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Perturbation theories in the complex plane

Abstract : *In this work, we explore the description of quantum chemistry in the complex plane. We see that the physics of the system can be connected to the position of the energy singularities in the complex plane. After a brief presentation of the fundamental notions of quantum chemistry and perturbation theory in the complex plane, we perform an historical review of the researches that have been done on the physic of singularities. Then we connect all those points of view on this problem using the spherium model (i.e., two opposite-spin electrons restricted to remain on the surface of a sphere of radius R) as a theoretical playground. In particular, we explore the effects of symmetry breaking of the wave functions on the singularity structure.*

Keywords : *Quantum chemistry, Perturbation theory, Spherium, Exceptional points, Symmetry breaking*

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1 Introduction

It has always been of great importance for theoretical chemists to better understand excited states and their properties because processes involving excited states are ubiquitous in nature (physics, chemistry and biology). One of the major challenges is to accurately compute energies of a chemical system (atoms, molecules, ..). Plenty of methods have been developed to this end and each of them have its own advantages but also its own flaws. The fact that none of all those methods is successful for every molecule in every geometry encourages chemists to continue the development of new methodologies to get accurate energies and to try to deeply understand why each method fails or not in each situation. All those methods rely on the notion of quantised energy levels of Hermitian quantum mechanics. In quantum chemistry, the ordering of the energy levels represents the different electronic states of a molecule, the lowest being the ground state while the higher ones are the so-called excited states. We need methods to accurately get how those states are ordered.

Within this quantised paradigm, electronic states look completely disconnected from one another. However, one can gain a different perspective on quantisation extending quantum chemistry into the complex domain. In a non-Hermitian complex picture, the energy levels are *sheets* of a more complicated topological manifold called *Riemann surface*, and they are smooth and continuous *analytic continuation* of one another. In other words, our view of the quantised nature of conventional Hermitian quantum mechanics arises only from our limited perception of the more complex and profound structure of its non-Hermitian variant.

Therefore, by analytically continuing the energy $E(\lambda)$ in the complex domain (where λ is a coupling parameter), the ground and excited states of a molecule can be smoothly connected. This connection is possible because by extending real numbers to the complex domain, the ordering property of real numbers is lost. Hence, electronic states can be interchanged away from the real axis since the concept of ground and excited states has been lost. Amazingly, this smooth and continuous transition from one state to another has recently been experimentally realized in physical settings such as electronics, microwaves, mechanics, acoustics, atomic systems and optics. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18]

Exceptional points (EPs) [19, 20, 21, 22] are non-Hermitian analogs of conical intersections (CIs) [23] where two states become exactly degenerate. CIs are ubiquitous in non-adiabatic processes and play a key role in photo-chemical mechanisms. In the case of auto-ionizing resonances, EPs have a role in deactivation processes similar to CIs in the decay of bound excited states. Although Hermitian and non-Hermitian Hamiltonians are closely related, the behavior of their eigenvalues near degeneracies is starkly different. For example, encircling non-Hermitian degeneracies at EPs leads to an interconversion of states, and two loops around the EP are necessary to recover the initial energy. Additionally, the wave function picks up a geometric phase (also known as Berry phase [24]) and four loops are required to recover the initial wave function. In contrast, encircling Hermitian degeneracies at CIs only introduces a geometric phase while leaving the states unchanged. More dramatically, whilst eigenvectors remain orthogonal at CIs, at non-Hermitian EPs the eigenvectors themselves become equivalent, resulting in a *self-orthogonal* state. [25] More importantly here, although EPs usually lie off the real axis, these singular points are intimately related to the convergence properties of perturbative methods and avoided crossing on the real axis are indicative of singularities in the complex plane. [26, 27]

2 Perturbation theory

Within perturbation theory, the Schrödinger equation is usually rewritten as

$$\mathbf{H}(\lambda)\Psi = (\mathbf{H}^{(0)} + \lambda\mathbf{V})\Psi(\lambda) = E(\lambda)\Psi, \quad (1)$$

with

$$\mathbf{V} = \mathbf{H} - \mathbf{H}^{(0)} \quad (2)$$

The energy can then be written as a power series of λ

$$E(\lambda) = \sum_{k=0}^{\infty} \lambda^k E^{(k)} \quad (3)$$

where λ is a coupling parameter set equal to 1 at the end of the calculation. However it is not guaranteed that the series $E(\lambda)$ has a radius of convergence $|\lambda_0| < 1$. It means that the series is divergent for the physical system at $\lambda = 1$. One can prove that $|\lambda_0|$ can be obtained by extending λ in the complex plane and looking for the singularities of $E(\lambda)$. This is due to the following theorem [28]: The Taylor series about a point z_0 of a function over the complex z plane will converge at a value z_1 if the function is non-singular at all values of z in the circular region centered at z_0 with radius $|z_1 - z_0|$. If the function has a singular point z_s such that $|z_s - z_0| < |z_1 - z_0|$, then the series will diverge when evaluated at z_1 . This theorem means that the radius of convergence of the perturbation series is equal to distance to the origin of the closest singularity of $E(\lambda)$.

The discovery of a partitioning of the Hamiltonian that allowed chemists to recover a part of the correlation energy (i.e. the difference between the exact energy and the Hartree-Fock energy) using perturbation theory has been a major step in the development of post-Hartree-Fock methods. This case of the Rayleigh-Schrödinger perturbation theory is called the Møller-Plesset perturbation theory [29]. In the MPPT the unperturbed Hamiltonian is the sum of the n mono-electronic Fock operators which are the sum of the one-electron core Hamiltonian $h(i)$, the Coulomb $J_j(i)$ and Exchange $K_j(i)$ operators.

$$H_0 = \sum_{i=1}^n f(i) \quad (4)$$

$$f(i) = h(i) + \sum_{j=1, j \neq i}^n [J_j(i) - K_j(i)] \quad (5)$$

In Hartree-Fock theory the exact wave function is approximated as a Slater-determinant (which is an anti-symmetric combination of mono-electronic orbitals) and those wave functions are eigenvectors of the Fock operators. In the perturbation theory the energy is a power series of λ and the physical energy is obtained by taking λ equal to 1. We will refer to the energy up to the n -th order as the MP n energy. The MP0 energy overestimates the energy by double counting the electron-electron interaction, the MP1 corrects this effect and the MP1 energy is equal to the Hartree-Fock energy. The MP2 energy starts to recover a part of the correlation energy.

$$E_{\text{MP}_n} = \sum_{k=0}^n E^{(k)} \quad (6)$$

But as mentioned before *a priori* there are no reasons that this power series is always convergent for $\lambda=1$ when n goes to infinity. In fact, it is known that when the Hartree-Fock wave function is a bad approximation of the exact wave function, for example for multi-reference states, the Møller-Plesset will give bad results[30, 31, 32, 33]. A smart way to investigate the convergence properties of the MP series is to transform the coupling parameter λ into a complex variable. By doing so the Hamiltonian and the energy become functions of this variable. The energy becomes a multivalued function on n Riemann sheets. As mentioned above by searching the singularities of the function $E(\lambda)$ we can get information on the convergence properties of the MPPT. Those singularities of the energy are exactly the exceptional points connecting the electronic states mentioned in the introduction. The direct computation of the terms of the series is quite easy up to the 4th order and the 5th and 6th order can be obtained at high cost. But to deeply understand the behavior of the MP series and how it is connected to the singularities, we need to have access to high order terms of the series. For small systems we can have access to the whole series using Full Configuration Interaction. If the Hamiltonian $H(\lambda)$ is diagonalized in the FCI basis set we get the exact energies (in this finite basis set) and expanding in λ allows to get the Møller-Plesset perturbation series at every order.

3 Historical overview

3.1 Behavior of the Møller-Plesset series

When we use Møller-Plesset perturbation theory it would be very convenient that each time a higher order term is computed the result obtained is closer to exact energy. In other words, that the Møller-Plesset series would be monotonically convergent. Assuming this, the only limiting process to get the exact correlation energy in a finite basis set is our ability to compute the terms of the perturbation series. Unfortunately this is not true in generic cases and rapidly some strange behaviors of the series were exhibited. In the late 80's Gill et al. reported deceptive and slow convergences in stretch systems[30, 31, 32, 33]. In the figure below we can see that the restricted Møller-Plesset series is convergent but oscillating which is not convenient if you are only able to compute few terms (for example here RMP5 is worse than RMP4). On the other hand, the unrestricted Møller-Plesset series is monotonically converging (except for the first few orders) but very slowly so we can't use it for systems where we can only compute the first terms.

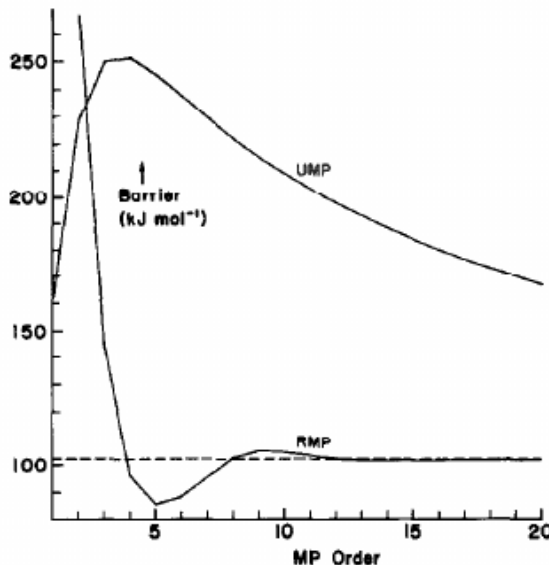


Figure 1: Barriers to homolytic fission of He_2^{2+} at $\text{MP}_n/\text{STO-3G}$ level ($n = 1-20$)[30].

When a bond is stretched the exact function can undergo a symmetry breaking becoming multi-reference during this process (see for example the case of H_2 in [34]). A restricted HF Slater determinant is a poor approximation of a broken symmetry wave function but even in the unrestricted formalism, where the spatial orbitals of electrons α and β are not restricted to be the same[35], which allows a better description of broken symmetry system, the series doesn't give accurate results at low orders. Even with this improvement of the zeroth order wave function the series doesn't have the smooth and rapidly converging behavior wanted.

In the unrestricted framework the ground state singlet wave function is allowed to mix with triplet states which leads to spin contamination. Gill et al. highlighted the link between the slow convergence of the unrestricted MP series and the spin contamination of the wave function as shown in the Table 1 in the example of H_2 in a minimal basis.

Handy and co-workers exhibited the same behaviors of the series (oscillating and monotonically slowly) in stretched H_2O and NH_2 systems [32]. Cremer and He performed the same analysis with 29 FCI systems [36] and regrouped all the systems in two classes. The class A systems which have a monotonic convergence to the FCI value and the class B which converge erratically after initial oscillations. The sample of systems contains stretched molecules and also some at equilibrium geometry, there are also some systems in various basis sets. They highlighted that systems with class A convergence have well-separated electrons pairs whereas class B systems present electrons clustering.

r	UHF	UMP2	UMP3	UMP4	$\langle S^2 \rangle$
0.75	0.0%	63.8%	87.4%	95.9%	0.00
1.35	0.0%	15.2%	26.1%	34.9%	0.49
2.00	0.0%	01.0%	01.8%	02.6%	0.95
2.50	0.0%	00.1%	00.3%	00.4%	0.99

Table 1: Percentage of electron correlation energy recovered and $\langle S^2 \rangle$ for the H_2 molecule as a function of bond length ($r, \text{\AA}$) in the STO-3G basis set [31].

This classification was encouraging in order to develop methods based on perturbation theory as it rationalizes the two different observed convergence modes. If it is possible to predict if a system is class A or B, then one can use extrapolation method of the first terms adapted to the class of the systems [36].

3.2 Cases of divergence

However Olsen et al. have discovered an even more preoccupying behavior of the MP series in the late 90's. They have shown that the series could be divergent even in systems that they considered as well understood like Ne and HF [26, 37]. Cremer and He had already studied those two systems and classified them as class B systems. But Olsen and his co-workers have done the analysis in larger basis sets containing diffuse functions and in those basis sets the series become divergent at high order.

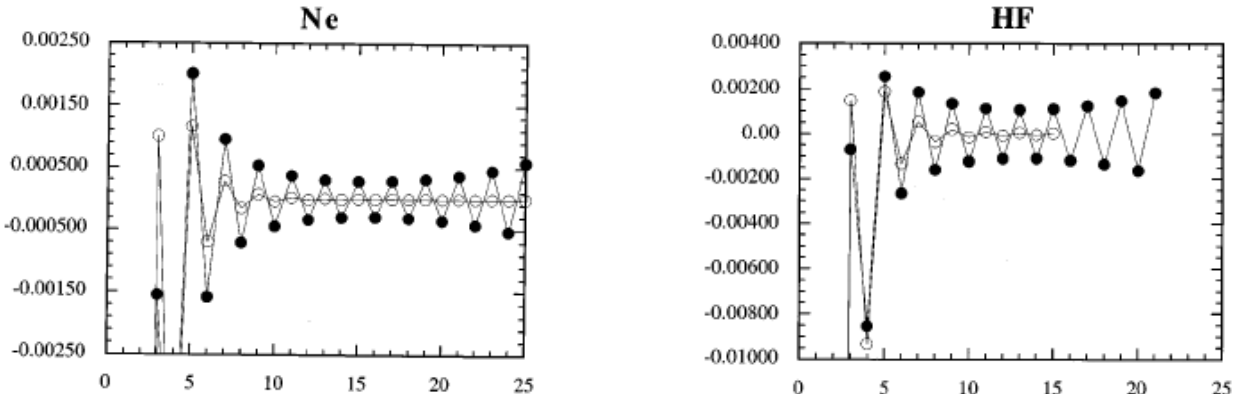


Figure 2: Correlation contributions for Ne and HF in the cc-pVTZ-(f/d) \circ and aug-cc-pVDZ \bullet basis sets.

The discovery of this divergent behavior was really worrying because in order to get more and more accurate results theoretical chemists need to work in large basis sets. As a consequence they investigated the causes of those divergences and in the same time the reasons of the different types of convergence. To do this they analyzed the relation between the dominant singularity (i.e. the closest singularity to the origin) and the convergence behavior of the series [27]. Their analysis is based on Darboux's theorem: in the limit of large order, the series coefficients become equivalent to the Taylor series coefficients of the singularity closest to the origin. Following the result of this theorem, the convergence patterns of the MP series can be explained by looking at the dominant singularity.

A singularity in the unit circle is designated as an intruder state, more precisely as a front-door (respectively back-door) intruder state if the real part of the singularity is positive (respectively negative). The method used is to do a scan of the real axis to identify the avoided crossing responsible for the pair of dominant singularity. Then by modeling this avoided crossing by a two-state Hamiltonian one can get an approximation of the dominant conjugate pair of singularity by finding the EPs of the $22 \times$ Hamiltonian. The diagonal matrix is the unperturbed Hamiltonian and the other matrix is the perturbative part of the Hamiltonian.

$$\begin{pmatrix} \alpha & \delta \\ \delta & \beta \end{pmatrix} = \begin{pmatrix} \alpha + \alpha_s & 0 \\ 0 & \beta + \beta_s \end{pmatrix} + \begin{pmatrix} -\alpha_s & \delta \\ \delta & -\beta_s \end{pmatrix} \quad (7)$$

They first studied molecules with low-lying doubly excited states of the same spatial and spin symmetry because in those systems the HF wave function is a bad approximation. The exact wave function has a non-negligible contribution from the doubly excited states, so those low-lying excited states were good candidates for being intruder states. For CH_2 in a large basis set, the series is convergent up to the 50th order. They showed that the dominant singularity lies outside the unit circle but close to it causing the slow convergence.

Then they demonstrated that the divergence for the Ne is due to a back-door intruder state. When the basis set is augmented with diffuse functions, the ground state undergo sharp avoided crossings with highly diffuse excited states leading to a back door intruder state. They used their two-state model on this avoided crossings and the model was actually predicting the divergence of the series. They concluded that the divergence of the series was due to the interaction with a highly diffuse excited state.

Moreover they proved that the extrapolation formula of Cremer and He [36] can't be used for all systems. Even more, that those formula were not mathematically motivated when looking at the singularity causing the divergence. For example the hydrogen fluoride molecule contains both back-door intruder states and low-lying doubly excited states which results in alternated terms up to order ten and then the series is monotonically convergent. This is due to the fact that two pairs of singularity are approximately at the same distance from the origin.

3.3 The singularity structure

In the 2000's Sergeev and Goodson [38, 39] analyzed this problem from a more mathematical point of view by looking at the whole singularity structure where Olsen and his co-workers were trying to find the dominant singularity causing the divergence. They regrouped singularities in two classes: the α singularities which have unit order imaginary parts and the β singularities which have very small imaginary parts. The singularities α are related to large avoided crossing between the ground state and a low-lying excited states. Whereas the singularities β come from a sharp avoided crossing between the ground state and a highly diffuse state. They succeeded to explain the divergence of the series caused by β singularities using a previous work of Stillinger [40].

The Møller-Plesset Hamiltonian is defined as below and by reassembling the term we get the expression (11).

$$H(\lambda) = H_0 + \lambda(H_{\text{phys}} - H_0) \quad (8)$$

$$H_{\text{phys}} = \sum_{j=1}^n \left[-\frac{1}{2} \nabla_j^2 - \sum_{k=1}^N \frac{Z_k}{|\mathbf{r}_j - \mathbf{R}_k|} + \sum_{j<l}^n \frac{1}{|\mathbf{r}_j - \mathbf{r}_l|} \right] \quad (9)$$

$$H_0 = \sum_{j=1}^n \left[-\frac{1}{2} \nabla_j^2 - \sum_{k=1}^N \frac{Z_k}{|\mathbf{r}_j - \mathbf{R}_k|} + V_j^{(scf)} \right] \quad (10)$$

$$H(\lambda) = \sum_{j=1}^n \left[-\frac{1}{2} \nabla_j^2 - \sum_{k=1}^N \frac{Z_k}{|\mathbf{r}_j - \mathbf{R}_k|} + (1 - \lambda)V_j^{(scf)} + \lambda \sum_{j<l}^n \frac{1}{|\mathbf{r}_j - \mathbf{r}_l|} \right] \quad (11)$$

The first two terms, the kinetic energy and the electron-nucleus attraction, form the mono-electronic core Hamiltonian which is independant of λ . The third term is the mean field repulsion of the Hartree-Fock calculation done to get H_0 and the last term is the Coulomb repulsion. If λ is negative, the Coulomb interaction becomes attractive but the mean field stays repulsive as it is proportional to $(1 - \lambda)$. If λ becomes more and more negative the mean field becomes more and more repulsive so

the nucleus can't bind the electrons anymore because the electron-nucleus attraction is not scaled with λ . The repulsive mean field is localized around nucleus whereas the electrons interactions persist away from nucleus. There is a real negative value λ_c where the electrons form a bound cluster and goes to infinity. According to Baker this value is a critical point of the system and by analogy with thermodynamics the energy $E(\lambda)$ exhibits a singularity at λ_c . Beyond λ_c there is a continuum of eigenstates with electrons dissociated from the nucleus.

This reasoning is done on the exact Hamiltonian and energy, this is the exact energy which exhibits this singularity on the negative real axis. But in finite basis set, one can prove that for a Hermitian Hamiltonian the singularities of $E(\lambda)$ occurs in complex conjugate pair with non-zero imaginary parts. Sergeev and Goodson proved, as predicted by Stillinger, that in a finite basis set the critical point on the real axis is modeled by a cluster of sharp avoided crossings with diffuse functions, equivalently by a cluster of β singularities in the negative half plane. They explain that Olsen et al., because they used a 2×2 model, only observed the first singularity of this cluster of singularities causing the divergence. Finally, it was shown that β singularities are very sensitive to the basis sets but not to the stretching of the system. On the contrary α singularities are relatively insensitive to the basis sets but very sensitive to bond stretching. According to Goodson the singularity structure from molecules stretched from the equilibrium geometry is difficult [41], this is consistent with the observation of Olsen and co-workers on the HF molecule at equilibrium geometry and stretched geometry [27]. To our knowledge the effect of bond stretching on singularities, its link with spin contamination and symmetry breaking of the wave function hasn't been as well understood as the ionization effect and its link with diffuse function. In this work we try to improve our understanding of the effect of symmetry breaking on the singularities of $E(\lambda)$ and we hope that it will lead to a deeper understanding of perturbation theory.

3.4 The physics of quantum phase transition

At a sharp avoided crossings the two eigenstates undergo

4 The spherium model

Simple systems that are analytically solvable (or at least quasi-exactly solvable) are of great importance in theoretical chemistry. Those systems are very useful benchmarks to test new methods as they are mathematically easy but retain much of the key physics. To investigate the physics of EPs we use one such system named spherium model. It consists of two electrons confined to the surface of a sphere interacting through the long-range Coulomb potential. The radius R of the sphere dictates the correlation regime, i.e., weak correlation regime at small R where the kinetic energy dominates, or strong correlation regime where the electron repulsion term drives the physics. We will use this model to try to rationalize the effects of the variables that may influence the physics of EPs:

- Partitioning of the Hamiltonian and the actual zeroth-order reference: weak correlation reference [restricted Hartree-Fock (RHF) or unrestricted Hartree-Fock (UHF) references, Møller-Plesset or Epstein-Nesbet (EN) partitioning], or strongly correlated reference.
- Basis set: minimal basis or infinite (i.e., complete) basis made of localized or delocalized basis functions
- Radius of the spherium that ultimately dictates the correlation regime.

4.1 Weak correlation regime

In the restricted Hartree-Fock formalism, the wave function can't model properly the physics of the system at large R because the spatial orbitals are restricted to be the same. Then a fortiori it can't represent two electrons on opposite side of the sphere. In the unrestricted formalism At a critical value of R , called the Coulson-Fischer point, a second unrestricted Hartree-Fock solution appear. This

solution is symmetry-broken as the two electrons tends to localize on opposite side of the sphere. By analogy with the case of H_2 [34], the unrestricted Hartree-Fock wave function is defined as: Then the mono-electronic wave function are expand in the spatial basis set of the zonal spherical harmonics:

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