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# THESIS

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**UNIVERSITY OF PAU AND THE COUNTRIES OF ADOUR**

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by

**Jeremy MARCHAIS**

In fulfillment for the Degree of

**DOCTOR OF PHILOSOPHY**

In CHEMICAL PHYSICS

## Research on unusual molecules and reactive intermediates

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# THESE

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**UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR**

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par

**Jérémy MARCHAIS**

Pour obtenir le grade de

**DOCTEUR**

en CHIMIE-PHYSIQUE

## Recherche de molécules à valences non-usuelles et étude des chemins de réactions

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*à mes parents et mon frère,  
à ma femme,*

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## Abstract

The complexity of the problems of traceability, isomerism, monitoring and fate of a set of ill-defined molecules involved in a chemical reaction often makes it difficult to use experimental characterisation techniques. These techniques, which are sometimes risky or even hazardous, need to be calibrated, which requires the use of complementary techniques or the support of predictive modelling. Among the available experimental techniques, infrared spectroscopy is still one of the most appreciated characterisation techniques due to its speed of acquisition and its ability to identify functional groups. It is therefore the approach of choice for analysing and studying highly reactive and/or short-lived compounds. The modelling of electronic and spectroscopic properties via quantum chemical methods turns out to be complementary to the experimental data and offers a precious help to the identification of the measured infrared bands. Nevertheless, if recent methodological developments, coupled with technological advances in computation, allow to provide accurate support for small systems (between 3 and 10 atoms), the theoretical chemist is very quickly limited when dealing with larger systems. Perturbation theory is one of the most widely used solutions to avoid these difficulties. Its implementation in all commercial computational chemistry software is in itself proof of its effectiveness and reliability. Although the "perturbation method" is extremely simple to implement at order 2, its use remains limited since it is strictly limited to the calculation of the lowest frequencies of a spectrum, i.e. in a domain where the density of vibrational states is low. This limitation of the perturbation theory is due to the phenomenon of resonance and the truncation of the method at order 2 in the modelling computer programs. The development of the perturbation method initiated by RAYLEIGH and SCHRÖDINGER and known as "many-body perturbation theory" (MBPT) was developed in the first chapter of this work up to order 6. The second part of this thesis was devoted to the study of reaction paths and in particular to the investigation of reaction intermediates on unusual valence molecules. These molecules are generally very reactive and specific characterisation methods are needed by the experimenters to generate and detect them - let's mention in particular flash vacuum pyrolysis, matrix trapping of reaction products at cryogenic temperatures, photochemistry, and of course spectrometry. Once again, infrared spectroscopy is one of the most suitable techniques for identifying reaction intermediates, so that the use of predictive modelling can provide experimenters with confidence in the nature of the reaction paths taken during their syntheses. Two studies have been carried out and published in the second part of this work. The first one focuses on the rearrangement of nitrile oxides and nitrile ylides, while the second one is devoted to solving the rearrangement of benzotriazole and triazoloquinone molecules to carbazoles, benzazirines, azepinediones and fulvenimines products. In both works, all possible synthesis paths were investigated. The multi-determinant properties of the intermediates studied (in particular the nitrenes) constrained us to carry out our calculations using a multi-determinant approach of the CASSCF (Complete Active Space) type, corrected, once again, using an MBPT perturbation method developed to order 2 (CASPT2).

Keywords: VPTn method, infrared spectroscopy, computational chemistry, isomerism, broken symmetry, multiconfigurational, density functional theory, CASPT2



## Résumé

La complexité des problèmes de traçabilité, d'isomérisation, de suivi et de devenir d'un ensemble de molécules mal définies intervenant lors d'une réaction chimique rend souvent délicate l'utilisation des techniques de caractérisation expérimentales. Ces dernières, parfois risquées sinon hasardeuses, nécessitent d'être calibrées, ce qui impose de recourir à l'emploi de techniques complémentaires ou au support de la modélisation prédictive. Parmi les techniques expérimentales disponibles, la spectroscopie infrarouge demeure encore à l'heure actuelle l'une des techniques de caractérisation les plus appréciées de par sa rapidité d'acquisition et sa capacité d'identification de groupes fonctionnels. C'est donc une approche de choix pour analyser et étudier des composés très réactifs et/ou de courte durée de vie. La modélisation des propriétés électroniques et spectroscopiques par le biais des méthodes de la chimie quantique s'avère complémentaire des données expérimentales et offre une aide précieuse à l'identification des bandes infrarouges mesurées. Néanmoins, si les développements méthodologiques récents, couplés aux avancées technologiques en matière de calcul, permettent d'apporter un support précis pour de petits systèmes (entre 3 et 10 atomes), le chimiste théoricien se retrouve très vite limité lorsqu'il doit faire face à des systèmes de plus grandes dimensions. La théorie de perturbation est une des solutions les plus utilisées pour contourner ces difficultés. Son implémentation dans tous les logiciels commerciaux de chimie calculatoire est à elle seule la preuve de son efficacité et de sa fiabilité. Si la "méthode de perturbation" est extrêmement simple à mettre en œuvre à l'ordre 2, il n'en demeure pas moins que son utilisation reste limitée puisqu'elle s'adresse en toute rigueur uniquement au calcul des fréquences les plus basses d'un spectre, soit dans un domaine où la densité d'états vibrationnels est peu élevée. Cette limitation de la théorie de perturbation est due au phénomène de résonance et à la troncature de la méthode à l'ordre 2 dans les programmes informatiques de modélisation. Le développement de la méthode de perturbation initiée par RAYLEIGH et SCHRÖDINGER et connue sous le nom de "théorie des perturbations à plusieurs corps" (MBPT) a été développée dans le premier chapitre de ce travail jusqu'à l'ordre 6. La seconde partie de ce travail de thèse a été consacrée à l'étude de chemins de réaction et tout particulièrement à la recherche d'intermédiaires réactionnels sur des molécules de valences non usuelles. Ces molécules sont généralement très réactives et des méthodes de caractérisation spécifiques sont nécessaires aux expérimentateurs pour les générer et les détecter - citons notamment la thermolyse sous vide flash, le piégeage en matrice des produits de réaction à des températures cryogéniques, la photochimie, et bien entendu les spectrométries. Ainsi et une fois encore, la spectroscopie infrarouge figure parmi les techniques les plus adaptées à l'identification des intermédiaires réactionnels, de sorte que le recours à la modélisation prédictive permet de conforter les expérimentateurs sur la nature des chemins réactionnels empruntés lors de leurs synthèses. Deux études ont été menées et publiées dans la seconde partie de ce travail. La première s'intéresse au réarrangement d'oxydes de nitriles et d'ylures de nitriles tandis que la seconde s'attache à résoudre le réarrangement de molécules de benzotriazoles et de triazoloquinones en produits de carbazoles, de benzazirines, d'azepinediones et de fulvenimines. Pour ces deux travaux, toutes les voies de synthèse envisageables ont été étudiées. Le caractère multi-déterminantal des espèces intermédiaires étudiées (en particulier les nitrènes) nous a contraint à réaliser nos calculs au moyen d'une approche pluri-déterminantale de type CASSCF (Complete Active Space) corrigée, une nouvelle fois, à l'aide d'une méthode de perturbation MBPT développée à l'ordre 2 (CASPT2).

Mots clefs: méthode VPTn, spectroscopie infrarouge, chimie computationnelle, isomérisation, symétrie brisée, multi-configurationnelle, théorie de la fonctionnelle de la densité, CASPT2

## List of Abbreviations

aug cc-pV(D,T,Q,...)Z	augmented Correlation-Consistent polarized (Double, Triple, Quadruple, ...) Zeta basis sets
A-VCI	Adaptive-Variational Configuration Interaction
BS	Broken Symmetry
CCSD(T)	Coupled-Cluster with Single/Double, Triple excitations
CC-VSCF	Correlation Corrected Vibrational Self-Consistent-Field
CAS	Complete Active Space
CASPT2	Complete Active Space Perturbation Theory at 2 <sup>nd</sup> order
CASSCF	Complete Active Space Self Consistent Field
CI	Configuration Interaction
CSF	Configuration State Functions
CSS	Closed Shell System
CVPT	Canonical Van Vleck Perturbation Theory
DFT	Density Functional Theory
ESR	Electron Spin Resonance
FTIR	Fourier Transform InfraRed
FVP	Flash Vacuum Pyrolysis
GGA	Generalized Gradient Approximation
(R/U)HF	(Restricted/Unrestricted) Hartree-Fock
HOMO	Highest Occupied Molecular Orbital
IEPA	Independent Electron Pair Approximation
IR	InfraRed
IRC	Intrinsic Reaction Coordinate
KS	Kohn-Sham
LUMO	Lowest Unoccupied Molecular Orbital
MBPT	Many Body Perturbation Theory
MCSCF	Multi-Configurational Self Consistent Field
MP2	Møller-Plesset at second order
MR(PT)	MultiReference (Perturbation Theory)

NMR	Nuclear Magnetic Resonance
OSS	Open Shell System
PES	Potential Energy Surface
P-MWCI	Parallel-Multiple Windows Configuration Interaction
QDPT	Quasi Degenerate Perturbation Theory
RAS	Restricted Active Space
RASSCF	Restricted Active Space Self-Consistent-Field
RSPT	Rayleigh-Schrödinger Perturbation Theory
RSVE	Resolution of the Schrodinger Vibrational Equation
SCF	Self-Consistent-Field
TD-DFT	Time-Dependant Density Function Theory
VCC	Vibrational Coupled Cluster
VPT <sub>n</sub>	Vibrational Perturbation Theory at order n
VSCF	Vibrational Self-Consistent-Field

## List of Publications

1. J. Marchais, D. Bégué, A. Dargelos and C. Wentrup, C., "Rearrangements of Aromatic Nitrile Oxides and Nitrile Ylides. Potential Ring Expansion to Cycloheptatetraene Derivatives Mimicking Arylcarbenes", *Chem. Eur. J.*, 2020, 26, 15700.
2. J. Marchais, D. Bégué, A. Dargelos and C. Wentrup, "Benzotriazoles and Triazoloquinones: Rearrangements to Carbazoles, Benzazirines, Azepinediones, and Fulvenimines", *J. Org. Chem.*, 2021.

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# 1 Introduction

In itself, the theme of identifying and characterising molecules in a given chemical environment is not new. Indeed, for many decades, chemists in all fields have been looking for this "grail" with varying degrees of success. Among the experimental techniques commonly used to answer this problem, vibrational spectroscopy (infrared, Raman, ...) is undoubtedly the one that has allowed the greatest number of advances in fields as varied as biochemistry, agri-food, interstellar chemistry and materials chemistry.

Recent developments in infrared spectroscopy (improvement in the resolution of lasers and detectors, use of cavity ring down systems, photoacoustics) have made it possible to improve the detection, traceability and quantification of molecules in their ambient environment. IR spectra are veritable fingerprints of molecules, allowing these systems to be identified irrevocably by comparison with reference spectra available on pure compounds (when they exist).

The use of these spectroscopic studies lies in the fact that the molecules constituting the environment studied (solvent and solute) are known *a minima*. The complexity of the problems of traceability, isomerism, monitoring and fate of a set of poorly defined molecules makes the use of experimental techniques delicate, sometimes risky and needing to be calibrated, so that it is essential to use complementary techniques or to resort to the support of predictive modelling.<sup>[1]</sup> It is undeniable that the joint progress of modelling techniques and computer resources now makes this tool an indispensable and effective tool for the identification of increasingly varied molecular systems. Moreover, the increasing power of computers and the regular development of computational methods and software make it possible to accurately process the electronic structure with *ab initio* quantum computations.

The advantage of modelling in the field of vibrational spectroscopy is that it allows us to work on a given, well-defined system in a controlled environment. In addition to this, the development of modelling has made dazzling progress over the last twenty years. Not a single year has passed without the computational limits and accuracies reached by these simulations being pushed back, thanks to the development of methods adapted and developed within the context of precise and controlled mathematical assumptions (which we will detail below). Nevertheless, in the field of vibrational spectroscopy, it is not yet possible to produce results of such precision that the comparison between experiment and theory is free of uncertainty.<sup>[2]</sup> This is the objective of our research group, which we have set up between IPREM and the HiePACS project-team of Inria Bordeaux Sud-Ouest. This consortium, which brings together partners from different disciplines, makes it possible to bring together a range of complementary expertise. Every day, it strives to remove the technological and conceptual obstacles to the development of calculation codes for spectral assignment.

The work presented in this first part of the manuscript (chapter 2, 3 and 4) is therefore part of these mathematical developments for the identification of complex chemical systems. The calculations that we are developing are carried out within the framework of the Resolution of the Schrodinger Vibrational Equation (RSVE), under the dual hypothesis of electrical and mechan-

ical anharmonic approximations allowing the determination of the intensities and frequencies of all the vibration modes intrinsic to a given chemical system, in a given environment. It is still commonly accepted that a calculation conducted in a simpler hypothesis, the so-called harmonic hypothesis, is sufficient to get a good deep insight of the molecular architecture. In reality, the fundamental reasons why researchers prefer the harmonic approximation are both related to the problem of computational cost and the lack of implementation of anharmonic approaches in large commercial codes. In the strategy that we are developing, our calculations differ from studies in the field in that they are placed precisely in the anharmonic hypothesis. Nevertheless, it is important to know that a calculation carried out in the harmonic hypothesis generates an error that the computational chemist usually "controls" by an adapted corrective factor that he applies to its results according to the calculation conditions used in the RSVE. Unfortunately, this method of calculation, which has been used for some fifty years and which has made vibrational spectroscopy modelling a somewhat empirical method in the minds of experimentalists, is still subject to doubt concerning the accuracy of the identification of vibrators, since it is fundamentally inconceivable that the error committed on each mode is the same for all and that the proposed correction is universally applicable to all the systems studied, whatever the environments in which they are found. Moreover, the calculations developed with this assumption do not allow the identification of other vibrators than the fundamental modes since no coupling between modes is taken into account.

The methods developed in our team are therefore based on theoretical infrared spectra, requiring the calculation of vibrational properties (positions and intensities), beyond the harmonic approximations usually used in standard theoretical chemistry software. If it is now possible to solve the vibrational problem under these conditions in the mid-infrared range<sup>[3]</sup>, we still have to continue to develop our approaches for the treatment of targeted spectral windows, of smaller dimensions and which can be extended to the near-IR spectral zone in which active bands of the harmonic type and/or combination bands develop (only accessible within the context of the mathematical approximations that we propose in our so-called 'anharmonic' approach).<sup>[4]</sup>

Some theoretical background to these modelling approaches is given in Chapter 2. The characterisation of the HCNO system and of the Formylnitrene, Cyanic, Isocyanic, Fulminic and Isofulminic acids that can be formed chemically from HCNO will be presented after these reminders as an illustration of the problems that such modelling generates. As of now, and even before going into the details of the calculations that will have to be performed in order to carry out such a study, it is important to remember from the beginning that the results of the modelling for vibrational spectroscopy depend mainly on two parameters, i.e. the quality of the potential energy surface (PES) and the mathematical method used to solve the Schrödinger Vibrational Equation. In addition, it is also accepted that variational or VCC (Vibrational Coupled Cluster)<sup>[5]</sup> approaches are the most capable of taking into account all the couplings between all the vibration modes of a given system and give the most accurate theoretical results. However, the recent upturn in the literature for perturbational approaches has led us to propose



in the last part of this chapter the development of the equations of the VPT<sub>n</sub> approaches (n=4 and 6) and to study the feasibility of their implementation with respect to the CVPT (Canonical Van Vleck Perturbational Theory) perturbation approaches, which are recognised as being the reference approaches in the perturbational domain.

In a second part of this thesis, in chapter 5, we introduce some multi-determinant methods that allow an approach applying a multi-configurational description of the system and taking into account the correlation (static and dynamic). We therefore deemed it suitable to use the CASSCF method.<sup>[6]</sup> This method takes into account both of the dynamic and static correlation energy. However, the CASSCF method is mainly static electron correlation. So, in order to recover the important part of the missed dynamic electron correlation, a multireference post-CASSCF as multireference perturbation theory (MRPT) can be used. Meanwhile the CASSCF calculations includes mostly the nondynamical (static) electron correlation, the post-CASSCF multireference perturbation theory (MRPT) bring the part of dynamical electron configuration, that explain the very good accuracy of this method. Several method are available and in this report, we decided to work with CASPT2 (Complete active space perturbation theory at second order) method because it is applicable to the CASSCF wavefunction.<sup>[7,8]</sup> But the major drawback of CASSCF is that the number of configuration statefunction scales factorially with the number of active orbitals. CASSCF calculations with a CAS larger than 16 electrons in 16 orbitals are currently not feasible. One solution to this problem is the BS (Broken-Symmetry) method. This latter allows the study of higher dimensional systems and is among the most widely used to "estimate" the energy of multi-configuration states in Kohn-Sham DFT. Thus, these computational methods, described above, have enabled a study which was carried out on the reaction paths and more specifically on the transition states and the reaction intermediates determination allowing the knowledge of the path followed during the synthesis.

The first study concerns the rearrangement of nitrile oxides and nitrile ylides. Nitrile oxides and nitrile ylides are really interesting 1,3-dipoles and often used in various cycloaddition reactions to produce five-membered heterocyclic compounds. There are six fundamental valence tautomers named 1,3-dipolar, reverse 1,3-dipolar, 1,3-diradical, propargylic, allenic and carbenic. The three last forms are predominant. It is also important to note that the energies of all different structures are highly substituent-dependant. We will use computational methods to examine the rearrangements of nitrile oxides and nitrile ylides under unimolecular reaction conditions, as obtained for example in gas phase pyrolyses (flash vacuum pyrolysis, FVP) or noble gas matrix photolyses. Then, the second study focuses on the analysis of the rearrangements to carbazoles, benzazirines, azepinediones and fulvenimines from benzotriazole and triazoloquinones. Thanks to the calculation of the energy profiles, we will look at possible competitions between Graebe-Ullmann-type cyclizations, benzazirine formation and Wolff-type ring contraction to fulvenimines. Benzotriazoles are of interest in many synthetic reactions, in particular due to their capacities to act as leaving groups, electron donors, electron withdrawers and radical or carbanion precursors.

## References

- [1] P. Barchewitz, *Spectroscopie atomique et moléculaire*, vol. 2. 1971.
- [2] J. M. Bowman, T. Carrington, and H. D. Meyer, “Variational quantum approaches for computing vibrational energies of polyatomic molecules,” *Mol. Phys.*, vol. 106, pp. 2145–2182, 2008.
- [3] P. S. Thomas and T. C. Jr, “An intertwined method for making low-rank, sum-of-product basis functions that makes it possible to compute vibrational spectra of molecules with more than 10 atoms,” *J. Chem. Phys.*, vol. 146, p. 204110, 2017.
- [4] T. Tassaing, P. A. Garrain, D. Bégué, and I. Baraille, “On the cluster composition of supercritical water combining molecular modeling and vibrational spectroscopic data,” *J. Chem. Phys.*, vol. 133, p. 034103, 2010.
- [5] P. Seidler, E. Matito, and O. Christiansen, “Vibrational coupled cluster theory with full two-mode and approximate three-mode couplings: The vcc [2pt3] model,” *J. Chem. Phys.*, vol. 131, p. 034115, 2009.
- [6] P. J. Knowles and H. J. Werner, “An efficient second-order mc scf method for long configuration expansions,” *Chem. Phys. Let.*, vol. 115, pp. 259–267, 1985.
- [7] T. Helgaker, P. Jorgensen, and J. Olsen, *Molecular electronic-structure theory*. 2014.
- [8] P. P. Pulay, “A perspective on the caspt2 method,” *Int. J. Quantum Chem.*, vol. 111, pp. 3273–3279, 2011.

## 2 Theoretical background of vibrational survey

The main objective of this section is to define the vocabulary and the fundamental notions that we will use later, as the detailed development of the classical treatment of vibration can be found in numerous works<sup>[1,2]</sup> and repeated in several thesis.<sup>[3,4]</sup>

In summary, all vibrational spectroscopy modelling, whether developed in the harmonic or anharmonic hypothesis, is directly dependent on the quality of the electronic molecular wave function, i.e. on the consideration of the electronic correlation. Even though it is now common to carry out RSVE for small systems, this criterion becomes almost prohibitive when it comes to solving these same problems in the anharmonic hypothesis on larger systems.

### 2.1 Separation of rotational and vibrational movements

In an additional  $0^{th}$  order approximation to the BORN-OPPENHEIMER approximation, nuclear motions can be separated into two classes: rotational motions and vibrational motions. To do this, it is necessary to explain the expression of the kinetic energy of the nuclei in the classical sense and to localize the molecule in a reference frame respecting the ECKART conditions.<sup>[5]</sup> Let us consider, in this space a mobile reference frame  $xyz$ , linked to the molecule, and a fixed reference frame  $OXYZ$ , defining the translational and rotational movements of the mobile reference frame. The motion of the mobile trihedron with respect to the fixed trihedron is defined by the distance  $R$  and the instantaneous angular velocity  $\alpha$ . The motion of the molecule is defined by the mobile trihedron representing at each moment the position  $\vec{r}_\alpha$  of the nuclei  $\alpha$  with respect to their equilibrium position  $\vec{a}_\alpha$ . Let us be:

$$\vec{\rho}_\alpha = \vec{r}_\alpha - \vec{a}_\alpha \quad (2.1)$$

The velocity  $\vec{v}_\alpha$  of the  $\alpha^{ieme}$  nucleus is therefore :  $\vec{v}_\alpha = \dot{\vec{r}}_\alpha = \dot{\vec{\rho}}_\alpha$  since by definition,  $\vec{a}_\alpha$  is constant over time.

Thus, in the fixed reference frame, the velocity of this core is written:

$$\vec{V}_\alpha = \dot{\vec{R}} + (\vec{\omega} \wedge \vec{r}_\alpha) + \vec{v}_\alpha \quad (2.2)$$

The total kinetic energy of the nuclei can be easily deduced from this expression:

$$\begin{aligned}
2T = \dot{R}^2 \sum_{\alpha} m_{\alpha} \left( \vec{\omega} \wedge \vec{r}_{\alpha} \right)^2 + \sum_{\alpha} m_{\alpha} v_{\alpha}^2 \\
+ 2 \vec{R} \sum_{\alpha} m_{\alpha} \vec{v}_{\alpha} \\
+ 2 \left( \vec{R} \wedge \vec{\omega} \right) \sum_{\alpha} m_{\alpha} \vec{r}_{\alpha} \\
+ 2 \vec{\omega} \sum_{\alpha} m_{\alpha} \left( \vec{r}_{\alpha} \wedge \vec{v}_{\alpha} \right)
\end{aligned} \tag{2.3}$$

If we assume that the nuclei have no translational motion in the mobile system and that the origin of the mobile system is the center of gravity of the molecule, then:

$$\sum_{\alpha} m_{\alpha} \vec{v}_{\alpha} = 0 \tag{2.4}$$

and

$$\sum_{\alpha} m_{\alpha} \vec{r}_{\alpha} = 0 \tag{2.5}$$

If, in addition, we consider that in the mobile trihedron the molecule has no rotational motion, we can write:

$$\sum_{\alpha} m_{\alpha} \left( \vec{a}_{\alpha} \wedge \vec{v}_{\alpha} \right) = 0 \tag{2.6}$$

and thus

$$\sum_{\alpha} m_{\alpha} \left( \vec{r}_{\alpha} \wedge \vec{v}_{\alpha} \right) = \sum_{\alpha} m_{\alpha} \left( \vec{\rho}_{\alpha} \wedge \vec{v}_{\alpha} \right) \tag{2.7}$$

The two conditions above are called ECKART conditions and simplify the expression (2.3):

$$2T = \dot{R}^2 \sum_{\alpha} m_{\alpha} + \sum_{\alpha} m_{\alpha} \left( \vec{\omega} \wedge \vec{r}_{\alpha} \right)^2 + \sum_{\alpha} m_{\alpha} v_{\alpha}^2 + 2 \vec{\omega} \sum_{\alpha} m_{\alpha} \left( \vec{r}_{\alpha} \wedge \vec{v}_{\alpha} \right) \tag{2.8}$$

The first term corresponds to the translational kinetic energy of the molecule. It does not contribute to the quantification of the energy. The second term is the rotational kinetic energy. The third term is the molecular vibrational energy. The last term is called the CORIOLIS term. It is related to the interaction between rotation and vibration, and can be neglected if we consider that the vibrational motions are of small amplitude:  $\vec{r}_{\alpha} \approx \vec{a}_{\alpha}$ . This approximation, called the CASIMIR condition<sup>[6]</sup>, is generally verified for elongation vibrations, as opposed to the very soft torsional modes, which often remain poorly translated in this framework.

Consequently, the kinetic energy of nuclei can be written, to a first approximation, as the sum of a rotational term and a vibrational term:

$$2T_n = 2T_R + 2T_V \quad \text{assuming that } 2T_{VR} = 0 \tag{2.9}$$

From a quantum point of view, the above considerations lead to separate the rotational and vibrational motions of the nuclear equation into two distinct equations:

$$\psi_{R_\alpha}^n = \psi_{R_\alpha}^R \bullet \psi_{R_\alpha}^V \quad (2.10)$$

$$E_n = E_V + E_R \quad (2.11)$$

with  $\psi_{R_\alpha}^R$  : rotational wave function,

$\psi_{R_\alpha}^V$  : vibrational wave function,

$E_R$  : energy corresponding to the rotational wave function,

$E_V$  : energy corresponding to the vibrational wave function.

This gives the Schrödinger equation for vibrational motion:

$$\left( \hat{T}_V + \hat{V}_V \right) \psi_{R_\alpha}^V = E_V \psi_{R_\alpha}^V \quad (2.12)$$

and the Schrödinger equation describing rotational motion, assuming that interatomic bonds do not elongate during rotation (rigid rotator hypothesis):

$$T_R \psi_{R_\alpha}^R = E_R \psi_{R_\alpha}^R \quad (2.13)$$

## 2.2 Kinetic energy of vibration

The kinetic energy of vibration of a molecule composed of  $n$  atoms in the ECKART frame is written:

$$2T_V = \sum_{\alpha}^n m_{\alpha} (\dot{x}_{\alpha}^2 + \dot{y}_{\alpha}^2 + \dot{z}_{\alpha}^2) \quad (2.14)$$

with  $\dot{x}_{\alpha}, \dot{y}_{\alpha}, \dot{z}_{\alpha}$  : components of the velocity  $\vec{\rho}_{\alpha}$  of the atom  $\alpha$ .

By expressing this energy in the Cartesian coordinate system weighted by the masses ( $q_x = m_{\alpha}^{1/2} x_{\alpha}, q_y = m_{\alpha}^{1/2} y_{\alpha}$  and  $q_z = m_{\alpha}^{1/2} z_{\alpha}$ ), and without labelling the Cartesian axes, we obtain a simplified expression, an explicit function of  $3n$  coordinates:

$$2T_V = \sum_i^{3n} \dot{q}_i^2 \quad (2.15)$$

Matrix-wise, the above equation takes the form:

$$2T_V = [\dot{q}]^t [\dot{q}] \quad (2.16)$$

with  $\dot{q}_i$  : derivative of  $q_i$  as a function of time  $\left(\frac{dq_i}{dt}\right)$ ,  
 $[\dot{q}]^t$  : transpose matrix of  $[\dot{q}]$ .

Note that, in the space of unweighted Cartesian coordinates, we have:

$$2T_V = [\dot{x}]^t [M_\alpha] [\dot{x}] \quad (2.17)$$

## 2.3 Harmonic potential energy

The potential function is generally written as a TAYLOR series expansion in the region of the equilibrium position. In the above coordinate space, it takes the form of a characteristic polynomial of order  $n$ , whose development we restrict to order 2 under the harmonic assumption:

$$V = V_{eq} + \sum_i^{3n} \left(\frac{\partial V}{\partial q_i}\right)_{eq} q_i + \frac{1}{2!} \sum_{i \leq j}^{3n, 3n} \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_{eq} q_i q_j \quad (2.18)$$

The coefficients of this polynomial represent the  $n^{th}$  derivatives of the potential function at the geometric equilibrium structure. For this equilibrium configuration,  $V$  is equal to  $V_{eq}$ ; this term of order 0 can be taken as a reference. Moreover, if the electronic state is a stable state, the first derivatives  $\left(\frac{\partial V}{\partial q_i}\right)_{eq}$  are zero. The coefficients of order 2 are called quadratic or harmonic force constants (denoted  $f_{ij}^{(q)}$  in this space) and constitute the harmonic force field. Thus, the harmonic potential function is written:

$$2V = \sum_{i \leq j}^{3n, 3n} f_{ij}^{(q)} q_i q_j \quad (2.19)$$

or, in its matrix form:

$$2V = [q]^t [f^q] [q] \quad (2.20)$$

## 2.4 Equations of Lagrange

### 2.4.1 Mass-weighted Cartesian coordinate space

The determination of the  $3n$  vibrational motions and their frequency is done by solving the  $3n$  LAGRANGE equations from the knowledge of the two fundamental functions of mechanics, expressed in the two previous sub-parts:

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{q}_i}\right) + \frac{\partial V}{\partial q_i} = 0 \quad (2.21)$$

i.e.:

$$\ddot{q}_i + \sum_j^{3n} f_{ij}^{(q)} q_j \quad (2.22)$$

The solutions are of the form  $q_i = q_i^{\tilde{r}} \cos \lambda^{1/2} t$ , where  $q_i^{\tilde{r}}$  is the maximum amplitude of the  $i$ -mode and  $\lambda^{1/2}$  is related to its vibration frequency. To determine the value of the  $3n$  frequencies, we inject these particular solutions into the  $3n$  equations. Matrix-wise, this is equivalent to diagonalizing the matrix  $[f^q]$ . We obtain 6 zero eigenvalues corresponding to the three translational and three rotational motions of the molecule (two rotational motions if the molecule is linear) and  $3n - 6$  non-zero eigenvalues (5 in the case of a linear molecule), corresponding to the vibrational motions of the molecule. From these eigenvalues we deduce the wave numbers  $\varpi$  (expressed in  $\text{cm}^{-1}$ ) and the vibration frequencies  $\omega$  (in Hz) by the relation :

$$\lambda^{1/2} = 2\pi c \varpi = 2\pi \omega \quad (2.23)$$

with  $c$  : celerity of light in vacuum.

When some eigenvalues are identical, corresponding to two or three different vibrational motions of the same frequency, these modes are said to be doubly or triply degenerate. The eigenvectors represent the motion of the atoms in mass-weighted Cartesian coordinates, induced by the  $3n - 6$  (or  $3n - 5$ ) vibrations. These motions, specific to each vibration, are called "normal modes of vibration". This new space, represented by an orthonormal reference frame where each dimension corresponds to a harmonic vibrational motion of the molecule, constitutes a basis for the construction of the vibrational Hamiltonian in quantum treatment.

#### 2.4.2 Internal coordinate space: resolution by the method of Wilson

The choice of this space allows to reduce the dimension of the equations to be treated by eliminating the zero eigenvalues corresponding to the translational and rotational motions of the molecule. This is possible if we choose a reference frame that obeys the ECKART conditions. Moreover, the molecular vibrations are studied in terms of variations in bond lengths and angular deformations, which allows to assign a physical meaning to the force constants calculated in this space.

Here, the expression of the kinetic energy is more complex, because it is necessary to define a passage matrix of dimension  $(3n - 6) \times 3n$  (noted  $[B]$ ) between the Cartesian coordinates of displacements  $x$  and the coordinates of displacement  $r$ :  $[r] = [B][x]$ . According to the equation (2.17), and assuming a transformation with constant coefficients, valid for small movements, the kinetic energy is written:

$$2T = [\dot{r}]^t [G^{-1}] [\dot{r}] \quad (2.24)$$

Hence :

$$[G^{-1}] = [B^{-1}]^t [M_\alpha] [B^{-1}] \quad (2.25)$$

The potential energy is written as a function of the harmonic force constants expressed in the internal coordinate basis:

$$2V = [r]^t [f^{(r)}] [r] \quad (2.26)$$

The resolution of the  $3n - 6$  equations of LAGRANGE amounts to diagonalizing the matrix product  $[G] [f^{(r)}]$  :

$$[G] [f^{(r)}] [L] = [\lambda] [L] \quad (2.27)$$

where  $[L]$  is the eigenvector matrix.

### 2.4.3 Internal symmetry coordinate space

An internal symmetry coordinate (denoted  $s_i$ ) is a linear combination of internal coordinates and can be a local mode of vibration. A mode of vibration can in turn be a linear combination of several local modes with the same symmetry. This property is extremely important since, in this space, it is possible to determine  $f_{ij}^{(s)}$ -zero harmonic force constants by simply applying the direct product calculation rules from group theory. The matrices  $[G^{(s)}]$  and  $[f^{(s)}]$  have here the property of being block-symmetric. An interesting study was carried out by PULAY<sup>[7]</sup> on the construction of this space according to the different functional groups of organic compounds.

## 2.5 Quantum processing of vibration

Whether the classical approach is carried out in the space of Cartesian, internal or internal symmetry coordinates, the aim is to express the normal coordinates, which are the only ones capable of leading to the quantum treatment of the vibrational equation. In this space, the two energies are expressed in quadratic form:

$$2T = \sum_{i=1}^{3n-6(5)} \dot{Q}_i^2 = [\dot{Q}]^t [\dot{Q}] \quad (2.28)$$

$$2V = \sum_{i=1}^{3n-6(5)} \lambda_i Q_i^2 = [Q]^t [\lambda] [Q] \quad (2.29)$$

and the corresponding Hamiltonian is written:

$$\hat{H} = \hat{T} + \hat{V} = \frac{1}{2} \sum_{i=1}^{3n-6(5)} (\dot{Q}_i^2 + \lambda_i Q_i^2) \quad (2.30)$$

By associating these quantities with their corresponding operator,



$$\hat{Q} = Q \quad (2.31)$$

$$\hat{Q} = \hat{P} = -i\hbar \frac{\partial}{\partial Q} \quad (2.32)$$

we obtain the vibrational Schrödinger equation:

$$\sum_{i=1}^{3n-6(5)} \frac{\partial^2 \Psi}{\partial Q_i^2} + \frac{2}{\hbar^2} \left( E - \frac{1}{2} \sum_{i=1}^{3n-6(5)} \lambda_i Q_i^2 \right) \Psi = 0 \quad (2.33)$$

Case of the non-degenerate oscillator: consider the following separations of variables,

$$\Psi(Q_1, Q_2, \dots, Q_{3n-6}) = \Psi_1(Q_1) \Psi_2(Q_2) \dots \Psi_{3n-6}(Q_{3n-6}) \quad (2.34)$$

$$E = E_1 + E_2 + \dots + E_{3n-6} \quad (2.35)$$

The equation (2.33) is therefore equivalent to solving  $(3n - 6)$  equations with only one variable:

$$\frac{d^2 \Psi_i(Q_i)}{dQ_i^2} + \frac{2}{\hbar^2} \left( E - \frac{\lambda_i}{2} Q_i^2 \right) \Psi_i(Q_i) = 0 \quad (2.36)$$

Usually, the normal coordinates  $Q_i$  are replaced by the dimensionless normal coordinates  $q_i$  (not to be confused with the mass-weighted Cartesian coordinates defined in part 2.4.1) *via* applying the relation:

$$Q_i = \left( \frac{\hbar^2}{\lambda_i} \right)^{1/4} q_i \quad (2.37)$$

In this coordinate system, the one-dimensional vibrational Schrödinger equation takes the well-known form:

$$\frac{d^2 \Psi_i(q_i)}{dq_i^2} + \left( \frac{2E_i}{\hbar \lambda_i^{1/2}} - q_i^2 \right) \Psi_i(q_i) = 0 \quad (2.38)$$

There are infinitely many pairs  $(E_i, \Psi_i)$  solution of this equation, whose characteristics in the dimensionless normal coordinate space are as follows:

$$\Psi_i(q_i) = N_{v_i} H_{v_i}(q_i) e^{-\frac{q_i^2}{2}} \quad (2.39)$$

$$E_i = \int \Psi_i H_i \Psi_i dq_i = hc\varpi_i \left( v_i + \frac{1}{2} \right) \quad (2.40)$$

with  $v_i$  : vibrational quantum number of the coordinate  $q_i$ , positive integer,

$N_{v_i}$  : normalisation factor for vibrational state functions (2.41),

$H_{v_i}(q_i)$  : a polynomial of HERMITE (2.42).

$$N_{v_i} = (2^{v_i} v_i! \sqrt{\pi})^{-1/2} \quad (2.41)$$

$$H_{v_i}(q_i) = (-1)^{v_i} e^{q_i^2} \frac{d^{v_i}}{dq_i^{v_i}} \left( e^{-q_i^2} \right) \quad (2.42)$$

Note further that according to the part 2.4.1, these state functions are expressed in terms of the normal coordinates and are therefore, in fact, orthogonal. This treatment is the most general and can of course be applied when some eigenvalues are degenerate. In this case, we do not explicitly discern a multiple degenerate mode but multiple single degenerate modes of the same eigenvalue. We will call this type of treatment "implicit degeneracy treatment" as opposed to "explicit degeneracy treatment" which we discuss in the next sub-section.

## 2.6 The anharmonic potential function

The concept of a normal mode of vibration is based on the assumption of infinitesimal displacements around the equilibrium position. In reality, excited vibrational states or soft modes correspond to large amplitude motions. In fact, the expression of the potential developed in the part 2.3 is no longer sufficient, and terms of orders higher than 2 of the potential function must be taken into account to model more accurately the vibrational spectrum of the molecule studied. In the space of curvilinear internal coordinates of  $s_i$  symmetry<sup>1</sup>, the analytical form of this function becomes:

$$\begin{aligned} V_v = V_{eq} + \sum_i^{3n-6} \left( \frac{\partial V}{\partial s_i} \right)_{eq} s_i + \frac{1}{2} \sum_{i \leq j}^{3n-6} \left( \frac{\partial^2 V}{\partial s_i \partial s_j} \right)_{eq} s_i s_j \\ + \frac{1}{3} \sum_{i \leq j \leq k}^{3n-6} \left( \frac{\partial^3 V}{\partial s_i \partial s_j \partial s_k} \right)_{eq} s_i s_j s_k \\ + \frac{1}{4} \sum_{i \leq j \leq k \leq l}^{3n-6} \left( \frac{\partial^4 V}{\partial s_i \partial s_j \partial s_k \partial s_l} \right)_{eq} s_i s_j s_k s_l \\ + \dots \end{aligned} \quad (2.43)$$

The derivatives of order 2, 3 and 4 are called quadratic, cubic and quartic force constants respectively. The fourth-order truncation of the potential expression is, according to MASLEN<sup>[9]</sup>, sufficient to properly study highly excited stretching modes up to 10,000 cm<sup>-1</sup>. The different force constants are determined, either classically by *ab initio* calculation (or DFT) of the molecular

<sup>1</sup>In the case of strongly anharmonic oscillators, coordinates of the type SIMONS-PARR-FINLAN or coordinates of the type MORSE<sup>[8]</sup> can also be used

energy for several nuclear configurations around the equilibrium position, or by a finite difference procedure of the second or first derivatives of the electronic energy with respect to the nuclear coordinates. The potential function is then expressed in the dimensionless normal mode space, so that the Hamiltonian can be constructed in this basis. It then takes the form :

$$\frac{V_v}{hc} = \frac{1}{2!} \sum_i \varpi_i q_i^2 + \frac{1}{3!} \sum_{i,j,k} \phi_{ijk} q_i q_j q_k + \frac{1}{4!} \sum_{i,j,k,l} \phi_{ijkl} q_i q_j q_k q_l \quad (2.44)$$

where  $\phi_{ijk}$  and  $\phi_{ijkl}$  are, respectively, the cubic and quartic force constants, expressed in  $cm^{-1}$ . The relations between the third- and fourth-order derivatives of the equation (2.43) and the  $\phi$ , which are obtained by the terms of the  $[L]$  transition matrix, are detailed in reference.<sup>[10]</sup> When it is necessary to explain the degeneracy of the coordinates, we will use the notation of NIELSEN<sup>[11]</sup> in the dimensionless normal mode basis:

$$V_{pot} = \sum_i^{3n-6} \frac{\omega_i}{2} q_i^2 + \sum_{\|S\|_1=3}^S K_S \prod_{i=1}^{3n-6} q_i^{S_i} \quad (2.45)$$

with  $\omega_i$  harmonic frequency (in  $cm^{-1}$ ) associated with the coordinate  $q_i$ ,  $\|S\|_1$  the sum of the elements of the multi-index  $S=(S_1, S_2, \dots, S_{3n-6})$  and  $S$  the maximum degree of the SEP.

The numerical values of the force constants can be determined in several ways. It is important to note beforehand that the number of coefficients of the PES is a function of the number of vibrators and the order of its expansion (although some terms can be determined simply by taking into account molecular symmetry). There are three main families of methods for determining force constants:

- Analytical methods: these consist of finding the analytical expression of the second, third and fourth derivatives of the energy and calculating these derivatives at the equilibrium configuration.
- Numerical methods: here, the value of the potential is calculated for different geometric structures of the system studied, and then an analytical function is fitted to the grid of points thus obtained. The expression of this function is determined by linear regression procedures. This approach is the most commonly used, because it leads to results of satisfactory accuracy on the condition that there is a suitable redundancy of information and a correct arrangement of the points on the field of calculation. On the other hand, the computational effort becomes very quickly gigantic, forcing the user to "degrade" the quality of the method of calculating the molecular wave function in order to be able to carry out the PES acquisition.
- Analytical-numerical methods: these approaches, proposed by Peter Pulay<sup>[12]</sup>, represent a compromise between the two previous derivation procedures. Here, a force field of order  $n$  is constructed by finite differences using the available analytical derivatives of order  $n - x$ . This method requires less computational efforts than the previous

approach, but is numerically very sensitive, sometimes leading to results that are difficult to use when one wants to know the analytical form of a fourth-order potential for large systems. Thus, a molecule of 10 atoms leads to 20475 *ab initio* calculations, a number that is generally doubled to ensure the convergence of the results.

Independently of the family of methods used for the determination of the force constants, it is important to underline the fact that the dimension of the problem increases in a very significant way with the number of atoms of the system to be studied. It is sufficient to recall that the study of a molecule of 12 atoms leads to 46376 *ab initio* calculations, i.e. more than double the number of calculations necessary to treat the system of 10 atoms mentioned above. Moreover, it is also important to recall that each of the terms (force constants) that constitute the analytical expression of the PES does not contribute with the same intensity to the description of the couplings between all modes.

Two approaches are currently being developed. The first is to remove from the PES the third and fourth order monomials below a force constant predetermined by the user. The second is to take into account the notion of "energetic proximity" in order to eliminate from the PES the third and fourth order monomials that couple the most energetically distant vibrational states. Both of these criteria are intimately linked to the energy formulas resulting from the standard perturbation method known as RAYLEIGH-SCHRÖDINGER, which we will develop hereafter and which makes it possible to evaluate the energy correction brought by each vibrational state to the energy of a given state through the mechanical anharmonicity. The first criterion is directly correlated to the numerical value of the force constants  $K$ s considered (present in the numerator of the perturbation formulae), while the second criterion is directly correlated to the energy difference of the modes coupled by this constant (term present in the denominator of the perturbation formulae). This observation should allow us, in the near future, to have an efficient and less "arbitrary" control tool to effectively reduce the size of the PES useful for RSVE.

## 2.7 Matrix representation of the Hamiltonian, calculation of integrals

The first term of the equation (2.45) represents the Hamiltonian of order 0. This term is diagonal. Therefore, the  $j$  ( $j \in [1, N]$ ) normalised eigenfunctions  $\psi_{j,v}^{(0)}$ , products of harmonic oscillators  $\Theta_{j,v}^{(0)}(q_k)$  resulting from the treatment of the vibrational equation of order 0 form a complete orthogonal system:

$$\psi_{j,v}^{(0)} = \prod_{k=1}^{nv} \Theta_{j,v}^{(0)}(q_k) \text{ with } \langle \Theta_{j,v}^{(0)} | \Theta_{j,v'}^{(0)} \rangle = \delta_{v_k v_{k'}} \quad (2.46)$$

This system constitutes a basis of development of the  $i$  ( $i \in [1, N_s]$ ) ( $N_s \leq N$ ) vibrational wave functions sought  $|v\rangle_i$ , constructed as linear combinations of eigenfunctions of order 0:

$$|v\rangle_i = |v_1, v_2, \dots, v_{nv}\rangle_i = \sum_j C_j \psi_{j,v}^{(0)} \quad (2.47)$$

In the case of doubly degenerate modes, we will note the vibrational wave function associated with the degenerate oscillator  $i$ :  $|v, l\rangle_i$ . It is then a question of solving the anharmonic vibrational Schrödinger equation:

$$\hat{H}_{v,l} |v, l\rangle_i = E_{v,l} |v, l\rangle_i \quad (2.48)$$

This is usually done using perturbation or variation methods, or combined variation-perturbation methods. For solving systems of equations such as (2.48), the computer tool becomes very valuable. Therefore, it is convenient to solve the problem in its algebraic form, i.e. to represent it matrix-wisely. For this purpose, we define the matrix representation of the Hamiltonian by projecting it into its basis of non-degenerate and doubly degenerate harmonic functions. The matrix elements  $H_{(v,l)(v',l')}$  are defined by the relation:

$$H_{(v,l)(v',l')} = \int \Psi_{(v,l)}^{(0)} \hat{H} \Psi_{(v',l')}^{(0)} dq_{(i,j,\dots, nv)} \quad (2.49)$$

$$= \langle (v, l)^{(0)} | \hat{H} | (v', l')^{(0)} \rangle \quad (2.50)$$

in which  $\hat{H}$  is partitioned as follows:

$$\hat{H} = \hat{H}^0 + \hat{H}^1 + \hat{H}^2 \quad (2.51)$$

where  $\hat{H}^0$  refers to the harmonic Hamiltonian,  $\hat{H}^1$  and  $\hat{H}^2$  translate the anharmonicity and involve respectively the operators  $q^3$  and  $q^4$ , these last ones being able to be decomposed in a product of operators  $q^{[13]}$ :  $q^3 = \prod_{i,j,k}^3 q_i q_j q_k$ ,  $q^4 = \prod_{i,j,k,l}^4 q_i q_j q_k q_l$ . Since the variables are separable, each matrix term decomposes into a product of single-mode integrals.

Case of non-degenerate modes: let the integral  $\langle v_\alpha | q | v'_\alpha \rangle$ , the monomode functions being in this case characterized by HERMITE polynomials, noted here  $\mathbf{H}$ , the integral is written:

$$\langle v | q | v' \rangle = N_v N_{v'} \int e^{-q^2} \mathbf{H}_v q \mathbf{H}_{v'} dq \quad (2.52)$$

It can be shown that there are recurrence relations between the polynomials, which leads to:<sup>[2]</sup>

$$\langle v | q | v' \rangle = N_v N_{v'} \int e^{-q^2} \mathbf{H}_{v'} \left( v \mathbf{H}_{v-1} + \frac{1}{2} \mathbf{H}_{v+1} \right) dq \quad (2.53)$$

Because these polynomials are orthogonal, this integral is non-zero if  $v' = v \pm 1$  and we obtain:

$$\langle v | q | v + 1 \rangle = \langle v + 1 | q | v \rangle = \sqrt{\frac{v+1}{2}} \quad (2.54)$$

$$\langle v | q | v - 1 \rangle = \langle v - 1 | q | v \rangle = \sqrt{\frac{v}{2}} \quad (2.55)$$

As the limited expansion of the potential function is truncated to order 6 in our study, the operators in the Hamiltonian are of type  $q, q^2, q^3, q^4, q^5$  and  $q^6$ . The result of the corresponding integrals is tabulated.<sup>[14]</sup>

## 2.8 Perturbation methods

There are two methods of perturbation calculation, namely the method known as the "contact transformation", which originates from the work of VAN VLECK<sup>[15,16]</sup>, and the standard method known as RAYLEIGH-SCHRÖDINGER.<sup>[17]</sup> The last one is relatively simple to set up and leads to the well known expressions of the energy :

$$E_{(v,l)}^{Tot} = E_{(v,l)}^{(0)} + H_{(v,l),(v,l)}^{(2)} + \sum_{v' \neq v'} \frac{(H_{(v,l),(v',l')}^{(1)})^2}{E_{(v,l)}^{(0)} - E_{(v',l')}^{(0)}} \quad (2.56)$$

$E_v^{(0)}$  et  $E_{v'}^{(0)}$  being respectively the harmonic energies of the  $v$  and  $v'$  states. The development of the wave function is usually deduced from a perturbation treatment of order 1:

$$|v, l\rangle^{(1)} = |v, l\rangle^{(0)} + \sum_{v' \neq v'} \frac{H_{(v,l),(v',l')}^{(1)}}{E_{(v,l)}^{(0)} - E_{(v',l')}^{(0)}} * |v', l'\rangle^{(0)} \quad (2.57)$$

Whatever the approach, the perturbational expression of the total vibration energy can be formulated as follows:

$$E_{(v,l)} = \sum_s \omega_s \left( v_s + \frac{1}{2} \right) + \sum_t \omega_t (v_t + 1) + \sum_{s \geq s'} x_{ss'} \left( v_s + \frac{1}{2} \right) \left( v_{s'} + \frac{1}{2} \right) \quad (2.58)$$

$$+ \sum_{s,t} x_{st} \left( v_s + \frac{1}{2} \right) (v_t + 1) + \sum_{t \geq t'} (v_t + 1) (v_{t'} + 1) + \sum_{t \geq t'} g_{tt'} l_t l_{t'} + \dots$$

For practical reasons:  $q_{\pm} = q_x \pm iq_y$ .

$$\begin{aligned}
E_{(v,l)} = & \sum_s \omega_s \langle v_s | q_s^2 | v_s \rangle + \sum_t \omega_t \sum_l \langle v_t, l | q_t^2 | v_t, l \rangle \\
& + \sum_{s \neq s'} k_{ss's'} \langle v_s | q_s^2 | v_s \rangle \langle v_{s'} | q_{s'}^2 | v_{s'} \rangle + \sum_{s=s'} k_{ssss} \langle v_s | q_s^4 | v_s \rangle \\
& + \sum_{s,t} k_{sstt} \langle v_s | q_s^2 | v_s \rangle \left( \sum_l \langle v_t, l | q_{t+} q_{t-} | v_t, l \rangle \right) \\
& + \sum_{t \neq t'} k_{ttt't'} \left( \sum_l \langle v_t, l | q_{t+} q_{t-} | v_t, l \rangle \right) \left( \sum_{l'} \langle v_{t'}, l' | q_{t'+} q_{t'-} | v_{t'}, l' \rangle \right) \\
& + \sum_{t=t'} k_{tttt} \left( \sum_l \langle v_t, l | q_{t+}^2 q_{t-}^2 | v_t, l \rangle \right) \\
& - \frac{1}{2} \sum_{t=t'} k_{tttt} l_t^2 + \Theta(q^3) \tag{2.59}
\end{aligned}$$

where the indexes  $s$  and  $t$  refer respectively to the non- and doubly degenerate states,  $x$  and  $g$  respectively anharmonicity constants depending on the cubic and quartic terms. While the perturbation method is easy to program, and despite the fact that it is one of the most widely used techniques for calculating an anharmonic spectrum<sup>[18]</sup>, its use remains limited since it is, strictly speaking, only intended for calculating the lowest frequencies of a spectrum, a spectral region where the density of vibrational states is low. This limitation of the perturbation theory is due to the resonance phenomena (type FERMI<sup>[19]</sup> or DARLING-DENNISON<sup>[20]</sup>) and to the fact that, by truncating the function to order 4 ((semi) diagonal terms), it is not possible to take into account all the interaction terms indispensable for the treatment of hot and combination bands.

Solutions to this problem have been developed over the last decade. We can cite, for example, the contact transform vibrational Hamiltonian method, coupled with an automated procedure for setting up and solving the relevant resonances specific to the systems of Martin and Taylor<sup>[21]</sup>, the canonical high-order perturbation theory of VAN VLECK<sup>[11]</sup>, or the Vibrational Self-Consistent Field (VSCF) approximation which includes corrections concerning the correlation between modes by the perturbation theory developed by JUNG, GERBER and NORRIS. It is called CC-VSCF for "Correlation Corrected VSCF"<sup>[22-24]</sup>.

## 2.9 Variational methods

The approximate solution of the vibrational Schrödinger equation by the variational method consists in developing the eigenstates of  $H_v$  in the basis of the known eigenfunctions of the Hamiltonian of order 0,  $H_v^{(0)}$ , and then to diagonalise the matrix representation of this Hamiltonian. Thus the problem amounts to computing the coefficients  $C_j$  of the eigenfunctions  $|v, l\rangle_i$  solutions of the vibrational Hamiltonian  $H_v$ , so that:

–  $|v, l\rangle$  be normalised :

$$\langle v, l | v, l \rangle = \sum_j^N C_j^2 \quad (2.60)$$

– vibrational energy :

$$E_{v,l} = \langle v, l | H_{v,l} | v, l \rangle = \sum_j^N C_j^2 \langle \psi_{j,v}^{(0)} | H_{v,l} | \psi_{j,v}^{(0)} \rangle + \sum_j^N \sum_{k \neq j}^N C_j C_k \langle \psi_{j,v}^{(0)} | H_{v,l} | \psi_{k,v}^{(0)} \rangle \quad (2.61)$$

$$E_{v,l} = \sum_j^N C_j^2 H_{jj} + 2 \sum_j^N \sum_{k \neq j}^N C_j C_k H_{jk} \quad (2.62)$$

be minimal in view of the normalisation condition.

– the variation in energy leads to an extremum:

$$dE_{v,l} = \sum_{j=1}^N \frac{\partial E_{v,l}}{\partial C_j} dC_j = 0 \quad (2.63)$$

where

$$\frac{\partial E_{v,l}}{\partial C_j} dC_j = 2C_j H_{jj} + 2 \sum_{k \neq j}^N C_k H_{jk} \quad (2.64)$$

The variations ( $\partial C_j$ ) are not independent of each other since they must simultaneously verify the normalisation condition. The method of Lagrange multipliers makes it possible to take these conditions into account. The application of the variation theorem thus leads to the calculation of the unitary transformation ( $C$ ) which diagonalizes the representation of the Hamiltonian ( $H$ ):

$$(H)(C) = E(C) \quad (2.65)$$

in the basis of the eigenfunctions of the unperturbed Hamiltonian in order to obtain the corresponding eigenvalues, energies of the vibrational levels, eigenvectors, vibrational states. The vibrational solutions will be all the closer to the exact solutions as the ( $N$ ) basis of development tends towards infinity. As this last one is always finite and limited, the problem then is based on the choice of the configurations of the space to be diagonalized. The selection strategies are numerous<sup>[25–30]</sup> and very close to those practised in quantum chemistry for the methods allowing to reach the electronic correlation energy.

### 2.9.1 Choice of the space to be diagonalized

The choice of the space to be diagonalized ( $N_s$ ) has a great influence on the precision and the speed of convergence of variational methods. The truncation of the complete space ( $N$ ) is a delicate problem that needs to be discussed as it is at the origin of the singularities of the



different approaches.

For a better interpretation of a resonant vibrational spectrum, it is therefore preferable to use a variational method, even if this type of method leads to known pitfalls. Indeed, the set of data extracted from the potential function  $V$  grows rapidly with the size of the molecule, i.e. proportionally to the number of vibrators and to the term  $g$  which represents the number of non-zero terms of the PES. It is possible to show that this growth behaves like  $O(gN)$ . However, the accuracy of the method is entirely dependent on the quality of  $V$  and the obligation to take into account a maximum of  $N$  vibrational configurations in the variational active space. The solution sought will be all the closer to the exact solution as the  $N$  basis tends towards infinity; however, this last being necessarily finite and limited, the problem thus lies in the choice of the  $N_s$  configurations to be diagonalized. This point is crucial because the precision and the convergence speed of the variational method depend greatly on this choice. The truncation made on the  $N$  space has become a major axis of research, which has led to different methods, each with its own specificities.

These selection methods are very similar to those used for the calculation of electronic correlation energy in quantum chemistry. There are almost as many selective strategies as there are programs based on configuration interaction (CI). In agreement with the two algorithms of WYATT et al<sup>[31]</sup>, a method called P\_MWCI (Parallel Multiple Windows CI) based on the iterative and parallelized construction ( $\gamma$  cycles) of  $\langle H_v \rangle$  of the configuration space has been implemented. The details are reported in reference.<sup>[32]</sup> More recently, a more efficient method, called A-VCI (Adaptive Variational CI) has been developed in the laboratory to select, no longer the complete matrix of the problem, but a sub-matrix sufficiently representative of the problem to allow us to be able to compute the first eigenvalues of interest for our analyses (without ever having to diagonalize the global matrix of the variational problem). Our analysis is based on a hierarchical method similar to the variational RAYLEIGH-RITZ method using a new way to write the residual error committed between two iterations. This adaptive algorithm was therefore developed in order to correlate three conditions simultaneously, namely: a suitable starting space that has no energy "holes", a controlled convergence criterion and a reasoned active space enrichment procedure. The use of the residual allows us to control the most relevant direction(s), in which it is necessary to enrich the active working space.

These methods are not unique, however, and among the various variational methods developed, we can cite as an example the innovative work of BOWMAN and GERBER on the VSCF approach<sup>[33-36]</sup>, to the development of the MULTIMODE<sup>[37]</sup> and to the very efficient VCC ("Vibrational Coupled Cluster") approach recently developed by CHRISTIANSEN.<sup>[38]</sup> More recently, an extension of the VSCF by introducing the Quasi-Degenerate Perturbation Theory (QDPT) has been developed, in order to improve the description of the vibrational resonance in the case of polyatomic molecules.<sup>[39]</sup> It is however important to recall here that the current average accuracy of variational calculations on small organic systems is 1 to 15  $\text{cm}^{-1}$ , depending on the nature of the motions studied. This is dependent on both the quality and the analytical form

chosen to describe the force field. Finally, it should be noted that these approaches, which are currently being developed, are only intended for the study of systems with less than 10 atoms in total.

### 2.9.2 Variation-perturbation methods

In front of the impossibility of solving the high-dimensional secular problem associated with a complete configuration interaction (CI), we have chosen in this work to use a variation-perturbation method similar to the one developed in the field of CIPSI electron spectroscopy<sup>[40]</sup>, which the ECP team has specialised in for over 20 years. In this method, the representation of the vibrational Hamiltonian will be diagonalized in an iteratively constructed basis, and the space of functions generated from an initial subspace  $S_0$  will have the information it contains treated in a more approximate way by a RAYLEIGH-SCHRÖDINGER type perturbation method at order 2 (on the energy).

The iterative process for the enrichment of the database is carried out with respect to the coefficients of the generated functions that will be tested in the correction of the zero-order wave function to the first order of perturbation. Only the functions that have a significant weight  $(C_{jj})^2$ , defined by the user, will be included in the database for the next iteration. This choice is based on the fact that we try to describe as well as possible the wave functions associated with the studied states. The description of the wave function is therefore improved by adding a correction that takes into account the excitations of the wave function, using a second order Rayleigh-Schrödinger perturbation method. For each state, the norm of the correction applied to the initial function is calculated. This norm makes it possible to follow the importance of the correction and to judge if the choice of the basis (the generator space) is judicious. The choice of the starting base  $S_0$  therefore determines the quality of the calculation. It is necessary to include all the vibrational functions (product functions of harmonic oscillators) that are considered important for describing the states under study. In practice, the dimension of the basis can be of the order of two hundred while the total space generated can be several thousands or tens of thousands.

A more precise detail of the variation-perturbation method is given below. The aim of the algorithm is to construct a basis of vibrational functions (the  $\psi^{(0)}$  eigenfunctions of  $H^{(0)}$ ) on which to develop the eigenstates of  $H$  ( $H = H^{(0)} + H'$ )

$$H^{(0)}\psi_i^{(0)} = E_i^{(0)}\psi_i^{(0)} \quad (2.66)$$

with

$$\psi_i^{(0)} = \prod_{k=1}^{nv} \Theta_{v_k}^{(0)}(q_k) \text{ with } v_k = 0, 1, 2, \dots \quad (2.67)$$

At each iteration, the process of generating  $\psi^{(0)}$  functions from the functions in  $S$  is as follows:

$$\langle \psi_i^{(0)} | H' | \psi_k^{(0)} \rangle \text{ with } \psi_k^{(0)} \notin S_0 \quad (2.68)$$

Let  $(S_m^{(n)}, \psi_{0m}^{(n)}, \eta_m^{(n)}, \psi_{1m}^{(n)}, E_{0m}^{(n)}, E_m^{(n)})$  represent the subspace  $S$ , the zeroth-order wave function, the selection threshold, the 1-order wave function, the zeroth-order energy and the (n)-corrected energy, respectively. The diagonalization of the Hamiltonian in the subspace  $S_m^{(n)}$  allows us to obtain the wave function  $\psi_{0m}^{(n)}$  associated to the studied state, with associated eigenvalues  $E_{0m}^{(n)}$ :

$$\psi_{0m}^{(n)} = \sum_{i \in S_m^{(n)}} C_i \psi_i^{(0)} \quad (2.69)$$

$$\langle \psi_{0m}^{(n)} | H | \psi_{0m}^{(n)} \rangle \quad (2.70)$$

At iteration  $n$ , the energy associated with the studied state will be:

$$E_m^{(n)} = E_{0m}^{(n)} + \epsilon_m^{(n)} \quad (2.71)$$

$$\epsilon_m^{(n)} = \sum_{j \notin S_m^{(n)}} \frac{|\langle \psi_i^{(0)} | H' | \psi_j^{(0)} \rangle|^2}{E_i^{(0)} - E_j^{(0)}} \quad (2.72)$$

$\epsilon_m^{(n)}$  is the correction due to the perturbation of the state  $m$ , described by the wave function  $\psi_{0m}^{(n)}$  by all the functions generated from the functions of  $S_m^{(n)}$ . This leads to the function :

$$|\psi_{1m}^{(n)}\rangle = |\psi_{0m}^{(n)}\rangle + \sum_{j \notin S_m^{(n)}} \frac{|\langle \psi_i^{(0)} | H' | \psi_j^{(0)} \rangle|}{E_i^{(0)} - E_j^{(0)}} |\psi_j^{(0)}\rangle = |\psi_{0m}^{(n)}\rangle + \sum_{j \notin S_m^{(n)}} C_{ij}^{(n)} |\psi_j^{(0)}\rangle \quad (2.73)$$

Only the functions generated  $|\psi_j^{(0)}\rangle$  whose coefficients of the development satisfy the condition :

$$|C_{ij}^{(n)}| > \eta_m^{(n)} \quad (2.74)$$

will contribute to the first order correction of the vibrational wave function. The subspace  $S_m^{(n)}$  will be enhanced by the functions which have a significant weight  $(C_{ij}^{(n)})^2$  (higher than a threshold chosen by the user) thus serving to define the subspace  $S_m^{(n+1)}$  which will allow us, by diagonalization, to generate the function  $\psi_{0m}^{(n+1)}$  and to restart a cycle, until we obtain a stable result. Let us specify however that this notion of "stable result" remains delicate to define, as proved by our recent developments concerning the notion of residue.<sup>[41]</sup> Nevertheless, in general, the vibrational wave function improves during the iterations, this improvement being obtained

by decreasing the selection threshold ( $\eta_m^{(n)}$ ) as well as the weight ( $(C_{ij}^{(n)})^2$ ) of the chosen functions. At the end of the iterative process, we will have :

- a carefully chosen subspace  $S$ , which will be treated by a variational method. The eigenfunctions obtained are good approximations to the true solutions for the lower energy states.
- a generated subspace, whose contribution to the vibrational energy will be evaluated by summing the contributions to the second-order perturbation correction of each of its constituent functions. The functions of the generated subspace must interact weakly with those of the complementary space, so that the wave function  $\psi_{1m}^{(n)}$  is normalised, which corresponds to :

$$\sum_{j \notin S_m^{(n)}} |C_{ij}^{(n)}|^2 \cong 0 \quad (2.75)$$

## References

- [1] P. Barchewitz, *Spectroscopie atomique et moléculaire*, vol. 2. Masson et Cie, 1971.
- [2] E. B. J. Wilson, J. G. Decius, and P. G. Cross, “Molecular vibrations,” *Am. J. Phys.*, vol. 23, pp. 550–550, 1955.
- [3] C. Pouchan, *Approche de la fonction potentielle nucléaire à partir du calcul de fonction d’onde (application à l’étude des modes de vibrations moléculaires)*. PhD thesis, 1978.
- [4] K. Zaki, *Etude des modes de vibration au-delà de l’approximation harmonique: application de la résolution des problèmes vibrationnels de molécules de type  $X_2CNX$  ( $X= F, H$ )*. PhD thesis, 1996.
- [5] C. Eckart, “Some studies concerning rotating axes and polyatomic molecules,” *Phys. Rev.*, vol. 47, p. 552, 1935.
- [6] H. B. G. Casimir, *Rotation of a rigid body in quantum mechanics*. PhD thesis, 1931.
- [7] P. Pulay, G. Fogarasi, F. Pang, and J. E. Boggs, “Systematic ab initio gradient calculation of molecular geometries, force constants, and dipole moment derivatives,” *J. Am. Chem. Soc.*, vol. 101, pp. 2550–2560, 1979.
- [8] W. Meyer, P. Botschwina, and P. Burton, “Ab initio calculation of near-equilibrium potential and multipole moment surfaces and vibrational frequencies of  $h+ 3$  and its isotopomers,” *J. Chem. Phys.*, vol. 84, pp. 891–900, 1986.
- [9] P. E. Maslen, D. Jayatilaka, S. M. Colwell, R. D. Amos, and N. C. Handy, “Higher analytic derivatives. ii. the fourth derivative of self-consistent-field energy,” *J. Chem. Phys.*, vol. 95, pp. 7409–7417, 1991.
- [10] A. R. Hoy, I. M. Mills, and G. Strey, “Anharmonic force constant calculations,” *Mol. Phys.*, vol. 24, pp. 1265–1290, 1972.
- [11] H. H. Nielsen, “The vibration-rotation energies of molecules,” *Rev. Mod. Phys.*, vol. 23, p. 90, 1951.
- [12] P. Pulay, “Ab initio calculation of force constants and equilibrium geometries in polyatomic molecules: I. theory,” *Mol. Phys.*, vol. 17, pp. 197–204, 1969.
- [13] P. Barchewitz, *Spectroscopie infrarouge*, vol. 1. 1961.
- [14] P. Carbonnière, *Calcul ab-initio de spectres vibrationnels anharmoniques: Développement méthodologique pour le traitement de systèmes de grande taille*. PhD thesis, 2002.
- [15] D. Papousek and M. R. Aliev, *Molecular vibrational-rotational spectra*, vol. 13. 1982.

- [16] J. H. V. Vleck, "On  $\sigma$ -type doubling and electron spin in the spectra of diatomic molecules," *Phys. Rev.*, vol. 33, p. 467, 1929.
- [17] T. Oka, "Vibration—rotation interaction in symmetric-top molecules and the splitting between a1 and a2 levels," *J. Chem. Phys.*, vol. 47, pp. 5410–5426, 1967.
- [18] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, "Gaussian 09 Revision A.2." Gaussian Inc. Wallingford CT 2009.
- [19] E. Fermi, "Über den ramaneffekt des kohlendioxys," *Z. Phys.*, vol. 71, pp. 250–259, 1931.
- [20] B. T. Darling and D. M. Dennison, "The water vapor molecule," *Phys. Rev.*, vol. 57, p. 128, 1940.
- [21] J. M. L. Martin and P. R. Taylor, "Accurate ab initio quartic force field for trans-hnnh and treatment of resonance polyads," *Spectroc. Acta A*, vol. 53, pp. 1039–1050, 1997.
- [22] J. O. Jung and R. B. Gerber, "Vibrational wave functions and spectroscopy of  $(\text{H}_2\text{O})_n$ ,  $n=2,3,4,5$ : Vibrational self-consistent field with correlation corrections," *J. Chem. Phys.*, vol. 105, pp. 10332–10348, 1996.
- [23] J. O. Jung and R. B. Gerber, "Vibrational wave functions and energy levels of large anharmonic clusters: A vibrational scf study of  $(\text{ar})_{13}$ ," *J. Chem. Phys.*, vol. 105, pp. 10682–10690, 1996.
- [24] L. S. Norris, M. A. Ratner, A. E. Roitberg, and R. B. Gerber, "Møller–Plesset perturbation theory applied to vibrational problems," *J. Chem. Phys.*, vol. 105, pp. 11261–11267, 1996.
- [25] C. Pouchan and K. Zaki, "Ab initio configuration interaction determination of the overtone vibrations of methyleneimine in the region 2800–3200  $\text{cm}^{-1}$ ," *J. Chem. Phys.*, vol. 107, pp. 342–345, 1997.
- [26] S. Carter, S. J. Culik, and J. M. Bowman, "Vibrational self-consistent field method for many-mode systems: A new approach and application to the vibrations of co adsorbed on cu (100)," *J. Chem. Phys.*, vol. 107, pp. 10458–10469, 1997.

- [27] J. Koput, S. Carter, and N. C. Handy, "Ab initio prediction of the vibrational-rotational energy levels of hydrogen peroxide and its isotopomers," *J. Chem. Phys.*, vol. 115, pp. 8345–8350, 2001.
- [28] P. Cassam-Chenaï and J. Liévin, "Alternative perturbation method for the molecular vibration–rotation problem," *Int. J. Quantum Chem.*, vol. 93, pp. 245–264, 2003.
- [29] N. Gohaud, D. Begue, C. Darrigan, and C. Pouchan, "New parallel software (p\_anhar) for anharmonic vibrational calculations: Application to  $(\text{ch}_3\text{li})_2$ ," *J. Comput. Chem.*, vol. 26, pp. 743–754, 2005.
- [30] F. Culot, F. Laruelle, and J. Liévin, "A vibrational casscf study of stretch-bend interactions and their influence on infrared intensities in the water molecule," *Theor. Chim. Acta*, vol. 92, pp. 211–226, 1995.
- [31] R. E. Wyatt, C. Iung, and C. Leforestier, "Toward ab initio intramolecular dynamics," *Acc. Chem. Res.*, vol. 28, pp. 423–429, 1995.
- [32] D. Bégué, N. Gohaud, C. Pouchan, P. Cassam-Chenai, and J. Liévin, "A comparison of two methods for selecting vibrational configuration interaction spaces on a heptatomic system: Ethylene oxide," *J. Chem. Phys.*, vol. 127, p. 164115, 2007.
- [33] J. M. Bowman, "Self-consistent field energies and wavefunctions for coupled oscillators," *J. Chem. Phys.*, vol. 68, pp. 608–610, 1978.
- [34] J. M. Bowman, "The self-consistent-field approach to polyatomic vibrations," *Acc. Chem. Res.*, vol. 19, pp. 202–208, 1986.
- [35] R. B. Gerber and M. A. Ratner, "Self-consistent-field methods for vibrational excitations in polyatomic systems," *Adv. Chem. Phys.*, vol. 70, pp. 97–132, 1988.
- [36] R. B. Gerber and M. A. Ratner, "A semiclassical self-consistent field (sc scf) approximation for eigenvalues of coupled-vibration systems," *Chem. Phys. Lett.*, vol. 68, pp. 195–198, 1979.
- [37] S. Carter, N. C. Handy, and J. M. Bowman, "High torsional vibrational energies of  $\text{h}_2\text{o}_2$  and  $\text{ch}_3\text{oh}$  studied by multimode with a large amplitude motion coupled to two effective contraction schemes," *Mol. Phys.*, vol. 107, pp. 727–737, 2009.
- [38] M. Sparta, M. B. Hansen, E. Matito, D. Toffoli, and O. Christiansen, "Using electronic energy derivative information in automated potential energy surface construction for vibrational calculations," *J. Chem. Theory Comput.*, vol. 6, pp. 3162–3175, 2010.
- [39] K. Yagi, S. Hirata, and K. Hirao, "Vibrational quasi-degenerate perturbation theory: Applications to fermi resonance in  $\text{co}_2$ ,  $\text{h}_2\text{co}$ , and  $\text{c}_6\text{h}_6$ ," *Phys. Chem. Chem. Phys.*, vol. 10, pp. 1781–1788, 2008.

- [40] B. Huron, J. P. Malrieu, and P. Rancurel, "Iterative perturbation calculations of ground and excited state energies from multiconfigurational zeroth-order wavefunctions," *J. Chem. Phys.*, vol. 58, pp. 5745–5759, 1973.
- [41] R. Garnier, M. Odunlami, V. L. Bris, D. Bégué, I. Baraille, and O. Coulaud, "Adaptive vibrational configuration interaction (a-vci): A posteriori error estimation to efficiently compute anharmonic ir spectra," *J. Chem. Phys.*, vol. 144, p. 204123, 2016.



### 3 Application to a small system : HCNO – Formylnitrene, Cyanic, Isocyanic, Fulminic and Isofulminic Acids and their Interrelationships at DFT and CASPT2 Levels of Theory.

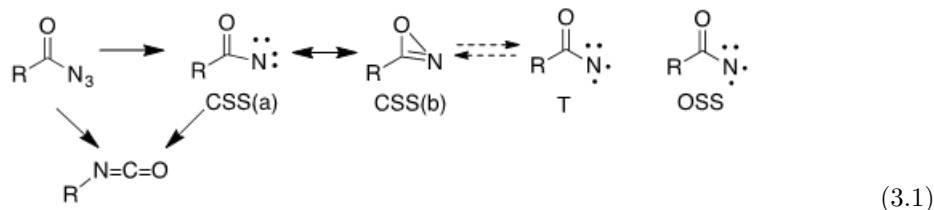
The four acids, fulminic EQ1 (HCNO), isocyanic EQ2 (HNCO), cyanic EQ9 (HOCN), and isofulminic EQ 5 (HONC) and their salts and esters are fundamental entities in chemistry. Silver Fulminate (AgCNO) and Silver Cyanate (AgOCN) played a crucial role in the formulation of the concept of Isomerism. Liebig had analyzed the elemental composition of silver fulminate, AgCNO.<sup>[1]</sup> Wöhler analyzed silver cyanate in 1824, and formulated it as a salt of then unknown cyanic acid, HOCN.<sup>[2]</sup> Since the two analyses were identical, Liebig concluded that Wöhler's analysis must be wrong, and Liebig's own analysis of (impure) silver cyanate actually showed that it contained less oxygen than the silver fulminate (71% AgO).<sup>[3]</sup> However, after conferring with Wöhler, Liebig analyzed a sample of pure silver cyanate himself and confirmed Wöhler's composition (75.5% AgO).<sup>[4,5]</sup> The two became life-long friends and collaborators. The realization that AgCNO and AgNCO have the same elemental composition contributed to Berzelius' formulation of the concept of isomerism.<sup>[6-9]</sup> Examples cited by Berzelius were cyanic and fulminic acids, tartaric and the racemic tartaric acids, ammonium cyanate and urea, and the stannic acids (then believed to be two different acids,  $\alpha$  and  $\beta$ , but now understood to be SnO<sub>2</sub> with different particle sizes and colloidal properties).

Fulminic acid EQ1 has the structure HCNO,<sup>[10,11]</sup> i.e. it is formonitrile oxide. The dangerously explosive, shock sensitive mercury and silver fulminates were prepared by Kunckel von Löwenstern,<sup>[12]</sup> and more recently by the Englishman Edward Howard<sup>[13]</sup> and the Italian Luigi Brugnatelli<sup>[14-16]</sup>. Howard isolated mercury fulminate as a grey powder by treating red mercuric oxide with nitric acid and ethanol and discovered that it exploded violently by addition of sulfuric acid. He was severely injured in the process. Hg(CNO)<sub>2</sub> has been used widely as a detonator, or blasting cap, to initiate the explosion of dynamite (nitroglycerin absorbed in diatomaceous earth). Fulminic acid EQ1 is obtained by acidification of a metal fulminate, but this is a dangerous process. It is safely and easily prepared by FVP of 4-oximinoisoxazol-5(4*H*)-ones.<sup>[17]</sup> Fulminic acid undergoes partial isomerization to isocyanic acid, EQ2 HNCO, at high temperature.<sup>[18]</sup> Gas phase photolysis results in dissociation reactions with only a low yield of HNCO formed.<sup>[18]</sup>

Cyanic acid, EQ9 HOCN, rearranges very easily to isocyanic acid, EQ2 HNCO, for example due to wall collisions when it is generated in FVP experiments, but it has been characterized by matrix IR and gas phase microwave spectroscopies.<sup>[19,20]</sup> Isofulminic acid, EQ5 HONC, was elusive until a few years ago, when it was characterized by pulsed microwave spectroscopy.<sup>[21]</sup>

A fifth isomer, formylnitrene EQ3 H-C(O)-N is a potential link between the four acids and the simplest member of the acylnitrenes, which are potential intermediate in the preparatively

and industrially important Curtius rearrangement<sup>[22]</sup> of acyl azides to isocyanates (Eq.3.1).<sup>[23]</sup> Photolysis of formyl azide, HCON<sub>3</sub>, yields EQ2 HNCO quantitatively (Eq.3.1, R = H).<sup>[24]</sup>



The thermal Curtius rearrangement is usually concerted, but it may be either concerted or stepwise in photolyses.<sup>[25]</sup> In addition to phenyl isocyanate (PhNCO) a very small amount of phenyl cyanate (PhOCN) were formed in the matrix photolysis of benzoyl azide.<sup>[26]</sup>

Autrey and Schuster suggested a closed-shell singlet ground state for aroylnitrene on chemical grounds and because they were not observable by ESR spectroscopy.<sup>[27]</sup> The singlet ground state arises due to partial bond formation between the acyl oxygen and the nitrene nitrogen, with the result that the singlets can be described as resonance hybrids of distorted closed-shell singlet nitrenes CSS(a) and oxazirines CSS(b) (Eq.3.1). This is the case for cyanofornitrene, NC-CO-N<sup>[28]</sup>, acetylnitrene<sup>[29]</sup> and the aroylnitrenes.<sup>[27,30-33]</sup> The corresponding triplets T and the higher-lying open-shell singlets OSS retain true nitrene structures. When the S-T gap is small enough, an equilibrium between a closed-shell singlet acylnitrene/oxazirine and a triplet acylnitrene may obtain, i.e. such nitrenes may become bistable.<sup>[23,34]</sup>

Calculations on the EQ1 HCNO isomers were performed at the STO-3G and 4-31G levels by Poppinger, Radom and Pople.<sup>[35]</sup> Neither formylnitrene nor the oxaziridine were found to be stable species at these levels.

Fueno et al.<sup>[36]</sup> described the oxazirine structure EQ3 (CSS(b)) of HC(O)N with a long N-O bond and an NCO angle of 94.1°. This was the ground state (<sup>1</sup>A') with the triplet (<sup>3</sup>A'') and the OSS (<sup>1</sup>A'') lying ~2 Kcal/mol and 20 Kcal/mol higher, respectively, both with a normal nitrene-type NCO angle of ~121° at the CASSCF(4,4) level. A very small barrier of 2.9 Kcal/mol was found for the isomerization of the oxazirine to HNCO and a 16.5 Kcal/mol higher barrier for the isomerization to HOCN. The barriers for isomerization to HCNO and HONC were 81 and 71 Kcal/mol, respectively, but the latter value was higher than the energy required for dissociation of HONC into HO + NC.

Calculations by Mebel et al.<sup>[37]</sup> at the B3LYP/6-311G(d,p) did not locate a transition state (TS) for rearrangement to HNCO, but a TS for rearrangement to HOCN was located just 0.7 Kcal/mol above the oxazirine CSS(b).

Shapley and Backskay located the TS for the rearrangement of the oxazirine EQ3 CSS(b) to EQ2 HNCO 30 Kcal/mol above the oxazirine at the G2 level, but a direct path from EQ3 H(CO)N to EQ9 HOCN was not located. The singlet triplet splitting was calculated as -2.5 Kcal/mol, i.e. the CSS is the ground state.<sup>[38]</sup>

Pritchina et al.<sup>[31,32]</sup> found the nitrene singlet-triplet splitting (EQ3) to be positive at B3LYP and CCSD levels but -0.13 Kcal/mol at the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ level, and this was further lowered to -0.72 Kcal/mol with complete basis set extrapolation.

DFT calculations at the PBE/TZ2P level gave an activation energy of 20.9 Kcal/mol for rearrangement of the singlet formylnitrene EQ3 to EQ2 HNCO, and a singlet-triplet splitting of -1 Kcal/mol was derived. The barrier was found to be significantly lower for MeC(O)N and PhC(O)N.<sup>[39]</sup>

Schaefer and al. calculated the heats of formation of the four acids and the NCO radical at the CCSD(T) level of theory.<sup>[40]</sup>

Recently, global reaction route mapping consisting of anharmonic downward distortion following and multi-component artificial force induced reaction methods was employed with the  $\omega$ B97-XD functional combined with the 6-311G(d,p) basis set to map the relationships between the HCNO isomers.<sup>[41]</sup> The nitrene HC(O)N EQ3 and oxazirine EQ6 HCON were considered as separate entities with a large energy separation (52 Kcal/mol), the oxazirine being of the lowest energy, and a high barrier between them (114 Kcal/mol from the nitrene), but the nitrene calculated this way was not the CSS.

In order to help the experimenters to identify the HCNO compounds present in their experiments, we started by determining the various reaction paths linking all the species potentially present in the experiments as recalled in the brief state of the art reported above. This study was carried out at the B3LYP/6-31+G\*\* and CASPT2(10,10)/6-311G\*\* levels (Figure 3.1 and Figure 3.2 respectively), taking into account the multi-determinant character of certain species present in the reaction paths. Our calculations show first of all that the number of reaction intermediates, canonical intersections and stable molecules in their singlet and triplet electronic states (for which it will be necessary to study the spectral signatures one by one) is very large and requires that we be able to provide very precise theoretical results (due to the presence of common chemical functions present for several species potentially present). The precise theoretical study of these spectral signatures requires that one be able to solve, *a minima*, the vibrational Schrödinger equation under the assumption of mechanical anharmonicity on each of the situations. This implies, for each system, dealing with two real challenges to these resolutions: the construction of the Potential Energy Surface (PES) and the resolution of the Vibrational Schrödinger Equation (RSVE)<sup>[2,9]</sup> in order to obtain the energy levels and consequently the fundamental harmonic and anharmonic wave numbers describing the vibrational spectra (frequencies).

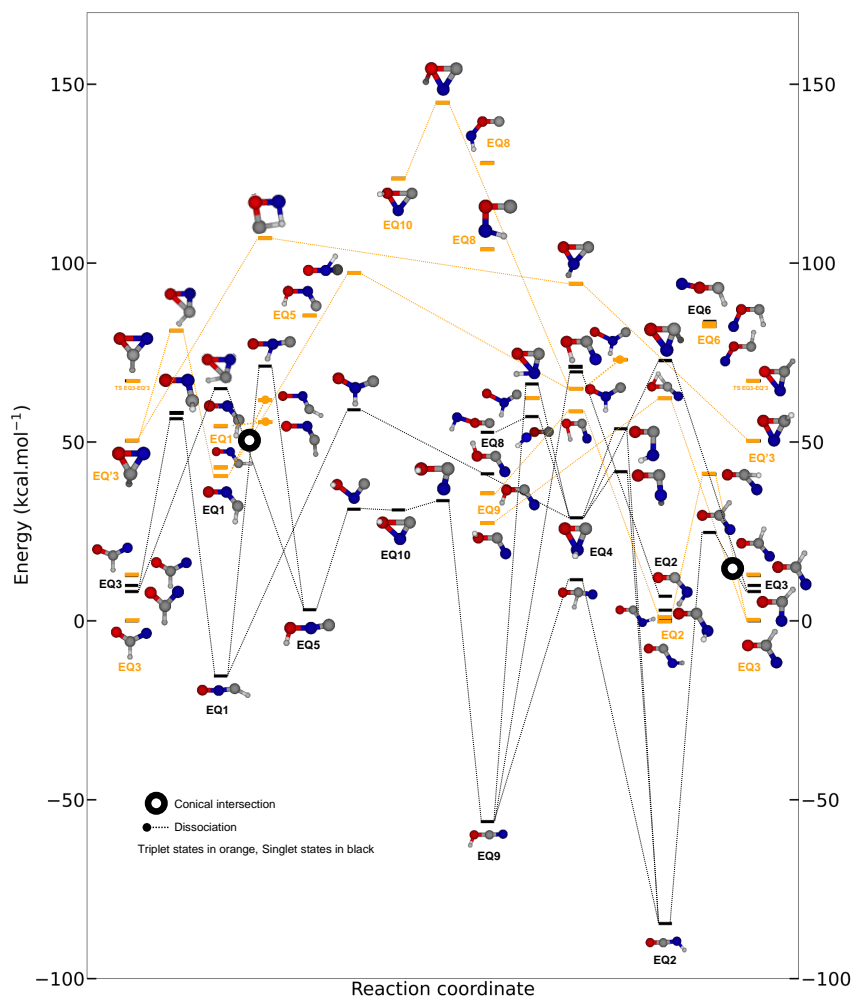


Figure 3.1: Reaction paths linking all the species potentially present in the experiments of the four acids, fulminic EQ1 (HCNO), isocyanic EQ2 (HNCO), cyanic EQ9 (HOCN), and isofulminic EQ5 (HONC) calculated at the DFT B3LYP/6-31+G\*\* level. All energies are in Kcal/mol.

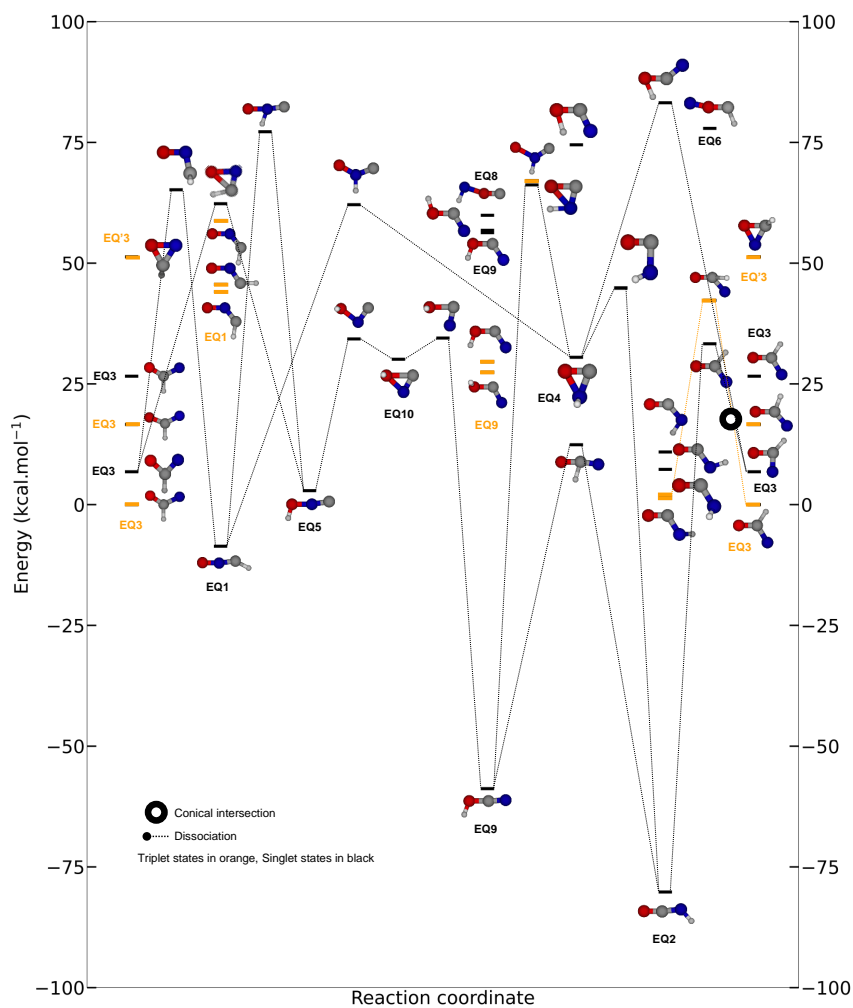


Figure 3.2: Reaction paths linking all the species potentially present in the experiments of the four acids, fulminic EQ1 (HCNO), isocyanic EQ2 (HNCO), cyanic EQ9 (HOCN), and isofulminic EQ5 (HONC) calculated at the CASPT2(10,10)/6-311G\*\* level. All energies are in Kcal/mol.

The work that we must undertake for such a problem consists first of all in questioning the precision that we seek to obtain on the final calculation (and thus on the PES) especially as the systems that we are studying (as a reminder - chemical systems made up of only 4 atoms i.e. H, C, N and O) will all generate, one by one, a size of PES such that for each system several hundreds of thousands of terms could be necessary to determine. The search for an optimal analytical expression of the PES is an ongoing discussion within the theoretical chemistry community. Among the existing solutions, the determination of the analytical form of the PES by means of a Taylor series extension using curvilinear displacement coordinates remains one of the most legitimate (2.43). In practice these series are truncated to fourth order. The quadratic, cubic, quartic force constants from these functions are obtained by fitting electronic energy data for various nuclear configurations close to their optimised geometry.

Another major problem related to the determination of the PES, and important to mention here, concerns the construction of functions that best describe the whole working space (of dimension  $3N-6$  with  $N$  representing the number of atoms present in the system studied). Unfortunately, in practice, and whatever the analytical function that is supposed to fit the PES, certain portions of the space (in general as far as possible from the equilibrium state under study) present areas that are poorly or not at all described electronically. The study of these 'holes' (loss of convexity, saddle point ...) is a problem that very few researchers have yet addressed. The absence of holes would allow us to ensure that we obtain a PES adapted to each chemical system without creating numerical limitations as is often the case in studies reported in the literature (in an insidious way and often ignored by most researchers in the field). In the absence of holes, the quality and accuracy of our results would be guaranteed. In practice, we are never sure that the truncated series at fourth order do not generate holes. One of the solutions currently recommended to avoid these holes is, failing to fill them efficiently, to push them back 'a little further'. This consists in using a truncation of the Taylor series beyond the fourth order. Another advantage of such a development is that it allows the force constants beyond fourth order to be obtained numerically - terms which are precisely necessary to implement a perturbation approach beyond the conventional VPT2 type approach and whose convergence can be very much questioned in some of the cases studied.

The second barrier to be removed is therefore the RSVE. As mentioned in the previous chapters, the perturbative approach is probably the simplest to implement and has long been the most widely used. The zero-order Hamiltonian (eq. 4.1) is in general the vibrational Hamiltonian in the harmonic approximation. Indeed, in this case, the Schrödinger equation admits an exact solution. All coupling terms between modes and anharmonicity are considered as perturbations (see chapter 4). In the case where the second order perturbation treatment is no longer restricted, the energy of the calculated vibrational states is then expressed as polynomial functions of the vibrational quantum numbers  $\bar{\nu}$ . This form is the same as the one used by experimenters to fit spectra, which therefore allows a simple comparison between experiment and theory.

This approach is, in principle, the simplest available. It is also ideal for the study of large

systems for which a variational approach is not feasible. However, it is necessary to be aware that such an approach:

- is less accurate for obtaining the wave function (than it is for obtaining the frequencies). Indeed, if we obtain the energy at order  $n$  from the perturbation theory, this corresponds, at the same time, to obtaining the wave function at order  $n-1$ ,
- does not (or hardly) allow to deal with strongly coupled systems (the partition given by the equation 4.2 to 4.8 is not adapted anymore),
- It is difficult to treat systems with a high degree of anharmonicity,
- and finally, becomes deficient when approaching near-degenerate problems.

In order to get around most of the problems mentioned above, the natural solution is to develop the perturbation approach at higher orders of the perturbation theory. To our knowledge, only two approaches have begun these developments. Firstly, the work of Stanton et al<sup>[42]</sup> in 2018, from which we have mainly drawn inspiration in this work (since their approach uses the standard Rayleigh-Schrödinger perturbation theory (RSPT) in the context of the Watson Hamiltonian in rectilinear normal coordinates). The equations for the perturbation corrections reported hereafter (chapter 4) and which are derived from our developments have been extended to order 6 (Stanton having stopped his development at order 4). The main purpose of these developments is to provide computer developers with all potentially programmable terms.

The other method that starts these difficulties is the one recently updated by S. Krasnoshcheko, used since the 1950s by Nielsen and essentially developed by Sibert et al in the 1990s. The basic idea of the Canonical Van Vleck Perturbation Theory approach is to transform the Hamiltonian of an initial complex representation<sup>[43]</sup> into a final representation in which the physical properties of interest are not modified. These properties can then be obtained simply by diagonalization in a basis of size restricted to the initial size. Formally, this amounts to finding change-of-base matrices (using the matrix  $T = \exp(i\lambda S)$ ) that allow the physical information to be reconcentrated in blocks that are much simpler to diagonalise. This approach has allowed, to this day, to study the vibrational and rovibrational spectra of many tetraatomic and pentaatomic systems. Its development in the form of an operator gives it a very high speed of calculation and requires very little memory space. The method has been successfully reviewed by Krasnoshcheko et al. on systems of up to eight atoms (diborane molecule) using a PES of order 6 and for which the results are in very good agreement (over 98% of the problem) with the most accurate variational results that can be achieved (at the same PES) using the AVCI (Adaptive Variational CI) approach<sup>[44–46]</sup>, method developed in the framework of our collaboration with INRIA researchers.

The study of the spectral signatures of the formaldehyde molecule is a representative illustration of the current performance of these perturbative VPTn approaches with respect to the most accurate variational calculations available. The potential energy surface used in the calculations reported in Table 1 is obviously common to each calculation and has been constructed on a grid

of 5000 points of electronic energies calculated at the CCSD(T) level in ANO1 basis. Similar calculations will have to be carried out on fulminic (HCNO), isocyanic (HNCO), cyanic (HOCN) and isofulminic (HONC) acids from a PES determined to order 8 (in collaboration with S. Krasnoshcheko and al) even if the example of the formaldehyde molecule leads us to believe that the correction of order 6 (VPT6) is certainly very weak with regard to the computer developments that its implementation will engender.

Table 1: Fundamental and overtones levels of formaldehyde molecule obtained at the CCSD(T)/ANO1 level of theory.

Level	Harmonic	VPT2	VPT4	Variational
$\nu_1$	3835.96	3659.07	3660.65	3660.33
$\nu_2$	1658.56	1605.56	1605.90	1605.36
$\nu_3$	3947.71	3756.68	3758.50	3758.33
$2\nu_1$	7671.92	7232.57	7208.67	7207.98
$2\nu_2$	3317.13	3176.35	3177.21	3174.46
$2\nu_3$	7895.42	7415.41	7450.75	7449.89
$\nu_1 + \nu_2$	5494.53	5248.11	5251.06	5249.12
$\nu_1 + \nu_3$	7783.67	7249.60	7256.51	7255.51
$\nu_2 + \nu_3$	5606.28	5342.25	5244.97	5344.09

The aim of this last part of this chapter is the comparison of the variational and perturbational approaches for the resolution of the vibrational Hamiltonian on an example equivalent to the four acids, fulminic EQ1 (HCNO), isocyanic EQ2 (HNCO), cyanic EQ9 (HOCN), and isofulminic EQ5 (HONC) on the  $\text{H}_2\text{CO}$  molecule, see below Figure 3.3. More precisely, the goal is to provide an analysis in order to compare the variational (A-VCI) and perturbational (VPT2, CVPT2 and CVPT4) approaches to compute a vibrational spectrum (see Figure 3.3 and Table 2). In all the following cases, the same sextic force field (PES), Coriolis coefficients and dipole moment coefficients are used in all methods. Moreover, codes give the same results for integral evaluation, Hamiltonian matrix coefficients and "raw" AVCI(4) calculation. Thus, the only differences that we can observe come from the way of solving the vibrational equation, with specific features for each method:

- The A-VCI method takes into consideration relevant highly excited wavefunctions to build the Hamiltonian matrix, without removing couplings. Eigen-pairs are then directly computed in this (often large) basis without any post-treatment.
- The CVPT method starts with the VCI(4) basis of wavefunctions, and uses unitary matrices to transform the Hamiltonian matrix into a quasi-diagonal form. This eliminates couplings except in the case of explicitly processed Fermi and Darlin-Dennison



resonances. Then, perturbative formulae are applied on the eigenvalues of this quasi-diagonal Hamiltonian.

- The VPT2 approach uses quadratic, all relevant cubic and quartic force constants to create a quartic force field.

It is important, at this level, to give final details on the force field used in this work. During the last decade, several anharmonic force fields of molecular systems consisting of three to twelve atoms were calculated with methods that were recognized as providing good vibrational predictions with wavenumbers being less than  $10\text{cm}^{-1}$  in agreement with the experimental data. Among those methods, MRCI (multireference CI) and CCSD(T)<sup>[47]</sup> were shown to provide very good spectroscopic predictions when the basis set used are of triple zeta quality or higher. When the size of the system becomes large, the anharmonic force field can be calculated by a Møller-Plesset perturbative method or by the popular DFT (Density Functional Theory) method. These last two methods have shown their ability to correctly account, at lower cost, the anharmonic constants in the study of organic systems.<sup>[48–50]</sup> These observations make it reasonable to expect that a new combined way of determining the hybrid force fields<sup>[51–54]</sup>, where the structural parameters and the harmonic constants are calculated by using CCSD(T) method, whereas the cubic, quartic, quintic and sextic force constants expressed in the basis of the normal CCSD(T) modes are determined by a MP2 or a DFT method, to be an adapted process for the treatment of large-scale molecular systems. The quadratic force constants which allow the calculation of the harmonic frequencies were determined at the CCSD(T)/cc-pVQZ level of theory. The cubic, quartic, quintic and sextic force constants were determined at the MP2/aug-cc-pVTZ level of theory.<sup>[55]</sup>

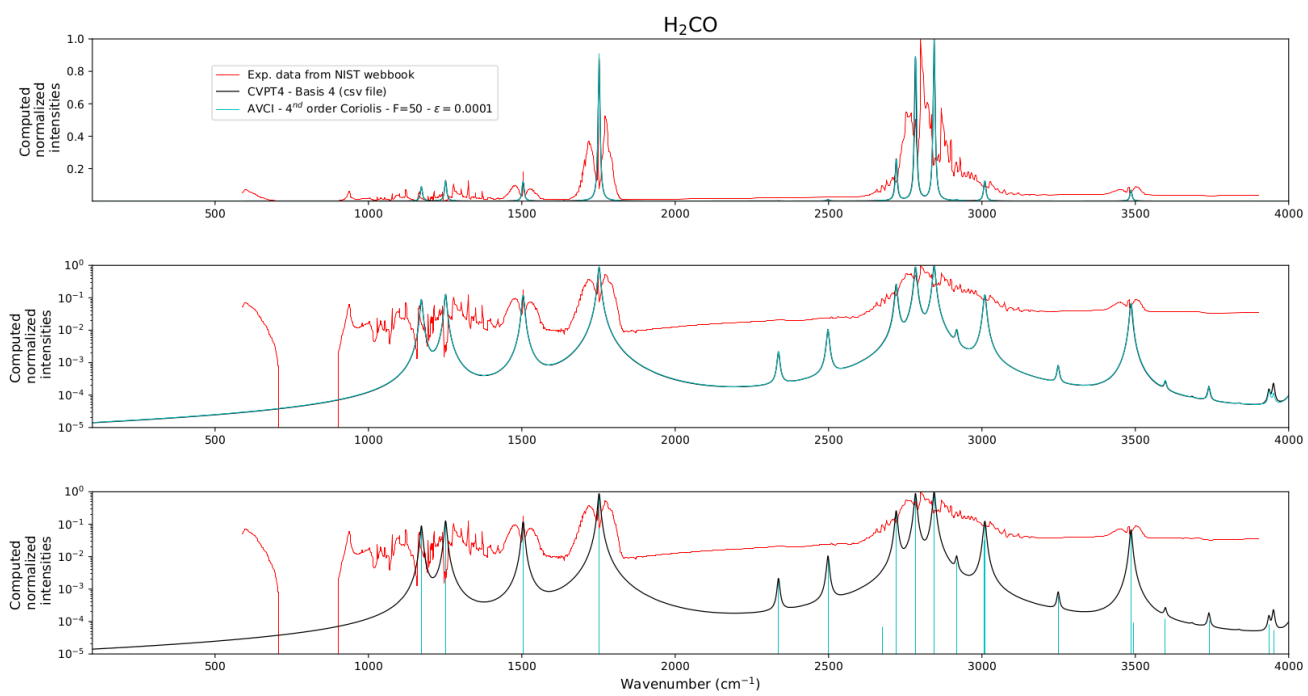


Figure 3.3:  $\text{H}_2\text{CO}$ : Comparison between experimental data, CVPT(4)-VCI(4) computation and A-VCI computation using  $\epsilon = 0.0001$ .

Table 2: H<sub>2</sub>CO: Comparison between experimental data, CVPT(4)-VCI(4) CVPT(2)-VCI(4), VPT2 computation and A-VCI computation using  $\epsilon = 0.0001$ .

N°	Exp.	CVPT(4) - VCI(4)		CVPT(2) - VCI(4)		VPT2		Harmonic		A-VCI(0.0001)	
		freq.	intens.	freq.	intens.	freq.	intens.	freq.	intens.	freq.	assign.
1	1167 <sup>[56]</sup>	1172.5293	6.9867	1173.7119	1180.2	1196.9	1172.4165	6.9855	$\nu_4$		
2	1249 <sup>[56]</sup>	1251.4909	10.0249	1252.4369	1247.1	1266.9	1251.4690	10.0120	$\nu_6$		
3	1500 <sup>[56]</sup>	1504.0975	9.4304	1505.1533	1503.2	1540.1	1503.9924	9.3840	$\nu_3$		
4	1746 <sup>[56]</sup>	1751.9143	69.5920	1751.7444	1752.9	1752.9	1751.9406	69.6546	$\nu_2$		
5	2328 <sup>[56]</sup>	2336.7252	0.1523	2336.7874			2336.7850	0.1513	$2\nu_4$		
6	2493 <sup>[56]</sup>	2497.9573	0.8022	2497.6580			2498.4087	0.8198	$2\nu_6$		
7	2656 <sup>[56]</sup>	2675.7034	0.0057	2679.1597			2675.6968	0.0058	$\nu_3 + \nu_4$		
8	2719 <sup>[56]</sup>	2720.4098	20.1978	2711.8626			2721.3685	19.8696	$\nu_3 + \nu_6, \nu_5$		
9	2782 <sup>[56]</sup>	2783.2001	69.9175	2788.8977	2814.0	2973.4	2784.0412	69.9089	$\nu_1$		
10	2843 <sup>[56]</sup>	2844.1602	78.7542	2851.8334			2844.4254	79.4082	$\nu_5, \nu_3 + \nu_6$		
11	2905 <sup>[56]</sup>	2917.4390	0.5157	2918.5929			2917.5884	0.5170	$\nu_2 + \nu_4$		
12	3000 <sup>[56]</sup>	3006.6927	2.5615	3010.7282			3006.7663	2.5726	$2\nu_3$		
13	3000 <sup>[56]</sup>	3009.9480	8.1041	3015.1618			3009.6634	7.8810	$\nu_2 + \nu_6$		
14	3238 <sup>[56]</sup>	3248.5002	0.0457	3249.9555			3248.7365	0.0478	$\nu_2 + \nu_3$		
15	3472 <sup>[56]</sup>	3485.7404	5.2530	3485.7359			3486.1384	5.2863	$2\nu_2$		
16	—	3493.6447	0.0006	3488.3030			3493.5113	0.0005	$3\nu_4$		
17	—	3597.9934	0.0093	3598.3548			3597.7912	0.0099	$2\nu_4 + \nu_6$		
18	—	3685.2083	0.0006	3687.1128			3685.9794	0.0007	$\nu_4 + 2\nu_6$		
19	—	3739.7431	0.0093	3735.8767			3740.9789	0.0088	$3\nu_6$		
20	—	3837.5392	0.0003	3840.0239			3837.1751	0.0003	$\nu_3 + 2\nu_4$		
21	—	3935.5562	0.0073	3918.3777			3936.6862	0.0069	$\nu_3 + 2\nu_6, \nu_5 + \nu_6$		
22	—	3950.3079	0.0138	3967.5309			3950.7260	0.0142	$\nu_1 + \nu_4, 3\nu_4$		

## References

- [1] J. Liebig and J. L. Gay-Lussac, "Analyse du fulminate d'argent," *Ann. chim. phys.*, vol. 25, pp. 285–311, 1824.
- [2] F. Wöhler, "Analytische versuche über die cyansäure," *Annalen der Physik*, vol. 77, pp. 117–124, 1824.
- [3] J. Liebig, "Über wöhler's cyansäure," *Arch. Ges. Nat.*, vol. 6, pp. 145–153, 1825.
- [4] J. Liebig, "Ueber cyan-und knallsäure," *Schweiggers Jahrbuch der Chemie und Physik*, vol. 18, pp. 376–381, 1826.
- [5] M. Faraday and W. Schweigger-Seidel, "For summaries of liebig's and wöhler's papers on fulminic and cyanic acids and their salts, see footnotes by m. faraday and w. schweigger-seidel in schweiggers jahrbuch der chemie und physik.," *Schweiggers Jahrbuch der Chemie und Physik*, no. 17, pp. 451–453, 1826.
- [6] J. Berzelius and J. Årsberättelse, "Defined isomeric entities as follows: "kroppar som hafva lika sammansätning och olika egenskaper foresla termen isomeriska af grekiska ordet  $\iota\sigma\mu\epsilon\rho\eta\sigma$ , som betydär sammansat af lika delar", that is, bodies that have the same composition and different properties, for which is proposed the term isomeric from the greek word  $\iota\sigma\mu\epsilon\rho\eta\sigma$ , which means composed of like parts.," *framstegen i Physik och Chemie*, pp. 45–48, 1831.
- [7] J. R. Partington, *A History of Chemistry*, vol. 4. 1964.
- [8] S. Esteban, "Liebig–wöhler controversy and the concept of isomerism," *J. Chem. Educ.*, vol. 85, p. 1201, 2008.
- [9] R. Winderlich, "Jons jakob berzelius.," *J. Chem. Educ.*, vol. 25, p. 500, 1948.
- [10] W. Beck, "The first chemical achievements and publications by justus von liebig (1803–1873) on metal fulminates and some further developments in metal fulminates and related areas of chemistry," *Europ. J. Inorg. Chem.*, vol. 2003, pp. 4275–4288, 2003.
- [11] W. Beck, G. Fischer, and P. Swoboda, "Some comments on fulminic acid (knallsäure) and a praise to heinrich wieland and his work on organic derivatives of nitrogen," *Zeitschrift für anorganische und allgemeine Chemie*, vol. 643, pp. 353–356, 2017.
- [12] J. Kunckel, *Johann Kunckel von Löwensterns... Collegium Physicochymicum experimentale, oder Laboratorium chymicum, in welchem... gründlich von den wahren Principiis in der Natur und denen gewürckten Dingen so wohl über als in der Erden, alls Vegetabilien, Animalien,... Metallen, wie auch deren wahrhafften Generation... und Scheidung, nebst der Transmutation und Verbesserung der Metallen gehandelt wird,... mit einem... Register und Vorrede herausgegeben von JC Engelleder, etc.* 1716.

- [13] E. Howard, "Xi. on a new fulminating mercury," *Philos. Trans. Roy. Soc. London*, no. 90, pp. 204–238, 1800.
- [14] L. Brugnatelli *Phil. Mag.*, no. 16, pp. 185–186 and 258, 1803.
- [15] L. Brugnatelli *Nicholson's J.*, no. VII, p. 285, 1804.
- [16] F. Kurzer, "Fulminic acid in the history of organic chemistry," *J. chem. educ.*, vol. 77, p. 851, 2000.
- [17] C. Wentrup, B. Gerecht, and H. Briehl, "A new synthesis of fulminic acid," *Angew. Chem. Int. Ed. Engl.*, vol. 18, pp. 467–468, 1979.
- [18] W. Feng and J. F. Hershberger, "Quantification of the 248 nm photolysis products of hcn (fulminic acid)," *J. Phys. Chem. A*, vol. 118, pp. 829–837, 2014.
- [19] V. E. Bondybey, J. H. English, C. W. Mathews, and R. J. Contolini, "Infrared spectra and isomerization of chno species in rare gas matrices," *J. Mol. Spectro.*, vol. 92, pp. 431–442, 1982.
- [20] S. Brünken, C. A. Gottlieb, M. C. McCarthy, and P. Thaddeus, "Laboratory detection of hcn and tentative identification in sgr b2," *Astrophys. J.*, vol. 697, p. 880, 2009.
- [21] M. Mladenović, M. Lewerenz, M. C. McCarthy, and P. Thaddeus, "Isofulminic acid, hnc: Ab initio theory and microwave spectroscopy," *J. Chem. Phys.*, vol. 131, p. 174308, 2009.
- [22] A. K. Ghosh, A. Sarkar, and M. Brindisi, "The curtius rearrangement: mechanistic insight and recent applications in natural product syntheses," *Org. Biomol. chem.*, vol. 16, pp. 2006–2027, 2018.
- [23] C. Wentrup, "Carbenes and nitrenes: recent developments in fundamental chemistry," *Angew. Chem. Int. Ed.*, vol. 57, pp. 11508–11521, 2018.
- [24] X. Zeng, E. Bernhardt, H. Beckers, K. Banert, M. Hagedorn, and H. Liu, "Formyl azide: Properties and solid-state structure," *Angew. Chem. Int. Ed.*, vol. 52, pp. 3503–3506, 2013.
- [25] C. Wentrup, "Flash vacuum pyrolysis of azides, triazoles, and tetrazoles," *Chem. rev.*, vol. 117, pp. 4562–4623, 2017.
- [26] C. Wentrup and H. Bornemann, "The curtius rearrangement of acyl azides revisited—formation of cyanate (r-o-cn)," 2005.
- [27] M. E. Sigman, T. Autrey, and G. B. Schuster, "Aroylnitrenes with singlet ground states: Photochemistry of acetyl-substituted aroyl and aryloxycarbonyl azides," *J. Am. Chem. Soc.*, vol. 110, pp. 4297–4305, 1988.

- [28] M. Barbieux-Flammang, S. V. and R. Flammang, M. W. Wong, H. Bibas, C. H. L. Kennard, and C. Wentrup, "Monomer, dimers and trimers of cyanogen n-oxide, n [triple bond, length as m-dash] c-c [triple bond, length as m-dash] n $\rightarrow$  o. an x-ray, fvt-ms/ir and theoretical investigation," *J. Chem. Soc., Perk. Trans. 2*, pp. 473–478, 2000.
- [29] J. Liu, S. Mandel, C. M. Hadad, and M. S. Platz, "A comparison of acetyl- and methoxycarbonylnitrenes by computational methods and a laser flash photolysis study of benzoylnitrene," *J. Org. chem.*, vol. 69, pp. 8583–8593, 2004.
- [30] N. P. Gritsan and E. A. Pritchina, "Are aroylnitrenes species with a singlet ground state?," *Mendeleev Comm.*, vol. 11, pp. 94–96, 2001.
- [31] E. A. Pritchina, N. P. Gritsan, A. Maltsev, T. Bally, T. Autrey, Y. Liu, Y. Wang, and J. P. Toscano, "Matrix isolation, time-resolved ir, and computational study of the photochemistry of benzoyl azide," *Phys. Chem. Chem. Phys.*, vol. 5, pp. 1010–1018, 2003.
- [32] E. A. Pritchina, N. P. Gritsan, and T. Bally, "Ground state multiplicity of acylnitrenes: computational and experimental studies," *Rus. chem. bul.*, vol. 54, pp. 525–532, 2005.
- [33] J. Kubicki, Y. Zhang, S. Vyas, G. Burdzinski, H. L. Luk, J. Wang, J. Xue, H. L. Peng, E. A. Pritchina, M. Sliwa, *et al.*, "Photochemistry of 2-naphthoyl azide. an ultrafast time-resolved uv-vis and ir spectroscopic and computational study," *J. Amer. Chem. Soc.*, vol. 133, pp. 9751–9761, 2011.
- [34] R. Feng, Y. Lu, G. Deng, J. Xu, Z. Wu, H. Li, Q. Liu, N. Kadowaki, M. Abe, and X. Zeng, "Magnetically bistable nitrenes: Matrix isolation of furylnitrenes in both singlet and triplet states and triplet 3-furylnitrene," *J. Amer. Chem. Soc.*, vol. 140, pp. 10–13, 2018.
- [35] D. Poppinger, L. Radom, and J. A. Pople, "A theoretical study of the chno isomers," *J. Amer. Chem. Soc.*, vol. 99, pp. 7806–7816, 1977.
- [36] K. Yokoyama, S. Y. Takane, and T. Fueno, "Computational studies of the isomerization pathways of isocyanic acid hncO," *Bul. Chem. Soc. Japan*, vol. 64, pp. 2230–2235, 1991.
- [37] A. M. Mebel, A. Luna, M. C. Lin, and K. Morokuma, "A density functional study of the global potential energy surfaces of the [h, c, n, o] system in singlet and triplet states," *J. Chem. Phys.*, vol. 105, pp. 6439–6454, 1996.
- [38] W. A. Shapley and G. B. Bacskay, "A gaussian-2 quantum chemical study of chno: isomerization and molecular dissociation reactions," *J. Phys. Chem. A*, vol. 103, pp. 6624–6631, 1999.
- [39] M. V. Zabalov and R. P. Tiger, "Mechanism and structural aspects of thermal curtius rearrangement. quantum chemical study," *Rus. chem. bul.*, vol. 54, pp. 2270–2280, 2005.

- [40] M. S. Schuurman, S. R. Muir, W. D. Allen, and H. F. S. III, "Toward subchemical accuracy in computational thermochemistry: Focal point analysis of the heat of formation of nco and [h, n, c, o] isomers," *J. Chem. Phys.*, vol. 120, pp. 11586–11599, 2004.
- [41] Y. Hayashi, Y. Ishiyama, T. Takata, and S. Kawauchi, "Exploration of unimolecular and bimolecular pathways for nitrile n-oxide isomerization to isocyanate through global reaction route mapping techniques," *Eur. J. Org. Chem.*, vol. 2019, pp. 6646–6654, 2019.
- [42] J. Z. Gong, D. A. Matthews, P. B. Changala, and J. F. Stanton, "Fourth-order vibrational perturbation theory with the watson hamiltonian: Report of working equations and preliminary results," *J. Chem. Phys.*, vol. 149, p. 114102, 2018.
- [43] S. V. Krasnoshchekov, E. O. Dobrolyubov, M. A. Syzgantseva, and R. V. Palvelev, "Rigorous vibrational fermi resonance criterion revealed: two different approaches yield the same result," *Mol. Phys.*, vol. 118, p. e1743887, 2020.
- [44] R. Garnier, M. Odunlami, V. L. Bris, D. Bégué, I. Baraille, and O. Coulaud, "Adaptive vibrational configuration interaction (a-vci): A posteriori error estimation to efficiently compute anharmonic ir spectra," *J. Chem. Phys.*, vol. 144, p. 204123, 2016.
- [45] V. L. Bris, M. Odunlami, D. Bégué, I. Baraille, and O. Coulaud, "Using computed infrared intensities for the reduction of vibrational configuration interaction bases," *Phys. Chem. Chem. Phys.*, vol. 22, pp. 7021–7030, 2020.
- [46] M. Odunlami, V. L. Bris, D. Bégué, I. Baraille, and O. Coulaud, "A-vci: A flexible method to efficiently compute vibrational spectra," *J. Chem. Phys.*, vol. 146, p. 214108, 2017.
- [47] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, "A fifth-order perturbation comparison of electron correlation theories," *Chem. Phys. Lett.*, vol. 157, pp. 479–483, 1989.
- [48] R. Janoschek, "Quantum chemical b3lyp/cc-pvqz computation of ground-state structures and properties of small molecules with atoms of  $z \leq 18$  (hydrogen to argon)(iupac technical report)," *Pure Appl. Chem.*, vol. 73, pp. 1521–1553, 2001.
- [49] N. J. Wright and R. B. Gerber, "Direct calculation of anharmonic vibrational states of polyatomic molecules using potential energy surfaces calculated from density functional theory," *J. Chem. Phys.*, vol. 112, pp. 2598–2604, 2000.
- [50] S. Dressler and W. Thiel, "Anharmonic force fields from density functional theory," *Chem. Phys. Lett.*, vol. 273, pp. 71–78, 1997.
- [51] P. Carbonniere, D. Begue, and C. Pouchan, "Anharmonic force field and vibrational spectra of perfluoromethanimine cf<sub>2</sub>nf," *J. Phys. Chem. A*, vol. 106, pp. 9290–9293, 2002.

- [52] A. Miani, V. Hänninen, M. Horn, and L. Halonen, “Anharmonic force field for methanol,” *Mol. Phys.*, vol. 98, pp. 1737–1748, 2000.
- [53] M. Shen, Y. Xie, Y. Yamaguchi, and H. F. S. III, “The silyl anion ( $\text{SiH}_3^-$ ): Cubic/quartic force field and anharmonic contributions to the fundamental vibrational frequencies,” *J. Chem. Phys.*, vol. 94, pp. 8112–8121, 1991.
- [54] W. D. Allen and A. G. Császár, “On the ab initio determination of higher-order force constants at nonstationary reference geometries,” *J. Chem. Phys.*, vol. 98, pp. 2983–3015, 1993.
- [55] S. V. Krasnoshchekov, V. B. Laptev, and I. K. Gainullin, “Infrared vibrational spectra and absolute intensities of fundamental bands of bis (trifluoromethyl) ketene: Ab initio interpretation using the second order operator van vleck perturbation theory,” *J. Quant. Spectrosc. Radiat. Transf.*, vol. 276, p. 107952, 2021.
- [56] D. E. Reisner, R. W. Field, J. L. Kinsey, and H. L. Dai, “Stimulated emission spectroscopy: A complete set of vibrational constants for  $\tilde{x}^1 a_1$  formaldehyde,” *J. Chem. Phys.*, vol. 80, pp. 5968–5978, 1984.



## 4 Development of the vibrational perturbation theory at order n (VPTn)

### 4.1 Development at the second, fourth and sixth order (VPT2, VPT4, VPT6)

The vibrational perturbation theory (VPT) method and the variational method are the two theoretical methods for establishing an infrared spectrum. The major advantage and disadvantage of these methods is that the variational method is a very accurate but expensive and slow method while the vibrational perturbation theory method is fast but less accurate. However, it is important to note that the VPT method is only developed to order 2 which means that there is a lack of information to describe the systems. Indeed, for small or simple systems, the second-order vibrational perturbation theory (VPT2) method is sufficient but when we have more complex systems and take into account physico-chemical effects, VPT2 is limited. Therefore, the development of the method to higher orders (4 and 6) would allow the addition of information and thus increase the accuracy of the method for an acceptable time and calculation cost.

#### 4.1.1 Hamiltonian operator and wave function: starting point

We took the harmonic solutions of systems as solutions to the zero order. For the harmonic solutions, the eigenfunctions and eigenvalues are well known and the Schrodinger's equation is the following:

$$H_0\Psi_v = E_v^{(0)}\Psi_v \quad (4.1)$$

with  $E_v^{(0)}$  the energy at the zero-order of the system, H the Hamiltonian operator and  $\Psi$  the wave function of the system.

In perturbation, for system with an infinite number of non-degenerate levels, we add some terms of perturbations and the wave function, the Hamiltonian and the energy become:

$$\begin{aligned} H &= H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots \\ E_v &= E_v^{(0)} + \lambda E_v^{(1)} + \lambda^2 E_v^{(2)} + \dots \\ \Psi &= \Psi_v^{(0)} + \lambda \Psi_v^{(1)} + \lambda^2 \Psi_v^{(2)} + \dots \end{aligned}$$

Let's note that  $\lambda$  is an arbitrary parameter.

We reintroduce in the (4.1) and we make the decision to take up to sixth-order. We treat, in a first time the left part and then the right part.

The left part corresponds to:

$$\begin{aligned}
H\Psi_v &= (H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \lambda^3 H^{(3)} + \lambda^4 H^{(4)} + \lambda^5 H^{(5)} + \lambda^6 H^{(6)})(\Psi_v^{(0)} + \lambda \Psi_v^{(1)} + \lambda^2 \Psi_v^{(2)} \\
&\quad + \lambda^3 \Psi_v^{(3)} + \lambda^4 \Psi_v^{(4)} + \lambda^5 \Psi_v^{(5)} + \lambda^6 \Psi_v^{(6)}) \\
&= H^{(0)}\Psi_v^{(0)} + \lambda H^{(0)}\Psi_v^{(1)} + \lambda^2 H^{(0)}\Psi_v^{(2)} + \lambda H^{(1)}\Psi_v^{(0)} + \lambda^2 H^{(1)}\Psi_v^{(1)} + \lambda^3 H^{(1)}\Psi_v^{(2)} + \lambda^2 H^{(2)}\Psi_v^{(0)} \\
&\quad + \lambda^3 H^{(2)}\Psi_v^{(1)} + \lambda^4 H^{(2)}\Psi_v^{(2)} + \lambda^3 H^{(0)}\Psi_v^{(3)} + \lambda^4 H^{(0)}\Psi_v^{(4)} + \lambda^4 H^{(1)}\Psi_v^{(3)} + \lambda^5 H^{(1)}\Psi_v^{(4)} \\
&\quad + \lambda^5 H^{(2)}\Psi_v^{(3)} + \lambda^6 H^{(2)}\Psi_v^{(4)} + \lambda^3 H^{(3)}\Psi_v^{(0)} + \lambda^4 H^{(3)}\Psi_v^{(1)} + \lambda^5 H^{(3)}\Psi_v^{(2)} + \lambda^6 H^{(3)}\Psi_v^{(3)} \\
&\quad + \lambda^7 H^{(3)}\Psi_v^{(4)} + \lambda^4 H^{(4)}\Psi_v^{(0)} + \lambda^5 H^{(4)}\Psi_v^{(1)} + \lambda^6 H^{(4)}\Psi_v^{(2)} + \lambda^7 H^{(4)}\Psi_v^{(3)} + \lambda^8 H^{(4)}\Psi_v^{(4)} \\
&\quad + \lambda^5 H^{(0)}\Psi_v^{(5)} + \lambda^6 H^{(1)}\Psi_v^{(5)} + \lambda^7 H^{(2)}\Psi_v^{(5)} + \lambda^8 H^{(3)}\Psi_v^{(5)} + \lambda^9 H^{(4)}\Psi_v^{(5)} + \lambda^{10} H^{(5)}\Psi_v^{(5)} \\
&\quad + \lambda^{11} H^{(6)}\Psi_v^{(5)} + \lambda^6 H^{(0)}\Psi_v^{(6)} + \lambda^7 H^{(1)}\Psi_v^{(6)} + \lambda^8 H^{(2)}\Psi_v^{(6)} + \lambda^9 H^{(3)}\Psi_v^{(6)} + \lambda^{10} H^{(4)}\Psi_v^{(6)} \\
&\quad + \lambda^{11} H^{(5)}\Psi_v^{(6)} + \lambda^{12} H^{(6)}\Psi_v^{(6)} + \lambda^5 H^{(5)}\Psi_v^{(0)} + \lambda^6 H^{(5)}\Psi_v^{(1)} + \lambda^7 H^{(5)}\Psi_v^{(2)} + \lambda^8 H^{(5)}\Psi_v^{(3)} \\
&\quad + \lambda^9 H^{(5)}\Psi_v^{(4)} + \lambda^6 H^{(6)}\Psi_v^{(0)} + \lambda^7 H^{(6)}\Psi_v^{(1)} + \lambda^8 H^{(6)}\Psi_v^{(2)} + \lambda^9 H^{(6)}\Psi_v^{(3)} + \lambda^{10} H^{(6)}\Psi_v^{(4)} \\
&= H^{(0)}\Psi_v^{(0)} + \lambda H^{(0)}\Psi_v^{(1)} + \lambda^2 H^{(0)}\Psi_v^{(2)} + \lambda H^{(1)}\Psi_v^{(0)} + \lambda^2 H^{(1)}\Psi_v^{(1)} + \lambda^2 H^{(2)}\Psi_v^{(0)} \\
&\quad + \lambda^3 H^{(1)}\Psi_v^{(2)} + \lambda^3 H^{(2)}\Psi_v^{(1)} + \lambda^3 H^{(0)}\Psi_v^{(3)} + \lambda^3 H^{(3)}\Psi_v^{(0)} + \lambda^4 H^{(0)}\Psi_v^{(4)} + \lambda^4 H^{(1)}\Psi_v^{(3)} \\
&\quad + \lambda^4 H^{(3)}\Psi_v^{(1)} + \lambda^4 H^{(4)}\Psi_v^{(0)} + \lambda^4 H^{(2)}\Psi_v^{(2)} + \lambda^5 H^{(0)}\Psi_v^{(5)} + \lambda^5 H^{(1)}\Psi_v^{(4)} + \lambda^5 H^{(2)}\Psi_v^{(3)} \\
&\quad + \lambda^5 H^{(3)}\Psi_v^{(2)} + \lambda^5 H^{(4)}\Psi_v^{(1)} + \lambda^5 H^{(5)}\Psi_v^{(0)} + \lambda^6 H^{(0)}\Psi_v^{(6)} + \lambda^6 H^{(1)}\Psi_v^{(5)} + \lambda^6 H^{(2)}\Psi_v^{(4)} \\
&\quad + \lambda^6 H^{(3)}\Psi_v^{(3)} + \lambda^6 H^{(4)}\Psi_v^{(2)} + \lambda^6 H^{(5)}\Psi_v^{(1)} + \lambda^6 H^{(6)}\Psi_v^{(0)}
\end{aligned}$$

We do exactly the same with the right part:

$$\begin{aligned}
E_v\Psi_v &= (E_v^{(0)} + \lambda E_v^{(1)} + \lambda^2 E_v^{(2)} + \lambda^3 E_v^{(3)} + \lambda^4 E_v^{(4)} + \lambda^5 E_v^{(5)} + \lambda^6 E_v^{(6)})(\Psi_v^{(0)} + \lambda \Psi_v^{(1)} + \lambda^2 \Psi_v^{(2)} \\
&\quad + \lambda^3 \Psi_v^{(3)} + \lambda^4 \Psi_v^{(4)} + \lambda^5 \Psi_v^{(5)} + \lambda^6 \Psi_v^{(6)}) \\
&= E_v^{(0)}\Psi_v^{(0)} + \lambda E_v^{(0)}\Psi_v^{(1)} + \lambda^2 E_v^{(0)}\Psi_v^{(2)} + \lambda E_v^{(1)}\Psi_v^{(0)} + \lambda^2 E_v^{(1)}\Psi_v^{(1)} + \lambda^3 E_v^{(1)}\Psi_v^{(2)} + \lambda^2 E_v^{(2)}\Psi_v^{(0)} \\
&\quad + \lambda^3 E_v^{(2)}\Psi_v^{(1)} + \lambda^4 E_v^{(2)}\Psi_v^{(2)} + \lambda^3 E_v^{(0)}\Psi_v^{(3)} + \lambda^4 E_v^{(0)}\Psi_v^{(4)} + \lambda^4 E_v^{(1)}\Psi_v^{(3)} + \lambda^5 E_v^{(1)}\Psi_v^{(4)} \\
&\quad + \lambda^5 E_v^{(2)}\Psi_v^{(3)} + \lambda^6 E_v^{(2)}\Psi_v^{(4)} + \lambda^3 E_v^{(3)}\Psi_v^{(0)} + \lambda^4 E_v^{(3)}\Psi_v^{(1)} + \lambda^5 E_v^{(3)}\Psi_v^{(2)} + \lambda^6 E_v^{(3)}\Psi_v^{(3)} \\
&\quad + \lambda^7 E_v^{(3)}\Psi_v^{(4)} + \lambda^4 E_v^{(4)}\Psi_v^{(0)} + \lambda^5 E_v^{(4)}\Psi_v^{(1)} + \lambda^6 E_v^{(4)}\Psi_v^{(2)} + \lambda^7 E_v^{(4)}\Psi_v^{(3)} + \lambda^8 E_v^{(4)}\Psi_v^{(4)} \\
&\quad + \lambda^5 E_v^{(0)}\Psi_v^{(5)} + \lambda^6 E_v^{(1)}\Psi_v^{(5)} + \lambda^7 E_v^{(2)}\Psi_v^{(5)} + \lambda^8 E_v^{(3)}\Psi_v^{(5)} + \lambda^9 E_v^{(4)}\Psi_v^{(5)} + \lambda^{10} E_v^{(5)}\Psi_v^{(5)} \\
&\quad + \lambda^{11} E_v^{(6)}\Psi_v^{(5)} + \lambda^6 E_v^{(0)}\Psi_v^{(6)} + \lambda^7 E_v^{(1)}\Psi_v^{(6)} + \lambda^8 E_v^{(2)}\Psi_v^{(6)} + \lambda^9 E_v^{(3)}\Psi_v^{(6)} + \lambda^{10} E_v^{(4)}\Psi_v^{(6)} \\
&\quad + \lambda^{11} E_v^{(5)}\Psi_v^{(6)} + \lambda^{12} E_v^{(6)}\Psi_v^{(6)} + \lambda^5 E_v^{(5)}\Psi_v^{(0)} + \lambda^6 E_v^{(5)}\Psi_v^{(1)} + \lambda^7 E_v^{(5)}\Psi_v^{(2)} + \lambda^8 E_v^{(5)}\Psi_v^{(3)} \\
&\quad + \lambda^9 E_v^{(5)}\Psi_v^{(4)} + \lambda^6 E_v^{(6)}\Psi_v^{(0)} + \lambda^7 E_v^{(6)}\Psi_v^{(1)} + \lambda^8 E_v^{(6)}\Psi_v^{(2)} + \lambda^9 E_v^{(6)}\Psi_v^{(3)} + \lambda^{10} E_v^{(6)}\Psi_v^{(4)} \\
&= E_v^{(0)}\Psi_v^{(0)} + \lambda E_v^{(0)}\Psi_v^{(1)} + \lambda^2 E_v^{(0)}\Psi_v^{(2)} + \lambda E_v^{(1)}\Psi_v^{(0)} + \lambda^2 E_v^{(1)}\Psi_v^{(1)} + \lambda^2 E_v^{(2)}\Psi_v^{(0)} \\
&\quad + \lambda^3 E_v^{(1)}\Psi_v^{(2)} + \lambda^3 E_v^{(2)}\Psi_v^{(1)} + \lambda^3 E_v^{(0)}\Psi_v^{(3)} + \lambda^3 E_v^{(3)}\Psi_v^{(0)} + \lambda^4 E_v^{(0)}\Psi_v^{(4)} + \lambda^4 E_v^{(1)}\Psi_v^{(3)} \\
&\quad + \lambda^4 E_v^{(3)}\Psi_v^{(1)} + \lambda^4 E_v^{(4)}\Psi_v^{(0)} + \lambda^4 E_v^{(2)}\Psi_v^{(2)} + \lambda^5 E_v^{(0)}\Psi_v^{(5)} + \lambda^5 E_v^{(1)}\Psi_v^{(4)} + \lambda^5 E_v^{(2)}\Psi_v^{(3)} \\
&\quad + \lambda^5 E_v^{(3)}\Psi_v^{(2)} + \lambda^5 E_v^{(4)}\Psi_v^{(1)} + \lambda^5 E_v^{(5)}\Psi_v^{(0)} + \lambda^6 E_v^{(0)}\Psi_v^{(6)} + \lambda^6 E_v^{(1)}\Psi_v^{(5)} + \lambda^6 E_v^{(2)}\Psi_v^{(4)} \\
&\quad + \lambda^6 E_v^{(3)}\Psi_v^{(3)} + \lambda^6 E_v^{(4)}\Psi_v^{(2)} + \lambda^6 E_v^{(5)}\Psi_v^{(1)} + \lambda^6 E_v^{(6)}\Psi_v^{(0)}
\end{aligned}$$

In order to simplify the resolution, we split the equation for each order.

$$\lambda^0 \rightarrow H^{(0)}\Psi_v^{(0)} = E_v^{(0)}\Psi_v^{(0)} \quad (4.2)$$

$$\lambda^1 \rightarrow H^{(0)}\Psi_v^{(1)} + H^{(1)}\Psi_v^{(0)} = E_v^{(0)}\Psi_v^{(1)} + E_v^{(1)}\Psi_v^{(0)} \quad (4.3)$$

$$\lambda^2 \rightarrow H^{(0)}\Psi_v^{(2)} + H^{(1)}\Psi_v^{(1)} + H^{(2)}\Psi_v^{(0)} = E_v^{(0)}\Psi_v^{(2)} + E_v^{(1)}\Psi_v^{(1)} + E_v^{(2)}\Psi_v^{(0)} \quad (4.4)$$

$$\lambda^3 \rightarrow H^{(0)}\Psi_v^{(3)} + H^{(1)}\Psi_v^{(2)} + H^{(2)}\Psi_v^{(1)} + H^{(3)}\Psi_v^{(0)} = E_v^{(0)}\Psi_v^{(3)} + E_v^{(1)}\Psi_v^{(2)} + E_v^{(2)}\Psi_v^{(1)} + E_v^{(3)}\Psi_v^{(0)} \quad (4.5)$$

$$\lambda^4 \rightarrow H^{(0)}\Psi_v^{(4)} + H^{(1)}\Psi_v^{(3)} + H^{(2)}\Psi_v^{(2)} + H^{(3)}\Psi_v^{(1)} + H^{(4)}\Psi_v^{(0)} + H^{(2)}\Psi_v^{(2)} = E_v^{(0)}\Psi_v^{(4)} + E_v^{(1)}\Psi_v^{(3)} + E_v^{(2)}\Psi_v^{(2)} + E_v^{(4)}\Psi_v^{(0)} + E_v^{(2)}\Psi_v^{(2)} \quad (4.6)$$

$$\lambda^5 \rightarrow H^{(0)}\Psi_v^{(5)} + H^{(1)}\Psi_v^{(4)} + H^{(2)}\Psi_v^{(3)} + H^{(3)}\Psi_v^{(2)} + H^{(4)}\Psi_v^{(1)} + H^{(5)}\Psi_v^{(0)} = E_v^{(0)}\Psi_v^{(5)} + E_v^{(1)}\Psi_v^{(4)} + E_v^{(2)}\Psi_v^{(3)} + E_v^{(3)}\Psi_v^{(2)} + E_v^{(4)}\Psi_v^{(1)} + E_v^{(5)}\Psi_v^{(0)} \quad (4.7)$$

$$\lambda^6 \rightarrow H^{(0)}\Psi_v^{(6)} + H^{(1)}\Psi_v^{(5)} + H^{(2)}\Psi_v^{(4)} + H^{(3)}\Psi_v^{(3)} + H^{(4)}\Psi_v^{(2)} + H^{(5)}\Psi_v^{(1)} + H^{(6)}\Psi_v^{(0)} = E_v^{(0)}\Psi_v^{(6)} + E_v^{(1)}\Psi_v^{(5)} + E_v^{(2)}\Psi_v^{(4)} + E_v^{(3)}\Psi_v^{(3)} + E_v^{(4)}\Psi_v^{(2)} + E_v^{(5)}\Psi_v^{(1)} + E_v^{(6)}\Psi_v^{(0)} \quad (4.8)$$

For the sake of clarity, we will write  $\Psi_v^{(0)}$ ,  $\Psi_k^{(0)}$ ,  $\Psi_l^{(0)}$ ,  $\Psi_m^{(0)}$ ,  $\Psi_n^{(0)}$ ,  $\Psi_p^{(0)}$  and  $\Psi_q^{(0)}$  like  $|v\rangle$ ,  $|k\rangle$ ,  $|l\rangle$ ,  $|m\rangle$ ,  $|n\rangle$ ,  $|p\rangle$ ,  $|q\rangle$  respectively. We will also shorten  $E_v^{(0)}$  in  $v$  and  $E_k^{(0)}$  in  $k$  and so one.

#### 4.1.2 The zero-order to the energy

In equation (4.2), we project on  $\langle v|$ :

$$\begin{aligned} \langle v| H^{(0)} |v\rangle &= \langle v| E_v^{(0)} |v\rangle \\ &= E_v^{(0)} \langle v|v\rangle \end{aligned}$$

Let's remember that  $\delta_{ij}$  is the Kronecker symbol and the property of orthonormality:

$$\begin{aligned} \langle i|j\rangle &= \delta_{ij} \\ \text{if } i=j & \quad \delta_{ij} = 1 \\ \text{if } i \neq j & \quad \delta_{ij} = 0 \end{aligned}$$

So, we obtain:

$$\boxed{E_v^{(0)} = \langle v| H^{(0)} |v\rangle} \quad (4.9)$$

We just recall that we choose to take the harmonic solutions like solutions of the zeroth order.

### 4.1.3 The first-order correction to the energy and to the wave function

By solving the equation above (4.3), we determine the correction at the first-order. Before to do the development, it is very important to mention the fact that in quantum mechanic, all linear combinations of solutions is also solution. Therefore, we can write the following equality:

$$\Psi_v^{(1)} = \sum_{k \neq v} \alpha_k \Psi_k^{(0)} \quad (4.10)$$

Let's take the equation (4.3):

$$\begin{aligned} H^{(0)}\Psi_v^{(1)} + H^{(1)}\Psi_v^{(0)} &= E_v^{(0)}\Psi_v^{(1)} + E_v^{(1)}\Psi_v^{(0)} \\ (H^{(0)} - E_v^{(0)})\Psi_v^{(1)} &= (E_v^{(1)} - H^{(1)})\Psi_v^{(0)} \end{aligned} \quad (4.11)$$

Knowing the solution at the zeroth order and according to the knowledge of linear combinations, we have:

$$\begin{aligned} H^{(0)}\Psi_v^{(1)} &= H^{(0)} \sum_{k \neq v} \alpha_k \Psi_k^{(0)} \\ &= \sum_{k \neq v} \alpha_k E_k^{(0)} \Psi_k^{(0)} \end{aligned}$$

Hence, we can write by substituting in equation (4.11):

$$\sum_{k \neq v} \alpha_k (k - v) |k\rangle = (E_v^{(1)} - H^{(1)}) |v\rangle \quad \text{with} \quad \sum_{k \neq v} \alpha_k (k - v) = \text{constant} \quad (4.12)$$

As in the part 4.1.2, we project on  $\langle v|$ , in order to research the energy correction to the first order

$$\begin{aligned} \langle v| \sum_{k \neq v} \alpha_k (k - v) |k\rangle &= \langle v| (E_v^{(1)} - H^{(1)}) |v\rangle \\ \sum_{k \neq v} \alpha_k (k - v) \langle v|k\rangle &= \langle v| (E_v^{(1)} - H^{(1)}) |v\rangle \\ \sum_{k \neq v} \alpha_k (k - v) \langle v|k\rangle &= \langle v| E_v^{(1)} |v\rangle - \langle v| H^{(1)} |v\rangle \\ \text{with} \quad \langle v|k\rangle &= 0 \\ \text{and} \quad \langle v| E_v^{(1)} |v\rangle &= E_v^{(1)} \langle v|v\rangle = E_v^{(1)} \end{aligned}$$

$$\begin{aligned} E_v^{(1)} - \langle v| H^{(1)} |v\rangle &= 0 \\ \boxed{E_v^{(1)} = \langle v| H^{(1)} |v\rangle} & \quad (4.13) \end{aligned}$$

As we can see, the first-order correction to the energy is equal to the mean value of the perturbed Hamiltonian operator when the system is in non-perturbed state. Let's move on the first-order correction to the wave function. To find it, we need to come back to the equation (4.12). This time, let's project on another wave function  $\langle j|$  with  $j \neq v$  and having the same property than the wave function  $\langle v|$ .

$$\begin{aligned} \sum_{k \neq v} \alpha_k (k - v) |k\rangle &= (E_v^{(1)} - H^{(1)}) |v\rangle \\ \langle j| \sum_{k \neq v} \alpha_k (k - v) |k\rangle &= \langle j| (E_v^{(1)} - H^{(1)}) |v\rangle \end{aligned} \quad (4.14)$$

If we focus on the left term:

$$\begin{aligned} \langle j| \sum_{k \neq v} \alpha_k (k - v) |k\rangle &= \langle j| \sum_{k \neq v} \alpha_1 (E_1^{(0)} - E_v^{(0)}) |\Psi_1^{(0)}\rangle + \langle j| \sum_{k \neq v} \alpha_2 (E_2^{(0)} - E_v^{(0)}) |\Psi_2^{(0)}\rangle + \dots \\ &+ \langle j| \sum_{k \neq v} \alpha_{j-1} (E_{j-1}^{(0)} - E_v^{(0)}) |j-1\rangle + \langle j| \sum_{k \neq v} \alpha_j (j - v) |j\rangle + \dots \end{aligned} \quad (4.15)$$

We have  $\langle j|k\rangle = 0$  for all the term except when  $k = j$ , where we have  $\langle j|j\rangle = 1$ . So this gives us:

$$\langle j| \sum_{k \neq v} \alpha_k (k - v) |k\rangle = \langle j| \sum_{k \neq v} \alpha_j (j - v) |j\rangle = \alpha_j (j - v)$$

We obtain the following equation:

$$\begin{aligned} \alpha_j (j - v) &= \langle j| (E_v^{(1)} - H^{(1)}) |v\rangle \\ \alpha_j (j - v) &= \langle j| (E_v^{(1)} |v\rangle - \langle j| H^{(1)} |v\rangle) \quad \langle j| (E_v^{(1)} |v\rangle) = 0 \\ \alpha_j (j - v) &= - \langle j| H^{(1)} |v\rangle \\ \alpha_j (v - j) &= \langle j| H^{(1)} |v\rangle \end{aligned}$$

$$\alpha_j = \frac{\langle j| H^{(1)} |v\rangle}{v - j} \quad (4.16)$$

Now that we know the value of the constant  $\alpha$ , we just have to replace in the formula of the linear combination:

$$\begin{aligned} \Psi_v^{(1)} &= \sum_{k \neq v} \alpha_k \Psi_k^{(0)} \\ \Psi_v^{(1)} &= \sum_{k \neq v} \frac{\langle k| H^{(1)} |v\rangle}{(v - k)} \Psi_k^{(0)} \end{aligned} \quad (4.17)$$

The equation (4.17) is the final result that correspond to the first-order correction to the wave function.

#### 4.1.4 The second-order correction to the energy and to the wave function

Now, we look for the second-order correction using the same technique. We introduce the wave function  $\Psi_v^{(2)}$  as the following linear combination:

$$\Psi_v^{(2)} = \sum_{l \neq v} \alpha_l \Psi_l^{(0)} \quad (4.18)$$

We start from equation (4.4) and we separate the second-order terms from the zero-order terms and from the first-order terms.

$$\begin{aligned} H^{(0)}\Psi_v^{(2)} + H^{(1)}\Psi_v^{(1)} + H^{(2)}\Psi_v^{(0)} &= E_v^{(0)}\Psi_v^{(2)} + E_v^{(1)}\Psi_v^{(1)} + E_v^{(2)}\Psi_v^{(0)} \\ (H^{(0)} - E_v^{(0)})\Psi_v^{(2)} &= (E_v^{(1)} - H^{(1)})\Psi_v^{(1)} + (E_v^{(2)} - H^{(2)})\Psi_v^{(0)} \end{aligned} \quad (4.19)$$

Thus, by replacing the  $\Psi_v^{(2)}$  (see equation ??) by its value in  $H^{(0)}\Psi_v^{(2)}$ , we have:

$$H^{(0)} \sum_{l \neq v} \alpha_l \Psi_l^{(0)} = \sum_{l \neq v} \alpha_l E_l^{(0)} \Psi_l^{(0)}$$

So, the equation (4.19) becomes (also note that we replace  $\Psi_v^{(1)}$ , see equation 4.10):

$$\sum_{l \neq v} \alpha_l (l - v) |l\rangle = \sum_{k \neq v} \alpha_k (E_v^{(1)} - H^{(1)}) |k\rangle + (E_v^{(2)} - H^{(2)}) |v\rangle \quad (4.20)$$

Then, we multiply by the wavefunction  $\langle v|$ ,

$$\begin{aligned} \langle v| \sum_{l \neq v} \alpha_l (l - v) |l\rangle &= \langle v| \sum_{k \neq v} \alpha_k (E_v^{(1)} - H^{(1)}) |k\rangle + \langle v| (E_v^{(2)} - H^{(2)}) |v\rangle \\ \sum_{l \neq v} \alpha_l (l - v) \langle v|l\rangle &= \langle v| \sum_{k \neq v} \alpha_k (E_v^{(1)} - H^{(1)}) |k\rangle + E_v^{(2)} \langle v|v\rangle - \langle v| H^{(2)} |v\rangle \\ \langle v|l\rangle &= 0 \quad \text{and} \quad \langle v|v\rangle = 1 \end{aligned}$$

$$\begin{aligned} \langle v| \sum_{k \neq v} \alpha_k (E_v^{(1)} - H^{(1)}) |k\rangle + E_v^{(2)} - \langle v| H^{(2)} |v\rangle &= 0 \\ \langle v| \sum_{k \neq v} \alpha_k E_v^{(1)} |k\rangle - \langle v| \sum_{k \neq v} \alpha_k H_v^{(1)} |k\rangle + E_v^{(2)} - \langle v| H^{(2)} |v\rangle &= 0 \\ - \langle v| \sum_{k \neq v} \alpha_k H_v^{(1)} |k\rangle + E_v^{(2)} - \langle v| H^{(2)} |v\rangle &= 0 \\ \langle v| H^{(2)} |v\rangle + \sum_{k \neq v} \alpha_k \langle v| H_v^{(1)} |k\rangle &= E_v^{(2)} \end{aligned}$$

Knowing  $\alpha_k$  (equation 4.16), we can deduce:

$$E_v^{(2)} = \langle v | H^{(2)} | v \rangle + \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle}{(v-k)} \langle v | H_v^{(1)} | k \rangle$$

$$\boxed{E_v^{(2)} = \langle v | H^{(2)} | v \rangle + \sum_{k \neq v} \frac{(\langle k | H^{(1)} | v \rangle)^2}{v-k}} \quad (4.21)$$

As previously, we are looking for the second order correction of the wave function following the same approach used to determine the first order correction of the wave function, i.e. by projection of the wave function  $\langle j |$  into the equation (4.20).

$$\sum_{l \neq v} \alpha_l (l-v) | l \rangle = \sum_{k \neq v} \alpha_k (E_v^{(1)} - H^{(1)}) | k \rangle + (E_v^{(2)} - H^{(2)}) | v \rangle$$

$$\sum_{l \neq v} \alpha_l (l-v) \langle j | l \rangle = \langle j | \sum_{k \neq v} \alpha_k (E_v^{(1)} - H^{(1)}) | k \rangle + \langle j | (E_v^{(2)} - H^{(2)}) | v \rangle$$

$$\alpha_j (j-v) = \sum_{k \neq v} \alpha_k E_v^{(1)} \langle j | k \rangle - \sum_{k \neq v} \alpha_k \langle j | H^{(1)} | k \rangle + E_v^{(2)} \langle j | v \rangle - \langle j | H^{(2)} | v \rangle$$

*with*  $j \neq k, \quad \langle j | k \rangle = 0 \quad \langle j | v \rangle = 0$

$$\alpha_j (j-v) = - \sum_{k \neq v} \alpha_k \langle j | H^{(1)} | k \rangle - \langle j | H^{(2)} | v \rangle$$

$$\alpha_j (v-j) = \sum_{k \neq v} \alpha_k \langle j | H^{(1)} | k \rangle + \langle j | H^{(2)} | v \rangle$$

$$\alpha_j = \sum_{k \neq v} \frac{\alpha_k \langle j | H^{(1)} | k \rangle}{(v-j)} + \frac{\langle j | H^{(2)} | v \rangle}{(v-j)}$$

Let's remember that  $\alpha_k$  is equal to the following equation:  $\alpha_k = \frac{\langle k | H^{(1)} | v \rangle}{(v-k)}$ . So we can determine  $\alpha_j$ ,

$$\boxed{\alpha_j = \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle j | H^{(1)} | k \rangle}{(v-k)(v-j)} + \frac{\langle j | H^{(2)} | v \rangle}{(v-j)}} \quad (4.22)$$

We deduce the correction of the wave function to the second order by replacing in equation 4.18,

$$\boxed{\Psi_v^{(2)} = \sum_{l \neq v} \left[ \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle}{(v-k)(v-l)} + \frac{\langle l | H^{(2)} | v \rangle}{(v-l)} \right] \Psi_l^{(0)}} \quad (4.23)$$

#### 4.1.5 The third-order correction to the energy and to the wave function

After the second-order correction, we seek the third order correction using the same method of resolution. We introduce the wave function  $\Psi_v^{(3)}$  as the following linear combination:

$$\Psi_v^{(3)} = \sum_{m \neq v} \alpha_m \Psi_m^{(0)} \quad (4.24)$$

Let's solve the equation (4.5),

$$\begin{aligned} H^{(0)}\Psi_v^{(3)} + H^{(1)}\Psi_v^{(2)} + H^{(2)}\Psi_v^{(1)} + H^{(3)}\Psi_v^{(0)} &= E_v^{(0)}\Psi_v^{(3)} + E_v^{(1)}\Psi_v^{(2)} + E_v^{(2)}\Psi_v^{(1)} + E_v^{(3)}\Psi_v^{(0)} \\ (H^{(0)} - E_v^{(0)})\Psi_v^{(3)} &= (E_v^{(1)} - H^{(1)})\Psi_v^{(2)} + (E_v^{(2)} - H^{(2)})\Psi_v^{(1)} + (E_v^{(3)} - H^{(3)})\Psi_v^{(0)} \end{aligned} \quad (4.25)$$

We begin by replacing the wavefunction  $\Psi_v^{(3)}$  by its value (see equation 4.24):

$$H^{(0)} \sum_{m \neq v} \alpha_m \Psi_m^{(0)} = \sum_{m \neq v} \alpha_m E_m^{(0)} \Psi_m^{(0)}$$

Let's replace also  $\Psi_v^{(2)}$  and  $\Psi_v^{(1)}$  by  $\sum_{l \neq v} \alpha_l \Psi_l^{(0)}$  and  $\sum_{k \neq v} \alpha_k \Psi_k^{(0)}$  respectively. So, the equation (4.25) becomes:

$$\sum_{m \neq v} \alpha_m (m - v) |m\rangle = \sum_{l \neq v} \alpha_l (E_v^{(1)} - H^{(1)}) |l\rangle + \sum_{k \neq v} \alpha_k (E_v^{(2)} - H^{(2)}) |k\rangle + (E_v^{(3)} - H^{(3)}) |v\rangle \quad (4.26)$$

By decomposition and projection on the wavefunction  $\langle v|$ , we write:

$$\begin{aligned} \sum_{m \neq v} \alpha_m (m - v) \langle v|m\rangle &= \sum_{l \neq v} \alpha_l E_v^{(1)} \langle v|l\rangle - \sum_{l \neq v} \alpha_l \langle v|H^{(1)}|l\rangle + \sum_{k \neq v} \alpha_k E_v^{(2)} \langle v|k\rangle \\ &\quad - \sum_{k \neq v} \alpha_k \langle v|H^{(2)}|k\rangle + E_v^{(3)} \langle v|v\rangle - \langle v|H^{(3)}|v\rangle \end{aligned}$$

If we look at the left side (i.e. to the the left of the equal),

$$\sum_{m \neq v} \alpha_m (m - v) \langle v|m\rangle = 0 \quad \text{like} \quad \langle v|m\rangle = 0$$

Knowing that  $\langle v|l\rangle$  and  $\langle v|k\rangle$  are equal to zero and  $\langle v|v\rangle = 1$ , the right side can be simplify and we obtain the following equation,



$$\begin{aligned}
& - \sum_{l \neq v} \alpha_l \langle v | H^{(1)} | l \rangle - \sum_{k \neq v} \alpha_k \langle v | H^{(2)} | k \rangle + E_v^{(3)} - \langle v | H^{(3)} | v \rangle = 0 \\
& E_v^{(3)} = \sum_{l \neq v} \alpha_l \langle v | H^{(1)} | l \rangle + \sum_{k \neq v} \alpha_k \langle v | H^{(2)} | k \rangle + \langle v | H^{(3)} | v \rangle
\end{aligned}$$

We just have now to substitute  $\alpha_k$  and  $\alpha_l$  (see eq.(4.16) and eq.(4.22)),

$$\begin{aligned}
E_v^{(3)} &= \langle v | H^{(3)} | v \rangle + \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle v | H^{(2)} | k \rangle}{(v-k)} + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle v | H^{(1)} | l \rangle}{(v-k)(v-j)} \\
&+ \sum_{l \neq v} \frac{\langle j | H^{(2)} | v \rangle \langle v | H^{(1)} | l \rangle}{(v-j)}
\end{aligned}$$

$$E_v^{(3)} = \langle v | H^{(3)} | v \rangle + 2 \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle v | H^{(2)} | k \rangle}{(v-k)} + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle v | H^{(1)} | l \rangle}{(v-k)(v-j)}$$

(4.27)

Let's take the equation (4.26) to find the third-order correction of the wave function. We decompose and then we multiply by  $\langle j |$  with  $j \neq v$ :

$$\begin{aligned}
\sum_{m \neq v} \alpha_m (m-v) \langle j | m \rangle &= \sum_{l \neq v} \alpha_l E_v^{(1)} \langle j | l \rangle - \sum_{l \neq v} \alpha_l \langle j | H^{(1)} | l \rangle + \sum_{k \neq v} \alpha_k E_v^{(2)} \langle j | k \rangle \\
&- \sum_{k \neq v} \alpha_k \langle j | H^{(2)} | k \rangle - \langle j | H^{(3)} | v \rangle + E_v^{(3)} \langle j | v \rangle
\end{aligned}$$

Because of  $j \neq v$ , only the last term is equal to zero, using the same principle than the equation (4.15), we have:

$$\begin{aligned}
\alpha_j (j-v) &= \sum_{l \neq v} \alpha_j'' E_v^{(1)} - \sum_{l \neq v} \alpha_l \langle j | H^{(1)} | l \rangle + \sum_{k \neq v} \alpha_j' E_v^{(2)} \\
&- \sum_{k \neq v} \alpha_k \langle j | H^{(2)} | k \rangle - \langle j | H^{(3)} | v \rangle \\
\alpha_j (v-j) &= - \sum_{l \neq v} \alpha_j'' E_v^{(1)} + \sum_{l \neq v} \alpha_l \langle j | H^{(1)} | l \rangle - \sum_{k \neq v} \alpha_j' E_v^{(2)} \\
&+ \sum_{k \neq v} \alpha_k \langle j | H^{(2)} | k \rangle + \langle j | H^{(3)} | v \rangle
\end{aligned}$$

Let's recall that:

$$E_v^{(1)} = \langle v | H^{(1)} | v \rangle$$

$$E_v^{(2)} = \langle v | H^{(2)} | v \rangle + \sum_{k \neq v} \frac{(\langle k | H^{(1)} | v \rangle)^2}{v - k}$$

According to a rule on integrals that shows the following relationships:

$$\begin{aligned} \langle \Psi^i | H^{(1)} | \Psi^{i \pm 1} \rangle &\neq 0 \quad \text{else} = 0 \\ \langle \Psi^i | H^{(2)} | \Psi^i \rangle &\neq 0 \quad \text{else} = 0 \\ \langle \Psi^i | H^{(2)} | \Psi^{i \pm 2} \rangle &\neq 0 \quad \text{else} = 0 \end{aligned}$$

We can substitute and remove the term equal to zero,

$$\begin{aligned} \alpha_j(v - j) &= \sum_{l \neq v} \alpha_l \langle j | H^{(1)} | l \rangle - \alpha'_j \langle v | H^{(2)} | v \rangle - \sum_{k \neq v} \alpha'_j \frac{(\langle k | H^{(1)} | v \rangle)^2}{v - k} \\ &\quad + \sum_{k \neq v} \alpha_k \langle j | H^{(2)} | k \rangle + \langle j | H^{(3)} | v \rangle \\ \alpha_j &= \frac{\langle j | H^{(3)} | v \rangle}{(v - j)} + \sum_{l \neq v} \alpha_l \frac{\langle j | H^{(1)} | l \rangle}{(v - j)} + \sum_{k \neq v} \alpha_k \frac{\langle j | H^{(2)} | k \rangle}{(v - j)} \\ &\quad - \alpha'_j \frac{\langle v | H^{(2)} | v \rangle}{(v - j)} - \sum_{k \neq v} \alpha'_j \frac{(\langle k | H^{(1)} | v \rangle)^2}{(v - k)(v - j)} \end{aligned}$$

$$\begin{aligned} \alpha_j &= \frac{\langle j | H^{(3)} | v \rangle}{(v - j)} + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle j | H^{(1)} | l \rangle}{(v - k)(v - l)(v - j)} \\ &\quad + \sum_{l \neq v} \frac{\langle j | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle}{(v - l)(v - j)} + \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle j | H^{(2)} | k \rangle}{(v - k)(v - j)} \\ &\quad - \frac{\langle j | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle}{(v - j)^2} - \sum_{k \neq v} \frac{\langle j | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2}{(v - k)(v - j)^2} \end{aligned} \tag{4.28}$$

with  $\alpha'_j$  is  $\alpha_k$  with the index  $j$ , so  $\alpha'_j = \frac{\langle j | H^{(1)} | v \rangle}{(v - j)}$ . We re-inject in the equation of the wave function that is give the third-order correction of the wave function,

$$\begin{aligned} \Psi_v^{(3)} &= \sum_{m \neq v} \left[ \frac{\langle m | H^{(3)} | v \rangle}{(v - m)} + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle}{(v - k)(v - l)(v - m)} \right. \\ &\quad + \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle}{(v - l)(v - m)} + \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle}{(v - k)(v - m)} \\ &\quad \left. - \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle}{(v - m)^2} - \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2}{(v - k)(v - m)^2} \right] \Psi_m^{(0)} \end{aligned} \tag{4.29}$$

#### 4.1.6 The fourth-order correction to the energy and to the wave function

First of all, we introduce the wave function  $\Psi_v^{(4)}$  as the following linear combination:

$$\Psi_v^{(4)} = \sum_{n \neq v} \alpha_n \Psi_n^{(0)} \quad (4.30)$$

We solve the equation (4.6) like previously for the lower order in order to obtain the correction for the energy as well the wave function. The first step is to rearrange the equation in order to isolate the term relating to the wavefunction at the fourth order.

$$\begin{aligned} H^{(0)}\Psi_v^{(4)} + H^{(1)}\Psi_v^{(3)} + H^{(3)}\Psi_v^{(1)} + H^{(4)}\Psi_v^{(0)} + H^{(2)}\Psi_v^{(2)} &= E_v^{(0)}\Psi_v^{(4)} + E_v^{(1)}\Psi_v^{(3)} + E_v^{(3)}\Psi_v^{(1)} \\ &+ E_v^{(4)}\Psi_v^{(0)} + E_v^{(2)}\Psi_v^{(2)} \\ (H^{(0)} - E_v^{(0)})\Psi_v^{(4)} &= (E_v^{(1)} - H^{(1)})\Psi_v^{(3)} + (E_v^{(2)} - H^{(2)})\Psi_v^{(2)} + (E_v^{(3)} - H^{(3)})\Psi_v^{(1)} \\ &+ (E_v^{(4)} - H^{(4)})\Psi_v^{(0)} \end{aligned} \quad (4.31)$$

As before for the lower orders, we use our introduction of the wavefunction  $\Psi_v^{(4)}$  by its value  $H^{(0)}\Psi_v^{(4)}$  which results in:

$$H^{(0)} \sum_{n \neq v} \alpha_n \Psi_n^{(0)} = \sum_{n \neq v} \alpha_n E_n^{(0)} \Psi_n^{(0)}$$

Let's substitute also  $\Psi_v^{(3)}$ ,  $\Psi_v^{(2)}$  and  $\Psi_v^{(1)}$ , the equation (4.31) becomes,

$$\begin{aligned} \sum_{n \neq v} \alpha_n (n - v) |n\rangle &= \sum_{m \neq v} \alpha_m (E_v^{(1)} - H^{(1)}) |m\rangle + \sum_{l \neq v} \alpha_l (E_v^{(2)} - H^{(2)}) |l\rangle \\ &+ \sum_{k \neq v} \alpha_k (E_v^{(3)} - H^{(3)}) |k\rangle + (E_v^{(4)} - H^{(4)}) |v\rangle \end{aligned} \quad (4.32)$$

If we multiply by the wavefunction  $\langle v|$ , this leads to the corresponding:

$$\begin{aligned} \sum_{n \neq v} \alpha_n (n - v) \langle v|n\rangle &= \sum_{m \neq v} \alpha_m \langle v| (E_v^{(1)} - H^{(1)}) |m\rangle + \sum_{l \neq v} \alpha_l \langle v| (E_v^{(2)} - H^{(2)}) |l\rangle \\ &+ \sum_{k \neq v} \alpha_k \langle v| (E_v^{(3)} - H^{(3)}) |k\rangle + \langle v| (E_v^{(4)} - H^{(4)}) |v\rangle \\ \sum_{n \neq v} \alpha_n (n - v) \langle v|n\rangle &= \sum_{m \neq v} \alpha_m E_v^{(1)} \langle v|m\rangle - \sum_{m \neq v} \alpha_m \langle v| H^{(1)} |m\rangle + \sum_{l \neq v} \alpha_l E_v^{(2)} \langle v|l\rangle \\ &- \sum_{l \neq v} \alpha_l \langle v| H^{(2)} |l\rangle + \sum_{k \neq v} \alpha_k E_v^{(3)} \langle v|k\rangle - \sum_{k \neq v} \alpha_k \langle v| H^{(3)} |k\rangle \\ &+ E_v^{(4)} \langle v|v\rangle - \langle v| H^{(4)} |v\rangle \end{aligned} \quad (4.33)$$

Firstly, we just work on the left term,

$$\sum_{n \neq v} \alpha_n (n - v) \langle v|n \rangle = 0 \quad \text{like} \quad \langle v|n \rangle = 0$$

Secondly, knowing that  $\langle v|m \rangle$ ,  $\langle v|l \rangle$  and  $\langle v|k \rangle$  are equal to zero and  $\langle v|v \rangle = 1$ , we can determine the right side and it can be simplified like this,

$$\begin{aligned} 0 &= - \sum_{m \neq v} \alpha_m \langle v|H^{(1)}|m \rangle - \sum_{l \neq v} \alpha_l \langle v|H^{(2)}|l \rangle \\ &\quad - \sum_{k \neq v} \alpha_k \langle v|H^{(3)}|k \rangle + E_v^{(4)} - \langle v|H^{(4)}|v \rangle \\ E_v^{(4)} &= \sum_{m \neq v} \alpha_m \langle v|H^{(1)}|m \rangle + \sum_{l \neq v} \alpha_l \langle v|H^{(2)}|l \rangle \\ &\quad + \sum_{k \neq v} \alpha_k \langle v|H^{(3)}|k \rangle + \langle v|H^{(4)}|v \rangle \end{aligned}$$

$$\begin{aligned} E_v^{(4)} &= \langle v|H^{(4)}|v \rangle + 2 \sum_{m \neq v} \frac{\langle m|H^{(3)}|v \rangle \langle v|H^{(1)}|m \rangle}{(v - m)} \\ &\quad + \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k|H^{(1)}|v \rangle \langle l|H^{(1)}|k \rangle \langle m|H^{(1)}|l \rangle \langle v|H^{(1)}|m \rangle}{(v - k)(v - l)(v - m)} \\ &\quad + 2 \sum_{l \neq v} \sum_{k \neq v} \frac{\langle l|H^{(1)}|k \rangle \langle k|H^{(2)}|v \rangle \langle v|H^{(1)}|l \rangle}{(v - l)(v - k)} \\ &\quad + \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k|H^{(1)}|v \rangle \langle m|H^{(2)}|k \rangle \langle v|H^{(1)}|m \rangle}{(v - k)(v - m)} - \sum_{m \neq v} \frac{(\langle m|H^{(1)}|v \rangle)^2 \langle v|H^{(2)}|v \rangle}{(v - m)^2} \\ &\quad - \sum_{m \neq v} \sum_{k \neq v} \frac{(\langle m|H^{(1)}|v \rangle)^2 (\langle k|H^{(1)}|v \rangle)^2}{(v - k)(v - m)^2} + \sum_{l \neq v} \frac{\langle l|H^{(2)}|v \rangle^2}{(v - l)} \end{aligned} \quad (4.34)$$

It's mandatory to determine the fourth-order correction of the wavefunction, if we want to go further and notably to the fifth- and sixth-order of the development. So, we go back to the equation (4.32), we are projecting on wavefunction  $\langle j|$  and apply the method seen in equation (4.15) to simplify the following equation:

$$\begin{aligned} \sum_{n \neq v} \alpha_n (n - v) \langle j|n \rangle &= \sum_{m \neq v} \alpha_m E_v^{(1)} \langle j|m \rangle - \sum_{m \neq v} \alpha_m \langle j|H^{(1)}|m \rangle + \sum_{l \neq v} \alpha_l E_v^{(2)} \langle j|l \rangle \\ &\quad - \sum_{l \neq v} \alpha_l \langle j|H^{(2)}|l \rangle + \sum_{k \neq v} \alpha_k E_v^{(3)} \langle j|k \rangle - \sum_{k \neq v} \alpha_k \langle \Psi_j^0|H^{(3)}|k \rangle \\ &\quad + E_v^{(4)} \langle j|v \rangle - \langle j|H^{(4)}|v \rangle \end{aligned}$$

$$\begin{aligned}
\alpha_j(j-v) &= - \sum_{m \neq v} \alpha_m \langle j | H^{(1)} | m \rangle + \alpha'_j E_v^{(2)} - \sum_{l \neq v} \alpha_l \langle j | H^{(2)} | l \rangle \\
&\quad - \sum_{k \neq v} \alpha_k \langle \Psi_j^0 | H^{(3)} | k \rangle - \langle j | H^{(4)} | v \rangle \\
\alpha_j(v-j) &= \sum_{m \neq v} \alpha_m \langle j | H^{(1)} | m \rangle - \alpha'_j E_v^{(2)} + \sum_{l \neq v} \alpha_l \langle j | H^{(2)} | l \rangle \\
&\quad + \sum_{k \neq v} \alpha_k \langle \Psi_j^0 | H^{(3)} | k \rangle + \langle j | H^{(4)} | v \rangle \\
\alpha_j &= \sum_{m \neq v} \alpha_m \frac{\langle j | H^{(1)} | m \rangle}{(v-j)} - \frac{\alpha'_j E_v^{(2)}}{(v-j)} + \sum_{l \neq v} \alpha_l \frac{\langle j | H^{(2)} | l \rangle}{(v-j)} \\
&\quad + \sum_{k \neq v} \alpha_k \frac{\langle \Psi_j^0 | H^{(3)} | k \rangle}{(v-j)} + \frac{\langle j | H^{(4)} | v \rangle}{(v-j)} \tag{4.35}
\end{aligned}$$

And in order to get the value of the constant  $\alpha_j$ , we reinject each term found previously:  $\alpha_m$ ,  $\alpha'_j$ ,  $\alpha_l$ , and  $\alpha_k$ .

$$\begin{aligned}
\alpha_j &= \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle j | H^{(1)} | m \rangle}{(v-m)(v-j)} + \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle j | H^{(1)} | m \rangle}{(v-l)(v-m)(v-j)} \\
&\quad + \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle j | H^{(1)} | m \rangle}{(v-k)(v-l)(v-m)(v-j)} \\
&\quad + \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle j | H^{(1)} | m \rangle}{(v-k)(v-m)(v-j)} \\
&\quad - \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle j | H^{(1)} | m \rangle}{(v-m)^2(v-j)} \\
&\quad - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle j | H^{(1)} | m \rangle}{(v-k)(v-m)^2(v-j)} \\
&\quad - \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle j | H^{(1)} | k \rangle}{(v-k)(v-j)^2} \\
&\quad - \sum_{l \neq v} \sum_{k \neq v} \frac{(\langle k | H^{(1)} | v \rangle)^2 \langle j | H^{(1)} | l \rangle \langle l | H^{(1)} | v \rangle}{(v-k)(v-l)(v-j)^2} - \frac{\langle j | H^{(2)} | v \rangle \langle v | H^{(2)} | v \rangle}{(v-j)^2} \\
&\quad - \sum_{k \neq v} \frac{(\langle k | H^{(1)} | v \rangle)^2 \langle j | H^{(2)} | v \rangle}{(v-k)(v-j)^2} + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle j | H^{(2)} | l \rangle \langle l | H^{(1)} | k \rangle}{(v-k)(v-l)(v-j)} \\
&\quad + \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle j | H^{(2)} | l \rangle}{(v-l)(v-j)} + \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle j | H^{(3)} | k \rangle}{(v-k)(v-j)} + \frac{\langle j | H^{(4)} | v \rangle}{(v-j)} \tag{4.36}
\end{aligned}$$

From now on, we can deduce the fourth-order correction of the wave function,

$$\begin{aligned}
\Psi_v^{(4)} = & \sum_{n \neq v} \left[ \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle n | H^{(1)} | m \rangle}{(v-m)(v-n)} \right. \\
& + \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle n | H^{(1)} | m \rangle}{(v-l)(v-m)(v-n)} \\
& + \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle n | H^{(1)} | m \rangle}{(v-k)(v-l)(v-m)(v-n)} \\
& + \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle n | H^{(1)} | m \rangle}{(v-k)(v-m)(v-n)} \\
& - \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle n | H^{(1)} | m \rangle}{(v-m)^2(v-n)} \\
& - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(1)} | m \rangle}{(v-k)(v-m)^2(v-n)} \\
& - \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle n | H^{(1)} | k \rangle}{(v-k)(v-n)^2} \\
& - \sum_{l \neq v} \sum_{k \neq v} \frac{(\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(1)} | l \rangle \langle l | H^{(1)} | v \rangle}{(v-k)(v-l)(v-n)^2} \\
& - \frac{\langle n | H^{(2)} | v \rangle \langle v | H^{(2)} | v \rangle}{(v-n)^2} - \sum_{k \neq v} \frac{(\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(2)} | v \rangle}{(v-k)(v-n)^2} \\
& + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle n | H^{(2)} | l \rangle \langle l | H^{(1)} | k \rangle}{(v-k)(v-l)(v-n)} + \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle n | H^{(2)} | l \rangle}{(v-l)(v-n)} \\
& \left. + \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle n | H^{(3)} | k \rangle}{(v-k)(v-n)} + \frac{\langle n | H^{(4)} | v \rangle}{(v-n)} \right] \Psi_n^{(0)}
\end{aligned} \tag{4.37}$$

#### 4.1.7 The fifth-order correction to the energy and to the wave function

We consider the wave function  $\Psi_v^{(5)}$  as the following linear combination:

$$\Psi_v^{(5)} = \sum_{p \neq v} \alpha_p \Psi_p^{(0)} \quad (4.38)$$

In a first step, we look for the energy correction at order 5. Starting from the equation (4.7) and by the fact that we are posed just above as  $\Psi_v^{(5)} = \sum_{p \neq v} \alpha_p \Psi_p^{(0)}$ , the equation can be expressed

$$\begin{aligned} \sum_{p \neq v} \alpha_p (p - v) |p\rangle &= \sum_{n \neq v} \alpha_n (E_v^{(1)} - H^{(1)}) |n\rangle + \sum_{m \neq v} \alpha_m (E_v^{(2)} - H^{(2)}) |m\rangle + \sum_{l \neq v} \alpha_l (E_v^{(3)} - H^{(3)}) |l\rangle \\ &+ \sum_{k \neq v} \alpha_k (E_v^{(4)} - H^{(4)}) |k\rangle + (E_v^{(5)} - H^{(5)}) |v\rangle \end{aligned} \quad (4.39)$$

Note that  $\Psi_v^{(4)}$ ,  $\Psi_v^{(3)}$ ,  $\Psi_v^{(2)}$  and  $\Psi_v^{(1)}$  have also been replaced by equations 4.30, 4.24, 4.18 and 4.10, respectively.

In order to produce the expression for the energy correction the wave function  $\langle v |$  is inserted as follows:

$$\begin{aligned} \sum_{p \neq v} \alpha_p (p - v) \langle v | p \rangle &= \sum_{n \neq v} \alpha_n \langle v | (E_v^{(1)} - H^{(1)}) |n\rangle + \sum_{m \neq v} \alpha_m \langle v | (E_v^{(2)} - H^{(2)}) |m\rangle \\ &+ \sum_{l \neq v} \alpha_l \langle v | (E_v^{(3)} - H^{(3)}) |l\rangle + \sum_{k \neq v} \alpha_k \langle v | (E_v^{(4)} - H^{(4)}) |k\rangle \\ &+ \langle v | (E_v^{(5)} - H^{(5)}) |v\rangle \\ \sum_{p \neq v} \alpha_p (p - v) \langle v | p \rangle &= \sum_{n \neq v} \alpha_n E_v^{(1)} \langle v | n \rangle - \sum_{n \neq v} \alpha_n \langle v | H^{(1)} |n\rangle + \sum_{m \neq v} \alpha_m E_v^{(2)} \langle v | m \rangle \\ &- \sum_{m \neq v} \alpha_m \langle v | H^{(2)} |m\rangle + \sum_{l \neq v} \alpha_l E_v^{(3)} \langle v | l \rangle - \sum_{l \neq v} \alpha_l \langle v | H^{(3)} |l\rangle \\ &+ \sum_{k \neq v} \alpha_k E_v^{(4)} \langle v | k \rangle - \sum_{k \neq v} \alpha_k \langle v | H^{(4)} |k\rangle + E_v^{(5)} \langle v | v \rangle \\ &- \langle v | H^{(5)} |v\rangle \end{aligned} \quad (4.40)$$

Using the properties of orthonormality i.e.  $\langle v|n\rangle$ ,  $\langle v|m\rangle$ ,  $\langle v|l\rangle$  and  $\langle v|k\rangle$  are equal to zero and  $\langle v|v\rangle = 1$ , the equation (4.40) becomes,

$$\begin{aligned}
0 &= - \sum_{n \neq v} \alpha_n \langle v|H^{(1)}|n\rangle - \sum_{m \neq v} \alpha_m \langle v|H^{(2)}|m\rangle - \sum_{l \neq v} \alpha_l \langle v|H^{(3)}|l\rangle \\
&\quad - \sum_{k \neq v} \alpha_k \langle v|H^{(4)}|k\rangle + E_v^{(5)} - \langle v|H^{(5)}|v\rangle \\
E_v^{(5)} &= \sum_{n \neq v} \alpha_n \langle v|H^{(1)}|n\rangle + \sum_{m \neq v} \alpha_m \langle v|H^{(2)}|m\rangle + \sum_{l \neq v} \alpha_l \langle v|H^{(3)}|l\rangle \\
&\quad + \sum_{k \neq v} \alpha_k \langle v|H^{(4)}|k\rangle + \langle v|H^{(5)}|v\rangle
\end{aligned}$$

Let's recall each term  $\alpha_k$ ,  $\alpha_l$ ,  $\alpha_m$ ,  $\alpha_n$ ,  $\alpha_n$ :

$$\begin{aligned}
\alpha_k &= \frac{\langle k|H^{(1)}|v\rangle}{v-k} \\
\alpha_l &= \sum_{k \neq v} \frac{\langle k|H^{(1)}|v\rangle \langle l|H^{(1)}|k\rangle}{(v-k)(v-l)} + \frac{\langle l|H^{(2)}|v\rangle}{(v-l)} \\
\alpha_m &= \frac{\langle m|H^{(3)}|v\rangle}{(v-m)} + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k|H^{(1)}|v\rangle \langle l|H^{(1)}|k\rangle \langle m|H^{(1)}|l\rangle}{(v-k)(v-l)(v-m)} + \sum_{l \neq v} \frac{\langle m|H^{(1)}|l\rangle \langle l|H^{(2)}|v\rangle}{(v-l)(v-m)} \\
&\quad + \sum_{k \neq v} \frac{\langle k|H^{(1)}|v\rangle \langle m|H^{(2)}|k\rangle}{(v-k)(v-m)} - \frac{\langle m|H^{(1)}|v\rangle \langle v|H^{(2)}|v\rangle}{(v-m)^2} - \sum_{k \neq v} \frac{\langle m|H^{(1)}|v\rangle (\langle k|H^{(1)}|v\rangle)^2}{(v-k)(v-m)^2} \\
\alpha_n &= \sum_{m \neq v} \frac{\langle m|H^{(3)}|v\rangle \langle n|H^{(1)}|m\rangle}{(v-m)(v-n)} + \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m|H^{(1)}|l\rangle \langle l|H^{(2)}|v\rangle \langle n|H^{(1)}|m\rangle}{(v-l)(v-m)(v-n)} \\
&\quad + \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k|H^{(1)}|v\rangle \langle l|H^{(1)}|k\rangle \langle m|H^{(1)}|l\rangle \langle n|H^{(1)}|m\rangle}{(v-k)(v-l)(v-m)(v-n)} \\
&\quad + \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k|H^{(1)}|v\rangle \langle m|H^{(2)}|k\rangle \langle n|H^{(1)}|m\rangle}{(v-k)(v-m)(v-n)} - \sum_{m \neq v} \frac{\langle m|H^{(1)}|v\rangle \langle v|H^{(2)}|v\rangle \langle n|H^{(1)}|m\rangle}{(v-m)^2(v-n)} \\
&\quad - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m|H^{(1)}|v\rangle (\langle k|H^{(1)}|v\rangle)^2 \langle n|H^{(1)}|m\rangle}{(v-k)(v-m)^2(v-n)} - \sum_{k \neq v} \frac{\langle k|H^{(1)}|v\rangle \langle v|H^{(2)}|v\rangle \langle n|H^{(1)}|k\rangle}{(v-k)(v-n)^2} \\
&\quad - \sum_{l \neq v} \sum_{k \neq v} \frac{(\langle k|H^{(1)}|v\rangle)^2 \langle n|H^{(1)}|l\rangle \langle l|H^{(1)}|v\rangle}{(v-k)(v-l)(v-n)^2} - \frac{\langle n|H^{(2)}|v\rangle \langle v|H^{(2)}|v\rangle}{(v-n)^2} \\
&\quad - \sum_{k \neq v} \frac{(\langle k|H^{(1)}|v\rangle)^2 \langle n|H^{(2)}|v\rangle}{(v-k)(v-n)^2} + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k|H^{(1)}|v\rangle \langle n|H^{(2)}|l\rangle \langle l|H^{(1)}|k\rangle}{(v-k)(v-l)(v-n)} \\
&\quad + \sum_{l \neq v} \frac{\langle l|H^{(2)}|v\rangle \langle n|H^{(2)}|l\rangle}{(v-l)(v-n)} + \sum_{k \neq v} \frac{\langle k|H^{(1)}|v\rangle \langle n|H^{(3)}|k\rangle}{(v-k)(v-n)} + \frac{\langle n|H^{(4)}|v\rangle}{(v-n)}
\end{aligned}$$



$$\begin{aligned}
E_v^{(5)} = & \langle v | H^{(5)} | v \rangle + \sum_{n \neq v} \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle n | H^{(1)} | m \rangle \langle v | H^{(1)} | n \rangle}{(v-m)(v-n)} \\
& + \sum_{n \neq v} \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle n | H^{(1)} | m \rangle \langle v | H^{(1)} | n \rangle}{(v-l)(v-m)(v-n)} \\
& + \sum_{n \neq v} \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle n | H^{(1)} | m \rangle \langle v | H^{(1)} | n \rangle}{(v-k)(v-l)(v-m)(v-n)} \\
& + \sum_{n \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle n | H^{(1)} | m \rangle \langle v | H^{(1)} | n \rangle}{(v-k)(v-m)(v-n)} \\
& - \sum_{n \neq v} \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle n | H^{(1)} | m \rangle \langle v | H^{(1)} | n \rangle}{(v-m)^2(v-n)} \\
& - \sum_{n \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(1)} | m \rangle \langle v | H^{(1)} | n \rangle}{(v-k)(v-m)^2(v-n)} \\
& - \sum_{n \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle n | H^{(1)} | k \rangle \langle v | H^{(1)} | n \rangle}{(v-k)(v-n)^2} \\
& - \sum_{n \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle l | H^{(1)} | v \rangle \langle n | H^{(1)} | l \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle v | H^{(1)} | n \rangle}{(v-k)(v-l)(v-n)^2} \\
& - \sum_{n \neq v} \frac{\langle n | H^{(2)} | v \rangle \langle v | H^{(2)} | v \rangle \langle v | H^{(1)} | n \rangle}{(v-n)^2} - \sum_{n \neq v} \sum_{k \neq v} \frac{(\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(2)} | v \rangle \langle v | H^{(1)} | n \rangle}{(v-k)(v-n)^2} \\
& + \sum_{n \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle n | H^{(2)} | l \rangle \langle l | H^{(1)} | k \rangle \langle v | H^{(1)} | n \rangle}{(v-k)(v-l)(v-n)} \\
& + \sum_{n \neq v} \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle n | H^{(2)} | l \rangle \langle v | H^{(1)} | n \rangle}{(v-n)(v-l)} \\
& + \sum_{n \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle n | H^{(3)} | k \rangle \langle v | H^{(1)} | n \rangle}{(v-k)(v-n)} + \sum_{n \neq v} \frac{\langle n | H^{(4)} | v \rangle \langle v | H^{(1)} | n \rangle}{(v-n)}
\end{aligned}$$

$$\begin{aligned}
& + \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle v | H^{(2)} | m \rangle}{(v - m)} \\
& + \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle v | H^{(2)} | m \rangle}{(v - k)(v - l)(v - m)} \\
& + \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle v | H^{(2)} | m \rangle}{(v - l)(v - m)} \\
& + \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle v | H^{(2)} | m \rangle}{(v - k)(v - m)} \\
& - \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle v | H^{(2)} | m \rangle}{(v - m)^2} \\
& - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle v | H^{(2)} | m \rangle}{(v - k)(v - m)^2} \\
& + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle v | H^{(3)} | l \rangle}{(v - k)(v - l)} + \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle v | H^{(3)} | l \rangle}{(v - l)} \\
& + \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle v | H^{(4)} | k \rangle}{(v - k)}
\end{aligned} \tag{4.41}$$

First we seek the value of the constant  $\alpha_j$  to deduce the expression for the correction of the wavefunction. So we pick up the equation (4.40) on which we integrate the wavefunction  $\langle j |$  and solve by the same procedure as used to solve the previous wave function corrections,

$$\begin{aligned}
\sum_{p \neq v} \alpha_p (p - v) \langle j | p \rangle & = \sum_{n \neq v} \alpha_n E_v^{(1)} \langle j | n \rangle - \sum_{n \neq v} \alpha_n \langle \Psi_j^0 | H^{(1)} | n \rangle + \sum_{m \neq v} \alpha_m E_v^{(2)} \langle j | m \rangle \\
& - \sum_{m \neq v} \alpha_m \langle j | H^{(2)} | m \rangle + \sum_{l \neq v} \alpha_l E_v^{(3)} \langle j | l \rangle - \sum_{l \neq v} \alpha_l \langle j | H^{(3)} | l \rangle \\
& + \sum_{k \neq v} \alpha_k E_v^{(4)} \langle j | k \rangle - \sum_{k \neq v} \alpha_k \langle j | H^{(4)} | k \rangle + E_v^{(5)} \langle j | v \rangle \\
& - \langle j | H^{(5)} | v \rangle
\end{aligned}$$

$$\begin{aligned}
\alpha_j(j-v) &= -\sum_{n \neq v} \alpha_n \langle j | H^{(1)} | n \rangle + \alpha'_j E_v^{(2)} - \sum_{m \neq v} \alpha_m \langle j | H^{(2)} | m \rangle \\
&\quad - \sum_{l \neq v} \alpha_l \langle j | H^{(3)} | l \rangle + \alpha''_j E_v^{(4)} - \sum_{k \neq v} \alpha_k \langle j | H^{(4)} | k \rangle \\
&\quad - \langle j | H^{(5)} | v \rangle \\
\alpha_j &= \sum_{n \neq v} \alpha_n \frac{\langle j | H^{(1)} | n \rangle}{(v-j)} - \frac{\alpha'_j E_v^{(2)}}{(v-j)} + \sum_{m \neq v} \alpha_m \frac{\langle j | H^{(2)} | m \rangle}{(v-j)} \\
&\quad + \sum_{l \neq v} \alpha_l \frac{\langle j | H^{(3)} | l \rangle}{(v-j)} - \frac{\alpha''_j E_v^{(4)}}{(v-j)} + \sum_{k \neq v} \alpha_k \frac{\langle j | H^{(4)} | k \rangle}{(v-j)} \\
&\quad + \frac{\langle j | H^{(5)} | v \rangle}{(v-j)} \tag{4.42}
\end{aligned}$$

We can define  $\alpha_j$  by replacing  $\alpha_n$ ,  $\alpha_m$ ,  $\alpha'_j$ ,  $\alpha_l$ ,  $\alpha''_j$  and  $\alpha_k$  by their values,

$$\begin{aligned}
\alpha_j &= \frac{\langle j | H^{(5)} | v \rangle}{(v-j)} + \sum_{n \neq v} \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle n | H^{(1)} | m \rangle \langle j | H^{(1)} | n \rangle}{(v-m)(v-n)(v-j)} \\
&\quad + \sum_{n \neq v} \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle n | H^{(1)} | m \rangle \langle j | H^{(1)} | n \rangle}{(v-l)(v-m)(v-n)(v-j)} \\
&\quad + \sum_{n \neq v} \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle n | H^{(1)} | m \rangle \langle j | H^{(1)} | n \rangle}{(v-k)(v-l)(v-m)(v-n)(v-j)} \\
&\quad + \sum_{n \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle n | H^{(1)} | m \rangle \langle j | H^{(1)} | n \rangle}{(v-k)(v-m)(v-n)(v-j)} \\
&\quad - \sum_{n \neq v} \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle n | H^{(1)} | m \rangle \langle j | H^{(1)} | n \rangle}{(v-m)^2(v-n)(v-j)} \\
&\quad - \sum_{n \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(1)} | m \rangle \langle j | H^{(1)} | n \rangle}{(v-k)(v-m)^2(v-n)(v-j)} \\
&\quad - \sum_{n \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle n | H^{(1)} | k \rangle \langle j | H^{(1)} | n \rangle}{(v-k)(v-n)^2(v-j)} \\
&\quad - \sum_{n \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle l | H^{(1)} | v \rangle \langle n | H^{(1)} | l \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle j | H^{(1)} | n \rangle}{(v-k)(v-l)(v-n)^2(v-j)} \\
&\quad - \sum_{n \neq v} \frac{\langle n | H^{(2)} | v \rangle \langle v | H^{(2)} | v \rangle \langle j | H^{(1)} | n \rangle}{(v-n)^2(v-j)} - \sum_{n \neq v} \sum_{k \neq v} \frac{(\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(2)} | v \rangle \langle j | H^{(1)} | n \rangle}{(v-k)(v-n)^2(v-j)}
\end{aligned}$$

$$\begin{aligned}
& + \sum_{n \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle n | H^{(2)} | l \rangle \langle l | H^{(1)} | k \rangle \langle j | H^{(1)} | n \rangle}{(v-k)(v-l)(v-n)(v-j)} \\
& + \sum_{n \neq v} \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle n | H^{(2)} | l \rangle \langle j | H^{(1)} | n \rangle}{(v-n)(v-l)(v-j)} + \sum_{n \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle n | H^{(3)} | k \rangle \langle j | H^{(1)} | n \rangle}{(v-k)(v-n)(v-j)} \\
& + \sum_{n \neq v} \frac{\langle n | H^{(4)} | v \rangle \langle j | H^{(1)} | n \rangle}{(v-n)(v-j)} + \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle j | H^{(2)} | m \rangle}{(v-m)(v-j)} \\
& + \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle j | H^{(2)} | m \rangle}{(v-k)(v-l)(v-m)(v-j)} \\
& + \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle j | H^{(2)} | m \rangle}{(v-l)(v-m)(v-j)} + \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle j | H^{(2)} | m \rangle}{(v-k)(v-m)(v-j)} \\
& - \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle j | H^{(2)} | m \rangle}{(v-m)^2(v-j)} - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle j | H^{(2)} | m \rangle}{(v-k)(v-m)^2(v-j)} \\
& + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle j | H^{(3)} | l \rangle}{(v-k)(v-l)(v-j)} + \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle j | H^{(3)} | l \rangle}{(v-l)(v-j)} \\
& + \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle j | H^{(4)} | k \rangle}{(v-k)(v-j)} - \frac{\langle j | H^{(3)} | v \rangle \langle v | H^{(2)} | v \rangle}{(v-j)^2} \\
& - \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle j | H^{(1)} | l \rangle \langle v | H^{(2)} | v \rangle}{(v-k)(v-l)(v-j)^2} - \sum_{l \neq v} \frac{\langle j | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle v | H^{(2)} | v \rangle}{(v-l)(v-j)^2} \\
& - \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle j | H^{(2)} | k \rangle \langle v | H^{(2)} | v \rangle}{(v-k)(v-j)^2} + \frac{\langle j | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle^2}{(v-j)^3} \\
& + \sum_{k \neq v} \frac{\langle j | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle v | H^{(2)} | v \rangle}{(v-k)(v-j)^3} - \sum_{m \neq v} \frac{\langle j | H^{(3)} | v \rangle (\langle m | H^{(1)} | v \rangle)^2}{(v-j)^2(v-m)} \\
& - \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle j | H^{(1)} | l \rangle (\langle m | H^{(1)} | v \rangle)^2}{(v-k)(v-l)(v-j)^2(v-m)} \\
& - \sum_{m \neq v} \sum_{l \neq v} \frac{\langle j | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle (\langle m | H^{(1)} | v \rangle)^2}{(v-l)(v-j)^2(v-m)}
\end{aligned}$$

$$\begin{aligned}
& - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle j | H^{(2)} | k \rangle (\langle m | H^{(1)} | v \rangle)^2}{(v-k)(v-j)^2(v-m)} \\
& + \sum_{m \neq v} \frac{\langle j | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle (\langle m | H^{(1)} | v \rangle)^2}{(v-m)(v-j)^3} \\
& + \sum_{m \neq v} \sum_{k \neq v} \frac{\langle j | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 (\langle m | H^{(1)} | v \rangle)^2}{(v-m)(v-k)(v-j)^3} \\
& - \frac{\langle v | H^{(4)} | v \rangle \langle j | H^{(1)} | v \rangle}{(v-j)^2} - 2 \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle v | H^{(1)} | m \rangle \langle j | H^{(1)} | v \rangle}{(v-m)(v-j)^2} \\
& - \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle v | H^{(1)} | m \rangle \langle j | H^{(1)} | v \rangle}{(v-k)(v-l)(v-m)(v-j)^2} \\
& - 2 \sum_{l \neq v} \sum_{k \neq v} \frac{\langle l | H^{(1)} | k \rangle \langle k | H^{(2)} | v \rangle \langle v | H^{(1)} | l \rangle \langle j | H^{(1)} | v \rangle}{(v-l)(v-k)(v-j)^2} \\
& - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle v | H^{(1)} | m \rangle \langle j | H^{(1)} | v \rangle}{(v-k)(v-m)(v-j)^2} \\
& + \sum_{m \neq v} \frac{(\langle m | H^{(1)} | v \rangle)^2 \langle v | H^{(2)} | v \rangle \langle j | H^{(1)} | v \rangle}{(v-m)^2(v-j)^2} \\
& + \sum_{m \neq v} \sum_{k \neq v} \frac{(\langle m | H^{(1)} | v \rangle)^2 (\langle k | H^{(1)} | v \rangle)^2 \langle j | H^{(1)} | v \rangle}{(v-k)(v-m)^2(v-j)^2} \\
& - \sum_{l \neq v} \frac{(\langle l | H^{(2)} | v \rangle)^2 \langle j | H^{(1)} | v \rangle}{(v-l)(v-j)^2}
\end{aligned} \tag{4.43}$$

We conclude the correction of the wave function to the fifth-order,

$$\begin{aligned}
\Psi_v^{(5)} = & \sum_{p \neq v} \left[ \frac{\langle p | H^{(5)} | v \rangle}{(v-p)} + \sum_{n \neq v} \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle n | H^{(1)} | m \rangle \langle p | H^{(1)} | n \rangle}{(v-m)(v-n)(v-p)} \right. \\
& + \sum_{n \neq v} \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle n | H^{(1)} | m \rangle \langle p | H^{(1)} | n \rangle}{(v-l)(v-m)(v-n)(v-p)} \\
& + \sum_{n \neq v} \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle n | H^{(1)} | m \rangle \langle p | H^{(1)} | n \rangle}{(v-k)(v-l)(v-m)(v-n)(v-p)} \\
& \left. + \sum_{n \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle n | H^{(1)} | m \rangle \langle p | H^{(1)} | n \rangle}{(v-k)(v-m)(v-n)(v-p)} \right]
\end{aligned}$$

$$\begin{aligned}
& - \sum_{n \neq v} \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle n | H^{(1)} | m \rangle \langle p | H^{(1)} | n \rangle}{(v-m)^2(v-n)(v-p)} \\
& - \sum_{n \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(1)} | m \rangle \langle p | H^{(1)} | n \rangle}{(v-k)(v-m)^2(v-n)(v-p)} \\
& - \sum_{n \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle n | H^{(1)} | k \rangle \langle p | H^{(1)} | n \rangle}{(v-k)(v-n)^2(v-p)} \\
& - \sum_{n \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle l | H^{(1)} | v \rangle \langle n | H^{(1)} | l \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle p | H^{(1)} | n \rangle}{(v-k)(v-l)(v-n)^2(v-p)} \\
& - \sum_{n \neq v} \frac{\langle n | H^{(2)} | v \rangle \langle v | H^{(2)} | v \rangle \langle p | H^{(1)} | n \rangle}{(v-n)^2(v-p)} \\
& - \sum_{n \neq v} \sum_{k \neq v} \frac{(\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(2)} | v \rangle \langle p | H^{(1)} | n \rangle}{(v-k)(v-n)^2(v-p)} \\
& + \sum_{n \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle n | H^{(2)} | l \rangle \langle l | H^{(1)} | k \rangle \langle p | H^{(1)} | n \rangle}{(v-k)(v-l)(v-n)(v-p)} \\
& + \sum_{n \neq v} \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle n | H^{(2)} | l \rangle \langle p | H^{(1)} | n \rangle}{(v-n)(v-l)(v-p)} \\
& + \sum_{n \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle n | H^{(3)} | k \rangle \langle p | H^{(1)} | n \rangle}{(v-k)(v-n)(v-p)} + \sum_{n \neq v} \frac{\langle n | H^{(4)} | v \rangle \langle p | H^{(1)} | n \rangle}{(v-n)(v-p)} \\
& + \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle p | H^{(2)} | m \rangle}{(v-m)(v-p)} \\
& + \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle p | H^{(2)} | m \rangle}{(v-k)(v-l)(v-m)(v-p)} \\
& + \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle p | H^{(2)} | m \rangle}{(v-l)(v-m)(v-p)} \\
& + \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle p | H^{(2)} | m \rangle}{(v-k)(v-m)(v-p)} \\
& - \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle p | H^{(2)} | m \rangle}{(v-m)^2(v-p)} \\
& - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle p | H^{(2)} | m \rangle}{(v-k)(v-m)^2(v-p)} \\
& + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle p | H^{(3)} | l \rangle}{(v-k)(v-l)(v-p)} + \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle p | H^{(3)} | l \rangle}{(v-l)(v-p)} \\
& + \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle p | H^{(4)} | k \rangle}{(v-k)(v-p)} - \frac{\langle p | H^{(3)} | v \rangle \langle v | H^{(2)} | v \rangle}{(v-p)^2}
\end{aligned}$$

$$\begin{aligned}
& + \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle p | H^{(2)} | m \rangle}{(v-k)(v-l)(v-m)(v-p)} \\
& + \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle p | H^{(2)} | m \rangle}{(v-l)(v-m)(v-p)} \\
& + \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle p | H^{(2)} | m \rangle}{(v-k)(v-m)(v-p)} \\
& - \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle p | H^{(2)} | m \rangle}{(v-m)^2(v-p)} \\
& - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle p | H^{(2)} | m \rangle}{(v-k)(v-m)^2(v-p)} \\
& + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle p | H^{(3)} | l \rangle}{(v-k)(v-l)(v-p)} + \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle p | H^{(3)} | l \rangle}{(v-l)(v-p)} \\
& + \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle p | H^{(4)} | k \rangle}{(v-k)(v-p)} - \frac{\langle p | H^{(3)} | v \rangle \langle v | H^{(2)} | v \rangle}{(v-p)^2} \\
& - \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle p | H^{(1)} | l \rangle \langle v | H^{(2)} | v \rangle}{(v-k)(v-l)(v-p)^2} \\
& - \sum_{l \neq v} \frac{\langle p | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle v | H^{(2)} | v \rangle}{(v-l)(v-p)^2} \\
& - \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle p | H^{(2)} | k \rangle \langle v | H^{(2)} | v \rangle}{(v-k)(v-p)^2} + \frac{\langle p | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle^2}{(v-p)^3} \\
& + \sum_{k \neq v} \frac{\langle p | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle v | H^{(2)} | v \rangle}{(v-k)(v-p)^3} - \sum_{m \neq v} \frac{\langle p | H^{(3)} | v \rangle (\langle m | H^{(1)} | v \rangle)^2}{(v-p)^2(v-m)} \\
& - \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle p | H^{(1)} | l \rangle (\langle m | H^{(1)} | v \rangle)^2}{(v-k)(v-l)(v-p)^2(v-m)} \\
& - \sum_{m \neq v} \sum_{l \neq v} \frac{\langle p | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle (\langle m | H^{(1)} | v \rangle)^2}{(v-l)(v-p)^2(v-m)} \\
& - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle p | H^{(2)} | k \rangle (\langle m | H^{(1)} | v \rangle)^2}{(v-k)(v-p)^2(v-m)} \\
& - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle p | H^{(2)} | k \rangle (\langle m | H^{(1)} | v \rangle)^2}{(v-k)(v-p)^2(v-m)} \\
& + \sum_{m \neq v} \frac{\langle p | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle (\langle m | H^{(1)} | v \rangle)^2}{(v-m)(v-p)^3} \\
& + \sum_{m \neq v} \sum_{k \neq v} \frac{\langle p | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 (\langle m | H^{(1)} | v \rangle)^2}{(v-m)(v-k)(v-p)^3}
\end{aligned}$$

$$\begin{aligned}
& - \frac{\langle v | H^{(4)} | v \rangle \langle p | H^{(1)} | v \rangle}{(v-p)^2} - 2 \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle v | H^{(1)} | m \rangle \langle p | H^{(1)} | v \rangle}{(v-m)(v-p)^2} \\
& - \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle v | H^{(1)} | m \rangle \langle p | H^{(1)} | v \rangle}{(v-k)(v-l)(v-m)(v-p)^2} \\
& - 2 \sum_{l \neq v} \sum_{k \neq v} \frac{\langle l | H^{(1)} | k \rangle \langle k | H^{(2)} | v \rangle \langle v | H^{(1)} | l \rangle \langle p | H^{(1)} | v \rangle}{(v-l)(v-k)(v-p)^2} \\
& - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle v | H^{(1)} | m \rangle \langle p | H^{(1)} | v \rangle}{(v-k)(v-m)(v-p)^2} \\
& + \sum_{m \neq v} \frac{(\langle m | H^{(1)} | v \rangle)^2 \langle v | H^{(2)} | v \rangle \langle p | H^{(1)} | v \rangle}{(v-m)^2(v-p)^2} \\
& + \sum_{m \neq v} \sum_{k \neq v} \frac{(\langle m | H^{(1)} | v \rangle)^2 (\langle k | H^{(1)} | v \rangle)^2 \langle p | H^{(1)} | v \rangle}{(v-k)(v-m)^2(v-p)^2} \\
& - \sum_{l \neq v} \frac{(\langle l | H^{(2)} | v \rangle)^2 \langle p | H^{(1)} | v \rangle}{(v-l)(v-p)^2} ] \Psi_p^{(0)}
\end{aligned} \tag{4.44}$$

#### 4.1.8 The sixth-order correction to the energy and to the wave function

We start by define the wave function  $\Psi_v^{(6)}$  as the following linear combination:

$$\Psi_v^{(6)} = \sum_{q \neq v} \alpha_q \Psi_q^{(0)} \tag{4.45}$$

Before to solve the correction energy to the sixth-order, we just note that the Wigner's  $2n+1$  rule stipulates that the  $2n+1^{st}$  energy derivatives can be determined when knowing the energy up to  $n^{th}$ -order. So, in our case we just didn't need to seek the sixth-order correction of the wavefunction. In this last part of the development, only the energy correction will be exposed. Using equation 4.8 and putting equation 4.45 in the latter as well as 4.17, 4.23, 4.29, 4.37 and 4.44, we obtain:

$$\begin{aligned}
\sum_{q \neq v} \alpha_q (q-v) |q\rangle &= \sum_{p \neq v} \alpha_p (E_p^{(1)} - H^{(1)}) |p\rangle + \sum_{n \neq v} \alpha_n (E_v^{(2)} - H^{(2)}) |n\rangle \\
&+ \sum_{m \neq v} \alpha_m (E_v^{(3)} - H^{(3)}) |m\rangle + \sum_{l \neq v} \alpha_l (E_v^{(4)} - H^{(4)}) |l\rangle \\
&+ \sum_{k \neq v} \alpha_k (E_v^{(5)} - H^{(5)}) |k\rangle + (E_v^{(6)} - H^{(6)}) |v\rangle
\end{aligned} \tag{4.46}$$



Now, we just have to allocate the wavefunction  $\langle v|$  to equation (4.46),

$$\begin{aligned}
\sum_{q \neq v} \alpha_q (q - v) \langle v|q\rangle &= \sum_{p \neq v} \alpha_p \langle v| (E_v^{(1)} - H^{(1)}) |p\rangle + \sum_{n \neq v} \alpha_n \langle v| (E_v^{(2)} - H^{(2)}) |n\rangle \\
&+ \sum_{m \neq v} \alpha_m \langle v| (E_v^{(3)} - H^{(3)}) |m\rangle + \sum_{l \neq v} \alpha_l \langle v| (E_v^{(4)} - H^{(4)}) |l\rangle \\
&+ \sum_{k \neq v} \alpha_k \langle v| (E_v^{(5)} - H^{(5)}) |k\rangle + \langle v| (E_v^{(6)} - H^{(6)}) |v\rangle \\
\sum_{q \neq v} \alpha_q (q - v) \langle v|q\rangle &= \sum_{p \neq v} \alpha_p E_v^{(1)} \langle v|p\rangle - \sum_{p \neq v} \alpha_p \langle v| H^{(1)} |p\rangle + \sum_{n \neq v} \alpha_n E_v^{(2)} \langle v|n\rangle \\
&- \sum_{n \neq v} \alpha_n \langle v| H^{(2)} |n\rangle + \sum_{m \neq v} \alpha_m E_v^{(3)} \langle v|m\rangle - \sum_{m \neq v} \alpha_m \langle v| H^{(3)} |m\rangle \\
&+ \sum_{l \neq v} \alpha_l E_v^{(4)} \langle v|l\rangle - \sum_{l \neq v} \alpha_l \langle v| H^{(4)} |l\rangle + \sum_{k \neq v} \alpha_k E_v^{(5)} \langle v|k\rangle \\
&- \sum_{k \neq v} \alpha_k \langle v| H^{(5)} |k\rangle + E_v^{(6)} \langle v|v\rangle - \langle v| H^{(6)} |v\rangle \tag{4.47}
\end{aligned}$$

Let's reduce the equation thanks with the following equalities:  $\langle v|p\rangle$ ,  $\langle v|n\rangle$ ,  $\langle v|m\rangle$ ,  $\langle v|l\rangle$  and  $\langle v|k\rangle$  are equal to zero and  $\langle v|v\rangle = 1$ , the simplification lead to,

$$\begin{aligned}
0 &= - \sum_{p \neq v} \alpha_p \langle v| H^{(1)} |p\rangle - \sum_{n \neq v} \alpha_n \langle v| H^{(2)} |n\rangle - \sum_{m \neq v} \alpha_m \langle v| H^{(3)} |m\rangle \\
&- \sum_{l \neq v} \alpha_l \langle v| H^{(4)} |l\rangle - \sum_{k \neq v} \alpha_k \langle v| H^{(5)} |k\rangle + E_v^{(6)} - \langle v| H^{(6)} |v\rangle \\
E_v^{(6)} &= \sum_{p \neq v} \alpha_p \langle v| H^{(1)} |p\rangle + \sum_{n \neq v} \alpha_n \langle v| H^{(2)} |n\rangle + \sum_{m \neq v} \alpha_m \langle v| H^{(3)} |m\rangle \\
&+ \sum_{l \neq v} \alpha_l \langle v| H^{(4)} |l\rangle + \sum_{k \neq v} \alpha_k \langle v| H^{(5)} |k\rangle + \langle v| H^{(6)} |v\rangle
\end{aligned}$$

Moreover, thanks to the knowledge of all constants, we finally get the result of the sixth-order correction of the energy,

$$\begin{aligned}
E_v^{(6)} = & \langle v | H^{(6)} | v \rangle + \sum_{p \neq v} \frac{\langle p | H^{(5)} | v \rangle \langle v | H^{(1)} | p \rangle}{(v-p)} \\
& + \sum_{p \neq v} \sum_{n \neq v} \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle n | H^{(1)} | m \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-m)(v-n)(v-p)} \\
& + \sum_{p \neq v} \sum_{n \neq v} \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle n | H^{(1)} | m \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-l)(v-m)(v-n)(v-p)} \\
& + \sum_{p \neq v} \sum_{n \neq v} \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle n | H^{(1)} | m \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-l)(v-m)(v-n)(v-p)} \\
& + \sum_{p \neq v} \sum_{n \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle n | H^{(1)} | m \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-m)(v-n)(v-p)} \\
& - \sum_{p \neq v} \sum_{n \neq v} \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle n | H^{(1)} | m \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-m)^2(v-n)(v-p)} \\
& - \sum_{p \neq v} \sum_{n \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(1)} | m \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-m)^2(v-n)(v-p)} \\
& - \sum_{p \neq v} \sum_{n \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle n | H^{(1)} | k \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-n)^2(v-p)} \\
& - \sum_{p \neq v} \sum_{n \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle l | H^{(1)} | v \rangle \langle n | H^{(1)} | l \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-l)(v-n)^2(v-p)} \\
& - \sum_{p \neq v} \sum_{n \neq v} \frac{\langle n | H^{(2)} | v \rangle \langle v | H^{(2)} | v \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-n)^2(v-p)} \\
& - \sum_{p \neq v} \sum_{n \neq v} \sum_{k \neq v} \frac{(\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(2)} | v \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-n)^2(v-p)} \\
& + \sum_{p \neq v} \sum_{n \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle n | H^{(2)} | l \rangle \langle l | H^{(1)} | k \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-l)(v-n)(v-p)} \\
& + \sum_{p \neq v} \sum_{n \neq v} \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle n | H^{(2)} | l \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-n)(v-l)(v-p)} \\
& + \sum_{p \neq v} \sum_{n \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle n | H^{(3)} | k \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-n)(v-p)} \\
& + \sum_{p \neq v} \sum_{n \neq v} \frac{\langle n | H^{(4)} | v \rangle \langle p | H^{(1)} | n \rangle \langle v | H^{(1)} | p \rangle}{(v-n)(v-p)} \\
& + \sum_{p \neq v} \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle p | H^{(2)} | m \rangle \langle v | H^{(1)} | p \rangle}{(v-m)(v-p)}
\end{aligned}$$

$$\begin{aligned}
& + \sum_{p \neq v} \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle p | H^{(2)} | m \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-l)(v-m)(v-p)} \\
& + \sum_{p \neq v} \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle p | H^{(2)} | m \rangle \langle v | H^{(1)} | p \rangle}{(v-l)(v-m)(v-p)} \\
& + \sum_{p \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle p | H^{(2)} | m \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-m)(v-p)} \\
& - \sum_{p \neq v} \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle p | H^{(2)} | m \rangle \langle v | H^{(1)} | p \rangle}{(v-m)^2(v-p)} \\
& - \sum_{p \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle p | H^{(2)} | m \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-m)^2(v-p)} \\
& + \sum_{p \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle p | H^{(3)} | l \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-l)(v-p)} \\
& + \sum_{p \neq v} \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle p | H^{(3)} | l \rangle \langle v | H^{(1)} | p \rangle}{(v-l)(v-p)} \\
& + \sum_{p \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle p | H^{(4)} | k \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-p)} - \sum_{p \neq v} \frac{\langle p | H^{(3)} | v \rangle \langle v | H^{(2)} | v \rangle \langle v | H^{(1)} | p \rangle}{(v-p)^2} \\
& - \sum_{p \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle p | H^{(1)} | l \rangle \langle v | H^{(2)} | v \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-l)(v-p)^2} \\
& - \sum_{p \neq v} \sum_{l \neq v} \frac{\langle p | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle v | H^{(2)} | v \rangle \langle v | H^{(1)} | p \rangle}{(v-l)(v-p)^2} \\
& - \sum_{p \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle p | H^{(2)} | k \rangle \langle v | H^{(2)} | v \rangle \langle v | H^{(1)} | p \rangle}{(v-k)(v-p)^2} \\
& + \sum_{p \neq v} \frac{(\langle p | H^{(1)} | v \rangle)^2 (\langle v | H^{(2)} | v \rangle)^2}{(v-p)^3} \\
& + \sum_{p \neq v} \sum_{k \neq v} \frac{(\langle p | H^{(1)} | v \rangle)^2 (\langle k | H^{(1)} | v \rangle)^2 \langle v | H^{(2)} | v \rangle}{(v-k)(v-p)^3} \\
& - \sum_{p \neq v} \sum_{m \neq v} \frac{\langle p | H^{(3)} | v \rangle (\langle m | H^{(1)} | v \rangle)^2 \langle v | H^{(1)} | p \rangle}{(v-p)^2(v-m)} \\
& - \sum_{p \neq v} \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle p | H^{(1)} | l \rangle (\langle m | H^{(1)} | v \rangle)^2 \langle v | H^{(1)} | p \rangle}{(v-k)(v-l)(v-p)^2(v-m)} \\
& - \sum_{p \neq v} \sum_{m \neq v} \sum_{l \neq v} \frac{\langle p | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle (\langle m | H^{(1)} | v \rangle)^2 \langle v | H^{(1)} | p \rangle}{(v-l)(v-p)^2(v-m)}
\end{aligned}$$

$$\begin{aligned}
& - \sum_{p \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle p | H^{(2)} | k \rangle (\langle m | H^{(1)} | v \rangle)^2 \langle v | H^{(1)} | p \rangle}{(v-k)(v-p)^2(v-m)} \\
& + \sum_{p \neq v} \sum_{m \neq v} \frac{(\langle p | H^{(1)} | v \rangle)^2 \langle v | H^{(2)} | v \rangle (\langle m | H^{(1)} | v \rangle)^2}{(v-m)(v-p)^3} \\
& + \sum_{p \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{(\langle p | H^{(1)} | v \rangle)^2 (\langle k | H^{(1)} | v \rangle)^2 (\langle m | H^{(1)} | v \rangle)^2}{(v-m)(v-k)(v-p)^3} \\
& - \sum_{p \neq v} \frac{\langle v | H^{(4)} | v \rangle (\langle v | H^{(1)} | p \rangle)^2}{(v-p)^2} \\
& - 2 \sum_{p \neq v} \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle v | H^{(1)} | m \rangle (\langle v | H^{(1)} | p \rangle)^2}{(v-m)(v-p)^2} \\
& - \sum_{p \neq v} \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle v | H^{(1)} | m \rangle (\langle v | H^{(1)} | p \rangle)^2}{(v-k)(v-l)(v-m)(v-p)^2} \\
& - 2 \sum_{p \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle l | H^{(1)} | k \rangle \langle k | H^{(2)} | v \rangle \langle v | H^{(1)} | l \rangle (\langle v | H^{(1)} | p \rangle)^2}{(v-l)(v-k)(v-p)^2} \\
& - \sum_{p \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle v | H^{(1)} | m \rangle (\langle v | H^{(1)} | p \rangle)^2}{(v-k)(v-m)(v-p)^2} \\
& + \sum_{p \neq v} \sum_{m \neq v} \frac{(\langle m | H^{(1)} | v \rangle)^2 \langle v | H^{(2)} | v \rangle (\langle v | H^{(1)} | p \rangle)^2}{(v-m)^2(v-p)^2} \\
& + \sum_{p \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{(\langle m | H^{(1)} | v \rangle)^2 (\langle k | H^{(1)} | v \rangle)^2 (\langle v | H^{(1)} | p \rangle)^2}{(v-k)(v-m)^2(v-p)^2} \\
& - \sum_{p \neq v} \sum_{l \neq v} \frac{(\langle l | H^{(2)} | v \rangle)^2 (\langle p | H^{(1)} | v \rangle)^2}{(v-l)(v-p)^2} \\
& + \sum_{n \neq v} \sum_{m \neq v} \frac{\langle m | H^{(3)} | v \rangle \langle n | H^{(1)} | m \rangle \langle v | H^{(2)} | n \rangle}{(v-m)(v-n)} \\
& + \sum_{n \neq v} \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle n | H^{(1)} | m \rangle \langle v | H^{(2)} | n \rangle}{(v-l)(v-m)(v-n)} \\
& + \sum_{n \neq v} \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle n | H^{(1)} | m \rangle \langle v | H^{(2)} | n \rangle}{(v-k)(v-l)(v-m)(v-n)} \\
& + \sum_{n \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle n | H^{(1)} | m \rangle \langle v | H^{(2)} | n \rangle}{(v-k)(v-m)(v-n)} \\
& - \sum_{n \neq v} \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle n | H^{(1)} | m \rangle \langle v | H^{(2)} | n \rangle}{(v-m)^2(v-n)}
\end{aligned}$$

$$\begin{aligned}
& - \sum_{n \neq v} \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(1)} | m \rangle \langle v | H^{(2)} | n \rangle}{(v-k)(v-m)^2(v-n)} \\
& - \sum_{n \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle n | H^{(1)} | k \rangle \langle v | H^{(2)} | n \rangle}{(v-k)(v-n)^2} \\
& - \sum_{n \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{(\langle k | H^{(1)} | v \rangle)^2 \langle n | H^{(1)} | l \rangle \langle l | H^{(1)} | v \rangle \langle v | H^{(2)} | n \rangle}{(v-k)(v-l)(v-n)^2} \\
& - \sum_{n \neq v} \frac{(\langle n | H^{(2)} | v \rangle)^2 \langle v | H^{(2)} | v \rangle}{(v-n)^2} - \sum_{n \neq v} \sum_{k \neq v} \frac{(\langle k | H^{(1)} | v \rangle)^2 (\langle n | H^{(2)} | v \rangle)^2}{(v-k)(v-n)^2} \\
& + \sum_{n \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle n | H^{(2)} | l \rangle \langle l | H^{(1)} | k \rangle \langle v | H^{(2)} | n \rangle}{(v-k)(v-l)(v-n)} \\
& + \sum_{n \neq v} \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle n | H^{(2)} | l \rangle \langle v | H^{(2)} | n \rangle}{(v-l)(v-n)} \\
& + \sum_{n \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle n | H^{(3)} | k \rangle \langle v | H^{(2)} | n \rangle}{(v-k)(v-n)} + \sum_{n \neq v} \frac{\langle n | H^{(4)} | v \rangle \langle v | H^{(2)} | n \rangle}{(v-n)} \\
& + \sum_{m \neq v} \frac{(\langle m | H^{(3)} | v \rangle)^2}{(v-m)} \\
& + \sum_{m \neq v} \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle m | H^{(1)} | l \rangle \langle v | H^{(3)} | m \rangle}{(v-k)(v-l)(v-m)} \\
& + \sum_{m \neq v} \sum_{l \neq v} \frac{\langle m | H^{(1)} | l \rangle \langle l | H^{(2)} | v \rangle \langle v | H^{(3)} | m \rangle}{(v-l)(v-m)} \\
& + \sum_{m \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle m | H^{(2)} | k \rangle \langle v | H^{(3)} | m \rangle}{(v-k)(v-m)} \\
& - \sum_{m \neq v} \frac{\langle m | H^{(1)} | v \rangle \langle v | H^{(2)} | v \rangle \langle v | H^{(3)} | m \rangle}{(v-m)^2} \\
& - \sum_{m \neq v} \sum_{k \neq v} \frac{\langle m | H^{(1)} | v \rangle (\langle k | H^{(1)} | v \rangle)^2 \langle v | H^{(3)} | m \rangle}{(v-k)(v-m)^2} \\
& + \sum_{l \neq v} \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle l | H^{(1)} | k \rangle \langle v | H^{(4)} | l \rangle}{(v-k)(v-l)} + \sum_{l \neq v} \frac{\langle l | H^{(2)} | v \rangle \langle v | H^{(4)} | l \rangle}{(v-l)} \\
& + \sum_{k \neq v} \frac{\langle k | H^{(1)} | v \rangle \langle v | H^{(5)} | k \rangle}{(v-k)}
\end{aligned} \tag{4.48}$$

## 5 Applications

### 5.1 Introduction

The study of the electronic structures of molecules requires the knowledge of the solutions of the SCHRÖDINGER equation at stationary states. The impossibility of reaching the analytical solutions of this integrodifferential equation has led theoretical chemists to develop a strategy and a set of methods that allow the main observables to be reached and calculated with a precision that continues to increase with the development of computational tools.

In the BORN-OPPENHEIMER approximation, the fundamental assumption is the independent particle model, which proposes to write an eigenfunction of the adiabatic electronic Hamiltonian (stationary state) at zero order as a product of functions depending on only one electronic variable (spin-orbit). This hypothesis completed, on the one hand, by the necessity to antisymmetrize the simple product of spin-orbitals, and on the other hand, by the adoption of the model of the double occupation of space functions, is the foundation of the SCF model whose objective is the determination of molecular orbitals.

In particular, the context of the RHF (Restricted Hartree Fock) methods makes it possible to account for multi-electron interactions by a model which stipulates that each electron is in an average field of the others (independent particle model) and this always within the context of the hypothesis of the double occupation of the molecular orbitals.

From these approximations results an error on the evaluation of the electronic energy which, while being small (a few percent of the total electronic energy) has disastrous consequences on the calculation of values such as the electronic energy, the binding energy, the description of the vibrational properties of the electronic states...

This deficiency of the monodeterminant approximation can be simply highlighted through the formalism of the density matrices directly involved in the HF expression of the total electronic energy (annex 7.1). In particular, the physical interpretation of the second order density function leads to the following conclusions:

- The probability of two simultaneous events is equal to the product of the isolated events: the events are not correlated
- In the context of the approximation imposing the double occupation of molecular orbitals, this result has serious consequences, i.e. the probability of finding two electrons with antiparallel spins in an element with a limited volume is not zero because the two electrons are not correlated (Coulomb hole): this possibility is, of course, impossible. This explains why the double occupancy hypothesis and the independent particle model have obvious defects. The correct description of the correlation effects, mentioned above, is one of the main obstacles in theoretical chemistry.

As opposed to the Restricted Hartree-Fock (RHF) solution which corresponds, as we have just recalled, to the description of a Slater determinant made up of  $N/2$  doubly occupied orbitals (the other orbitals being empty), the exact solution that we are trying to describe by taking into account the correlation is in fact made up of an infinite number of configurations that can be seen as excitations with respect to the  $N$ -electron RHF determinant in an infinitely large basis. Obviously, it is impossible to work in a complete or infinite basis. Various methods are then proposed by theoretical chemists to evaluate this correlation as accurately as possible. Three types of approach are used:

- Methods that aim to solve the Schrödinger eigenstate equation variationally using a Slater determinant or configuration basis. These are Configuration Interaction (C.I.) approaches,
- Perturbational methods require the definition of a minimal basis and a partition of the Hamiltonian operator adapted to ensure the convergence of the perturbational series in a Rayleigh-Schrodinger type approach (a method we will discuss in chapter 4),
- The pairing methods, which consist of evaluating the correlation energy of electron pairs assumed to be without interactions (Independent Electron Pair Approximation - IEPA) or interacting (Coupled Pair Theory).

All these approaches have in common that they build the basis for the development of the searched function from single-electron functions optimised at the Hartree-Fock level (generally ground-state monodeterminant).

In contrast, in Multi Configurational Self Consistent Field (MCSCF) methods the objective is to variationally optimise both the single-electron functions used and the multi-configurational development of the eigenfunction of the electronic Hamiltonian.

Among the numerous developments proposed, the Complete Active Space Self Consistent Field (CASSCF) approaches that we have used in this work<sup>[1-4]</sup> lead to the development of the multiconfigurational wave function on the totality of the configurations generated by the set of all possible excitations in a restricted space of occupied molecular orbitals and virtual molecular orbitals (active space).

The aim of this chapter is not, as you will have understood, to present the mathematical details of all these calculation methods, but rather to set out the general considerations for applying these approaches when describing one or more electronic states of more or less strongly correlated electrons. Thus, in a system where static correlation is not involved, the RHF determinant remains a relatively good approximation for the description of the wave function. The addition of a method taking into account the dynamic correlation is done with respect to this determinant (as for the DFT, CCSD(T) ... methods). The RHF determinant is considered as the reference determinant. Conversely, in the case of a system of strongly correlated electrons, several Slater determinants must be taken into account to describe this state. The wave function

used is most often a CAS wave function and the dynamic correlation is taken into account on the latter. As this CAS wave function is made up of several determinants, the system has several references. The term Multi-Reference (MR) thus translates the fact of taking into account the dynamic correlation on several reference determinants. The problem of MR methods is multiple. Firstly, the choice of references is not always obvious. As mentioned, the choice is usually made for a CAS wave function as a starting point, which is dependent on the chosen active space. Secondly, the fact of having several references leads to a great complexity in the consideration of the dynamic correlation. The choice of a perturbation treatment of the MBPT (Many Body Perturbation Theory) type at second order remains probably the most accessible and the most used. We have therefore chosen, in this work, to use the  $2^{nd}$  order perturbation method based on the Møller-Plesset (MP2) type partition, implemented by Anderson and al<sup>[5,6]</sup> from a simple multiconfiguration reference function resulting from a CASSCF calculation. This method is known as CASPT2 (Complete Active Space  $2^{nd}$  Order Perturbation Theory).<sup>[5-9]</sup> If, as we will see in chapter 5.2 and chapter 5.3 of this work, the results are in general of high numerical accuracy, they can only be carried out on the smallest of molecular systems containing no more than a dozen atoms. The study of higher dimensional systems requires the use of faster approaches, although more approximate.

The BS (Broken-Symmetry) approach is one of the approaches that allows the study of higher dimensional systems and is among the most widely used to "estimate" the energy of multi-configuration states in Kohn-Sham DFT. Indeed, its implementation does not require any additional methodological input to that commonly found in a standard quantum chemistry program. The principle is to approximate the "multi-determinant" state by a single Slater determinant, which thus allows the use of DFT-KS. This determinant, which is not an eigenvector of the  $S^2$  operator, is called broken symmetry (BS). The only way to obtain such a determinant is to use the unrestricted formalism. This formalism allows the space parts of the  $\alpha$  and  $\beta$  orbitals to be different, unlike the restricted formalism. Nevertheless, this formalism suffers from the spin contamination problem which limits the accuracy of such an approach compared to the multi-determinant approaches mentioned above. The Yamaguchi method<sup>[10-12]</sup> is the most widely used BS approach at present.

The simplest open shell state consists of two electrons located in two orbitals leading to the description of a singlet state (called "OSS" for Open Shell System) and a triplet state. The Yamaguchi method is based on the approximation that the unique determinant BS sought is a pure linear combination between the singlet and triplet states and that the spin polarisation introduced by the unrestricted formalism is negligible in the triplet state. The BS determinant can thus be expressed very easily and cheaply, such that:

$$\Psi_{BS} = \lambda\Psi_S + \mu\Psi_T \quad (5.1)$$

with  $\lambda$  et  $\mu$  such as  $\lambda^2 + \mu^2 = 1$ . The energy of this determinant can be expressed as:

$$E_{BS} = \lambda^2 E_S + \mu^2 E_T \quad (5.2)$$



The average value of the operator  $\hat{S}^2$ , in the case of the above approximations, is given by:

$$\begin{aligned}\langle \Psi_{BS} | \hat{S}^2 | \Psi_{BS} \rangle &= \langle \lambda \Psi_S + \mu \Psi_T | \hat{S}^2 | \lambda \Psi_S + \mu \Psi_T \rangle \\ &= \lambda^2 \langle \Psi_S | \hat{S}^2 | \Psi_S \rangle + \mu^2 \langle \Psi_T | \hat{S}^2 | \Psi_T \rangle + 2\lambda\mu \langle \Psi_S | \hat{S}^2 | \Psi_T \rangle \\ &= \mu^2 \langle \hat{S}^2 \rangle_T\end{aligned}\tag{5.3}$$

Hence,

$$\lambda^2 = 1 - \frac{\langle \hat{S}^2 \rangle_{BS}}{\langle \hat{S}^2 \rangle_T}\tag{5.4}$$

$$\mu^2 = \frac{\langle \hat{S}^2 \rangle_{BS}}{\langle \hat{S}^2 \rangle_T}\tag{5.5}$$

The energy of the BS determinant can thus be very easily expressed as:

$$E_{BS} = \left(1 - \frac{\langle \hat{S}^2 \rangle_{BS}}{\langle \hat{S}^2 \rangle_T}\right) E_S + \frac{\langle \hat{S}^2 \rangle_{BS}}{\langle \hat{S}^2 \rangle_T} E_T\tag{5.6}$$

Let for  $E_S$ ,

$$E_S = \frac{\langle \hat{S}^2 \rangle_T}{\langle \hat{S}^2 \rangle_T - \langle \hat{S}^2 \rangle_{BS}} (E_{BS} - \frac{\langle \hat{S}^2 \rangle_{BS}}{\langle \hat{S}^2 \rangle_T} E_T)\tag{5.7}$$

Another advantage of these approaches is that it is generally accepted that for the most classical functionals in the molecular domain (hybrid-Generalized Gradient Approximation (GGA) such as B3LYP, PBE0, etc.), the BS approach with the Yamaguchi formula represents the OSS state more or less correctly and at lower computational cost.<sup>[10-12]</sup>

Despite this, we should not forget the main limitation of this approach. One is entitled to ask what is the meaning of using the mean value of the  $\hat{S}^2$  operator in DFT. Indeed, this value is most often calculated as in wave function theory on the determinant KS by a 2-body operator. This determinant is that of a fictitious system without interaction and this average value should normally be calculated on the wave function of the real system. Experience shows that the BS method is effective when the difference between the average value obtained for the KS determinant and the real system is small, which is unfortunately not often the case. Even a very limited estimation of the CASPT2 and BS-KS states obtained in this work (chapter 5.2 and 5.3) for the study of the OSS states of nitrene molecules and their reaction paths shows the weakness of the BS approach when the energies of the singlet and triplet electronic states are quasi-degenerate. However, the BS approach remains by default one of the standard approaches to describe a multi-configurational system in DFT-KS. Contrary to CASPT2 type approaches, one can find a very large number of applications of the BS method in the literature, for both organic and inorganic molecules and for all system sizes.

A last alternative to the BS method exists in DFT but for which the Palois group has no

experience. This is the Spin-Flip approach.<sup>[13]</sup> Time-Dependent DFT (TD-DFT) is well known for its application to excited states. Shao, Head-Gordon and Krylov have proposed an approach to calculate low spin and open shell states using TD-DFT. In a very general way, the principle is to calculate the state of the triplet  $m_s = 1$  (unrestricted formalism) and make a time-dependent perturbation with a spin flip. In this way, we obtain all the mono-excitations with a spin change. The aim is to obtain *in fine* the states characterised by the determinants  $m_s = 0$  allowing to describe correctly the low spin state.

## 5.2 Rearrangements of Aromatic Nitriles Oxides and Nitriles Ylides. Potential Ring Expansion to Cycloheptatetraene Derivatives Mimicking Arylcarbenes

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**Abstract:** Nitrile imines, nitrile oxides and nitrile ylides are widely used in 1,3-dipolar cycloaddition reactions. They also undergo thermal and photochemical rearrangements to carbodiimides, isocyanates, and ketenimines, respectively. Calculations at DFT and CASPT2 levels of theory reveal novel, potential rearrangements, in which the aromatic 1,3-dipoles mimic phenylcarbene and undergo ring expansion to cycloheptatetraene derivatives. These rearrangements can potentially take place in both the singlet ground states and the triplet excited states, and they are accelerated by *m,m'*-bis(dimethylamino) substitution on the phenyl moieties. The new rearrangement becomes the energetically preferred path for *m,m'*-bis(dimethylamino)benzoxonitrile oxide in the triplet state. In the *m,m'*-bis(dimethylamino)benzo nitrile ylide, the cyclization to the 2-phenyl-1-azirine is favoured over the ring expansion to a cycloheptatetraene by ca. 5 Kcal/mol in the singlet state. In the bent triplet states, 1,3-hydrogen shifts interconverting nitrile ylides are potentially possible.

### Introduction

Nitrile imines, nitrile oxides and nitrile ylides are widely used 1,3-dipoles employed in numerous cycloaddition reactions to produce five-membered heterocyclic compounds.<sup>[14–17]</sup> In addition, their electronic structures and the mechanisms of their reactions are of continuing theoretical interest.<sup>[18–24]</sup> Six basic structures are commonly formulated: propargylic, allenic, carbenic, 1,3-dipolar, reverse 1,3-dipolar, and 1,3-diradical forms (Figure 5.1), but their relative energies are highly substituent-dependent, and one particular mesomer may dominate for individual molecules, thereby making it the minimum energy structure. Based on their calculated and spectroscopic properties, nitrile imines can be divided into predominantly propargylic, allenic,<sup>[25,26]</sup> and carbenic forms.<sup>[27–29]</sup>

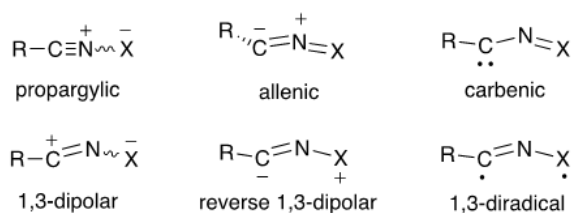
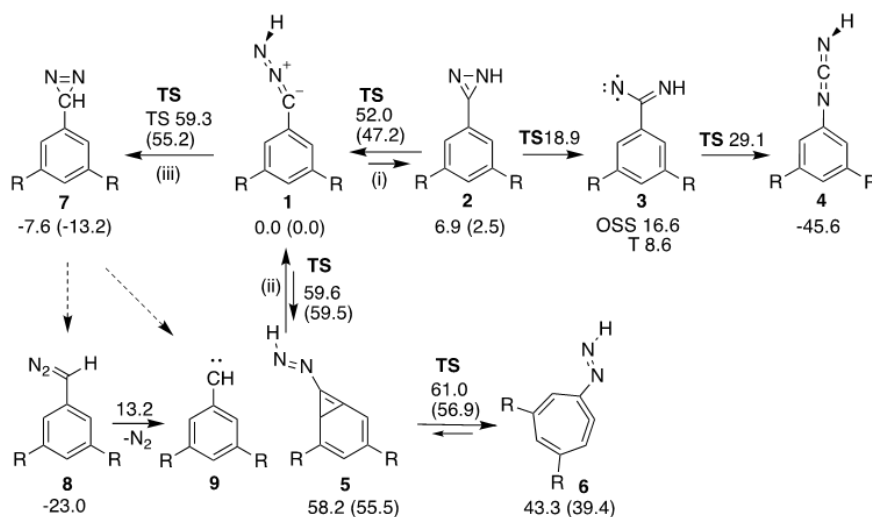


Figure 5.1: Six fundamental valence tautomers of nitrilium betaines (nitrile imines, X = NR'; nitrile oxides, X = O; nitrile ylides, X = CR'R'')

In the case of nitrile imines **1**, several types of rearrangement, depicted in Scheme 5.1, are known. Here, the rearrangement to carbodiimides **4** is commonly observed under both thermal (Flash Vacuum Pyrolysis, FVP) and photochemical conditions.



Scheme 5.1: Rearrangements of nitrile imines. Relative energies in Kcal/mol for R = H at the DFT and (CASPT2) levels of theory.<sup>[30]</sup>

The reaction (route (i)) takes place via a diazirine **2** and an imidoylnitrene **3**.<sup>[31,32]</sup> We will refer to route (i) as the “classical” route. Route (ii) is the recently described<sup>[30,33]</sup> ring expansion, in which the nitrile imine behaves like an arylcarbene, cyclizing to the cyclopropene derivative **5** and ring expanding to the cycloheptatetraene **6**. There is a third potential route (iii) yielding 3-phenyl-3*H*-diazirine **7**. The activation energy for route (ii) is higher than that for route (i) by roughly 10 Kcal/mol, but these energies and the energy difference are lowered significantly by meta-substitution with electron-donating groups. Thus, for R = NMe<sub>2</sub> the activation energies for **1** → **2**, **1** → **5** and **1** → **7** are 49.2, 51.6, and 58.8 Kcal/mol, respectively, at the DFT level; i.e. routes (i) and (ii) are now nearly competitive and much preferred over route (iii).<sup>[30]</sup> This effect of meta-substitution can be understood in terms of the LUMO of **1**, which exhibits a large, vacant sigma-type orbital at C (Figure 5.2).

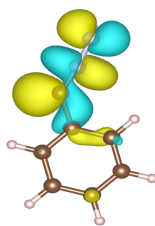
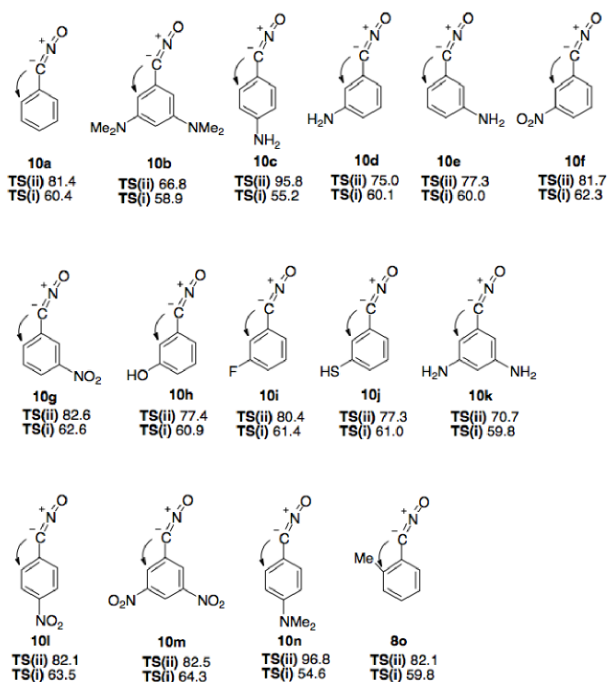


Figure 5.2: LUMO of C-phenylnitrile imine **1** at the B3LYP/6-311G(d,p) level.<sup>[30]</sup>

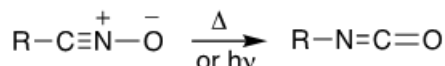
Since electron-donating *meta*-substituents will increase the electron densities at the ortho-carbons, *meta*-substituents such as amino, hydroxy, and sulfanyl facilitate the cyclization (route ii), and the dimethylamino group was found to have the strongest effect. In contrast, electron-donating *para*-substituents lower the barrier for route (i) but have relatively little effect on route (ii). A *meta*-NO<sub>2</sub> group had little effect, but a *para*-NO<sub>2</sub> group increased the barrier for route (i) (Scheme 5.2).



TS(i) and TS(ii) are the energies of the transition states for routes (i) and (ii), respectively, in kcal/mol at the DFT level

Scheme 5.2: Effects of different *meta*- and *para*-substituents on the activation energies of routes (i) and (ii) for benzonitrile oxide. Relative energies (Kcal/mol) of the singlet transition states calculated at the B3LYP/6-311G(d,p) level of theory

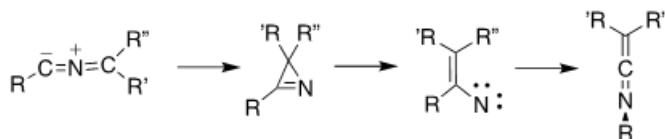
In this paper the possibility of analogous rearrangements occurring in nitrile oxides and nitrile ylides will be examined computationally. In the case of nitrile oxides, the rearrangement to isocyanates (Scheme 5.3) has long been known.<sup>[34–48]</sup> Already Gabriel and Koppe observed 135 years ago that vaporization of diphenylfuroxan (3,4-diphenyl-1,2,5-oxadiazole 2-oxide) resulted in the quantitative formation of “Phenylcyanat”, that is, phenyl isocyanate, PhNCO, which undoubtedly was due to the thermal cleavage of the furoxan into two molecules of benzonitrile oxide, PhCNO, which then rearranged.<sup>[49]</sup>



Scheme 5.3: Rearrangement of nitrile oxides to isocyanates.

There is, however, little understanding of the reaction mechanism. Oxazirines<sup>[37,38,44]</sup> and acylnitrenes<sup>[37,44]</sup> have been suggested as reactive intermediates, as has a dyotropic rearrangement,<sup>[38,41]</sup> in which the group R and the oxygen atom migrate simultaneously. For reactions in solution it has been suggested that aggregates or oligomers are involved.<sup>[43,47]</sup>

Like nitrile imines, nitrile ylides can exist in propargylic or allenic forms,<sup>[50]</sup> and they can cyclize to 3*H*-azirines and rearrange to ketenimines (Scheme 5.4).<sup>[42,51]</sup> The ketenimines often rearrange further to phenylacetone nitriles.<sup>[51]</sup>



Scheme 5.4: Rearrangement of nitrile ylides to ketenimines.<sup>[50]</sup>

Further rearrangements of nitrile oxides and nitrile ylides analogous to Scheme 5.1a are not known. We will use computational methods to examine the rearrangements of nitrile oxides and nitrile ylides under unimolecular reaction conditions, as obtained for example in gas phase pyrolyses (flash vacuum pyrolysis, FVP) or noble gas matrix photolyses.

## Computational methods

Ground-state geometries and energies were determined at the DFT level using the B3LYP exchange-correlation functional with the 6-311G(d,p) basis set using the Gaussian 09 program package.<sup>[52]</sup> Transition state optimization and IRC calculations were performed for all reactions at this DFT level. In order to properly characterize the electronic states of nitrenes and take any multiconfigurational effects into account, calculations were also carried out at the CASSCF and CASPT2(14,12)sp/6-311G(d,p) levels of theory using the Molpro program package.<sup>[53,54]</sup> Calculated energies *E* are at 0 K. Calculated free energies *G* are at 298 K.

## Results and Discussion

### 1. Rearrangements of Benzonitrile Oxides

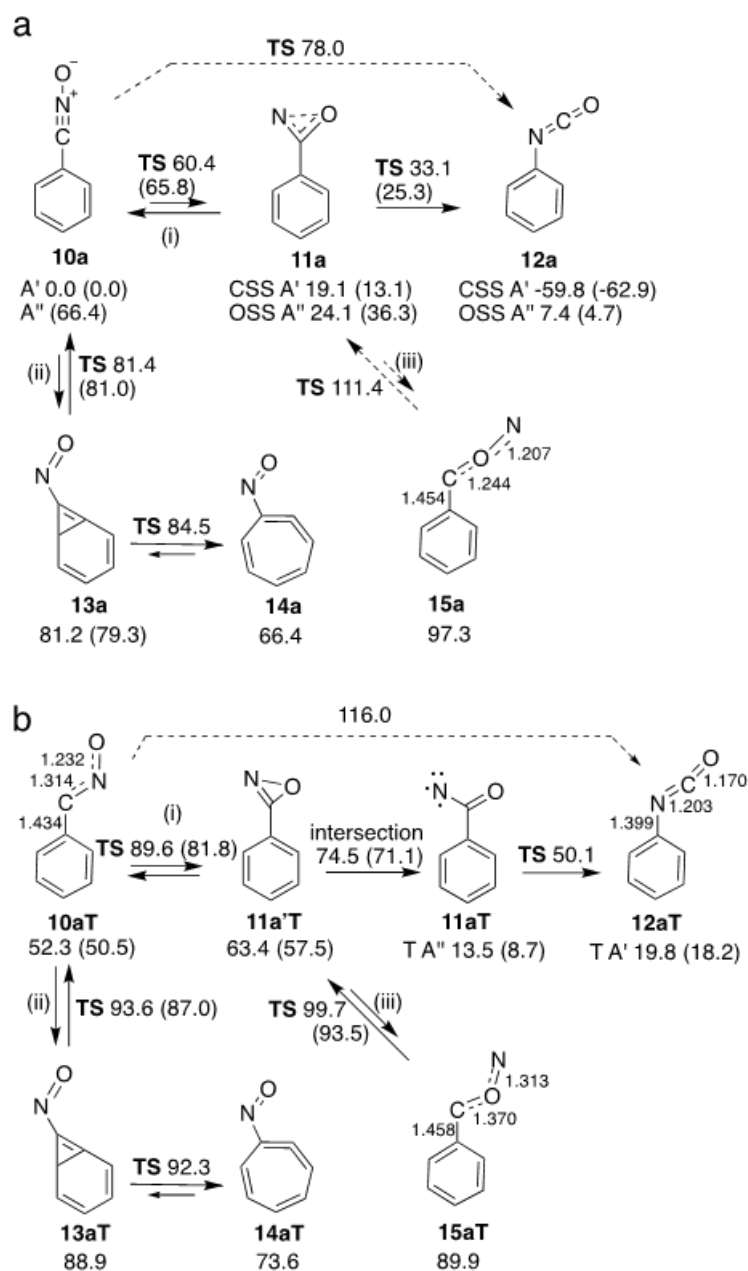
Two intramolecular rearrangement routes of benzonitrile oxide **10a** are set out in Scheme 5.5. The compounds depicted in Scheme 5.5 are designated the ‘a’ series. The corresponding compounds with *m,m'*-dimethylamino substituents form the ‘b’ series. Route (i) is the ring closure to the putative oxazirine/acylnitrene **11a**. Route (ii) describes the new ring expansion of benzonitrile oxide to 1-diazenylcycloheptatetraene **14a**.

The benzylnitrene **11a** in Scheme 5.5 is depicted in its closed-shell singlet (CSS) state, A' (see Figure 5.3), in which a bonding interaction between N and O causes an acute NCO angle of 94° and a C-O bond length of 1.86 Å in agreement with previous calculations on this nitrene.<sup>[55–57]</sup> The open-shell singlet (OSS) is higher in energy by 23 Kcal/mol at the CASPT2 level. The triplet A" is the ground state. There is a crossing of the CSS and the triplet A" of **11** lying 5 Kcal/mol above the CSS. Therefore, facile interconversion of the singlet and triplet states of the nitrene can be expected.



Figure 5.3: Structures of four electronic states of benzylnitrene **11a** at the CASPT2 level. From left (N-O distance (Å) and NCO angle (°) given, (a) CSS A' (1.86, 94.2), (b) OSS A' (2.23, 116.1), (c) T A'' (2.25, 118.8), (d) T A' (2.29, 123.3) at the CASPT2 level.

The activation energy for the rearrangement of benzylnitrene **11a** (CSS, A') to phenyl isocyanate **12a** in its closed-shell singlet electronic state, A', is very modest, about 12 Kcal/mol (Scheme 5.5a). The direct dyotropic rearrangement of **10a** to **12a** has a considerably higher activation energy (78 Kcal/mol; Scheme 5.5). The activation energy for the ring expansion **10a** → **13a** → **14a** (route ii) is about 20 Kcal/mol higher than that for the isocyanate formation (Scheme 5.5). Substitution with two *meta*-NMe<sub>2</sub> groups cause a lowering of the two activation energies to 58.9 Kcal/mol for route (i) and 66.8 Kcal/mol for route (ii), i.e. the energy difference is now only 12 Kcal/mol (Scheme 5.6a). Similar to what was observed previously for the nitrile imines, electron-donating *meta*-substituents generally lower the activation energy for route (ii), electron-withdrawing *meta*-substituents have a mild, opposite effect, electron-donating *para*-substituents raise the barrier for route (ii) and lower the barrier for route (i), thereby widening the gap. Although the “classical” rearrangement to isocyanate **12a** remains the thermochemically preferred path, both paths may very well become possible under photochemical conditions. There is a potential third path (iii) leading to PhCON **15a**, but the high activation energy required makes this reaction (Scheme 5.5a) unlikely in the singlet state.



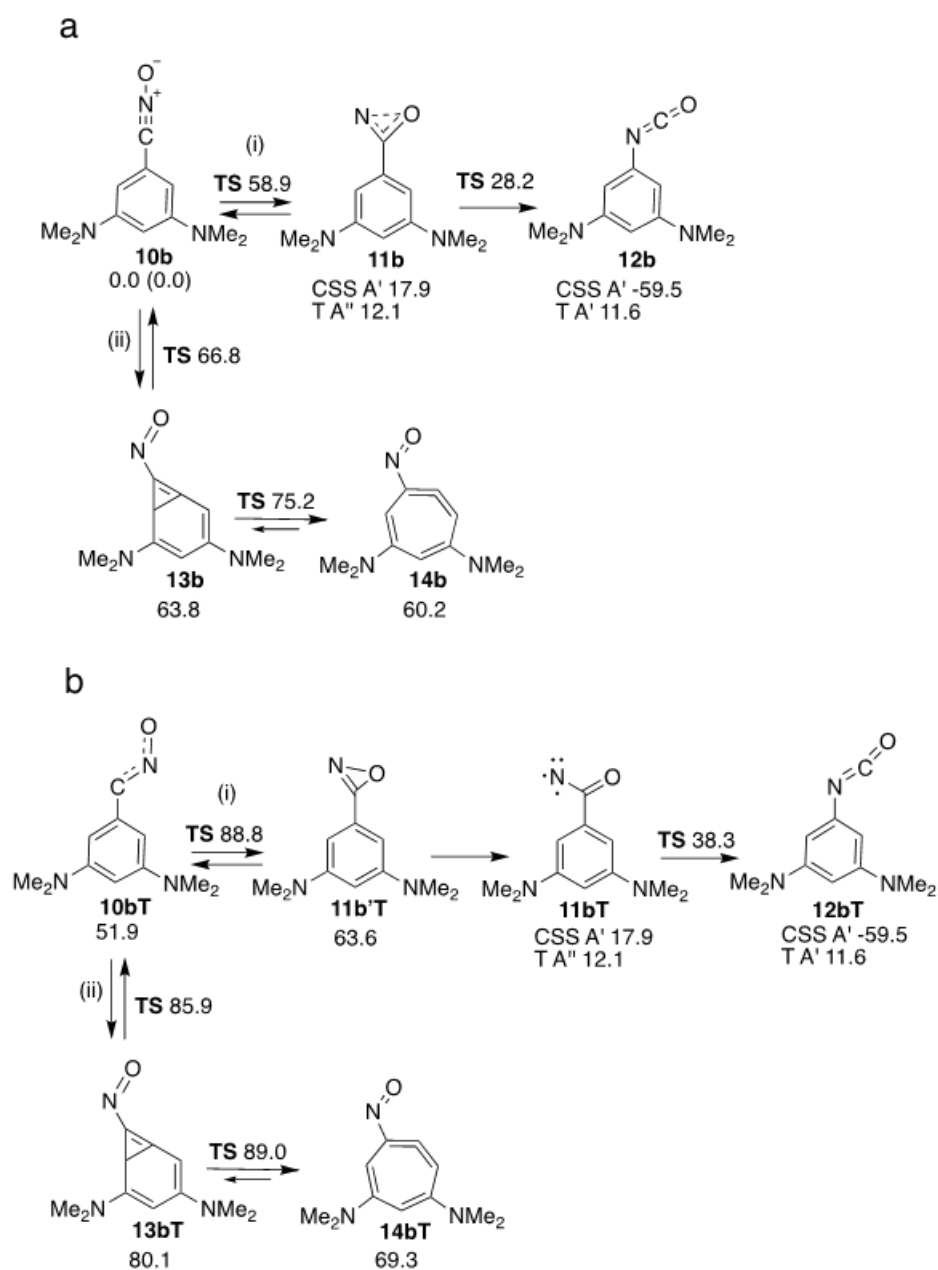
Scheme 5.5: Rearrangements of benzonitrile oxide **10a** in the singlet (a) and triplet, **T** (b) states. Energies relative to **10a** A' in Kcal/mol at the B3LYP/6-311G(d,p) level, and in parentheses at the CASPT2(14,12)/6-311G(d,p) level. The singlet benzoylnitrene **11a** is shown in its closed-shell singlet state, **11a** CSS A' and the triplet **11aT** in the A'' state. We refrain from indicating charges on the excited state structures. Note that the CNO, NCO, and CON moieties are not linear in the triplet states.



The ground state of **11a** is the triplet A" **11aT** which, as observed for many other acylnitrenes,<sup>[58]</sup> is very likely formed on photolysis. Therefore, examination of the triplet energy surface is of interest. It is recognized that singlet excited species may also be involved, but their rearrangements are not considered in this paper.

The triplet state of benzonitrile oxide **10aT** lies only ~50 Kcal/mol above the singlet ground state, and thus it would be expected to be readily accessible photochemically. The rearrangements on the triplet energy surface are similar to those presented for the singlets in Scheme 5.5a, but now the activation energy differences between routes (i) and (ii) is reduced to just 4 Kcal/mol (Scheme 5.5b). In other words, both paths may be (nearly) competitive under photochemical conditions. Also note that the triplet oxazirine **11a'T** can now in principle exist as a true three-membered ring, although it is much higher in energy (63.4 (57.5) Kcal/mol) than the nitrene **11aT A"** (13.5 (8.7) Kcal/mol). The energy profiles of **11a'T** and **11aT** intersect at an energy of 74.5 (71.1) Kcal/mol, i.e. only 11-14 Kcal/mol above **11a'T** (Scheme 5.5b). The third path, (iii), leading to PhCON **15aT** is now more likely than in the singlet state. The activation energy for this path is about 6 Kcal/mol higher than that for route (ii). The triplet **15aT** is the ground state of this species. The lengths of the C-O and O-N bonds in **15aT** are between typical single and double bond lengths, whereas for the singlet **15a** they both have double bond character (Scheme 5.5). In both **15a** and **15aT** the C-C bond between the benzene ring and the CON moiety has the typical length of a single bond between two double bonds.

Substitution with two *meta*-dimethylamino groups in **10bT** makes route (ii) even more favorable. The activation energies are now 88.8 for route (i) and 85.9 for route (ii) in the triplet state (Scheme 5.6b) at the DFT level. Thus, route (ii) should now be preferred, and both paths may be experimentally observable. Concerted rearrangements of the nitrile oxides to the isocyanates are also theoretically possible, but they have much higher activation energies. Note again that the triplet oxazirine **11b'T** is now capable of separate existence, although the nitrene **11bT** is much lower in energy (Scheme 5.6).

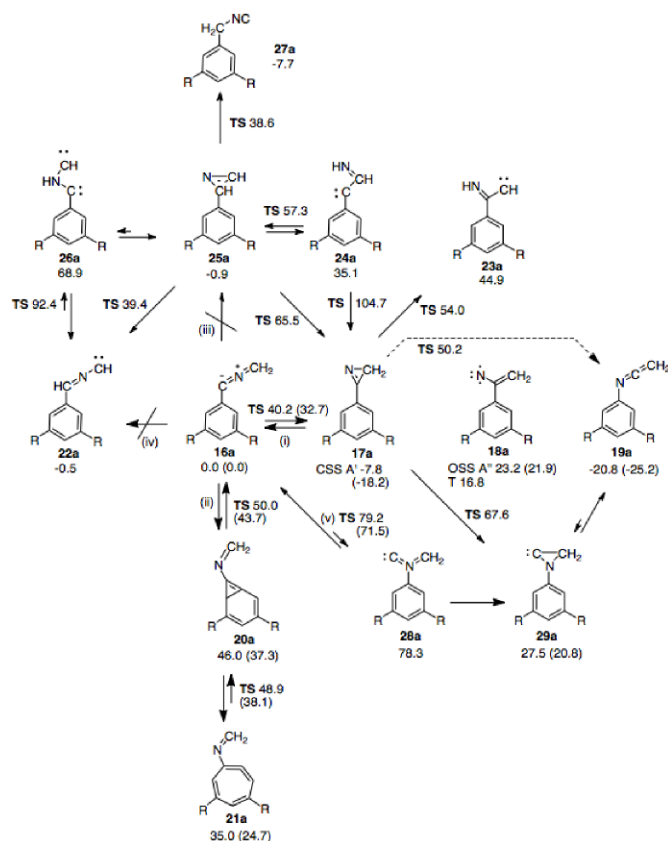


Scheme 5.6: Rearrangements of *m,m'*-bis(dimethylamino)benzotrile oxide **10b** in the singlet (a) and triplet, **T** (b) states. Relative energies in Kcal/mol at the B3LYP/6-311G(d,p) level. We refrain from indicating charges on the excited state structures. Note that the CNO and NCO moieties are not linear in the triplet states.

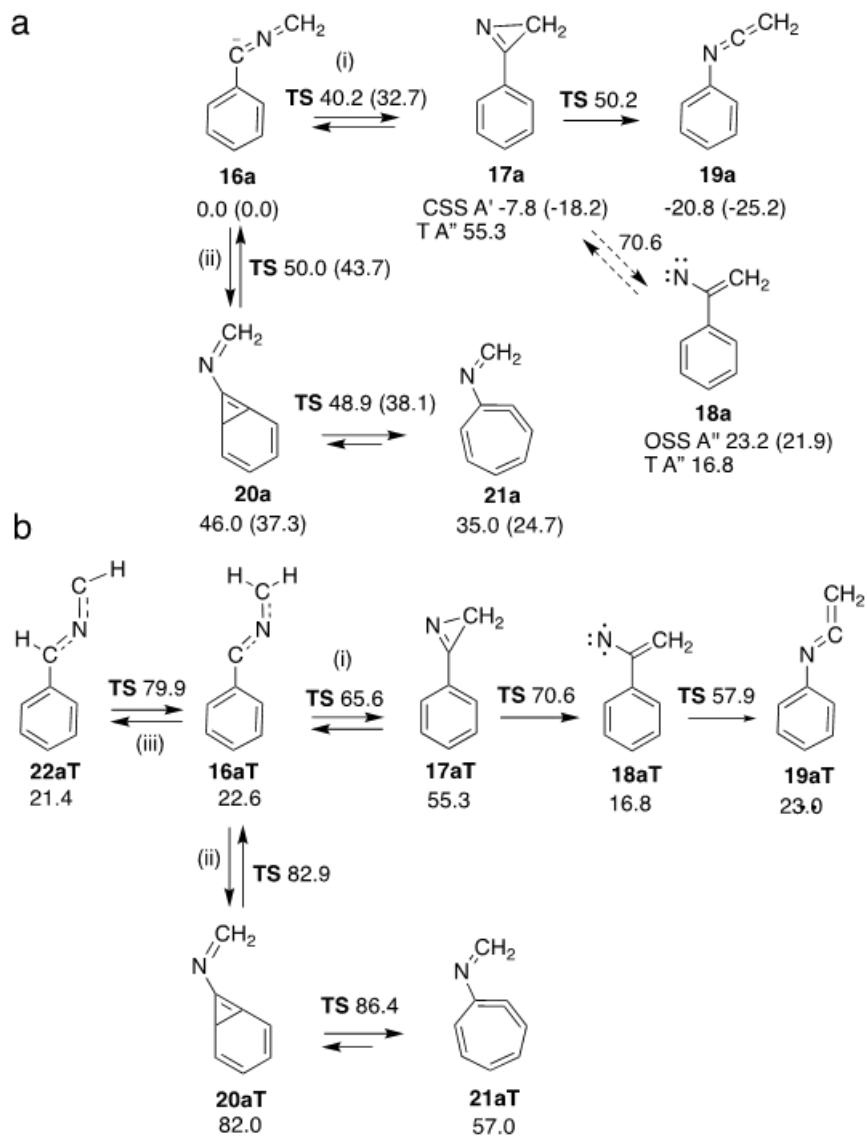
## 2. Rearrangements of Benzonitrile Methylides

Two intramolecular rearrangement routes of benzonitrile methylide **16a** are shown in Scheme 5.8. In this case, the ring closure route (i) generates the stable 2-phenyl-3*H*-azirine **17a**, which can ring-open to the  $\alpha$ -Styrylnitrene **18a** or rearrange in a concerted manner to *N*-phenylketenimine **19a**. The azirine **17a** has been obtained previously by FVP of  $\alpha$ -styryl azide at 350°C, which may react either concertedly or via the nitrene **18a**.<sup>[59]</sup> Similarly, the azirine **17a** may rearrange to ketenimine **19a** concertedly or via the vinylnitrene **18a**, although the concerted reaction has the lower activation energy (Scheme 5.8a). Previously, several vinylnitrenes have been generated and observed in their triplet states by ESR spectroscopy in photolyses of vinyl azides, azirines, or isoxazoles at cryogenic temperatures.<sup>[60–62]</sup> The structures of **17a** and the three lowest electronic states of the vinylnitrene **18a** are illustrated in Figure 5.4.

Route (ii) describes the new ring expansion to the cyclopropane **20a** and the cycloheptatraene **21a**. Further rearrangements requiring considerably higher activation energies are reported in the Supporting Information (Scheme 5.7).



Scheme 5.7: Rearrangements of Benzonitrile Methylide **16a** Energies in Kcal/mol at the B3LYP/6-311g(d,p) level, and in parentheses at the CASPT2(14,12)/6-311G(d,p) level.



Scheme 5.8: Rearrangements of benzonitrile methylene **16a** in the singlet (a) and triplet, **T** (b) states.  $\alpha$ -Styrylnitrene **18a** is shown in its open-shell singlet state (OSS), A'' (see also Figure 5.4). Note that the CNC and NCC moieties in **22aT** and **19aT** are not linear. We refrain from indicating charges on the excited state structures. Relative energies in Kcal/mol at the B3LYP/6-311G(d,p) and (CASPT2) levels.

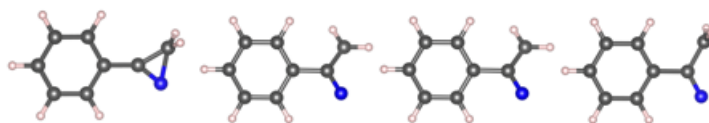
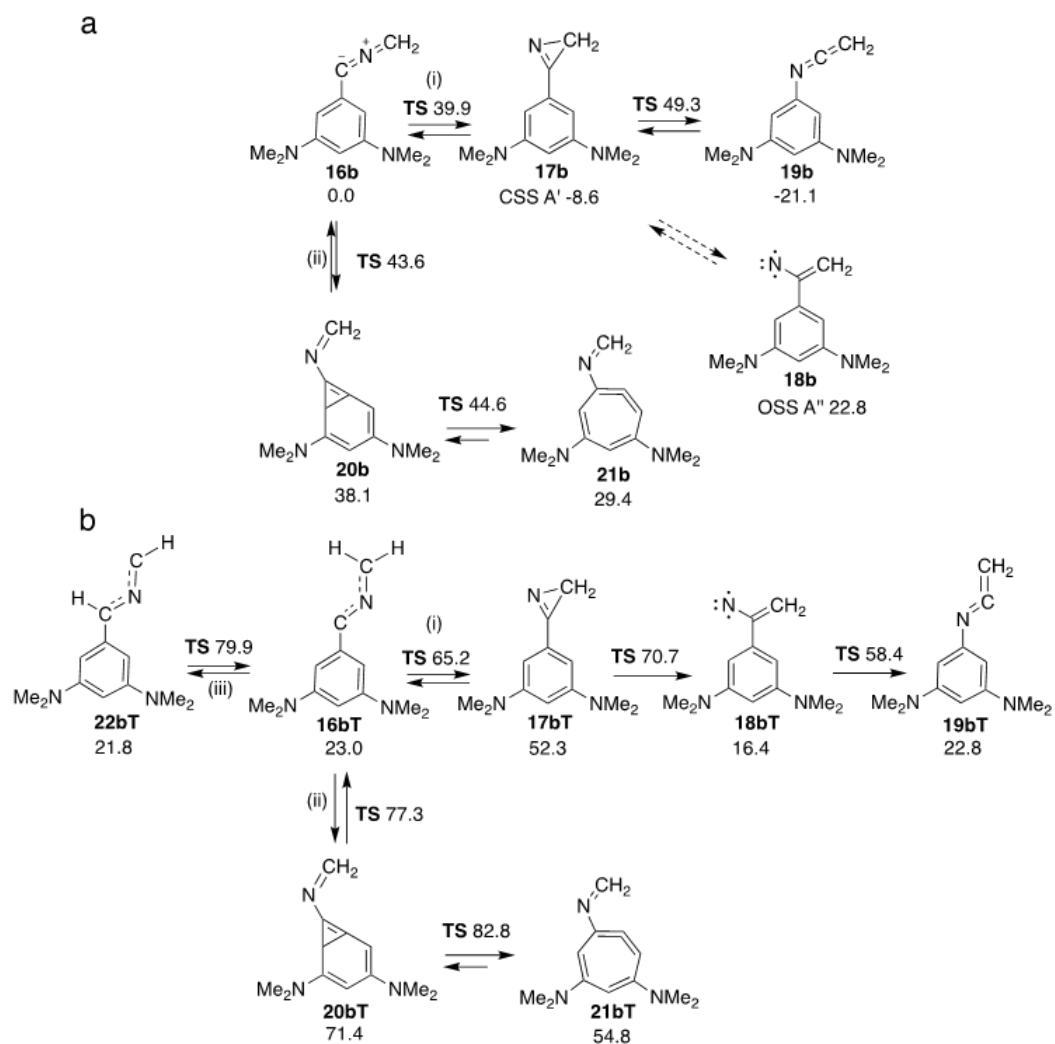


Figure 5.4: Structures of 2-phenyl-1-azirine **17a** and  $\alpha$ -Styrylnitrene **18a** at the CASPT2 level. From left (N-CH<sub>2</sub> distance (Å) and NCCH<sub>2</sub> angle (°) given), (a) **17a** CSS A' (1.55, 69.1), (b) **18a** CSS (1.35, 120.1), (c) **18aT** A' (2.35, 119.8), (d) **18aT** A' (2.41, 122.1).

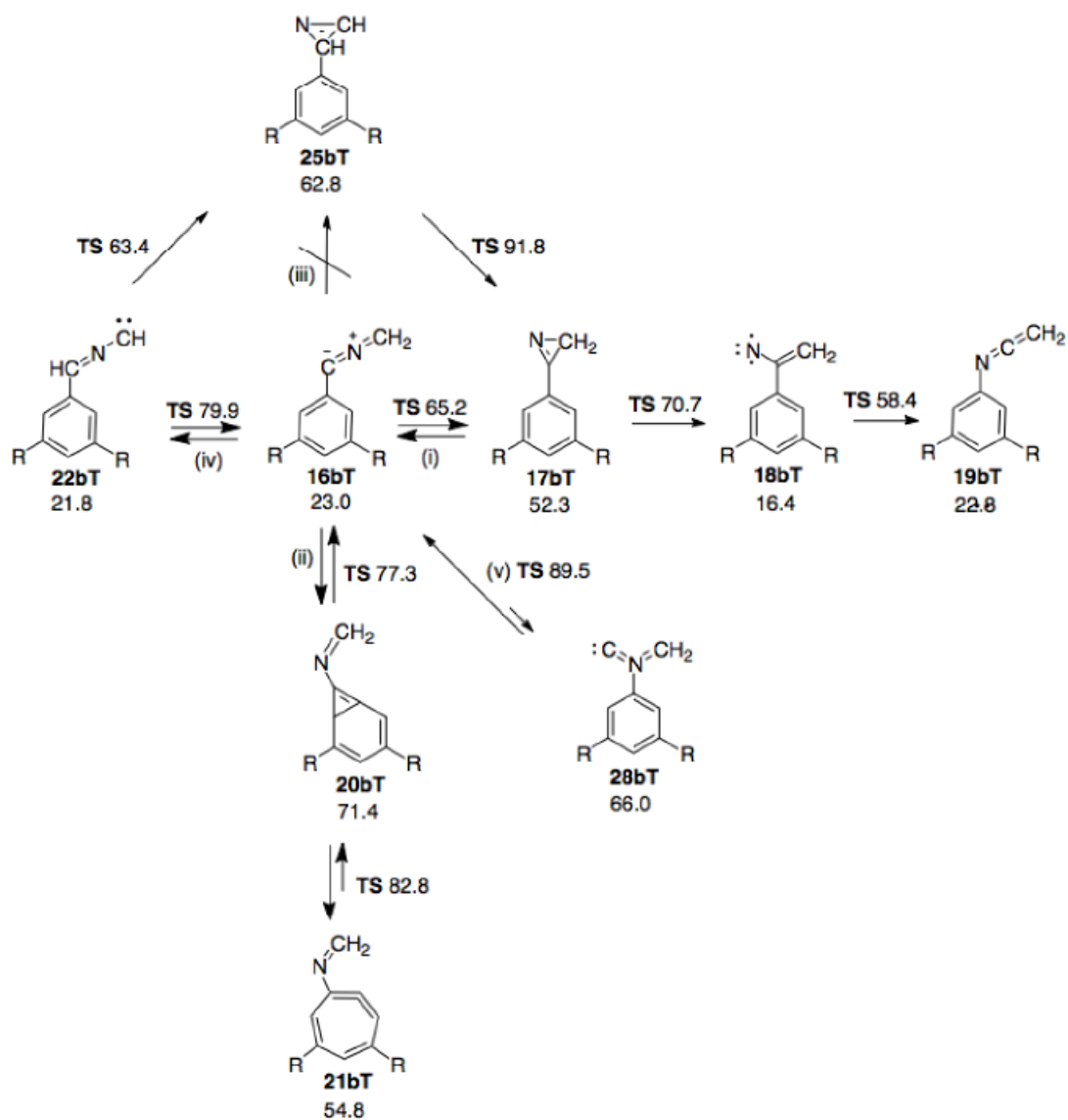
In this case there is a  $\sim 10$  Kcal/mol difference in the activation energies for routes (i) and (ii) (Scheme 5.8a). However, *meta*-substitution with dimethylamino groups in **16b** lower this difference to just 4 Kcal/mol (Scheme 5.9a). Thus, it is possible that route (ii) may become competitive in high-temperature pyrolysis reactions or in photolysis reactions.

In the triplet state of the nitrile ylide **16aT** there is still a 17 Kcal/mol difference between the activation energies for routes (i) and (ii), the former being preferred (Scheme 5.8b). However, thanks to the bent structure of the nitrile ylide, a 1,3-shift of a hydrogen atom on the terminal carbon atom of the nitrile ylide now becomes possible (route (iii), Scheme 5.8b), leading to the isomeric nitrile ylide **22aT**. This takes place in a single step through a symmetrical transition state with an activation energy of  $\sim 80$  Kcal/mol. In contrast, 1,3-H shifts in linear systems have very high activation energies, e.g.  $\sim 90$  Kcal/mol for the direct isomerization of C-phenylnitrile imine **1** to phenyldiazomethane **8**. Therefore, such formal 1,3-shifts often occur by dissociation-recombination or roaming mechanisms.<sup>[63]</sup>

Surprisingly, the dimethylamino groups do not help to lower the energy barrier for route (ii) in the triplet state **16bT** in this case (Scheme 5.9b). The 'classical' route (i) is still preferred by  $\sim 12$  Kcal/mol. As in the case of ylide **16bT**, a 1,3-hydrogen shift with an activation energy of 80 Kcal/mol is potentially possible (route (iii), Scheme 5.9b) and leads to the isomeric nitrile ylide **22bT**. However, these 1,3-H shifts require higher activation energies than either of the other routes, (i) and (ii), and are not, therefore, expected to be readily observable.



Scheme 5.9: Rearrangements of *m,m'*-bis(dimethylamino)benzonitrile methylene **16b** in the singlet (a) and triplet **T** (b) states. Relative energies in Kcal/mol at the B3LYP/6-311G(d,p) level. We refrain from indicating charges on the excited state structures. Note that the CNC and CNC and NCC moieties in **16bT**, **19bT** and **22bT** are not linear (More details in the Scheme 5.10, see below).



Scheme 5.10: Rearrangements of *m,m'*-bis(dimethylamino)benzonitrile Methylene **16bT**. Energies in Kcal/mol at the B3LYP/6-311g(d,p) level.

## Conclusion

The ring expansion of benzonitrile imine **1** to a diazenylcycloheptatetraene **6**, in which the nitrile imine mimics a phenylcarbene,<sup>[30]</sup> has analogues in the benzonitrile oxide **10** and benzonitrile methylene **6** series. The activation energy for the ‘classical’ rearrangement of benzonitrile oxide **10a** in its singlet ground state to phenyl isocyanate **12a** is lower than that for the potential cyclization to the cyclopropene **13a** and ring expansion to cycloheptatetraene **14a** by ~20 Kcal/mol, but in the triplet state **10aT** this difference is reduced to 4 Kcal/mol. Substitution with *m,m'*-bis(dimethylamino) groups in **10b** reduces this energy difference to 8 Kcal/mol in the singlet state, and to -3 Kcal/mol in the triplet **10bT**; in other words, the ring expansion becomes the preferred path in the triplet state, and it can be expected that this reaction will be observable under photolysis conditions. Formation of the species Ph-CON **15aT** is also in principle possible.

In the case of benzonitrile methylene **16a**, the ‘classical’ rearrangement to the ketenimine **19a** is favoured over the ring expansion to the cyclopropane **20a** and cycloheptatetraene **21a** by ~10 Kcal/mol in the singlet state, and the substitution with *m,m'*-bis(dimethylamino) groups in **16b** reduced this activation energy difference to ~5 Kcal/mol, the ‘classical’ reaction still being preferred. Here, the substitution with *m,m'*-bis(dimethylamino) groups does not lead to significant changes in the reactions of the triplet state **16bT**, where the ‘classical’ reaction is still preferred over the ring expansion by 12-17 Kcal/mol. In addition, 1,3-H shifts interconverting the nitrile ylides **16aT** and **16bT** with the isomeric nitrile ylides **22aT** and **22bT** are potentially possible in the triplet state.

## Acknowledgements

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## Conflict of interest

The authors declare no conflict of interest.

## Keywords

Nitrile imines; nitrile oxides; nitrile ylides; cycloheptatetraenes; DFT and CASPT2 calculations



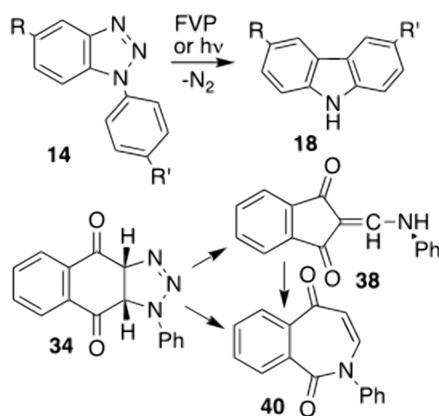
### 5.3 Benzotriazoles and Triazoloquinones: Rearrangements to Carbazoles, Benzazirines, Azepinediones, and Fulvenimines

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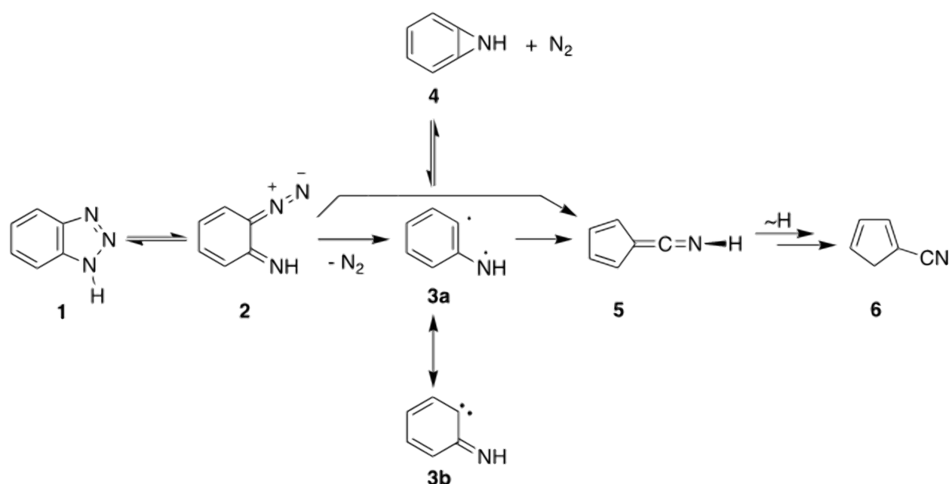
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**Abstract:** The denitrogenative rearrangements of several types of benzotriazoles were investigated by DFT (B3LYP/6-311G(d,p)) and CASPT2(10,10)sp/6-311G(d,p) calculations. The Graebe-Ullmann synthesis of carbazoles **18** by pyrolysis or photolysis of 1-arylbenzotriazoles **14** proceeds without the involvement of benzazirines and without Wolff-type ring contraction to fulvenimines. However, 1-aryltetrahydrobenzotriazoles undergo both the cyclization to tetrahydrocarbazole and the ring contraction. Triazoloquinones like **34** undergo predominant ring contraction to aminofulvenediones like **38** but also ring expansion to azepinediones like **40** and cyclization to *N*-arylbenzaziridinediones such as **39**, whereas carbazolidiones are not formed. Denitrogenation of 1-methylbenzotriazole **64** results in a facile 1,2-H shift with formation of *N*-phenylmethanimine **67**. 1-Cyanobenzotriazole **71** undergoes destructive pyrolysis with charring, and the calculations predict the occurrence of several low-activation energy reaction pathways.



## Introduction

Benzotriazoles are used in numerous synthetic reactions<sup>[64–66]</sup>, where they can act as leaving groups, electron donors, electron withdrawers, and radical or carbanion precursors. The denitrogenative cyclization<sup>[67,68]</sup> is of particular interest for the synthesis of heterocycles. Computational investigations of the denitrogenation of benzotriazole **1** at the CASPT2 level of theory demonstrated that nitrogen loss from the initially formed diazo valence tautomers **2** results in a 1,3-diradical/carbene **3a/3b**, which has a triplet ground state, but a low-lying open-shell singlet state is responsible for further reactions.<sup>[69,70]</sup> This diradical/carbene can cyclize to benzazirine **4**, the formation of which has been demonstrated experimentally by carbon labeling,<sup>[71]</sup> or it can undergo the aza-Wolff rearrangement to fulvenimine **5** followed by tautomerization yields to 1-cyanocyclopentadiene **6** in high yield (Scheme 5.11).<sup>[69]</sup> The concerted reaction **2**→**5** bypassing the diradical **3** was only located at the DFT level.<sup>[69,72]</sup>

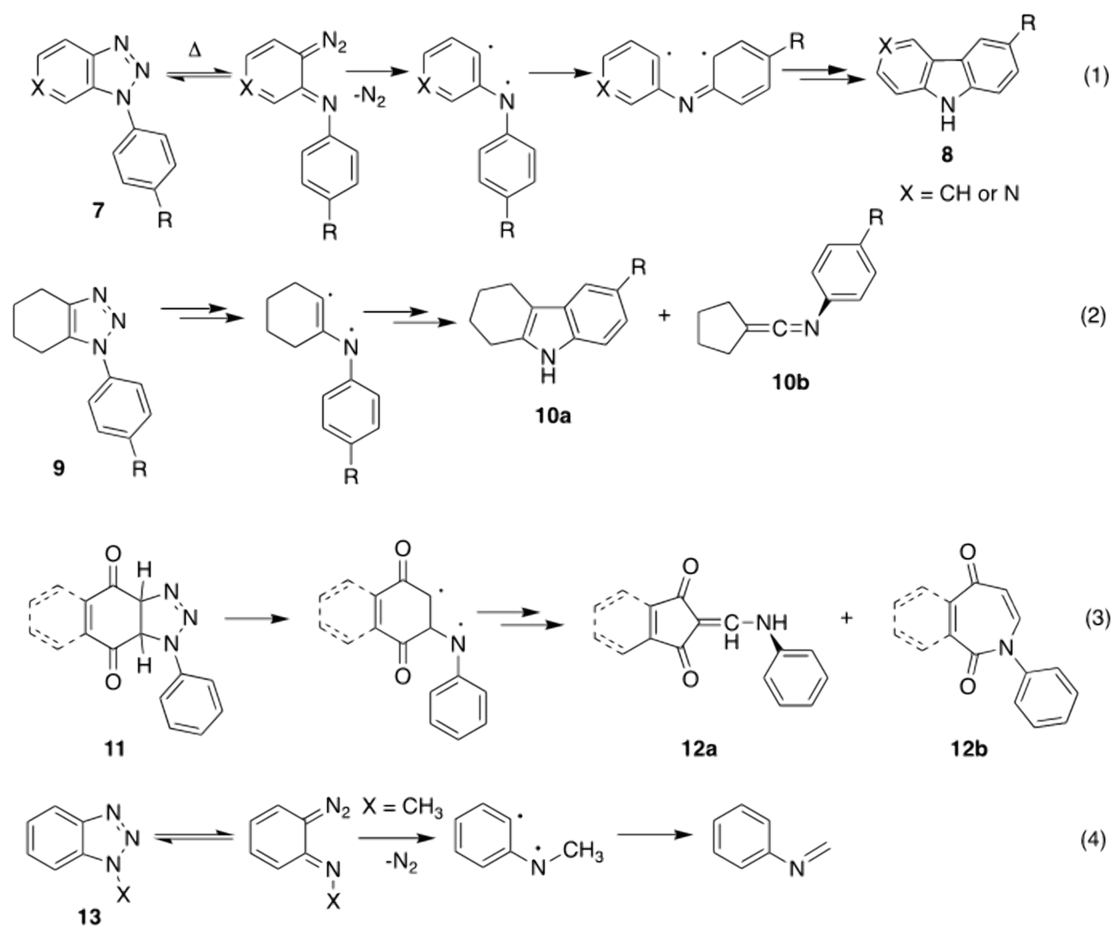


Scheme 5.11: Rearrangements of benzotriazole to fulvenimine, cyanocyclopentadiene, and benzazirine.

Several different type of rearrangement can take place on pyrolysis of 1-substituted benzotriazoles.<sup>[73]</sup> The preparation of carbazoles and carbolines such as **8** by pyrolysis of 1-arylbenzotriazoles and -triazolopyridines such as **7** (Scheme 5.12, Eq.1) is the well-known Graebe-Ullmann reaction, first reported 125 years ago.<sup>[74]</sup> In the original experiment 1-phenylbenzotriazole was decomposed by heating to about 360°C in a distillation flask.<sup>[74]</sup> Further procedures used heating in sealed tubes, distillation with or without CaO, or heating with ZnCl<sub>2</sub> or (poly)phosphoric acid.<sup>[74–80]</sup> Numerous variants of the reaction have been reported.<sup>[73,81,82]</sup> Nowadays flash vacuum pyrolysis (FVP)<sup>[73]</sup> is a convenient and usually high-yielding method. The falling solid FVP procedure<sup>[83,84]</sup> allows a straightforward synthesis of carbazoles on a preparative scale. Carbazoles and heterocyclic analogs are also obtained on photolysis;<sup>[85,86]</sup> carbazole was obtained in 78% yield in the photolysis of **7** in MeOH at 300 nm.<sup>[87]</sup>

In contrast, tetrahydrobenzotriazoles **9** undergo both the carbazole-type cyclization to **10a** and Wolff-type ring contraction to a tetrahydroiminofulvene derivative **10b** (Eq.2). Triazoloquinones and tiazolobenzoquinones **11** undergo the Wolff-type ring contraction to **12a** as the principal products, but ring expansion to azepinedione derivatives **12b** also takes place, whereas carbazole-type cyclizations have not been observed at all (Eq.3). 1-Methylbenzotriazole **13** (X = CH<sub>3</sub>) yields N-phenylmethanimine cleanly (Eq.4), whereas N-acyl and N-alkoxycarbonylbenzotriazoles (**13**, X = RCO or ROCO) undergo ring contraction to iminofulvenes,<sup>[31,70,73]</sup> but N-cyanobenzotriazole **13** (X = CN) has not so far yielded any definite pyrolysis product.

In this paper we will examine the possible competitions between Graebe-Ullmann-type cyclizations, benzazirine formation, and Wolff-type ring contraction to fulvenimines by calculation of the energy profiles. Depending on the molecular structure, all three types of rearrangement can become energetically feasible.

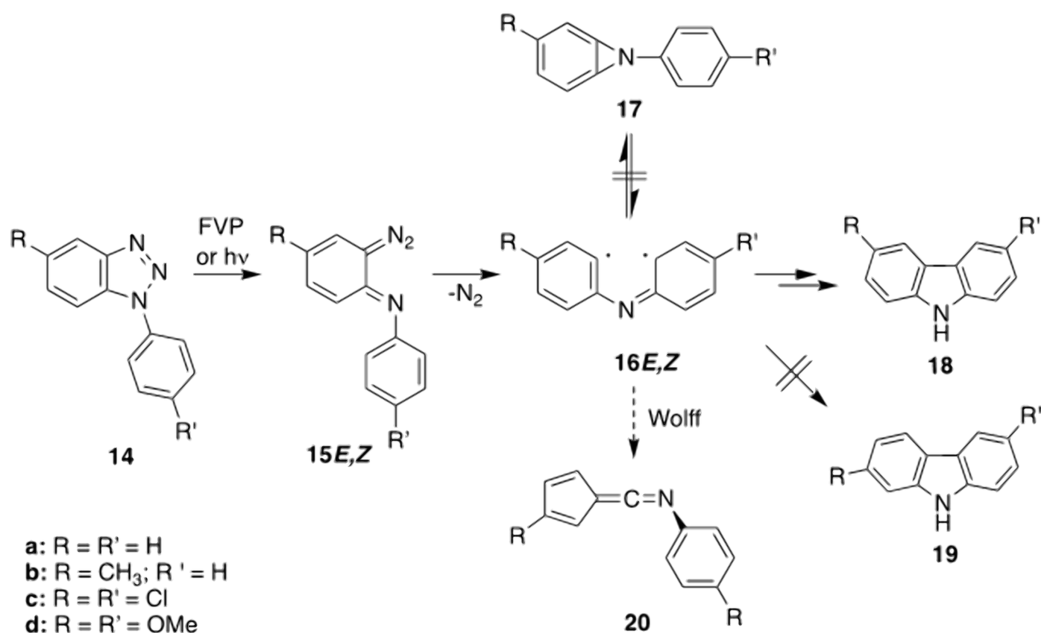


Scheme 5.12: The different types of rearrangement of benzotriazoles, tetrahydrobenzotriazoles, triazoloquinones, and simple 1-substituted benzotriazoles described in this paper.

## Results and Discussion

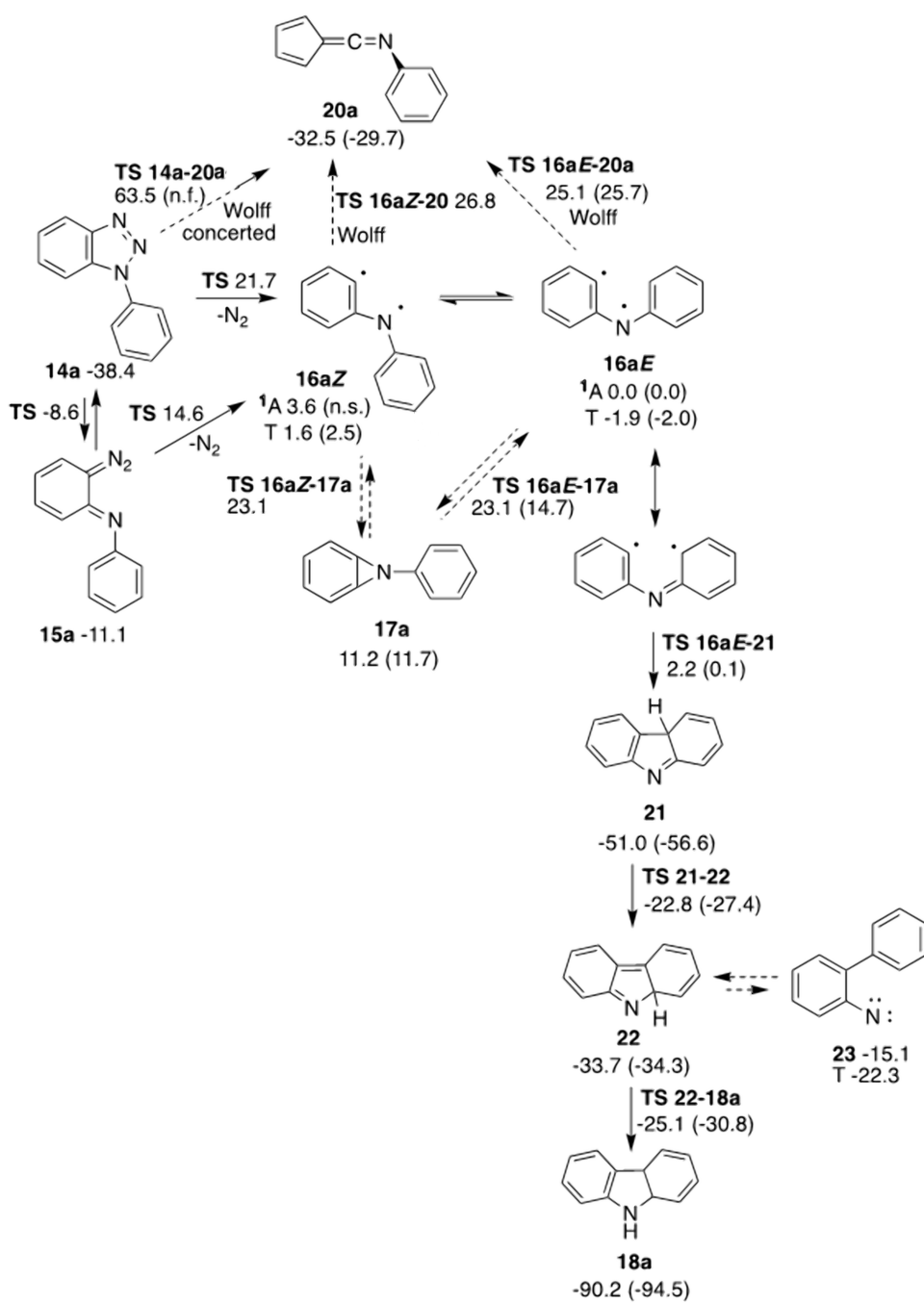
### 1. 1-Arylbenzotriazoles

Pyrolysis<sup>[70,88]</sup>, and photolysis<sup>[89–91]</sup> of 1-arylbenzotriazoles **14** yield carbazoles **18** in high yields (Scheme 5.13). Diazo compounds **15** have been detected as intermediates in matrix photolysis reactions.<sup>[73]</sup> The triplet diradicals **16E,Z** have been characterized by ESR spectroscopy in the photolysis of **7** at 77 K.<sup>[92]</sup> Compound **14b** was examined by FVP at 780–1100°C,<sup>[88]</sup> compound **14c** by low-pressure Hg arc photolysis,<sup>[89,90]</sup> and **14d** by photolysis at 254nm.<sup>[91]</sup> Involvement of benzazirines **17** would have led to formation of positional isomers **19** of the carbazoles, and such isomers have not been detected in either pyrolysis or photolysis reactions. This excludes the involvement of benzazirines **17**. The potential fulvenimines **20** arising from Wolff-type ring contractions have never been described either. The yields of carbazoles are nearly quantitative in the FVP reactions, but they are usually far from quantitative in the photolyses.



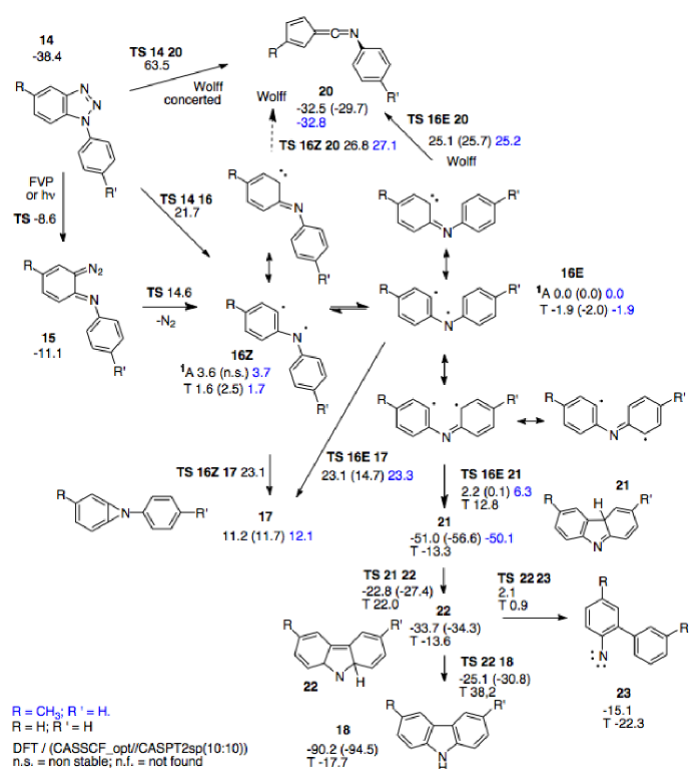
Scheme 5.13: Potential products of decomposition of 1-phenylbenzotriazoles **14**.

We have investigated the potential rearrangements of 1-phenylbenzotriazole **14a** at the DFT (B3LYP/6-311G(d,p)) and CASPT2(10,10)sp/6-311G(d,p) computational levels with the results shown in Scheme 5.14.



Scheme 5.14: Potential products of decomposition of 1-phenylbenzotriazole **14a**. Energies in Kcal/mol calculated at the DFT and (CASPT2) levels; n.s. = not stable; n.f = not found (a TS could not be found at the CASPT2 level).

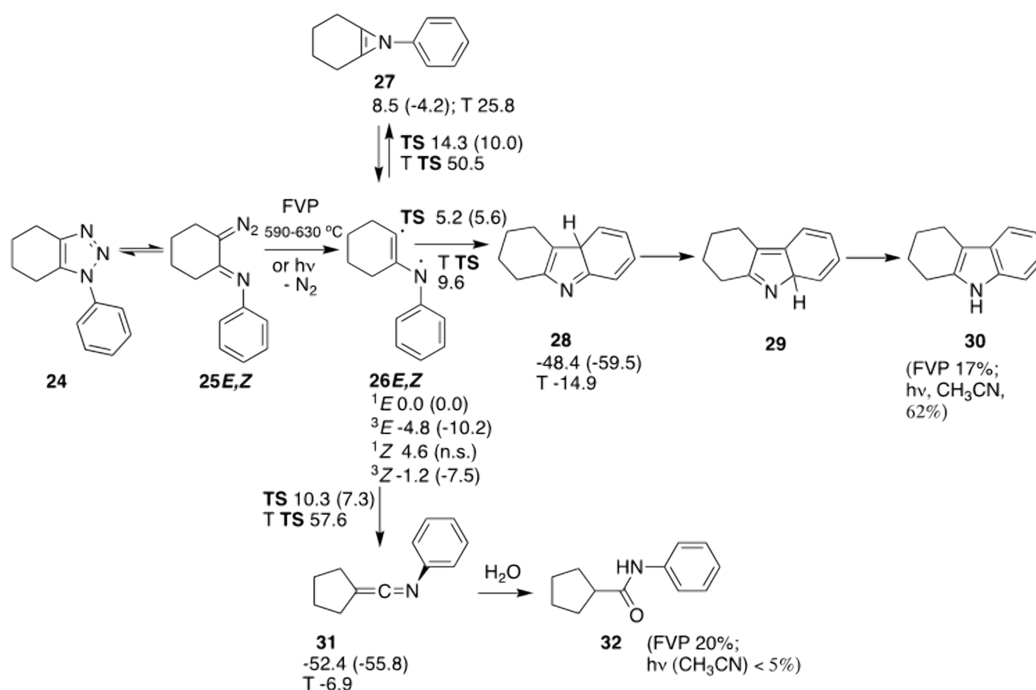
As in the case of the unsubstituted benzotriazole,<sup>[71]</sup> the concerted ring contraction **14a** → **20a** was only found at the DFT level, and the energy barrier is very high at ~ 102 Kcal/mol. The stepwise reaction via the diradicals **16aE** and **16aZ** could lead to the fulvenimine **20a** with a barrier of ~26 Kcal/mol, and benzazirine **17a** could be formed with a barrier of 15-23 Kcal/mol, but the cyclization to the carbazole derivative **21** is by far the preferred reaction with a barrier of only 0.1-2 Kcal/mol depending on the level of calculation. This reaction is highly exothermic (-51 to -57 Kcal/mol), and the subsequent 1,5-H shifts to carbazole **18a** via **21** and **22** have low barriers relative to the energy of **14a**. Therefore, clean carbazole formation without the involvement of the benzazirine **17a** is expected in full agreement with the experimental observations. Analogous calculations were also performed for compound **14b**, with very similar results (Scheme 5.15). It is interesting to note that the isocarbazole **22** is an isomer of the higher energy 2-biphenylnitrene **23**, with which it may interconvert. This reaction has been demonstrated in the laser flash photolysis of 2-biphenyl azide, where the products were identified by transient UV absorption spectroscopy.<sup>[93]</sup> The calculated barrier for the reaction of singlet **23** to **22** was 4-6 Kcal/mol, and this reaction was computed to be exothermic by ~28 Kcal/mol.



Scheme 5.15: Potential products of decomposition of 1-phenylbenzotriazoles **14**. Energies in Kcal/mol calculated at the B3LYP/6-311G(d,p) and CASPT2(10,10)sp/6-311G(d,p) (values in parenthesis) levels related to Scheme 5.14.

## 2. 1-Phenyl-4,5,6,7-tetrahydrobenzotriazole

Pyrolysis and photolysis of 1-phenyl-4,5,6,7-tetrahydrobenzotriazole **24** lead to formation of both tetrahydrocarbazole **30** and tetrahydrofulvenimine **31** (Scheme 5.16).<sup>[94]</sup> The latter was detected by its IR absorption at 2020 cm<sup>-1</sup> and isolated as the amide **32**. The pyrolysis was carried out by FVP at 590-630°C at a pressure <10<sup>-2</sup> hPa. The photolysis was in CH<sub>3</sub>CN using a 5W low-pressure Hg arc. The yield of **30** was 17% in the pyrolysis and 62% in the photolysis. The yield of **32** was 20% in the pyrolysis and less than 5% in the photolysis.

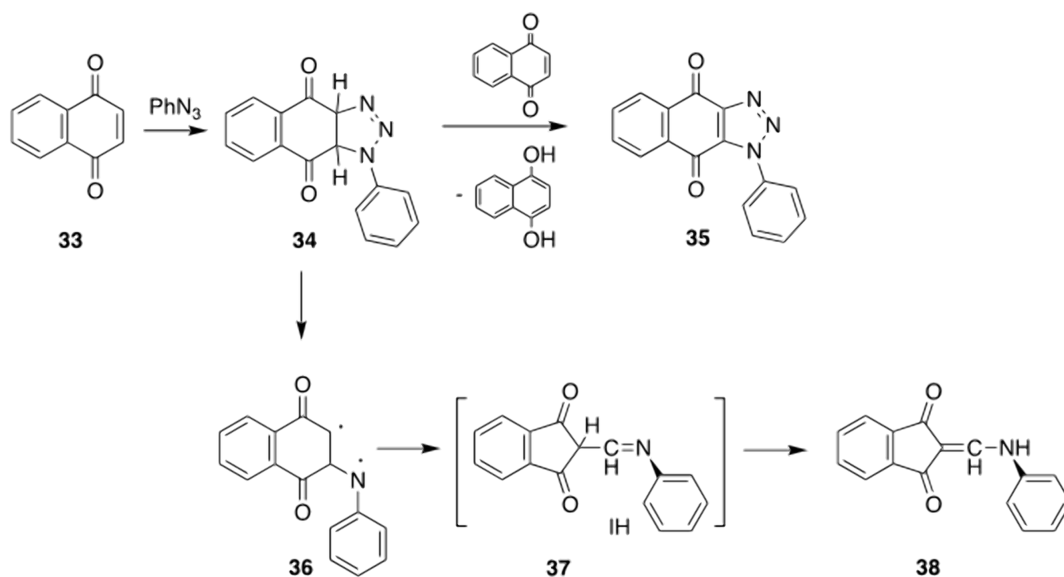


Scheme 5.16: Products of decomposition of 1-phenyltetrahydrobenzotriazole **24**. Energies in Kcal/mol calculated at the DFT and (CASPT2) levels; n.s = not stable.

Our calculations show that, after formation of the E and Z forms of the open-shell singlet diradical **26**, the activation barriers for ring closure to the carbazole derivative **28** and to the fulvenimine **31** are both very small, about 6 and 7 Kcal/mol, respectively, at the CASPT2 level (Scheme 5.16). Given the computational accuracy, these two barriers are in effect indistinguishable and are in at least qualitative agreement with the experimental observation of roughly equal yields of the two compounds under FVP conditions. However, for the triplet diradical<sup>[69]</sup> **26** the two activation energies are ca. 10 and 58 Kcal/mol, respectively. This suggests that the photochemical reaction takes place in the triplet manifold, thus resulting in predominant formation of **30**. Reversible formation of the tetrahydrobenzazirine **27** is possible on the singlet surface but unlikely in the triplet, the calculated barriers being ca. 14 and 55 Kcal/mol, respectively.

### 3. N-Phenyltriazolo[*b*]naphthoquinone

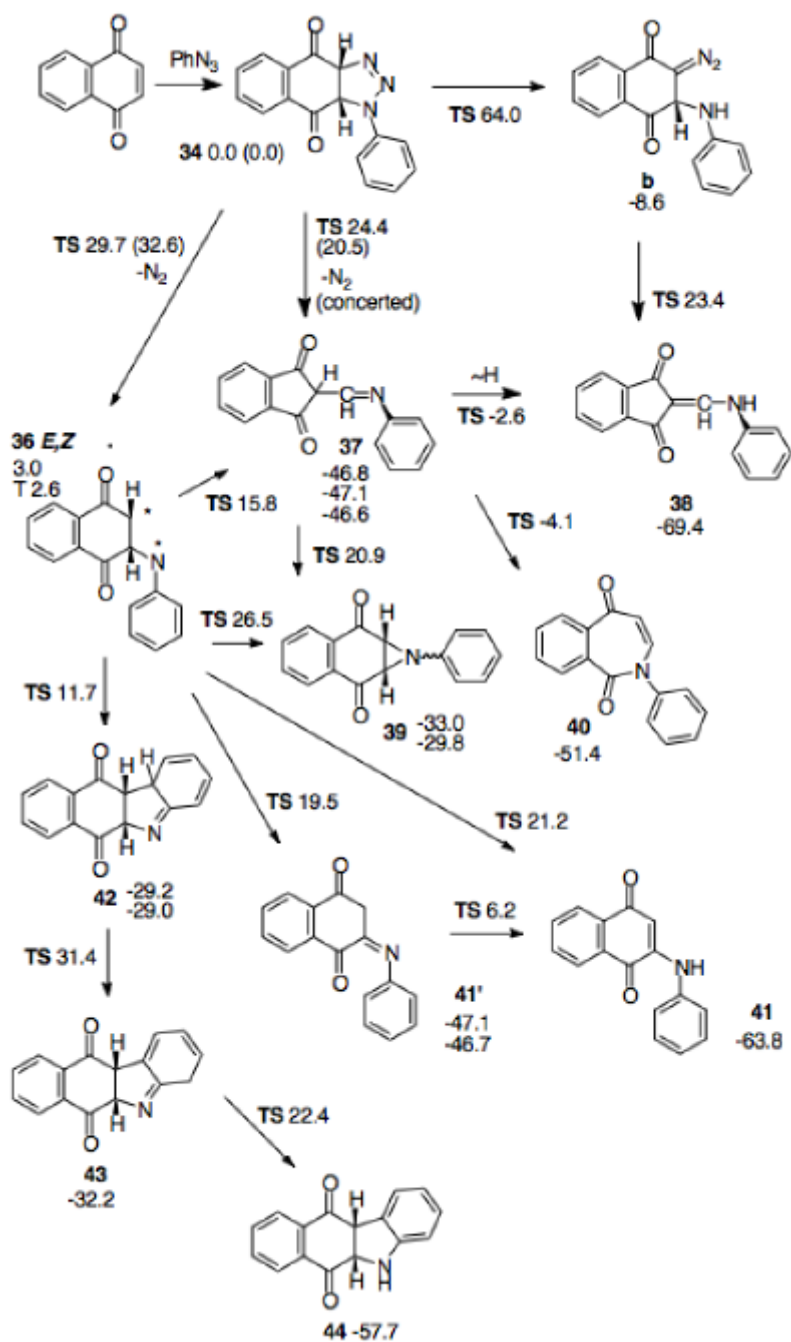
Ludwig Wolff obtained the triazolone naphthoquinone **35** by reaction of 1,4-naphthoquinone **33** with phenyl azide (Scheme 5.17). The product was explained in terms of oxidation of the initially formed dihydro compound **34** by the quinone. Moreover, a ring contraction product formulated as the imine **37** was also formed, in low yield at 60-65°C, and in substantial yield at 100°C.<sup>[95-97]</sup> More recent work has shown that the product is actually the enamine **38**.<sup>[95-100]</sup> Wolff suggested the diradical **36** (formulated as a compound with two open valencies) as the precursor of **37**. Formation of a carbazole derivative was not reported.



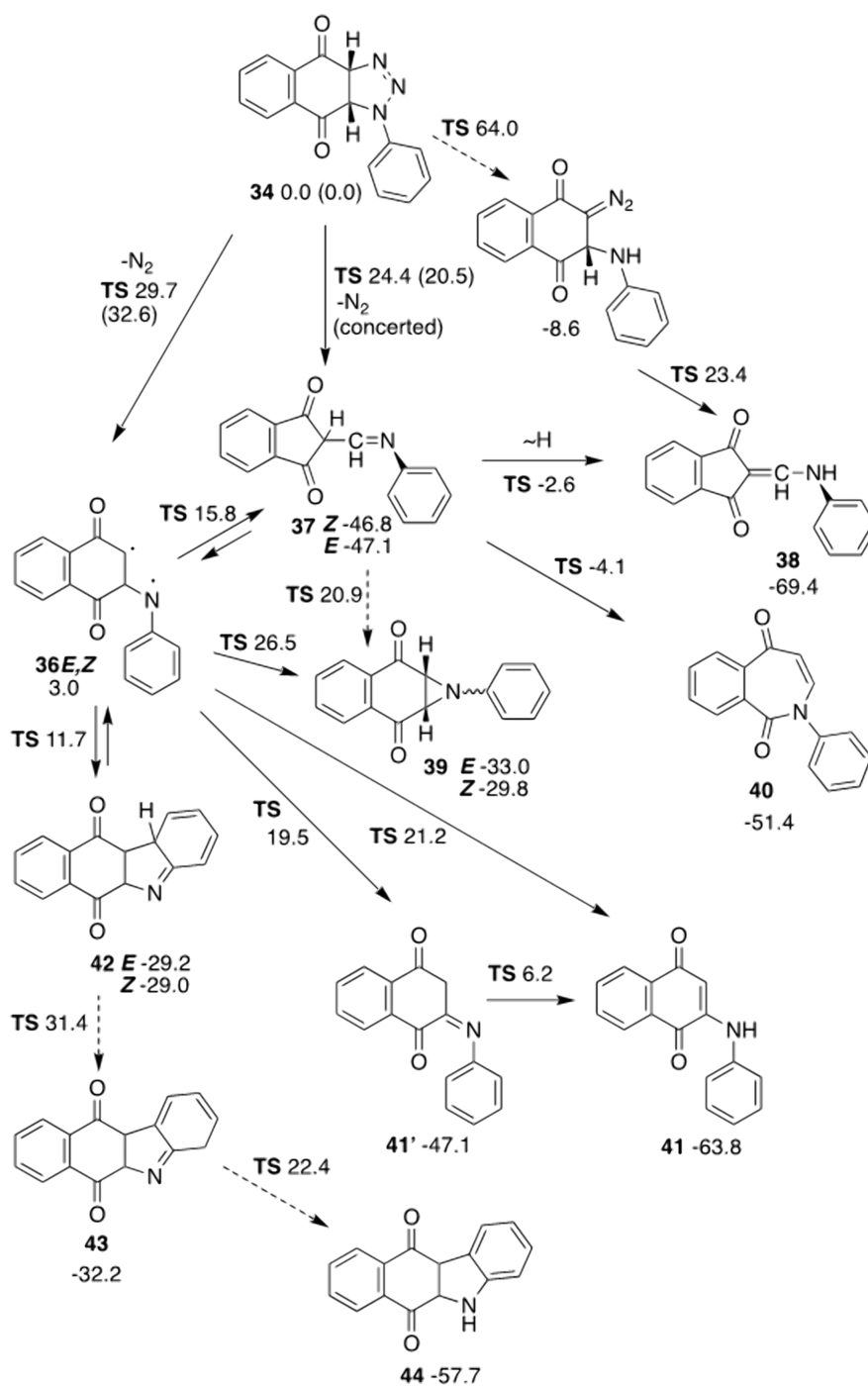
Scheme 5.17: Wolff's mechanism.

Our calculations at the DFT, and in part CASPT2, levels (Scheme 5.19) indicate that the indanedione derivatives **37** and **38** may be reached from the triazolone **34** via two indirect routes with barriers below 30 Kcal/mol. Wolff's intermediate **36** is a diradical with only ca. 1 Kcal/mol, difference between the singlet ground state and the triplet at CASPT2 level; i.e. the two states are virtually isoenergetic (see Scheme 5.18). Ring closure of **36** affords the aziridine **39**, and such compounds have in fact been isolated.<sup>[95-100]</sup> The carbazole derivative **44** would in principle be obtainable from the diradical **36**, but lower energy H-shift paths to the anilinoquinone **41** available, thus preventing the formation of **42** - **44**. The imine-amine tautomerization  $\mathbf{41}' \rightarrow \mathbf{41}$  would take place rapidly by intermolecular H-exchange in solution. Compound **44** has not been reported as a product, but anilinoquinones like **41** are often obtained in decompositions of triazolines.<sup>[99,101]</sup> The predicted, easy formation of the benzazepinedione **40** by rearrangement of **37** accounts for the otherwise unexplained isolation of such compounds in the reactions of azides with quinones.<sup>[102-105]</sup>



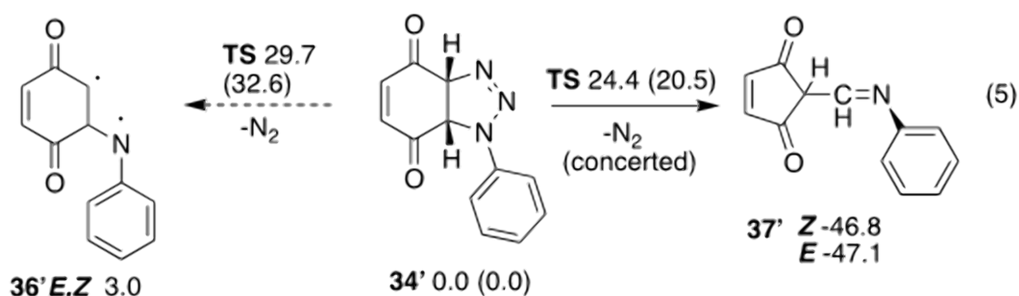


Scheme 5.18: *N*-Phenyltriazo[b]naphthoquinone **35** : Calculations related to Wolff's mechanism. Energies in Kcal/mol calculated at the B3LYP/6-311G(d,p) and CASPT2(10.10)sp/6-311G(d,p) (values in parenthesis) levels related to Scheme 5.17



Scheme 5.19: Calculations related to Wolff's mechanism. DFT and (CASPT2) energies in Kcal/mol.<sup>a</sup>

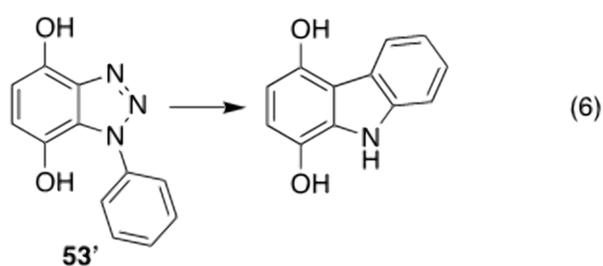
<sup>a</sup> The CASPT2 calculations (values in parentheses) are for the analogous benzoquinone derivatives (Eq. 5).

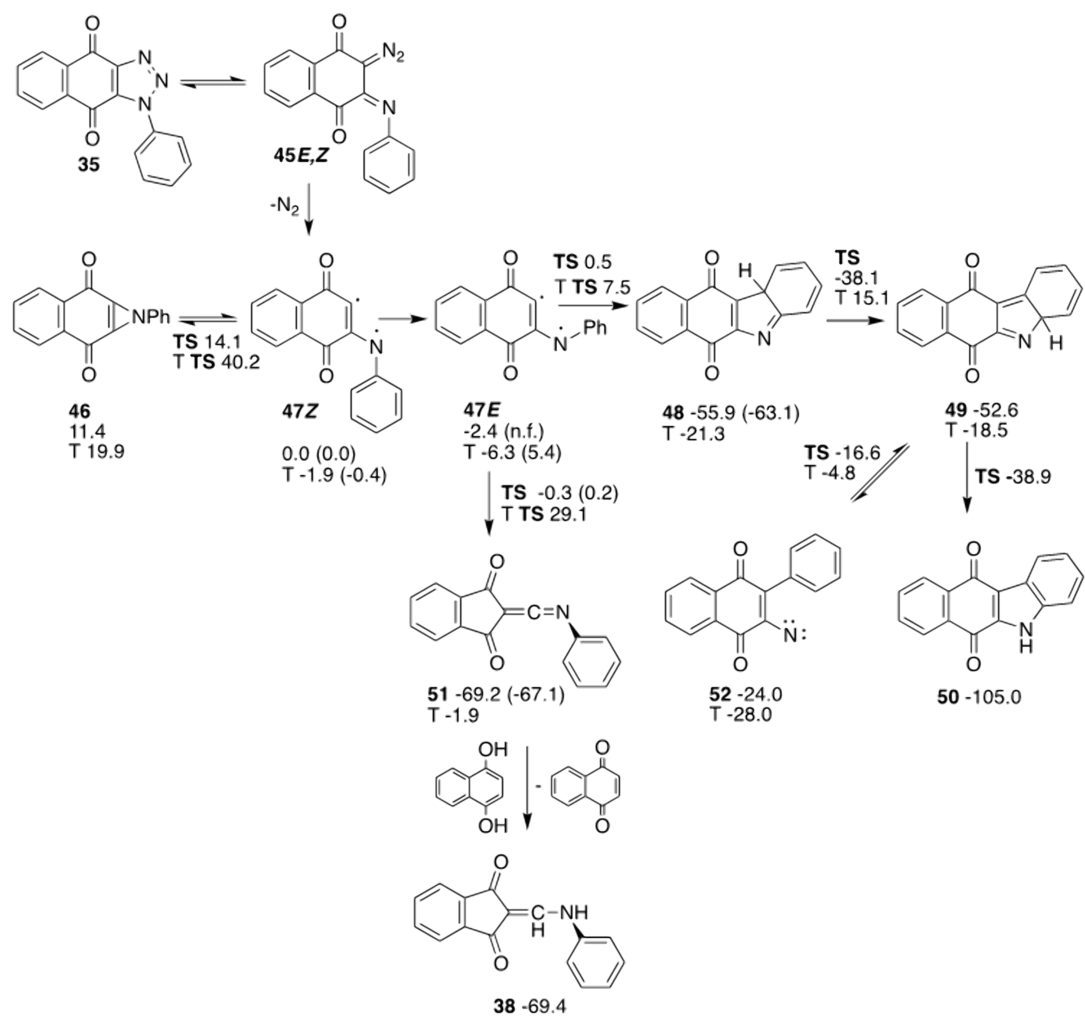


While the reactions described in Scheme 5.19 provide a satisfactory explanation of the observed products, alternate reaction mechanisms need to be considered. Boyer proposed the isolated triazolobenzoquinone **35**, formed by oxidation on the initial addition product **34** by excess naphthoquinone, as the key starting material.<sup>[105]</sup> The 2-diazo-p-naphthoquinone-3-imine valence tautomer **45** can then undergo a Wolff-type rearrangement to the ketenimine **51**. Reduction of this by benzohydroquinone would afford the imine **37** or its isomer, the enamine **38** (Scheme 5.20).

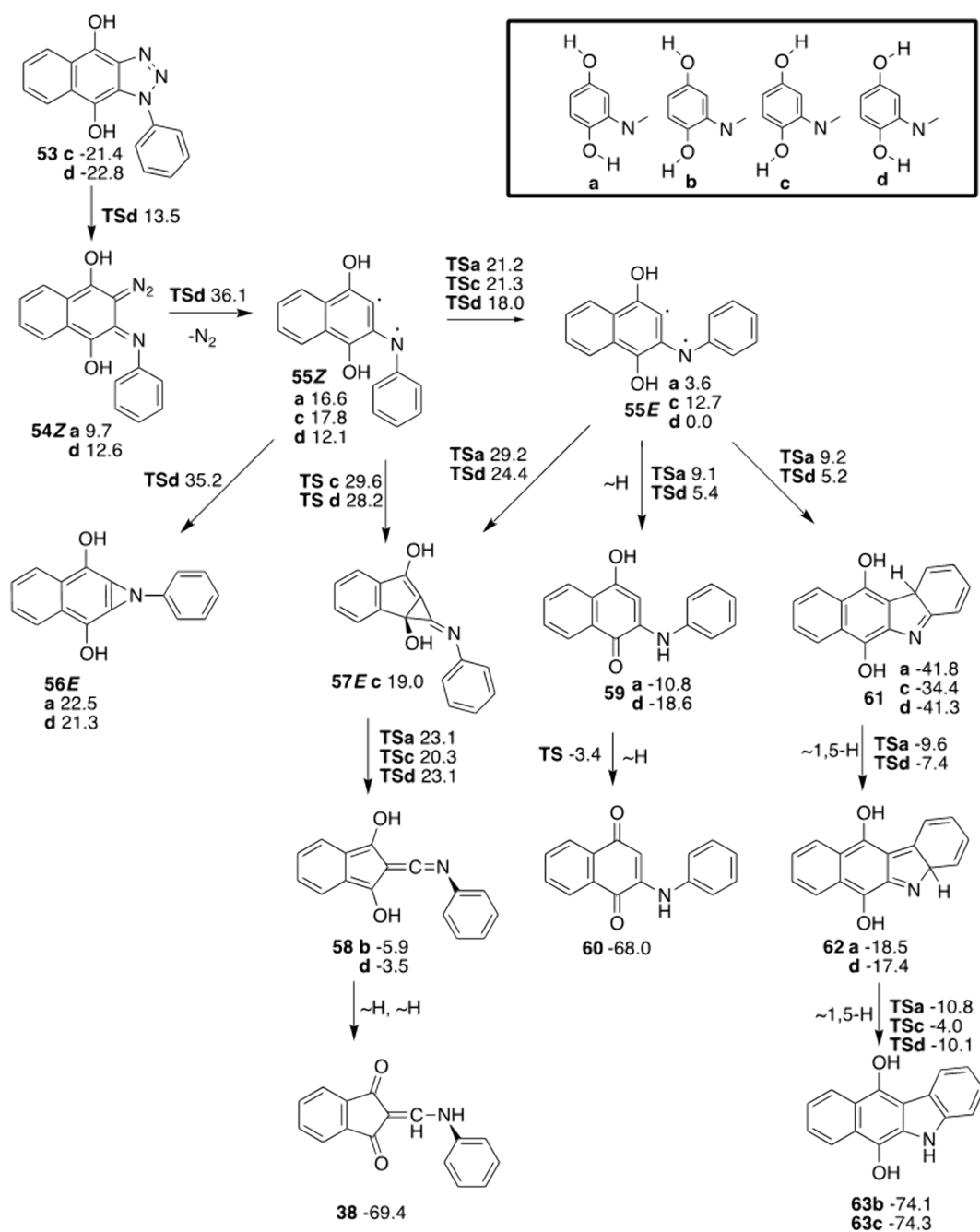
Alternatively, either **34** or **35** could be converted to the hydroquinone **53** and hence the diazoimine **54** (Scheme 5.21). The resulting diradicals **55Z** and **55E** can in principle undergo a number of rearrangements, leading to the ring contraction product **38**, 2-phenylaminobenzoquinone **60**, and carbazole derivative **63**. The calculations at the DFT level clearly show that the formation of **60** and **63** would be preferred. Since carbazole derivatives have never been reported in this chemistry, the mechanism in Scheme 5.21 can be excluded.

The same trend and the same conclusion resulted from our calculations on the simple triazolobenzoquinone **53'** at the DFT level: the formation of 1,4-dihydroxycarbazole would be vastly preferred by this mechanism (Eq. 6).



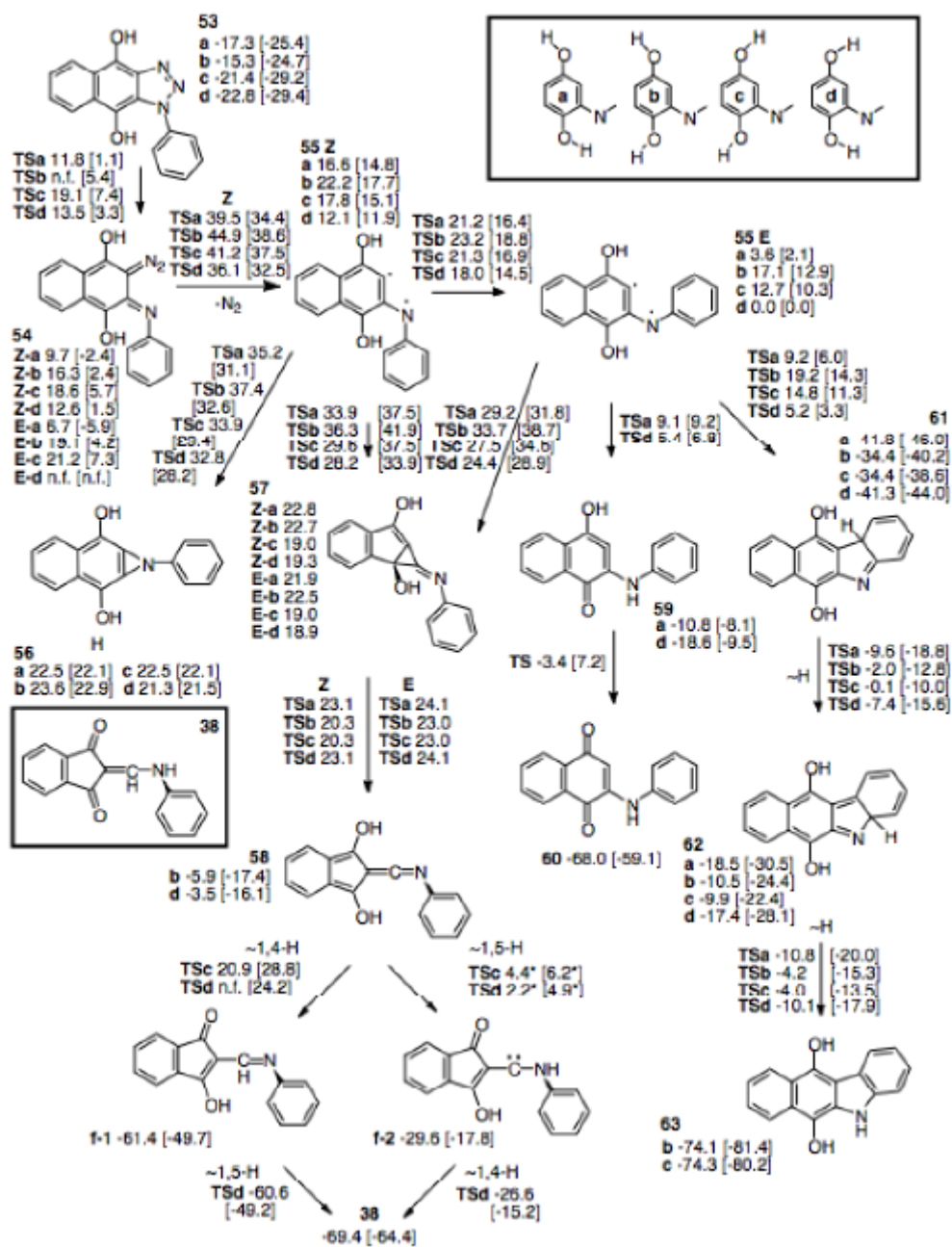


Scheme 5.20: Boyer's mechanism. DFT and (CASPT2) energies in Kcal/mol relative to **47Z** (n.f. = not found).



Scheme 5.21: Hydroquinone mechanism. Energies in Kcal/mol relative to **55Ed** at the DFT level.<sup>a</sup>

<sup>a</sup> Only the data for the lowest energy isomers a-d are shown. Data for all the isomers are available in Scheme 5.22.

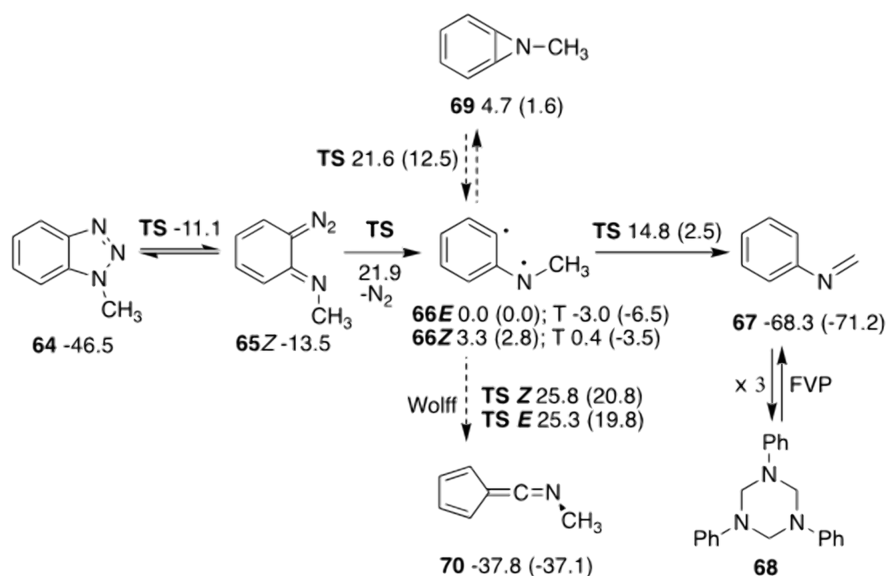


Scheme 5.22: Hydroquinone **53** mechanism. Energies in Kcal/mol calculated at the B3LYP/6-311G(d,p) level related to Scheme 5.21. (values in bracket are obtained for the triazolobenzoquinone **53'** mechanism).

#### 4. 1-Methylbenzotriazole

The FVP of 1-methylbenzotriazole **64** at 660°C yields N-phenylmethanimine **67** in better than 94% yield (Scheme 5.23).<sup>[106,107]</sup> The compound was isolated in the form of its trimer **68** from which it can be regenerated by FVP.<sup>[106]</sup> The Wolff-type ring contraction product, N-methylfulvenimine **69** was not formed. The efficient and exothermic formation of **67** suggests that formation of the benzazirine **69** may be too slow for it to be involved.

Neither **67** nor **70** were reported as products of photolysis of **64** in methanol at 300nm. Instead, N-methylaniline and o-methoxy-N-methylaniline were isolated in 63% and 3.8% yields, respectively.<sup>[85,86]</sup> The triplet diradical<sup>[69]</sup> **66E,Z** has been observed by ESR spectroscopy at 77 K.<sup>[92]</sup>

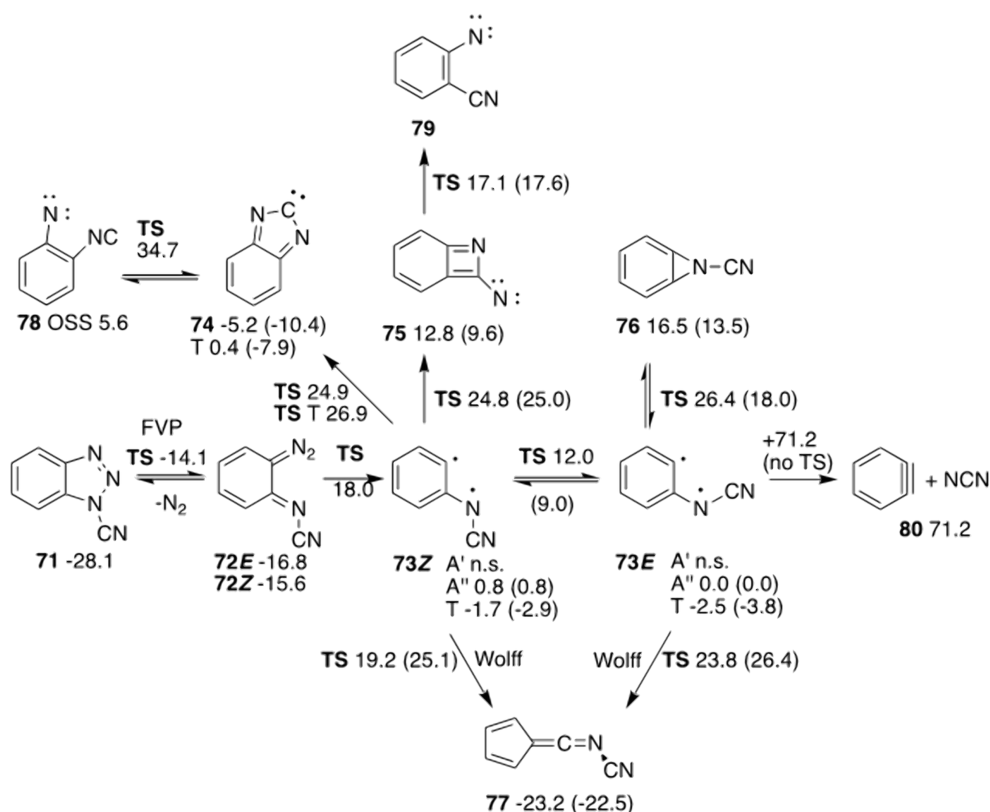


Scheme 5.23: Reactions of 1-methylbenzotriazole. Energies in Kcal/mol at the DFT and (CASPT2) levels.

Our calculations at DFT and CASPT2 levels (Scheme 5.23) are in agreement with the rapid formation of the methanimine **67**, slower potential formation of the unobserved benzazirine **69**, and much slower formation of the unobserved fulvenimine **70**.

## 5. 1-Cyanobenzotriazole

1-Cyanobenzotriazole **71** (Scheme 5.24) undergoes FVP at relatively low temperatures, around 450°C, and kinetic measurements have yielded a first order rate constant several orders of magnitudes higher than for a series of 1-benzotriazolylketones.<sup>[108]</sup> Color changes occurring on heating of **71** in solution or on melting suggest that the diazo compound **72** is readily formed.<sup>[109]</sup> This is in agreement with our low, calculated activation barrier of ~14 Kcal/mol. However, in spite of the facile pyrolysis, it has not afforded any definite, isolable product. Instead, extensive charring occurred inside the pyrolysis tube.



Scheme 5.24: Potential pyrolysis reactions of 1-cyanobenzotriazole; n.s. = not stable; OSS = open shell singlet. Energies in Kcal/mol at the DFT and (CASPT2) levels.

The calculations (Scheme 5.24) indicate that a variety of unstable compounds **74** - **77** can be formed from the initial diradical **73** with comparable and rather modest activation energies of the order of 25 Kcal/mol. Furthermore, the carbene **74** may interconvert with the nitrene **78**, and the nitrene **75** may ring open rather easily to the nitrene **79**. The diradical **73** could decompose to benzyne and NCN (**80**) with a much higher activation barrier. Further, potential reactions are described in Scheme 5.19. All these compounds are very reactive and may explain why no discrete product is formed in an appreciable yield.



## Conclusion

The denitrogenative rearrangement of 1-arylbenzotriazoles **14** to carbazoles **18** is energetically preferred over the ring contraction to fulvenimines **20** by about 25 Kcal/mol. The cyclization of biradicals **16** to benzazirines **17** is disfavoured by about 21 Kcal/mol. These results are in accord with the experimentally observed, clean formation of carbazoles without substituent migration under both thermal (FVP) and photochemical reaction conditions.

In contrast, the two reaction paths, cyclization to tetrahydrocarbazole **30** and ring contraction to tetrahydrofulvenimine **31**, have similar, small, activation barriers of the order of 6-7 Kcal/mol, and both products were in fact formed with comparable yields on pyrolysis of 1-phenyltetrahydrobenzotriazole **24**. However, compound **30** is the major product in the photolysis reaction. The formation of a tetrahydrobenzazirine **27** is not predicted to be competitive.

Consideration of different reaction mechanisms for the thermal decomposition of triazolobenzo- and -naphthoquinones lead to the conclusion that denitrogenation of the product **34** of 1,3-cycloaddition of phenyl azide to 1,4-naphthoquinone results in ring contraction to the indanedione **37** and the benzofulvenedione derivative **38**. In addition, compound **37** can rearrange to the benzazepinedione **40**. Furthermore, **37** can also rearrange to the aziridine **39** and the phenylaminoquinone **41** via the diradical **36** originally proposed by Wolff. These reactions explain all the experimentally observed products as well as the absence of the carbazole derivative **44**.

Pyrolysis of 1-methylbenzotriazole **64** gives N-phenylmethanimine **67** in virtually quantitative yield, and neither cyclization to a benzazirine **69** nor ring contraction to the fulvenimine **70** are favoured energetically. In contrast, 1-cyanobenzotriazole **71** has not yielded any definite product but much charring inside the pyrolysis tube in FVP experiments. Calculations indicate the operation of several reaction paths with very similar, low activation energies, all leading to unstable compounds, whose subsequent reactions may explain the experimental observations.

## Computational Details

Ground-state geometries and energies were determined at the DFT level using the B3LYP exchange-correlation functional with the 6-311G(d,p) basis set. In order to take any potential multiconfigurational effects into account, calculations were also carried out at CASSCF\_opt // CASPT2(10,10)sp/6-311G(d,p) levels. In the case of Scheme 5.19, due to the size of the molecules, the CASPT2 calculations were for the analogous p-benzoquinone derivatives. These procedures allow direct comparison with previous calculations on benzotriazoles.<sup>[69]</sup> All calculations were performed using the Gaussian 09 and Molpro program packages.<sup>[110,111]</sup> Calculated energies are at 0 K. The reported energies are always for the singlet species, except when the triplet is indicated with a T.

## References

- [1] H. J. Werner and P. J. Knowles, "A second order multiconfiguration scf procedure with optimum convergence," *J. Chem. Phys.*, vol. 82, pp. 5053–5063, 1985.
- [2] P. J. Knowles and H. J. Werner, "An efficient second-order mc scf method for long configuration expansions," *Chem. Phys. Lett.*, vol. 115, pp. 259–267, 1985.
- [3] H. J. Werner and W. Meyer, "A quadratically convergent multiconfiguration self consistent field method with simultaneous optimization of orbitals and ci coefficients," *J. Chem. Phys.*, vol. 73, pp. 2342–2356, 1980.
- [4] H. J. Werner and W. Meyer, "A quadratically convergent mcsf method for the simultaneous optimization of several states," *J. Chem. Phys.*, vol. 74, pp. 5794–5801, 1981.
- [5] K. Andersson, P. A. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, "Second-order perturbation theory with a casscf reference function," *J. Phys. Chem.*, vol. 94, pp. 5483–5488, 1990.
- [6] K. Andersson, P. A. Malmqvist, and B. O. Roos, "Second-order perturbation theory with a complete active space self-consistent field reference function," *J. Chem. Phys.*, vol. 96, pp. 1218–1226, 1992.
- [7] J. J. Finley, P. A. Malmqvist, B. O. Roos, and L. Serrano-Andrés, "The multi-state caspt2 method," *Chem. phys. let.*, vol. 288, pp. 299–306, 1998.
- [8] T. Shiozaki and H. J. Werner, "Communication: Second-order multireference perturbation theory with explicit correlation: Caspt2-f12," *J. Chem. Phys.*, vol. 133, p. 141103, 2010.
- [9] T. Shiozaki, C. Woywod, and H. J. Werner, "Pyrazine excited states revisited using the extended multi-state complete active space second-order perturbation method," *Phys. Chem. Chem. Phys.*, vol. 15, pp. 262–269, 2013.
- [10] K. Yamaguchi, H. Fukui, and T. Fueno, "Molecular orbital (mo) theory for magnetically interacting organic compounds. ab-initio mo calculations of the effective exchange integrals for cyclophane-type carbene dimers," *Chem. Lett.*, vol. 15, pp. 625–628, 1986.
- [11] K. Yamaguchi, Y. Takahara, T. Fueno, and K. Houk, "Extended hartree-fock (ehf) theory of chemical reactions," *Theoretica chimica acta*, vol. 73, pp. 337–364, 1988.
- [12] K. Yamaguchi, F. Jensen, A. Dorigo, and K. Houk, "A spin correction procedure for unrestricted hartree-fock and møller-pleeset wavefunctions for singlet diradicals and polyradicals," *Chem. phy. let.*, vol. 149, pp. 537–542, 1988.
- [13] D. Casanova and A. I. Krylov, "Spin-flip methods in quantum chemistry," *Phys. Chem. Chem. Phys.*, vol. 22, pp. 4326–4342, 2020.

- [14] A. Padwa, *1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products*. Wiley-Interscience, 1984.
- [15] A. Padwa and W. H. Pearson, *Synthetic applications of 1,3-dipolar cycloaddition chemistry toward heterocycles and natural products*, vol. 59. Wiley, 2002.
- [16] S. Kobayashi and K. A. Jørgensen, *Cycloaddition reactions in organic synthesis*. 2002.
- [17] G. Bertrand and C. Wentrup, “Nitrile imines: from matrix characterization to stable compounds,” *Angew. Chem. Int. Ed. Engl.*, vol. 33, pp. 527–545, 1994.
- [18] D. H. Ess and K. N. Houk, “Theory of 1,3-dipolar cycloadditions: distortion/interaction and frontier molecular orbital models,” *J. Am. Chem. Soc.*, vol. 130, pp. 10187–10198, 2008.
- [19] R. C. Mawhinney, H. M. Muchall, and G. H. Peslherbe, “The electronic structure of nitrilimines revisited,” *Chem. Comm.*, pp. 1862–1863, 2004.
- [20] F. Cargnoni, G. Molteni, D. Cooper, M. Raimondi, and A. Ponti, “The electronic structure of nitrilimine: absence of the carbenic form,” *Chem. Comm.*, pp. 1030–1032, 2006.
- [21] G. Haberhauer, R. Gleiter, and S. Woitschetzki, “Anti-diradical formation in 1,3-dipolar cycloadditions of nitrile oxides to acetylenes,” *J. Org. Chem.*, vol. 80, pp. 12321–12332, 2015.
- [22] B. Braida, C. Walter, B. Engels, and P. C. Hiberty, “A clear correlation between the diradical character of 1,3-dipoles and their reactivity toward ethylene or acetylene,” *J. Am. Chem. Soc.*, vol. 132, pp. 7631–7637, 2010.
- [23] T. M. Sexton, M. Freindorf, E. Kraka, and D. Cremer, “A reaction valley investigation of the cycloaddition of 1,3-dipoles with the dipolarophiles ethene and acetylene: solution of a mechanistic puzzle,” *J. Phys. Chem. A*, vol. 120, pp. 8400–8418, 2016.
- [24] A. Toyota, T. Muramatsu, and S. Koseki, “Multiconfiguration self-consistent field study on formonitrile imine and n-substituted nitrile imines hcn<sub>2</sub>-r: Energy component analysis of the pseudo-jahn-teller effect,” *J. Phys. Chem. A*, vol. 121, pp. 2298–2310, 2017.
- [25] D. Bégué, G. G. Qiao, and C. Wentrup, “Nitrile imines: matrix isolation, ir spectra, structures, and rearrangement to carbodiimides,” *J. Am. Chem. Soc.*, vol. 134, pp. 5339–5350, 2012.
- [26] C. M. Nunes, I. Reva, R. Fausto, D. Bégué, and C. Wentrup, “Bond-shift isomers: the co-existence of allenic and propargylic phenylnitrile imines,” *Chem. Comm.*, vol. 51, pp. 14712–14715, 2015.

- [27] D. Bégué and C. Wentrup, “Carbenic nitrile imines: properties and reactivity,” *J. Org. Chem.*, vol. 79, pp. 1418–1426, 2014.
- [28] E. G. Baskir, D. N. Platonov, Y. V. Tomilov, and O. M. Nefedov, “Infrared-spectroscopic study of amino-substituted nitrilimines and their photochemical transformations in an argon matrix,” *Mendeleev Commun.*, vol. 24, pp. 197–200, 2014.
- [29] C. M. Nunes, I. Reva, M. T. S. Rosado, and R. Fausto, “The quest for carbenic nitrile imines: Experimental and computational characterization of *c*-amino nitrile imine,” *Eur. J. Org. Chem.*, vol. 2015, pp. 7484–7493, 2015.
- [30] D. Bégué, A. Dargelos, and C. Wentrup, “Rearrangements of nitrile imines: Ring expansion of benzonitrile imines to cycloheptatetraenes and ring closure to 3-phenyl-3H,” *J. Org. Chem.*, vol. 84, pp. 8668–8673, 2019.
- [31] D. Bégué, H. Santos-Silva, A. Dargelos, and C. Wentrup, “Imidoynitrenes  $r^1c(=nr)-n$ , nitrile imines, 1*H*-diazirines, and carbodiimides: Interconversions and rearrangements, structures, and energies at dft and caspt2 levels of theory,” *J. Phys. Chem. A*, vol. 121, pp. 8227–8235, 2017.
- [32] M. Abe, D. Bégué, H. Santos-Silva, A. Dargelos, and C. Wentrup, “Direct observation of an imidoynitrene: Photochemical formation of  $phc(=nme)-n$  and  $me-n$  from 1-methyl-5-phenyltetrazole,” *Angew. Chem.*, vol. 130, pp. 3266–3270, 2018.
- [33] D. Bégué, A. Dargelos, and C. Wentrup, “Aryl nitrile imines and diazo compounds. formation of indazole, pyridine *n*-imine, and 2-pyridyldiazomethane from tetrazoles,” *J. Org. Chem.*, vol. 85, pp. 7952–7958, 2020.
- [34] H. Wieland, “Zur kenntnis der nitriloxyde (ii),” *Ber. deu. chem. Ges.*, vol. 42, pp. 803–816, 1909.
- [35] H. Wieland, “Zur kenntnis der nitriloxyde (ii),” *Ber. deu. chem. Ges.*, vol. 43, pp. 4207–4209, 1910.
- [36] C. Grundmann and J. M. Dean, “Nitrile oxides. v. stable aromatic nitrile oxides<sup>1,2</sup>,” *J. Org. Chem.*, vol. 30, pp. 2809–2812, 1965.
- [37] G. Just and W. Zehetner, “Photolysis of podocarponitrile oxide and mesitonitrile oxide,” *Tetrahedron Letters*, vol. 8, pp. 3389–3391, 1967.
- [38] C. Grundmann and P. Kochs, “An investigation of the nitrile oxide-isocyanate rearrangement,” *Angew. Chem. Int. Ed. Engl.*, vol. 9, p. 635, 1970.
- [39] F. J. Holsboer and W. Beck, “Indo calculation of the fulminate-cyanate rearrangement,” *J. Chem. Soc.: Chem. Commun.*, p. 262, 1970.

- [40] C. Grundmann, P. Kochs, and J. R. Boal, "Nitriloxide, xv. zur kenntnis der thermischen umlagerung von nitriloxiden in isocyanate," *Justus Liebigs Ann. Chem.*, vol. 761, pp. 162–181, 1972.
- [41] G. Trickes and H. Meier, "Catalyzed rearrangement of nitrile oxides to isocyanates," *Angew. Chem. Int. Ed. Engl.*, vol. 16, p. 555, 1977.
- [42] C. Wentrup, "Carbenes and nitrenes in heterocyclic chemistry: intramolecular reactions," in *Advances in Heterocyclic Chemistry*, vol. 28, pp. 231–361, 1981.
- [43] G. A. Taylor, "J. chem. soc., perkin trans. i," pp. 1181–1184, 1985.
- [44] E. Eibler, J. Käsbauer, H. Pohl, and J. Sauer, "Konkurrenzexperimente zum nachweis von acylnitrenen," *Tetrahedron letters*, vol. 28, pp. 1097–1100, 1987.
- [45] M. Barbieux-Flammang, S. Vandevorde, R. Flammang, M. W. Wong, H. Bibas, C. H. Kennard, and C. Wentrup, "Monomer, dimers and trimers of cyanogen n-oxide,  $n\equiv c-c\equiv n\rightarrow o$ . an x-ray, fvt-ms/ir and theoretical investigation," *J. Chem. Soc., Perkin Trans. II*, pp. 473–478, 2000.
- [46] H. Feuer, *Nitrile oxides, nitrones and nitronates in organic synthesis: novel strategies in synthesis*, vol. 6. 2008.
- [47] S. Bando, Y. Koyama, and T. Takata, "Concentration-dependent thermal isomerization of nitrile n-oxide," *Eur. J. Org. Chem.*, vol. 2020, pp. 4982–4987, 2020.
- [48] C. Grundmann and P. Grünanger, "Physiological properties and applications of nitrile oxides," in *The Nitrile Oxides*, pp. 184–187, 1971.
- [49] S. Gabriel and M. Koppe, "Zur kenntniss des phenylnitromethans," *Ber. deut. chem. Ges.*, vol. 19, pp. 1145–1148, 1886.
- [50] D. Bégué, C. Addicott, R. Burgard, P. Bednarek, E. Guille, I. Baraille, and C. Wentrup, "Nitrile ylides: allenic and propargylic structures from pyrazinyl nitrenes. experimental and theoretical characterization," *J. Org. Chem.*, vol. 79, pp. 2148–2155, 2014.
- [51] D. Bégué, A. Dargelos, H. M. Berstermann, K. P. Netsch, P. Bednarek, and C. Wentrup, "Nitrile imines and nitrile ylides: Rearrangements of benzonitrile n-methylimine and benzonitrile dimethylmethylyde to azabutadienes, carbodiimides, and ketenimines. chemical activation in thermolysis of azirenes, tetrazoles, oxazolones, isoxazolones, and oxadiazolones," *J. Org. Chem.*, vol. 79, pp. 1247–1253, 2014.
- [52] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara,

- K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, "Gaussian 09 Revision A.2." Gaussian Inc. Wallingford CT 2009.
- [53] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, "Molpro: a general-purpose quantum chemistry program package," *WIREs: Comput. Mol. Sci.*, vol. 2, pp. 242–253, 2012.
- [54] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and M. Wang, "Molpro, version 2012.1, a package of ab initio programs," See <http://www.molpro.net> (retrived 4.9.2020), 2012.
- [55] E. A. Pritchina, N. P. Gritsan, A. Maltsev, T. Bally, T. Autrey, Y. Liu, Y. Wang, and J. P. Toscano, "Matrix isolation, time-resolved ir, and computational study of the photochemistry of benzoyl azide," *Phys. Chem. Chem. Phys.*, vol. 5, pp. 1010–1018, 2003.
- [56] E. A. Pritchina, N. P. Gritsan, and T. Bally, "Ground state multiplicity of acylnitrenes: computational and experimental studies," *Russ. chem. bull.*, vol. 54, pp. 525–532, 2005.
- [57] C. Wentrup and H. Bornemann, "The curtius rearrangement of acyl azides revisited—formation of cyanate (r-o-cn)," 2005.
- [58] C. Wentrup, "Carbenes and nitrenes: recent developments in fundamental chemistry," *Angew. Chem. Int. Ed.*, vol. 130, pp. 11680–11693, 2018.
- [59] C. Wentrup and B. Freiermuth, "Pyrolysis of benzotriazoles. relationships between 1-and 2-vinylbenzotriazoles,  $\alpha$ -and  $\beta$ -azidostyrenes, n-phenylketenimine and indole. pitfalls in the use of pyrolysis-mass spectrometry in mechanistic studies," *J. Anal. Appl. Pyrolysis*, vol. 121, pp. 67–74, 2016.
- [60] U. Banerjee, K. Thenna-Hewa, and A. D. Gudmundsdottir, "Triplet vinylnitrenes," *Patai's chemistry of functional groups*, 2019.

- [61] H. D. M. Sriyathne, S. K. Sarkar, S. Hatano, M. Abe, and A. D. Gudmundsdottir, "Photolysis of 3,5-diphenylisoxazole in argon matrices," *J. Phys. Org. Chem.*, vol. 30, p. e3638, 2017.
- [62] X. Zhang, S. Sarkar, G. Weragoda, S. Rajam, B. S. Ault, and A. D. Gudmundsdottir, "Comparison of the photochemistry of 3-methyl-2-phenyl-2*H*-azirine and 2-methyl-3-phenyl-2*H*-azirine," *J. Org. Chem.*, vol. 79, pp. 653–663, 2014.
- [63] C. Wentrup, D. Bégué, and R. Leung-Toung, "Ethyamine – ketenimine – acetonitrile rearrangements: A computational study of flash vacuum pyrolysis processes.," <https://doi.org/10.26434/chemrxiv.5373964.v1>, 2017.
- [64] R. Gérardy and J.-C. M. Monbaliu, "Preparation, reactivity, and synthetic utility of simple benzotriazole derivatives," *The Chemistry of Benzotriazole Derivatives*, pp. 1–66, 2015.
- [65] A. R. Katritzky and S. Rachwal, "Synthesis of heterocycles mediated by benzotriazole. 1. monocyclic systems," *Chem. Rev.*, vol. 110, pp. 1564–1610, 2010.
- [66] A. R. Katritzky, X. Lan, J. Z. Yang, and O. V. Denisko, "Properties and synthetic utility of *n*-substituted benzotriazoles.," *Chem. Rev.*, vol. 98, pp. 409–548, 1998.
- [67] A. S. Singh, D. Kumar, N. N. Mishra, and V. K. Tiwari, "An efficient one-pot synthesis of *n,n'*-disubstituted ureas and carbamates from *n*-acylbenzotriazoles," *RSC advances*, vol. 6, pp. 84512–84522, 2016.
- [68] W. Li and J. Zhang, "Frontispiece: Synthesis of heterocycles through denitrogenative cyclization of triazoles and benzotriazoles," *Chem. Eur. J.*, vol. 26, 2020.
- [69] D. Bégué, H. Santos-Silva, A. Dargelos, and C. Wentrup, "Iminocyclohexadienylienes: Carbenes or diradicals ? the hetero-wolff rearrangement of benzotriazoles to cyanocyclopentadienes and 1 *H*-benzo[b]azirines," *J. Phys. Chem. A*, vol. 121, pp. 5998–6003, 2017.
- [70] C. Wentrup, B. Freiermuth, and N. Aylward, "Pyrolysis of benzotriazoles. 1-acyl-and 1-alkoxycarbonylbenzotriazoles: Hetero-wolff rearrangement to *n*-acyl-and *n*-alkoxycarbonylfulvenimines and free radical routes to cyanocyclopentadienes," *J. Anal. Appl. Pyrolysis*, vol. 128, pp. 187–195, 2017.
- [71] C. Thetaz and c. Wentrup, "1*H*-benzazirines. intermediates in the ring contraction of iminocyclohexadienylienes and arylnitrenes," *J. Am. Chem. Soc.*, vol. 98, pp. 1258–1259, 1976.
- [72] E. S. Gil, B. B. de Araújo, and P. F. B. Gonçalves, "Caspt2, casscf and non-adiabatic molecular dynamics (namd) studies on the low-lying electronic states of 1*H*-1, 2,3-triazole photolysis," *Physical Chemistry Chemical Physics*, vol. 21, pp. 25809–25819, 2019.

- [73] C. Wentrup, "Flash vacuum pyrolysis of azides, triazoles, and tetrazoles," *Chem. Rev.*, vol. 117, pp. 4562–4623, 2017.
- [74] C. Graebe and F. Ullmann, "Ueber eine neue carbazolsynthese," *Justus Liebigs Ann. Chem.*, vol. 291, pp. 16–17, 1896.
- [75] F. Ullmann, "Ueber synthesen in der carbazolgruppe," *Ber. dtsh. chem. Ges.*, vol. 31, pp. 1697–1698, 1898.
- [76] F. Ullmann, "Studien in der carbazolreihe," *Justus Liebigs Ann. Chem.*, vol. 332, pp. 82–104, 1904.
- [77] W. Borsche and M. Feise, "Ueber einige neue carbazolderivate," *Ber. dtsh. chem. Ges.*, vol. 40, pp. 378–386, 1907.
- [78] W. Lawson, W. H. Perkin, and R. Robinson, "Lxxvi.—harmine and harmaline. part vii. a synthesis of apo harmine and of certain carboline and copyrine derivatives," *J. Chem. Soc. Trans.*, vol. 125, pp. 626–657, 1924.
- [79] N. Campbell and B. M. Barclay, "Recent advances in the chemistry of carbazole.," *Chem. Rev.*, vol. 40, pp. 359–380, 1947.
- [80] W. Freudenberg, "Heterocyclic compounds," 1952.
- [81] N. A. Al-Awadi, A. S. Mohamed, O. M. Habib, F. H. Al-Awadhi, N. A. Al-Jalal, and Y. A. Ibrahim, "Flash vacuum pyrolysis of acetylenic esters: A mechanistic study," *J. Anal. Appl. Pyrolysis*, vol. 146, pp. 65–78, 2020.
- [82] C. Wentrup, "Carbenes and nitrenes in heterocyclic chemistry: intramolecular reactions," in *Adv. Heterocycl. Chem.*, vol. 28, pp. 231–361, 1981.
- [83] C. Wentrup, J. Becker, and H. W. Winter, "Falling-solid flash vacuum pyrolysis: An efficient preparation of arylacetylenes," *Angew. Chem.*, vol. 127, pp. 5794–5796, 2015.
- [84] C. Wentrup, "Flash vacuum pyrolysis: Techniques and reactions," *Angew. Chem. Int. Ed.*, vol. 56, pp. 14808–14835, 2017.
- [85] A. J. Hubert, "Photochemistry of benzotriazoles," *J. Chem. Soc. C*, pp. 1334–1336, 1969.
- [86] A. J. Hubert, "A comparison of the thermolysis and photochemistry of benzotriazoles," *J. Chem. Soc. D: Chem. Commun.*, p. 328, 1969.
- [87] J. H. Boyer and R. Selvarajan, "Photo-elimination of nitrogen from fused-ring triazoles," *J. Heterocycl. Chem.*, vol. 6, pp. 503–506, 1969.
- [88] C. Wentrup, "The relationship between  $c_6h_5n$  isomers. pyrolysis of isatins," *Helv. Chim. Acta*, vol. 55, pp. 1613–1617, 1972.



- [89] M. Ohashi, K. Tsujimoto, and T. Yonezawa, "Nature of the intermediates in the photolysis of benzotriazoles," *J. Chem. Soc. D: Chem. Commun.*, pp. 1089–1090, 1970.
- [90] K. Tsujimoto, M. Ohashi, and T. Yonezawa, "The photochemical decomposition of benzotriazoles," *Bull. Chem. Soc. Japan*, vol. 45, pp. 515–519, 1972.
- [91] I. Alimi, R. Remy, and C. G. Bochet, "Photochemical c-h activation: generation of indole and carbazole libraries, and first total synthesis of clausenawalline d," *Eur. J. Org. Chem.*, vol. 2017, pp. 3197–3210, 2017.
- [92] H. Murai, M. Torres, and O. P. Strausz, "Electron spin resonance of iminocyclohexadienylidenes: photoinduced triplet geometrical isomerization," *J. Am. Chem. Soc.*, vol. 102, pp. 1421–1422, 1980.
- [93] M. L. Tsao, N. Gritsan, T. R. James, M. S. M. S. Platz, D. A. Hrovat, and W. T. Borden, "Study of the chemistry of ortho-and para-biphenylnitrenes by laser flash photolysis and time-resolved ir experiments and by b3lyp and caspt2 calculations," *J. Am. Chem. Soc.*, vol. 125, pp. 9343–9358, 2003.
- [94] K. Tsujimoto, M. Ohashi, and T. Yonezawa, "Thermal and photochemical decompositions of 4,5,6,7-tetrahydro-1,2,3-benzotriazole analogues," *Bull. Chem. Soc. Japan*, vol. 46, pp. 3605–3607, 1973.
- [95] L. Wolff, "Anlagerung von diazobenzolimid an chinone," *Justus Liebigs Ann. Chem.*, vol. 399, pp. 274–297, 1913.
- [96] L. Wolff, "Anlagerung von diazobenzolimid an chinone," *Justus Liebigs Ann. Chem.*, vol. 394, pp. 68–85, 1912.
- [97] G. Caronna and S. S. Palazzo, "Reazioni tra p-nitrofenilazide e alcuni chinoni," *Gazz. Chim. Ital.*, vol. 82, pp. 292–296, 1952.
- [98] I. T. Barnish and M. S. Gibson, "The reaction of aryl azides with 1,4-quinones," *J. chem. Res. (S)*, p. 208, 1992.
- [99] I. T. Barnish and M. S. Gibson, "The reaction of aryl azides with 1,4-quinones," *J. chem. Res. (M)*, pp. 1740–1757, 1992.
- [100] C. K. Sha, S. L. Ouyang, D. Y. Hsieh, R. C. Chang, and S. C. Chang, "Intramolecular 1,3-dipolar cycloaddition of alkyl azide enones and rearrangements of the triazoline intermediates. formal total synthesis of ( $\pm$ )-desamylperhydrohistrionicotoxin," *J. Org. Chem.*, vol. 51, pp. 1490–1494, 1986.
- [101] W. I. Awad, S. M. A. R. Omran, and F. Nagieb, "Action of hydrazoic acid and arylazides on n-arylmaleimides, with special note on the pyrolysis of the resulting triazolines," *Tetrahedron*, vol. 19, pp. 1591–1601, 1963.

- [102] A. G. Schultz and W. G. McMahon, "Intramolecular reactions of azidoalkenes. the 2-(azidoalkyl) quinone rearrangement," *J. Org. Chem.*, vol. 49, pp. 1676–1678, 1984.
- [103] J. Zhang and C. T. Chang, "One-pot synthesis of 1-and 2-substituted naphtho [2,3-d][1,2,3] triazole-4,9-diones," *J. Org. Chem.*, vol. 74, pp. 4414–4417, 2009.
- [104] J. J. Zhang and C.-W. T. C. W. Chang, "Divergent synthesis of three classes of aryl glycosides by solvent control," *The Journal of organic chemistry*, vol. 74, no. 2, pp. 685–695, 2009.
- [105] J. H. Boyer and f. C. Canter, "Alkyl and aryl azides.," *Chemical Reviews*, vol. 54, pp. 1–57, 1954.
- [106] C. Wentrup, "Rearrangements and interconversions of carbenes and nitrenes," in *Synthetic and Mechanistic Organic Chemistry*, pp. 173–251, 1976.
- [107] W. K. Janowski, R. H. Prager, and J. A. Smith, "A comparison of some pyrolysis reactions of benzotriazoles, benzisoxazolones and benzisothiazolones," *J. Chem Soc, Perkin Trans. 1*, pp. 3212–3216, 2000.
- [108] H. H. Dib, N. A. Al-Awadi, Y. A. Ibrahim, and O. M. E. El-Dusouqui, "Gas-phase thermolysis of benzotriazole derivatives: part 1—synthesis of  $\alpha$ -n (1)-and n (2)-benzotriazolyl ketones and kinetics and mechanism of their gas-phase pyrolysis," *J. Phys. Org. Chem.*, vol. 17, pp. 267–272, 2004.
- [109] M. E. Hermes and F. D. Marsh, "1-cyano-1,2,3-triazole- $\alpha$ -diazo-n-cyanoimine tautomers from cyanogen azide and acetylenes," *J. Am. Chem. Soc.*, vol. 89, pp. 4760–4764, 1967.
- [110] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, "Gaussian 09 Revision A.2." Gaussian Inc. Wallingford CT 2009.
- [111] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert,

E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and M. Wang, "Molpro, version 2012.1, a package of ab initio programs," See <http://www.molpro.net> (retrived 02.18.2019), 2012.

## 6 Conclusions and perspectives

Quantum chemistry is a discipline that allows a theoretical approach of chemical phenomena. The increasing power of computer and the regular development of methods and softwares used for computation make it possible to process kind the chemical problem. However, methods and approximations need to be carefully chosen to ensure both reliability and accuracy of the computations. In some cases, depending on the nature of the chemical species studied and on the physicochemical properties to be modelled, it can be necessary to improve or extend an existing method. One way to develop the most suitable approach is to analyse and correct the limitations of the existing methods. It starts by identifying all the structural and chemical informations the existing methods don't take into account but which are, however, essential to the description of the physical properties studied. By implementing those informations, we obviously increase the precision of the model used.

In the first chapter of this thesis work, we develop the classical vibrational approach. The resolution of a vibrational problem for a chemical system under the harmonic assumption is well-known and easy to implement with common computational softwares. However, when working on systems that require a very specific determination in the near infrared region or yet in far infrared, the harmonic assumption is no longer sufficient and anharmonicity must be taken into account. This is the case for the many HCNO isomers studied in this work, for which the anharmonicity allows a better understanding of the reaction paths through the rearrangement of the molecule as shown in chapter 3.

Three main kinds of methods may be used for the theoretical resolution of a vibrational problem: i) the perturbation theory, ii) the variation method and iii) the perturbation-variation theory. The perturbation method can be seen as the faster, and it can be used for the study of large systems (with more than 10 atoms). Unfortunately, those advantages go with a low accuracy. In its common use, the development of this method does not exceed order 4. We decided to implement its development at higher orders so that missing informations like physicochemical effects could be taken into account, allowing us to reach a better accuracy. The VPTn method thus developed is able to determine all the energy and wavefunction corrections at orders 1 to 6. Thanks to this better approximation of the potential function, it becomes possible to solve with a good precision the identification of unusual molecules by infrared spectroscopy. The VPTn method is a powerful theoretical tool accessible to all theoretical and experimental researchers who work on infrared spectroscopy problems.

In the second part of this thesis, we briefly present the different multi-determinantal methods, as the systems studied have a multi-configurational behaviour. We first studied the rearrangements of aromatic nitrile oxides and nitrile ylides. We noticed that those rearrangements could take place in both the singlet ground states and the triplet excited states, and that they were accelerated by *m,m'*-bis(dimethylamino) substitution on the phenyl moieties. The new rearrangement leads to the preferential energy pathway, *m,m'*-bis(dimethylamino)benzonitrile oxide

in the triplet state: *m,m'*-bis(dimethylamino)benzotrile ylide, the cyclization to the 2-phenyl-1-azirine is favoured over the ring expansion to acycloheptatetraene by ca. 5 Kcal/mol in the singlet state. In the bent triplet states, 1,3-hydrogen shifts interverting nitrile ylides are theoretically possible.

We also examined the competition between mechanisms as the Graebe-Ullmann-type cyclizations, benzazirine formation and Wolff-type ring contraction to fulvenimines. The energy profiles computed for the different paths agree with the experimental data. The reaction path is clearly determined, as well as all the reaction intermediates, in the study of 1-Arylbenzotriazoles. For the 1-Phenyl-4,5,6,7-tetrahydrobenzotriazole compound, two reaction paths show small activation barriers, so that both products (tetrahydro-carbazole **30** and tetrahydrofulvenimine **31**) have comparable yield on pyrolyse as experimentally observed. The computed mechanisms for the thermal decomposition of triazolobenzo- and -naphtoquinone can explain all the experimentally observed products. Regarding the study of 1-Methylbenzotriazole, there is no doubt about the product obtained (theoretically and experimentally) as well as the reaction path followed. Concerning the study of 1-Cyanobenzotriazole, calculations show that several reaction paths lead to unstable compounds, whose subsequent reactions may explain the experimental observations.

This thesis highlights the challenge of experience-theory confrontations and the way computational chemistry has to adapt to answer ever more complex problems. We developed all the equations underlying the VPTn method and implemented it in a code. However, our work is not yet sufficient to make this method operational. The results obtained using this method should be compared with the one obtained with the A-VCI method, in order to ensure the consistency of the method.

One of the remaining challenges is the acquisition of a PES at higher orders which is necessary for the resolution of the vibrational Schrodinger equation (RSVE). As the size of the PES increases in a very significant way with the number of atoms of the system studied, it quickly becomes impossible to calculate each term (force constants) of the analytical expression of the PES.

As we can see in chapter 5, the large number of electrons in such systems do not allow the use of a multiconfigurational method like CASPT2, due to the computational cost. It is therefore necessary to develop some alternative methods until technology will have made enough improvements to no longer use approximations. A close collaboration between theory and experiment appears essential to face those problems and build some suitable strategies.

## 7 Appendices

### 7.1 Functions and density matrices

#### 7.1.1 General definitions

Quantum computational methods provide increasingly sophisticated molecular wavefunctions, but their analysis is becoming more and more difficult due to their complicated description (based on determinants which are themselves built on molecular orbitals developed on atomic orbital bases).

It is therefore convenient to link the physical properties of the molecular wave function to a concept such as the electronic distribution, which is easy to interpret.

In the remainder of this paper, the indices  $i, j, k, l$  will be reserved for molecular orbitals, the indices  $\mu, \nu, \sigma, \lambda$  for atomic orbitals and the indices  $a$  and  $b$  for electrons.

#### 7.1.2 Density function

If  $\psi(x_1, x_2, \dots, x_n)$  denotes the wave function describing an  $n$ -electron system  $n!$   $\psi^*(x_1, x_2, \dots, x_n)\psi(x_1, x_2, \dots, x_n)$  represents the probability of the distribution corresponding to particle 1 at  $x_1$ , 2 at  $x_2$ , etc. ( $x_a$  denoting the generalised space coordinate and spin of electron  $a$ ).

Similarly, the function  $\rho_1(x_1)$  such that:

$$\rho_1(x_1) = n \int \psi^*(x_1, x_2, \dots, x_n)\psi(x_1, x_2, \dots, x_n)dx_2 \dots dx_n \quad (7.1)$$

gives the probability of having a particle at  $x_1$ , the others being distributed in space.  $\rho_1(x_1)$  is the density function of order 1.

In the case of the separation of space and spin variables, and after integration on the spin, we obtain:

$$P_1(r_1) = \int \rho_1(x_1)ds_1$$

$r_1$  is the space coordinate of electron 1 and  $s_1$  is the spin coordinate.  $P_1$  is the electron density function determined by crystallographers. Similarly, we can define the density function of order 2  $\rho_2(x_1, x_2)$ :

$$\rho_2(x_1, x_2) = n(n-1) \int \psi^*(x_1, x_2, \dots, x_n)\psi(x_1, x_2, \dots, x_n)dx_3 \dots dx_n \quad (7.2)$$

Which is written, after integration on the spin:

$$P_2(r_1, r_2) = \int \rho_2(x_1, x_2)ds_1ds_2$$

And so on until order  $n$ .

### 7.1.3 Density matrix

As for the density function, the density matrix<sup>[1]</sup> can be defined at various orders. At order 1, it takes the form:

$$\rho_1(x_1, x'_1) = n \int \psi^*(x'_1, x_2, \dots, x_n) \psi(x_1, x_2, \dots, x_n) dx_2 \dots dx_n \quad (7.3)$$

This function has no physical meaning and depends on the couple chosen  $(x_1, x'_1)$  (hence the name of matrix). At order 2, its expression is such that :

$$\rho_2(x_1, x_2; x'_1, x'_2) = n(n-1) \int \psi^*(x'_1, x'_2, \dots, x_n) \psi(x_1, x_2, \dots, x_n) dx_3 \dots dx_n \quad (7.4)$$

Let us notice that the application of the antisymmetry properties of the wave function with respect to the exchange of two particles, makes it possible to find the principle of PAULI. Indeed we will have:

$$\rho_2(x_1, x_2; x'_1, x'_2) = -\rho_2(x_2, x_1; x'_1, x'_2)$$

This equality implies that two particles cannot have the same space and spin coordinates. The transition from density matrices to density functions is immediate:

$$\begin{aligned} \rho_1(x_1) &= \rho_1(x_1, x'_1) & \text{for } x_1 &= x'_1 \\ \rho_2(x_1, x_2) &= \rho_2(x_1, x_2; x'_1, x'_2) & \text{for } x_1 &= x'_1 \text{ and } x_2 = x'_2 \end{aligned}$$

## 7.2 Density functions and density matrices in the independent particle model

The impact of the independent particle model on the expression of the density functions and matrices written for a general wave function describing an n-electron system can be briefly analysed. We will distinguish the case of the monodeterminantal approximation used in RHF methods from the more general case of multi-determinantal functions.

### 7.2.1 Case of a single-determinant wave function

If the total electronic wave function  $\Psi$  is implemented as an antisymmetric product of orthonormal single-electron functions (spin-orbitals) denoted  $u_i$  :

$$\psi(x_1, x_2, \dots, x_n) = (n!)^{-1/2} \mathcal{A}[u_1(x_1), u_2(x_2), \dots, u_n(x_n)] \quad (7.5)$$

$\mathcal{A}$  representing the antisymmetry operator. Considering the orthonormality of the  $(2m)$  spin-orbitals used, the density matrices are simply expressed.

At order 1:

$$\rho(x_1, x'_1) = \sum_{i=1}^{2m} \sum_{j=1}^{2m} \rho_{ij} u_i^*(x'_1) u_j(x_1) \quad (7.6)$$

With:

$$\begin{aligned} \rho_{ij} &= 0 && \text{if } i \neq j \\ \rho_{ii} &= 1 && \text{if } u_i \text{ is occupied} \\ \rho_{ii} &= 0 && \text{if } u_i \text{ is virtual} \end{aligned}$$

And to order 2:

$$\rho_2(x_1, x_2; x'_1, x'_2) = \sum_{i=1}^{2m} \sum_{j=1}^{2m} \sum_{k=1}^{2m} \sum_{l=1}^{2m} \rho_{ijkl} u_i^*(x'_1) u_j^*(x'_2) u_k(x_1) u_l(x_2) \quad (7.7)$$

The elements of the second-order  ${}^2p$  tensor are given by:

$$\begin{aligned} {}^2p_{ii,ii} &= 0 \\ {}^2p_{ij,ij} &= 1 \\ {}^2p_{ij,ji} &= -1 \\ {}^2p_{ij,kl} &= 0 \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \begin{array}{l} \text{if the spin-orbitals } u_i \text{ and } u_j \text{ are occupied (} i \neq j \text{)} \\ \text{in all other cases} \end{array}$$

Therefore, we can write:

$$\rho_2(x_1, x_2; x'_1, x'_2) = \sum_i^{occ} \sum_j^{occ} [u_i^*(x'_1) u_j^*(x'_2) u_i(x_1) u_j(x_2) - u_i^*(x'_1) u_j^*(x'_2) u_j(x_1) u_i(x_2)]$$

It is immediately apparent that the second order density matrix can be written in terms of the first order density matrices:

$$\rho_2(x_1, x_2; x'_1, x'_2) = \rho_1(x_1, x'_1) \rho_1(x_2, x'_2) - \rho_1(x_2, x'_1) \rho_1(x_1, x'_2) \quad (7.8)$$

This can be expressed as the determinant:

$$\rho_2(x_1, x_2; x'_1, x'_2) = \begin{vmatrix} \rho_1(x_1, x'_1) & \rho_1(x_1, x'_2) \\ \rho_1(x_2, x'_1) & \rho_1(x_2, x'_2) \end{vmatrix}$$

Note that the off-diagonal terms of this determinant constitute a generalisation of the notion of density matrices and correspond to exchange terms. The passage to the density functions being immediate, after integration on the spin, the equation (7.8) is written :



$$P_2(r_1, r_2) = P_1(r_1)P_1(r_2) - P_1(r_2, r_1)P_1(r_1, r_2) \quad (7.9)$$

In the expressions (7.6) and (7.7), we can easily separate the  $\alpha$  and  $\beta$  contributions because of the orthonormalisation of the spin functions. One will obtain,

$$\begin{aligned} \text{at order 1: } P_1(r_1) &= P_1^\alpha(r_1) + P_1^\beta(r_1) \\ \text{at order 2: } P_2(r_1, r_2) &= P_2^{\alpha\alpha}(r_1, r_2) + P_2^{\beta\beta}(r_1, r_2) + P_2^{\alpha\beta}(r_1, r_2) + P_2^{\beta\alpha}(r_1, r_2) \end{aligned}$$

With, according to the expression (7.9),

$$\begin{aligned} P_2^{\alpha\alpha}(r_1, r_2) &= P_1^\alpha(r_1)P_1^\alpha(r_2) - P_1^{\alpha\alpha}(r_1, r_2)P_1^{\alpha\alpha}(r_2, r_1) \\ P_2^{\alpha\beta}(r_1, r_2) &= P_1^\alpha(r_1)P_1^\beta(r_2) \end{aligned}$$

Note that similar terms are obtained for  $P_2^{\beta\beta}(r_1, r_2)$  and  $P_2^{\beta\alpha}(r_1, r_2)$ .

### 7.2.2 Case of a multi-determinant wave function

Let us consider the case where the wave function is developed on a basis of determinants  $\Delta_I$ , themselves constructed on a basis of spin-orbitals supposed to be orthonormal:

$$\Psi = \sum_I A_I \Delta_I$$

In practice, this is the usual case that is encountered, in particular, when spectroscopic properties involving several states must be interpreted. This leads to the introduction of the notion of transition density matrix.<sup>[1]</sup> The first-order density function associated with a multi-determinant wave function is expressed in terms of the coefficients  $A_I$  of the development:

$$\rho_1(x_1) = \sum_{IJ} A_I^* A_J \rho_1(IJ|x_1) \quad (7.10)$$

We define:

$$\rho_1(IJ|x_1) = n \int \Delta_I^*(x_1, x_2, \dots, x_n) \Delta_J(x_1, x_2, \dots, x_n) dx_2 \dots dx_n$$

Like the first-order transition density function, the first-order density function associated with the  $\Psi = \Delta_I$  state corresponding to  $\rho_1(IJ|x_1)$ .

$$\rho_1(IJ|x_1) = \sum_{ij}^{2m} \rho_{ij}^{II} u_i^*(x_1) u_j(x_1)$$

The  $\rho_{ij}^{II}$  terms are to be compared with the  $\rho_{ij}$  terms introduced in the expression (7.6). This matrix-wise writing can be extended to the functions  $\rho_1(IJ|x_1)$  for  $I \neq J$ , that is :

$$\rho_1(IJ|x_1) = \sum_{ij}^{2m} \rho_{ij}^{IJ} u_i^*(x_1) u_j(x_1) \quad (7.11)$$

In practice,  $\rho_1(IJ|x_1)$  is a non-zero function only if the determinants  $\Delta_I$  and  $\Delta_J$  differ at most by one spin-orbital ( $u_p$  for  $\Delta_I$  and  $u_q$  for  $\Delta_J$ ) in an orthonormal spin-orbital basis. In this case, the only non-zero  $\rho_{ij}^{IJ}$  term is  $\rho_{pq}^{IJ}$  (equal to 1):

$$\rho_1(IJ|x_1) = u_p^*(x_1) u_q(x_1) \quad (7.12)$$

The first order density function is then written :

$$\rho_1(x_1) = \sum_{ij}^{2m} \left( \sum_{I,J} A_I^* A_J \rho_{i,j}^{IJ} \right) u_i^*(x_1) u_j(x_1)$$

The expression is comparable to that obtained in the single-determinant case. The second-order density function is similarly expressed in terms of the expansion coefficients:

$$\rho_2(x_1, x_2) = \sum_{IJ} A_I^* A_J \rho_2(IJ|x_1 x_2) \quad (7.13)$$

This leads to the definition of the second order transition function:

$$\rho_2(IJ|x_1 x_2) = n(n-1) \int \Delta_I^*(x_1, x_2, \dots, x_n) \Delta_J(x_1, x_2, \dots, x_n) dx_3 \dots dx_n \quad (7.14)$$

which can also be written by introducing a tensor of order 2  $\rho^{IJ}$ :

$$\rho_2(IJ|x_1 x_2) = \sum_{ijkl}^{2m} \rho_{ijkl}^{IJ} u_i^*(x_1) u_j^*(x_2) u_k(x_1) u_l(x_2) \quad (7.15)$$

The second order density function can then be expressed as follows:

$$\rho_2(IJ|x_1 x_2) = \sum_{ijkl}^{2m} \left( \sum_{I,J} A_I^* A_J \rho_{ijkl}^{IJ} \right) u_i^*(x_1) u_j^*(x_2) u_k(x_1) u_l(x_2) \quad (7.16)$$

The first and second order transition functions can be defined after integration on the spin coordinates:

$$\rho_1(IJ|r_1) = \int \rho_1(IJ|x_1) ds_1 \quad (7.17)$$

$$\rho_2(IJ|r_1 r_2) = \int \rho_2(IJ|x_1 x_2) ds_1 ds_2 \quad (7.18)$$

### 7.2.3 Mean value of an operator: example of the non-relativistic electron Hamiltonian in the Born-Oppenheimer approximation

We will treat the non-relativistic electron Hamiltonian (note  $\hat{H}$ ), which is written for a system with  $n$  electrons  $a$ , space coordinates  $r_a$  and  $N$  nuclei  $A$ , as the sum of single-electron terms and double-electron terms such that:

$$\hat{H} = \sum_{a=1}^n \hat{T}_a(r_a) + \underbrace{\sum_{a=1}^n \sum_{A=1}^N \hat{V}_{aA}(r_a)}_{\text{single-electron term}} + \underbrace{\sum_{a=1}^n \sum_{b>a}^n \hat{g}_{ab}(r_a, r_b)}_{\text{double-electron term}} \quad (7.19)$$

with:  $\hat{V}_{aA}$  :electron-nucleus potential  
 $\hat{g}_{ab}$  :electron-electron potential  
 $\hat{T}_a$  :electronic kinetic operator

The total electronic energy of the system given by the mean value of the Hamiltonian is written, for any wave function  $\Psi$ :

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{T} | \Psi \rangle + \langle \Psi | \hat{V} | \Psi \rangle + \langle \Psi | \hat{g} | \Psi \rangle$$

with:  $\langle \Psi | \hat{O} | \Psi \rangle = \int \Psi^*(x_1, x_2, \dots, x_n) \hat{O} \Psi(x_1, x_2, \dots, x_n) dx_1 \dots dx_n$

$\hat{O}$  representing the three operators  $\hat{T}$ ,  $\hat{V}$  or  $\hat{g}$ . Taking the definition of the density function<sup>[2]</sup> to order 1, we can write:

$$\langle \Psi | \hat{T} | \Psi \rangle = \frac{1}{n} \sum_{a=1}^n \int \hat{T}_a(x_a) \rho_1(x_a) dx_a \quad (7.20)$$

$$\langle \Psi | \hat{V} | \Psi \rangle = \frac{1}{n} \sum_{a=1}^n \sum_{A=1}^N \int \hat{V}_{aA}(x_a) \rho_1(x_a) dx_a \quad (7.21)$$

$$\langle \Psi | \hat{g} | \Psi \rangle = \frac{1}{n(n-1)} \sum_{a=1}^n \sum_{a>b}^n \int \hat{g}_{ab}(x_a, x_b) \rho_2(x_a, x_b) dx_a dx_b \quad (7.22)$$

It is quite clear from the discussion above that these mean values can also be expressed in terms of the density matrices, i.e.:

$$\langle \Psi | \hat{T} | \Psi \rangle = \frac{1}{n} \sum_{a=1}^n \int_{x_a=x'_a} \hat{T}_a(x_a) \rho_1(x_a, x'_a) dx_a \quad (7.23)$$

$$\langle \Psi | \hat{V} | \Psi \rangle = \frac{1}{n} \sum_{a=1}^n \sum_{A=1}^N \int_{x_a=x'_a} \hat{V}_{aA}(x_a) \rho_1(x_a, x'_a) dx_a \quad (7.24)$$

$$\langle \Psi | \hat{g} | \Psi \rangle = \frac{1}{n(n-1)} \sum_{a=1}^n \sum_{a>b}^n \int_{\substack{x_a=x'_a \\ x_b=x'_b}} \hat{g}_{ab}(x_a, x_b) \rho_2(x_a, x_b; x'_a, x'_b) dx_a dx_b \quad (7.25)$$

Thus, taking into account the principle of indiscernibility of electrons, the energy associated with the electronic Hamiltonian has the expression:

$$E = \int_{x_a=x'_a} \hat{h}_a(x_a) \rho_1(x_a, x'_a) dx_a + \frac{1}{2} \int_{\substack{x_a=x'_a \\ x_b=x'_b}} \hat{g}_{ab}(x_a, x_b) \rho_2(x_a, x_b; x'_a, x'_b) dx_a dx_b \quad (7.26)$$

with  $\hat{h}_a$  a single-electron operator such that:

$$\hat{h}_a(x_a) = \hat{T}_a(x_a) + \sum_{A=1}^N \hat{V}_{aA}(x_a) \quad (7.27)$$

After integration on the spin, we obtain :

$$E = \int_{r_a=r'_a} \hat{h}_a(r_a) \rho_1(r_a, r'_a) dr_a + \frac{1}{2} \int_{\substack{r_a=r'_a \\ r_b=r'_b}} \hat{g}_{ab}(r_a, r_b) P_2(r_a, r_b; r'_a, r'_b) dr_a dr_b \quad (7.28)$$

Or, by showing the integrals calculated in the  $m$  molecular orbital basis  $\phi_i$ :<sup>[1]</sup>

$$E = \sum_{ij} D_{ij} h_{ij} + \frac{1}{2} \sum_{ijkl} P_{ijkl} \langle ij|kl \rangle \quad (7.29)$$

$$\text{Where } \langle ij|kl \rangle = \int \phi_i^*(r_a) \phi_j^*(r_b) \hat{g}_{ab} \phi_k(r_a) \phi_l(r_b) dr_a dr_b$$

$$\text{And } h_{ij} = \int \phi_i^*(r_a) \phi_j(r_a) \hat{h}_a(r_a) dr_a$$

The elements of the matrix  $D$  and the tensor  $P$  of second order being related to the density functions of first and second order by the expressions:

$$P_1(r_1) = \sum_{i=1}^m \sum_{j=1}^m D_{ij} \phi_i^*(r_1) \phi_j(r_1) \quad (7.30)$$

$$P_2(r_1, r_2) = \sum_{i=1}^m \sum_{j=1}^m \sum_{k=1}^m \sum_{l=1}^m P_{ijkl} \phi_i^*(r_1) \phi_j^*(r_2) \phi_k(r_1) \phi_l(r_2) \quad (7.31)$$

The matrix  $D$  and the tensor  $P$  of second order are commonly referred to as first and second order density matrices, which can lead to some confusion since this vocabulary is also associated to functions of several variables defined in paragraphs 7.1.2 and 7.1.3. The difference between the single and multi-determinant cases is entirely contained in  $D$  and  $P$ . At the single-determinant level, the elements of the matrix  $D$  and the tensor  $P$  are given by :

$$\begin{aligned} D_{ii} &= 2 && \text{if } \phi_i \text{ is occupied} \\ D_{ii} &= 0 && \text{if } \phi_i \text{ is virtual} \\ D_{ii} &= 0 && \text{if } \phi_i \text{ and } \phi_j \text{ are different} \\ \\ P_{iii} &= 0 \\ P_{ijij} &= 2 \\ P_{ijji} &= -1 && \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{if } \phi_i \text{ and } \phi_j \text{ are occupied and } i \neq j \\ \\ P_{ijkl} &= 0 && \text{in all other cases} \end{aligned}$$

In the case of a multi-determinant wave function  $\Psi = \sum_I A_I \Delta_I$ , the expression of these matrices is more complex because it takes into account the coefficients  $A_I$  of the development. Taking into account the expressions (7.11) and (7.12), we obtain the elements  $D_{ij}$ :

$$D_{ij} = \sum_{I,J} A_I^* A_J D_{ij}^{IJ}$$

$D_{ij}^{IJ}$  is non-zero only if  $\Delta_I$  and  $\Delta_J$  differ by at most one spin-orbit ( $u_i$  for  $\Delta_I$  and  $u_j$  for  $\Delta_J$ )

## References

- [1] R. McWeeny, "Method of molecular quantum mechanics," *2nd edition*, 1989.
- [2] D. Liotard, *Etude topologique des surfaces de potentiel en vue de l'interprétation de la réactivité chimique*. PhD thesis, 1979.

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