three clusters of Figure 8.3 – **C-enol**, **C-cis-keto** and **C-trans-keto** – were investigated by means of TD-DFT through the use of a QM/QM' ONIOM model with charge embedding, in order to evaluate accurately the effect of the surrounding environment on the excited-state properties of the SA molecule.

The cluster size (15 molecules: fourteen explicit molecules of SA treated at low QM' level, one central molecule of SA treated at high QM level) were chosen on the basis of the network of intermolecular interactions discussed before in Section 8.2.

In particular, the molecules considered are related to the central one via intermolecular interactions that span from about 2.5 Å to 3.8 Å. This range can be safely considered for including all the most relevant $\text{H}\cdots\pi$, $\text{H}\cdots\text{O}$ interactions and weaker – van der Waals type – effects. Moreover, we can reasonably assume that the molecules of the low layer form a cage that screens all further interactions that may be envisaged with more distant molecules. The most relevant optimized intramolecular parameters corresponding to the three tautomers of SA – obtained for both clusters and isolated molecules – are collected in Table 8.3.

Clusters - B3LYP-D*	C-enol	C-cis-keto	C-trans-keto
N...H/ N-H	1.757	1.033	1.014
N...O	2.645	2.645	4.021
C-O-H/ C-O...H	107.390	102.982	55.697
C5-C6-N-C7	8.483	2.696	-178.116
O-H /O...H	0.994	1.786	4.684
C-O	1.348	1.266	1.246
C7-N	1.289	1.329	1.335
Gas-phase - B3LYP-D	C-enol	C-cis-keto	C-trans-keto
N...H/ N-H	1.780	1.035	1.010
N...O	2.656	2.611	4.095
C-O-H/ C-O...H	108.198	103.672	53.767
C5-C6-N-C7	40.165	18.952	-164.720
O-H /O...H	0.988	1.742	4.717
C-O	1.340	1.256	1.233
C7-N	1.287	1.333	1.347

Table 8.3: B3LYP-D* optimized C-enol, C-cis-keto and C-trans-keto clusters: intramolecular parameters of the central molecule of SA – compared with isolated molecules in the gas phase (B3LYP). Distances in Å, angles in degrees. For the trans-keto form, the same atoms of enol and cis-keto were considered: distances and angles greatly differ because of the rotation around the C7-N bond.

Since in this case the dispersive interactions are negligible, the B3LYP-D* data computed for clusters models are directly compared to the B3LYP results obtained for isolated molecules.

The analysis of the data listed in Table 8.3 shows that – at a structural level – the embedding in crystal environment only affects the planarity of the molecule. Indeed, within the clusters, the SA molecule presents a quasi-planar conformation independent of the tautomer considered, whereas in the gas-phase a marked non-planarity of the molecular skeleton is observed.

It is worth noting that, as expected, the **C-enol** form is predicted to be the most energetically stable but the **C-cis-keto** tautomer is predicted to be very close in energy, in agreement with the experimentally observed [10] presence of the cis-keto impurity in SA crystals, that gives rise to the yellow colour.

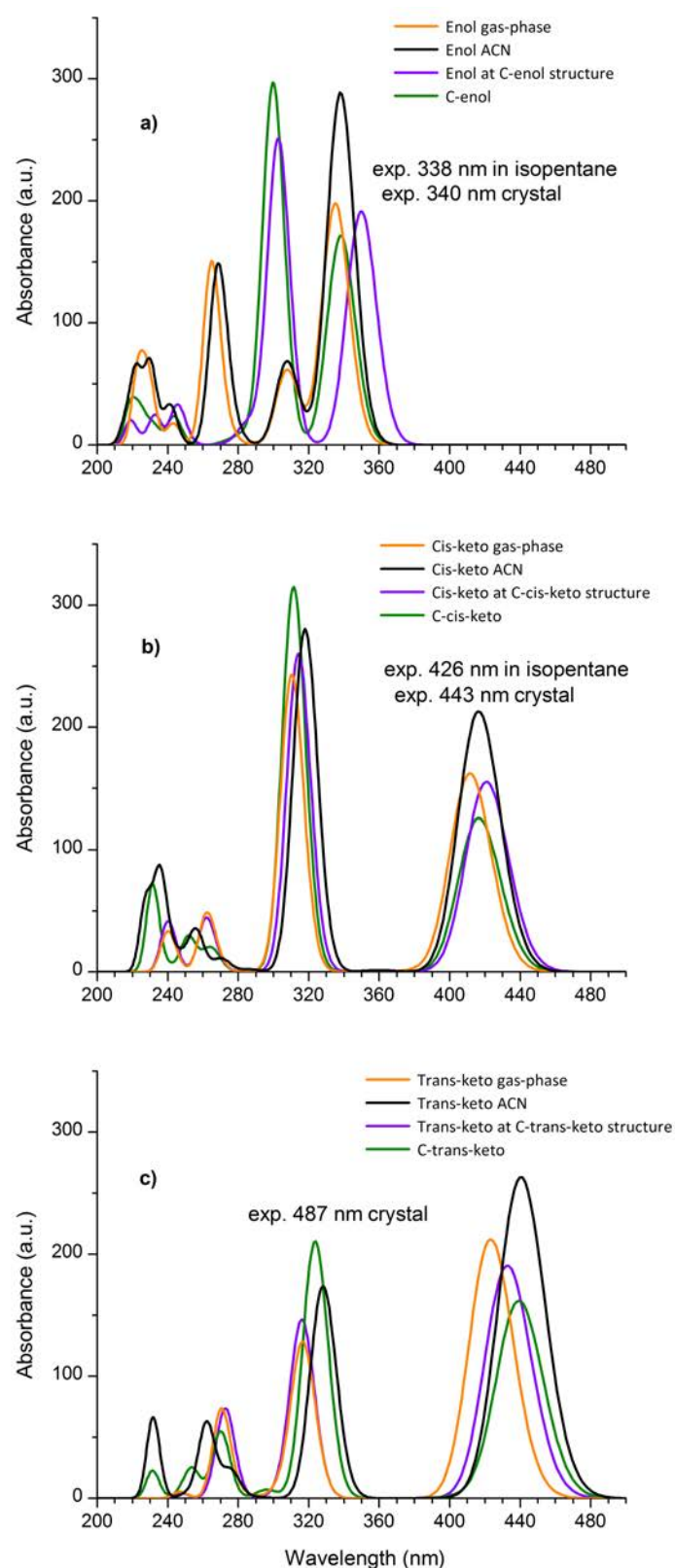
The **C-trans-keto** form, on the other hand, is computed to be sizeably destabilized also due to the enol environment of the surrounding molecules.

From an experimental point of view, the spectra of SA are available both for crystals and in non-polar solvent (such as isopentane). These spectra are all characterized by a well isolated band attributed to the enol form (at 300-350 nm), that is red-shifted (in the range of 400-500 nm) in the case of the cis-keto and trans-keto forms.

In Figure 8.7, the UV-Visible absorption spectra simulated from the calculated TD-DFT vertical electronic excitations energies are depicted, whereas the most relevant data are collected in Table 8.4.

Overall, the simulated spectra compare well with the experiment – both in terms of global spectral shape and energy maxima position. Each spectrum presents a characteristic band which can be assigned either to the enol form or to the cis-keto and trans-keto forms. Moreover, even if computed spectra are blue-shifted with respect to experiment, the relative energy gap between the absorption maxima predicted for the different tautomeric forms is in agreement with experimental results. This feature further confirms the reliability of the computational protocol adopted here.

Figure 8.7: Simulated UV-Visible spectra of the **C-enol**, **C-cis-keto**, and **C-trans-keto** clusters. The spectra computed for the isolated SA molecule are also reported at the fixed PBC-optimized geometry, the gas-phase geometry, and in acetonitrile solvent. Exp. values for SA in isopentane and crystal are taken from Ref. [13] and Ref. [10], respectively.



By analyzing in more detail the spectra computed for the isolated SA molecule, it can be noticed that the peak (λ_{max}) corresponding to the colourless gas-phase enol form (Figure 8.7a) is predicted at 336 nm, which nicely compares with the one experimentally measured in isopentane ($\lambda_{max} = 338$ nm). Analogously, the cis-keto form of SA, which is produced as thermochromic excitation from the enol form, is predicted to absorb at 413 nm (in the gas-phase, Figure 8.7b) – the corresponding experimental value in isopentane being 426 nm.

Finally, the trans-keto form (in gas-phase) is predicted to absorb at 429 nm (Figure 8.7c). Unfortunately, in this case, no experimental data for comparison is available. For all tautomers the λ_{max} corresponds to a vertical excitation from the HOMO to LUMO orbitals, whose characteristics have been already discussed.

Table 8.4: Computed vertical excitation energies (nm). Experimental λ_{max} are given in parentheses. ACN stands for acetonitrile.

	enol	cis-keto	trans-keto
gas-phase	335 (338) ^a	412 (426) ^a	429
ACN	338	416	440
PBC structure	350	421	432
cluster	338 (340) ^b	416 (443) ^b	439 (487) ^b

a: Expt. data collected in isopentane [13]; *b*: Expt. data corresponding to crystal data [10].

In order to consider the effect of crystal embedding on the vertical excitation energies, we start by analyzing the spectra computed for the enol form – that are reported in Figure 8.7a. These spectra show that the inclusion of the environment produces a sizable red-shift. Indeed, a lower excitation energy is observed for the **C-enol** model, with respect to the gas-phase molecule (336 nm to 338 nm). Such trend compares well with what was observed experimentally, going from isopentane to solid SA (i.e. from 338 nm to 340 nm).

The red-shift observed is also somehow qualitatively expected, considering the trend discussed for the HOMO-LUMO gap going from the isolated molecule to the crystal. Indeed, the HOMO-LUMO gap of the gas-phase enol form (4.17 eV) is larger than the one of the isolated molecule at PBC geometry (3.97 eV), thus larger

transition energies are expected in the former case. One may question if this red-shift is somehow related to geometric or electronic factors. Figure 8.7a shows that electronic effects of the surrounding molecules are non-negligible: this is highlighted by the difference of computed λ_{max} between the cluster (338 nm) and the isolated molecule at PBC geometry (350 nm). From this data it clearly appears that if one would consider only the steric effects due to the presence of the environment, the red-shift would be much more marked, and the observed behaviour is the sum of two opposite effects: the structural one – red-shifting – and the electronic one – blue-shifting.

Similar conclusions can be drawn also for the cis-keto form. In particular, Figure 8.7b shows that a red-shift of the HOMO-LUMO excitation is observed – going from 413 nm (in gas-phase) to 416 nm (in the cluster).

The larger deviation – compared with the enol form – observed with respect to the data measured in solid state (443 nm), is indeed related to the fact that the central molecule (in the cis-keto form) is enclosed within a layer of molecules in the enol form. Strictu sensu, the quantity here computed actually corresponds to the absorption spectra of the “nucleating” cis-keto form, more than those of the bulk cis-keto material. Analogously to the enol form, steric and electronic effects due to the presence of the environment play an opposite role: the structural one – red-shifting – and the electronic one – blue-shifting.

Contrary to the previous cases, for the trans-keto form both structural and electronic effects, induced by the environment, cause a red-shift in absorption – although structural effects seem to be more relevant than the electronic ones.

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Conclusions and perspectives

This work of thesis was focused on the application of quantum chemistry methods to the investigation of structural and electronic properties of some technologically relevant molecular crystals. Many important achievements were obtained. In particular:

- The results of a study of the polymorphs of the p-diiodobenzene (p-DIB) molecular crystal, whose packing is governed by dispersive forces confirmed that – oppositely to what claimed before in literature, for p-DIB – when properly set up dispersion-corrected DFT calculations can successfully predict the relative stability of the α and β phases at zero temperature, in good agreement with Diffusion Monte Carlo calculations.

Between the two schemes employed for dispersion-correction, the TS – combined with the PBE density functional – performed much better than the original scheme of Grimme. This is due to the accurate nearly-nonempirical method used to obtain the molecular $C_{6,ij}$ coefficients in the former approach. Accordingly to experiment and to DMC, the α phase of p-DIB results more stable than the β one. Moreover, all dispersion-corrected methods – except for B3LYP-D – furnish an energy difference that fall within large error bar of DMC.

Our work demonstrated that the PBE-TS functional can be safely used to predict the relative stabilities and structural packing of organic molecular crystals, with a relatively low computational cost with respect to more sophisticated QM methods.

- We showed that between the two semiempirical DFT approaches used for dispersion-correction, PBE-TS and PBE-D2, the former provides better results on the crystal structure of the five forms of the oxalyl dihydrazide (ODH) molecular crystal and on the prediction of relative stabilities. The comparison with previous calculations and with fully periodic LMP2 calculations, reported here for the first time, shows that a stability ordering can be defined, although spanning on a larger range of energies.

Dispersion-correction schemes such as TS and D3 lead to results that are reliable, even if relative stabilities of the polymorphs are slightly overestimated with respect to LMP2 results. The B3LYP-D3(BJ)+E⁽³⁾ method furnished promising results, but it did not ameliorate relative stability predictions with respect to the methods mentioned before. Furthermore, its combination with the gCP correction, designed to remove the BSSE and devised to compute BSSE-corrected interaction energies, appears to be not suitable to predict this kind of properties on ODH. The energy ranking (in terms of stability) that can be deduced from the different methods adopted here is: $\alpha > \epsilon > \gamma \sim \delta > \beta$, whereas partial experimental results suggest $\alpha \sim \epsilon \sim \delta > \gamma > \beta$.

- The PBE-GIPAW method was used to compute the ¹³C/¹H NMR parameters and ¹³C MAS NMR chemical shifts (δ_{iso}) and the related spectra of the **1** α , **1**·**H**₂**O**, **1** β and **1** γ forms of [(p-cymene)Ru(*k*N-INA)Cl₂].

The results demonstrated that, in order to obtain good agreement with the spectroscopic data, full geometry optimizations of the experimental structures or, at least, computational refinement of the hydrogen atoms is mandatory. Moreover, the addition of a dispersion-correction term (e.g. the -D* scheme) to the pure B3LYP functional used for the geometry optimization protocol (carried out in periodic boundary conditions) is remarkably important to ameliorate the prediction of structures and spectra. The experimental and computed ¹³C and ¹H δ_{iso} data values differences, expressed as mean absolute deviations, lie in the range 1.3-2.9 ppm and 0.3-1.0 ppm, respectively.

Some revisions in the experimental assignment of the ¹³C/¹H NMR δ_{iso} parameters of the **1**·**H**₂**O**, **1** β and **1** γ forms were also suggested on the basis of computed δ_{iso} . The mismatch in the assignment seems to be mainly due to the rotation of the COOH moiety, which occurs at the **1** α - **1**·**H**₂**O** transition and that was not considered in the experiments.

Moreover, the results obtained suggest the presence of two $\text{COOH}\cdots\text{Cl}$ hydrogen bonds of comparable strength established by the two molecules in the asymmetric unit of the **1** γ polymorph, in partial disagreement with previous findings.

- A novel approach combining periodic and QM/QM' ONIOM cluster calculations was used to investigate the structural and photophysical UV-Visible absorption properties of the β thermochromic polymorph of salicylidene aniline (SA). The approach consisted in the description of the molecular crystal using periodic dispersion corrected DFT, and the subsequent identification of reliable finite models – clusters – for the calculation of vertical transition energies. These last have been computed by including environmental effects by coupling the QM/QM' ONIOM model with the electronic embedding. The results obtained here, encouraging both in terms of accuracy and computational cost, open the way to the simulation and the prediction of the photophysical behaviour of other molecular crystals that show interesting excited-state properties.

Appendix A

A.1 – p-DIB: computational methods

The crystal structures (fractional coordinates and lattice constants) of the α and β polymorphs, used as input, were taken from the original paper by Alcobé et al. [1]. Both polymorphs have orthorhombic lattices belonging to the *Pbca* and *Pccn* space groups, respectively, and contain four p-DIB molecules (48 atoms) per unit cell.

Three exchange and correlation functionals have been tested, that is, the pure PBE [2] functional and the PBE0 [3] and B3LYP [4] hybrid functionals coupled with the dispersion correction proposed by Grimme [5] and by Tkatchenko and Scheffler [6], that will be indicated, respectively, as D and TS hereafter. While the latter correction can be applied to all the functionals mentioned, the former has been parameterized only for the PBE and B3LYP functionals. The TS scheme has already been benchmarked against several systems [7–13] but, to the best of our knowledge, it has never been applied before to study the polymorphism of an important benchmark system like p-DIB.

The CASTEP code [14, 15] – which adopts plane-waves as basis-set, within the pseudopotential approach – was used to perform DFT calculations under periodic boundary conditions. We chosen a 1x3x4 Monkhorst-Pack k -point mesh for both crystalline phases, as previously employed by Hongo et al. [16], which gives energies converged to 0.1 meV per atom.

In CASTEP, non-local functionals are only implemented with norm-conserving pseudopotentials (NCPP), while local functional can be used with ultrasoft pseudopotentials (USPP). Therefore, we employed NCPP in all the B3LYP and PBE0

calculations and USPP for all PBE calculations. We set the kinetic energy cutoff at 680 and 410 eV for NCPP and USPP, respectively. Such values are enough to reach an energy convergence at less than 1.7 meV per atom.

For a better comparison with the previously published DMC calculations [16], the zero-point energy (ZPE) contributions to the energy stability were neglected. This can be also justified by the fact that for p-DIB, a relatively weakly bound molecular crystal, the majority of the ZPE would come from intramolecular vibrations – which should be almost the same for both polymorphs.

A.2 – ODH: computational methods

The starting experimental structures of ODH were taken from the original work of Ahn et al. [17]. The polymorphs, all belonging to the $P2_1/c$ symmetry, include two molecules (28 atoms) per unit cell in the case of α , β , δ and ϵ , whereas the γ phase contains four molecules (56 atoms). Since three-dimensional structures from databases were obtained from X-ray diffraction (XRD) techniques, we carried out geometry optimizations of the hydrogen atoms with the PBE-TS method to obtain refined experimental structures. These, within the text, are called “revised experimental geometries”.

Full relaxations of cell parameters and atomic positions have then also been performed at both PBE-TS and PBE-D2 levels of theory.

For the mentioned methods (PBE-TS and PBE-D2), periodic calculations have been carried out by using the CASTEP [14, 15] software, which employs plane-waves (PWs) as basis-set in conjunction with norm-conserving pseudo-potentials (NCPP). The energy cutoff (800 eV) and the k -points mesh (7x4x3) – converged, respectively, to less than 1 meV/atom and 0.01 meV/atom – were chosen.

The fully optimized structures were compared with the experimental ones in order to assess the accuracy of these dispersion corrected functionals in the prediction of the crystal structure of the five oxalyl dihydrazide polymorphs. The last SCF ground-state energies were also collected to calculate the relative stability of the five polymorphs at the fully relaxed geometry.

Single-point energy calculations on the revised experimental geometries have also been carried out with the PBE0-D2, B3LYP-D2 and B3LYP-D3(BJ) functionals by using a development version of the CRYSTAL code [18, 19]. The B3LYP-D3(BJ) calculations were performed with and without the gCP correction and including both two- and three-body corrections. All-electron basis-sets were adopted: the large QZVP [20] basis-set has been considered for PBE0-D2, B3LYP-D2 and B3LYP-D3(BJ) calculations, while the 6-31G(d) basis-set has been used for the calculation including the gCP correction.

Periodic Local-MP2 energies have been computed by means of the CRYSCOR program [21–23] on the revised experimental structures. A p-aug-6-31G(d,p) Gaussian basis-set has been chosen, as it has already proved to be a good compromise between computational cost and accuracy of the results in the study of molecular crystals [24] and graphane-based nanostructures.[25] CRYSCOR implements the local correlation approach [26] that – together with fast integral evaluation techniques [27] – allows to exploit the fundamentally local character of dynamic electron correlation and to lead the code to scale linearly with the size of the system. It employs the periodic Hartree–Fock solution in the basis of Gaussian-type orbitals (GTO) provided by the CRYSTAL code.[18, 19]

All calculations (DFT and LMP2) were performed at 0 K temperature. Zero-point energy (ZPE) effects were evaluated through vibrational frequencies calculations with CASTEP – employing the linear-response phonon DOS (Density Of States) [28] approach on the fully optimized PBE-TS structures – that are, however, very close to the revised experimental ones. As shown below, ZPE effects have in this case a negligible impact on relative stabilities.

A.3 – SA: computational methods

Ground state periodic calculations. A parallel version of the CRYSTAL09 package [18, 19], within the frame of all-electron atom-centred Gaussian basis-sets, was employed for ground- state calculations of bulk molecular crystals. After checking convergence on the Monkhorst- Pack k -points grid, we set the number of k -points to 27, in the Irreducible Brillouin Zone (IBZ). The DFT grid consisted of 75 radial and 974 angular points. The tolerances on bielectronic integrals (Coulomb and Exchange series) were set to 10^{-7} , 10^{-7} , 10^{-7} , 10^{-7} , 10^{-18} . A full geometry op-

timization – both of cell parameters and atomic displacements – of the enol-form of the β polymorph of SA was carried out at the B3LYP, B3LYP-D2 and B3LYP-D* level of theory starting from the experimental structure [29], imposing periodic boundary conditions (PBC) and using default convergence criteria on gradients and atoms displacements. We decided to adopt the B3LYP functional [30] because it is well known that hybrid functionals describe the ground and excited states – e.g. valence excitations – of molecular systems with 20% to 40% accuracy [31]. In general, they also provide a correct description of hydrogen bonding. The -D2 [5] and -D* [32] a posteriori dispersion-correction terms have been used since other more recent and accurate schemes (i.e. D3 [33], TS [6], MBD [34] and XDM [35]) are not available in the present version of the CRYSTAL code. It is worth to highlight that the -D* consists of a modified version of the Grimme -D2 scheme, especially devised for molecular crystals.

Three basis sets (namely the 6-311G(d), 6-311G(d,p) and pob-TZVP basis sets [36, 37]) were tested in conjunction with the B3LYP functional. Based on Single Point energy results (convergence of energy, computational cost), and on previous structural optimizations (convergence of energy, cost and accuracy in predicting lattice constants), the 6-311G(d) basis-set was selected for full geometry optimizations – since it represents a good balance between quality of the results and computational cost.

Excited state QM/QM' calculations. A cluster of 15 molecules of SA was extracted from the fully optimized crystal in the enol form to be used for ONIOM QM/QM' calculations. One SA molecule was treated at high-level (QM layer), while fourteen molecules were kept at low-level (QM' layer). The innermost SA molecule (high-level) was fully optimized with CRYSTAL09 (B3LYP-D*/6-311G(d)), keeping fixed the coordinates of surrounding molecules. The same optimization procedure was pursued, maintaining fixed the low-level layer in the enol form, but while fully relaxing the central molecule in its cis-keto or trans- keto forms.

Vertical Excited States of the so-optimized clusters were computed at ONIOM QM/QM' level, with charge embedding (Mulliken charges) [38, 39], using the development version of the Gaussian package [40]. The hybrid B3LYP/6-31+G(d) functional was adopted as high- level method, whereas the HF/3-21+G(d) model

was used as low-level approximation.

Optimizations of the SA molecule in acetonitrile were performed including solvent effects through a Polarizable Continuum Model (PCM) [41]. TD-DFT calculations were computed subsequently at the B3LYP/6-31+G(d) level, which is almost as accurate as PBE0 for most organic molecules [42–44].

In such a way, just one exchange functional is used for molecular, cluster and periodic calculations, allowing for an easier comparison of the results obtained. UV-Visible absorption spectra were obtained from the computed vertical excitation energies and oscillator strengths through a Gaussian convolution using a fixed full width at half maximum (FWHM) of 0.2 eV.

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Riassunto

I cristalli molecolari hanno applicazioni rilevanti sia nel contesto della ricerca accademica sia in quella industriale poichè vengono utilizzati, a seconda dei casi, in elettronica/optoelettronica (come per schermi o periferiche di archiviazione), sistemi 'host-guest', per esempio per applicazioni di rilascio dei farmaci, o per sistemi meccanici fotoattivati (attuatori).

Le proprietà menzionate, in particolare, sono largamente influenzate dal polimorfismo e dal comportamento strutturale ed elettronico che da esso derivano, per ogni composto che si trova in una forma cristallina definita. Questo è complicato dalla presenza delle forze vdW e/o dai legami a idrogeno, che governano la struttura molecolare all'interno del cristallo.

Con l'obiettivo di descrivere questo tipo di interazioni e predire proprietà elettroniche avanzate (come spettroscopia NMR di stato solido, assorbimento UV-Visibile), è stato adottato un approccio quantistico (QM) computazionale, a livello della Teoria del Funzionale della Densità (DFT) – sia nella sua formulazione indipendente dal tempo, sia in quella dipendente dal tempo. La DFT ha permesso di concludere con successo i diversi studi, bilanciando accuratezza e costo computazionale.

In particolare, il bisogno di tenere conto delle forze di vdW tramite la DFT corretta per le interazioni dispersive è stato messo in evidenza e differenti tipi di approccio (D2, D*, TS) sono stati adottati e comparati.

Questi approcci ci hanno permesso di ottenere un avanzamento notevole nella comprensione del polimorfismo e di altre proprietà dei sistemi studiati, in particolare di dimostrare che:

i) una ragionevole combinazione tra DFT e correzioni semiempiriche per la dispersione a basso costo può portare ad una predizione della stabilità relativa tra polimorfi allo stesso livello di accuratezza di tecniche più rigorose e costose (per esempio, Diffusion Monte Carlo);

ii) la stabilità relativa di composti complessi può essere calcolata con metodi DFT corretti per la dispersione: gli approcci disponibili offrono spesso risultati compatibili con quelli forniti dai metodi post-HF, ed il benchmarking con tali metodi può essere utile per l'individuazione di nuovi schemi per la dispersione;

iii) la predizione strutturale delle quattro forme cristalline di un sistema 'host-guest', per il quale abbiamo riportato e chiarito alcune lacune nell'interpretazione sperimentale della spettroscopia NMR, grazie al calcolo dei chemical shifts NMR;

iv) l'ottimizzazione di un protocollo computazionale – basato sulla caratterizzazione QM di clusters di molecole estratte dal solido – per lo studio dei processi fotofisici e fotochimici di un cristallo molecolare termocromatico.

Résumé

Les cristaux moléculaires présentent des applications importantes tant pour la recherche universitaire que dans l'industrie, et peuvent être utilisés, le cas échéant, pour l'électronique/l'optoélectronique (comme les écrans ou appareils de stockage), les systèmes 'host-guest' avec, par exemple, des applications concernant le relâchement de médicaments, ou encore pour des systèmes mécaniques photo-actifs ('actuators').

Les propriétés mentionnées ci-dessus sont sensiblement affectées par le polymorphisme, qui influence le comportement structural/électronique de chaque composé présent dans une forme cristalline définie. Ce phénomène est rendu difficile à étudier de par la présence d'interactions de dispersion et/ou liaisons hydrogène.

Avec l'objectif de décrire précisément ces interactions, et pour prédire des propriétés électroniques avancées (par exemple, spectre RMN à l'état solide, absorption UV-Visible), une approche de mécanique quantique (QM) a été adoptée, utilisant la Théorie de la Fonctionnelle de la Densité (DFT) – tant dans sa formulation indépendante du temps, que dans son expression dépendante du temps. Cette méthode a été choisie de par le bon ratio entre la précision atteignable et le temps de calcul nécessaire.

La nécessité de prendre en compte les forces de vdW a été mise en évidence et une étude comparative a été réalisée entre les différentes approches telles que le modèle de dispersion D2, D* ou encore TS.

Les avancements les plus importants dans la compréhension du polymorphisme, ainsi que des autres propriétés des cristaux examinées, sont:

i) une prédiction correcte de la stabilité relative entre polymorphes, similaire aux résultats prévus par des méthodes plus coûteuses en termes de temps de calcul (diffusion Monte Carlo par exemple), peut être obtenue par l'utilisation d'une combinaison entre la DFT et des corrections semi-empiriques moins coûteuses;

ii) la stabilité relative de systèmes complexes peut être obtenue avec de bonnes performances avec la DFT incluant des corrections pour la dispersion, les modèles disponibles donnant des résultats comparables à ceux fournis par les méthodes post-HF. Le benchmark réalisé ici pourrait également être utile dans le cadre de la création de nouveaux modèles correctifs pour la dispersion en DFT;

iii) la prédiction de la structure de quatre formes cristallines d'un composé 'host-guest' précédemment synthétisé a été réalisée, notamment grâce aux calculs des déplacements chimiques (RMN) ayant permis de compléter et corriger l'interprétation RMN des résultats expérimentaux;

iv) un protocole calculatoire pour l'étude des procédés photophysiques et photochimiques d'un cristal moléculaire thermochromique a été mis en place, basé sur la caractérisation des clusters de molécules extraits du cristal 'bulk' par la mécanique quantique.

Publications

1. P. Pernot, B. Civalleri, **D. Presti** and A. Savin, "Prediction uncertainty of density functional approximations for properties of crystals with cubic symmetry", *J. Phys. Chem. A* 2014, *Just Accepted* - **Journal Article**
2. **D. Presti**, F. Labat, A. Pedone, M. J. Frisch, H. P. Hratchian, I. Ciofini, M. C. Menziani and C. Adamo, "A computational protocol for modeling thermochromic molecular crystals: salicylidene aniline as a case study", *J. Chem. Theory Comput.*, **10**, 2014, 5577–5585, IF(2013): 5.310 - **Journal Article**
3. **D. Presti**, A. Pedone and M. C. Menziani, "Unraveling the Polymorphism of [(p-cymene)Ru(kN-INA)Cl₂] through Dispersion-Corrected DFT and NMR-GIPAW Calculations.", *Inorg. Chem.* **53**, 2014, 7926–7935, IF(2013): 4.794 - **Journal Article**
4. **D. Presti**, A. Pedone, M. C. Menziani, B. Civalleri and L. Maschio "Oxalyl Dihydrazide Polymorphism: a Periodic Dispersion-Corrected DFT and MP2 Investigation.", *CrystEngComm* **16**, 2014, 102–109, IF(2013): 3.858 - **Journal Article**
5. **D. Presti**, A. Pedone and M. C. Menziani, "Computational prediction of molecular crystal polymorphism in p-diiodobenzene: on the ability of dispersion-corrected DFT calculations", *La Chimica e l'Industria*, Vol. 4 (Maggio) 2013, 114–115 - **Conference Proceeding** from 'XII Giornata della Chimica dell'Emilia-Romagna' - December 17, 2012 - Università di Ferrara
6. A. Pedone, **D. Presti** and M. C. Menziani, "On the ability of periodic dispersion-corrected DFT calculations to predict molecular crystal polymorphism in p-diiodobenzene", *Chem. Phys. Lett.* **541**, 2012, 12–15, IF(2011): 2.337, **Journal Article**
7. B. Civalleri, **D. Presti**, R. Dovesi and A. Savin, "On choosing the best density functional approximation", *Chem. Modell.* **9** (2012), 168–185, M. Springborg Ed., RSC Specialist Periodical Reports, ISBN: 978-1-84973-412-7 - **Book Chapter**