

Perturbation theory in the complex plane: Exceptional points and where to find them

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In this review, we explore the extension of quantum chemistry in the complex plane. We observe that the physics of a quantum system is intimately connected to the position of the energy singularities in the complex plane. After a presentation of the fundamental notions of quantum chemistry and perturbation theory in the complex plane, we provide a historical overview of the various research activities that have been performed on the physics of singularities.

I. INTRODUCTION

A. Background

Due to the ubiquitous influence of processes involving electronic excited states in physics, chemistry, and biology, their faithful description from first principles has been one of the grand challenges faced by theoretical chemists since the dawn of computational chemistry. Accurately predicting ground- and excited-state energies (hence excitation energies) is particularly valuable in this context, and it has concentrated most of the efforts within the community. An armada of theoretical and computational methods have been developed to this end, each of them being plagued by its own flaws. The fact that none of these methods is successful in every chemical scenario has encouraged chemists to carry on the development of new excited-state methodologies, their main goal being to get the most accurate excitation energies (and properties) at the lowest possible computational cost in the most general context.

One common feature of all these methods is that they rely on the notion of quantized energy levels of Hermitian quantum mechanics, in which the different electronic states of a molecule or an atom are energetically ordered, the lowest being the ground state while the higher ones are excited states. Within this quantized paradigm, electronic states look completely disconnected from one another. Many current methods study excited states using only ground-state information, creating a ground-state bias that leads to incorrect excitation energies. However, one can gain a different perspective on quantization 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 quantized nature of conventional Hermitian quantum mechanics arises only from our limited perception of the more complex and profound structure of its non-Hermitian variant.^{1,2} The realization that ground and excited states both emerge from one single mathematical structure with equal importance suggests that excited-state energies can be computed from first principles in their own right. One could then exploit the structure of these Riemann surfaces to develop methods that directly target excited-state energies without needing ground-state information.^{3,4}

By analytically continuing the electronic 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.^{5–22}

Exceptional points (EPs) are branch point singularities where two (or more) states become exactly degenerate.^{1,23–29} They are the non-Hermitian analogs of conical intersections,³⁰ which 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 conical intersections in the decay of bound excited states.²⁹ 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.^{1,28,29} Additionally, the wave function picks up a geometric phase (also known as Berry phase³¹) and four loops are required to recover the initial wave function. In contrast, encircling Hermitian degeneracies at conical intersections only introduces a geometric phase while leaving the states unchanged. More dramatically, whilst eigenvectors remain orthogonal at conical intersections, at non-Hermitian EPs the eigenvectors themselves become equivalent, resulting in a *self-orthogonal* state.¹ 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.^{32–38}

B. An illustrative example

In order to highlight the general properties of EPs mentioned above, we propose to consider the following 2×2 Hamiltonian commonly used in quantum chemistry

$$\mathbf{H} = \begin{pmatrix} \epsilon_1 & \lambda \\ \lambda & \epsilon_2 \end{pmatrix}, \quad (1)$$

which represents two states of energies ϵ_1 and ϵ_2 coupled with a strength of magnitude λ . This Hamiltonian could represent,

for example, a minimal-basis configuration interaction with doubles (CID) for the hydrogen molecule.³⁹

For real λ , the Hamiltonian (1) is clearly Hermitian, and it becomes non-Hermitian for any complex λ value. Its eigenvalues are

$$E_{\pm} = \frac{\epsilon_1 + \epsilon_2}{2} \pm \frac{1}{2} \sqrt{(\epsilon_1 - \epsilon_2)^2 + 4\lambda^2}. \quad (2)$$

One notices that the two states become degenerate only for a pair of complex conjugate values of λ

$$\lambda_{\text{EP}} = \pm i \frac{\epsilon_1 - \epsilon_2}{2}, \quad (3)$$

with energy

$$E_{\text{EP}} = \frac{\epsilon_1 + \epsilon_2}{2}, \quad (4)$$

which correspond to square-root singularities in the complex- λ plane. These two λ values, given by Eq. (3), are the so-called EPs and one can clearly see that they connect the ground and excited states. Starting from λ_{EP} , two square-root branch cuts run on the imaginary axis towards $\pm i\infty$. In the real λ axis, the point for which the states are the closest ($\lambda = 0$) is called an avoided crossing and this occurs at $\lambda = \text{Re}(\lambda_{\text{EP}})$. The ‘‘shape’’ of the avoided crossing is linked to the magnitude of $\text{Im}(\lambda_{\text{EP}})$: the smaller $\text{Im}(\lambda_{\text{EP}})$, the sharper the avoided crossing is.

Around $\lambda = \lambda_{\text{EP}}$, Eq. (2) behaves as¹

$$E_{\pm} = E_{\text{EP}} \pm \sqrt{2\lambda_{\text{EP}}} \sqrt{\lambda - \lambda_{\text{EP}}}, \quad (5)$$

and following a complex contour around the EP, *i.e.*, $\lambda = \lambda_{\text{EP}} + R \exp(i\theta)$, yields

$$E_{\pm}(\theta) = E_{\text{EP}} \pm \sqrt{2\lambda_{\text{EP}}R} \exp(i\theta/2), \quad (6)$$

and we have

$$E_{\pm}(2\pi) = E_{\mp}(0), \quad E_{\pm}(4\pi) = E_{\pm}(0).$$

This evidences that 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 and four loops are required to recover the starting wave function.¹

II. PERTURBATION THEORY

A. Rayleigh-Schrödinger perturbation theory

Within the Born-Oppenheimer approximation,

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_A \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (7)$$

is the exact electronic Hamiltonian for a chemical system with n electrons (where \mathbf{r}_i is the position of the i th electron) and N (fixed) nuclei (where \mathbf{R}_A and Z_A are the position and the

charge of the A th nucleus respectively). The first term is the kinetic energy of the electrons, the two following terms account respectively for the electron-nucleus attraction and the electron-electron repulsion. Note that we use atomic units throughout unless otherwise stated.

Within (time-independent) Rayleigh-Schrödinger perturbation theory, the Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad (8)$$

is recast as

$$\hat{H}(\lambda)\Psi(\lambda) = (\hat{H}^{(0)} + \lambda\hat{V})\Psi(\lambda) = E(\lambda)\Psi(\lambda), \quad (9)$$

where $\hat{H}^{(0)}$ is the zeroth-order Hamiltonian and $\hat{V} = \hat{H} - \hat{H}^{(0)}$ is the so-called perturbation. The ‘‘physical’’ system of interest is recovered by setting the coupling parameter λ to unity. This decomposition is obviously non-unique and motivated by several factors as discussed below.³⁷

Accordingly to Eq. (9), the energy can then be written as a power series of λ

$$E(\lambda) = \sum_{k=0}^{\infty} \lambda^k E^{(k)}. \quad (10)$$

However, it is not guaranteed that the series (10) has a radius of convergence $|\lambda_0| < 1$. In other words, the series might well be divergent for the physical system at $\lambda = 1$. One can prove that the actual value of the radius of convergence $|\lambda_0|$ can be obtained by looking for the singularities of $E(\lambda)$ in the complex λ plane. This is due to the following theorem:⁴⁰

‘‘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 the distance to the origin of the closest singularity of $E(\lambda)$. To illustrate this result we consider the simple function³²

$$f(x) = \frac{1}{1 + x^4}. \quad (11)$$

This function is smooth for $x \in \mathbb{R}$ and infinitely differentiable in \mathbb{R} . One would expect that the Taylor series of such a function would be convergent $\forall x \in \mathbb{R}$. However this series is divergent for $x \geq 1$. This is because the function has four singularities in the complex plane ($x = e^{i\pi/4}$, $e^{-i\pi/4}$, $e^{i3\pi/4}$, and $e^{-i3\pi/4}$) with a modulus equal to 1. This simple yet powerful example emphasizes the importance of the singularities in the complex plane to understand the convergence properties on the real axis.

B. The Hartree-Fock Hamiltonian

In the Hartree-Fock (HF) approximation, the many-electron wave function is approximated as a single Slater determinant

$\Psi^{\text{HF}}(\mathbf{x}_1, \dots, \mathbf{x}_n)$ [where $\mathbf{x} = (\sigma, \mathbf{r})$ is a composite vector gathering spin and spatial coordinates] defined as an antisymmetric combination of n (real-valued) one-electron spin-orbitals $\phi_p(\mathbf{x})$, which are, by definition, eigenfunctions of the one-electron Fock operator

$$f(\mathbf{x})\phi_p(\mathbf{x}) = [h(\mathbf{x}) + v^{\text{HF}}(\mathbf{x})]\phi_p(\mathbf{x}) = \epsilon_p\phi_p(\mathbf{x}), \quad (12)$$

where

$$h(\mathbf{x}) = -\frac{\nabla^2}{2} + \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \quad (13)$$

is the core Hamiltonian and

$$v^{\text{HF}}(\mathbf{x}) = \sum_i [J_i(\mathbf{x}) - K_i(\mathbf{x})] \quad (14)$$

is the HF mean-field potential with

$$J_i(\mathbf{x})\phi_p(\mathbf{x}) = \left[\int d\mathbf{x}' \phi_i(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_i(\mathbf{x}') \right] \phi_p(\mathbf{x}) \quad (15a)$$

$$K_i(\mathbf{x})\phi_p(\mathbf{x}) = \left[\int d\mathbf{x}' \phi_i(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_p(\mathbf{x}') \right] \phi_i(\mathbf{x}) \quad (15b)$$

being the Coulomb and exchange operators (respectively) in the spin-orbital basis.³⁹ If the spatial part of the spin-orbitals are restricted to be the same for spin-up and spin-down electrons, one talks about restricted HF (RHF) theory, whereas if one does not enforce this constrain it leads to the so-called unrestricted HF (UHF) theory. From hereon, i and j are occupied orbitals, a and b are unoccupied (or virtual) orbitals, while $p, q, r,$ and s indicate arbitrary orbitals.

Rather than solving Eq. (8), HF theory uses the variational principle to find an approximation of Ψ as a single Slater determinant. Hence a Slater determinant is not an eigenfunction of the exact Hamiltonian \hat{H} . However, it is, by definition, an eigenfunction of the so-called (approximated) HF many-electron Hamiltonian defined as the sum of the one-electron Fock operators

$$\hat{H}^{\text{HF}} = \sum_i f(\mathbf{x}_i). \quad (16)$$

C. Møller-Plesset perturbation theory

The HF Hamiltonian (16) can be used as the zeroth-order Hamiltonian of Eq. (9). This partitioning of the Hamiltonian leads to the so-called Møller-Plesset (MP) perturbation theory.⁴¹ The discovery of a partitioning of the Hamiltonian that allowed chemists to recover a large chunk 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-HF methods. This yields

$$\hat{H}(\lambda) = \sum_i^n \left[-\frac{\nabla_i^2}{2} - \sum_A \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + (1 - \lambda)v^{\text{HF}}(\mathbf{x}_i) + \lambda \sum_{i < j}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right]. \quad (17)$$

If one considers a RHF or UHF reference wave functions, it leads to the RMP or UMP series, respectively.

As mentioned earlier, in perturbation theory, the energy is a power series of λ and the physical energy is obtained at $\lambda = 1$. The MP m energy is defined as

$$E_{\text{MP}m} = \sum_{k=0}^m E^{(k)}, \quad (18)$$

where $E^{(k)}$ is the k th-order MP correction, and it is well known that $E_{\text{MP}1} = E^{(0)} + E^{(1)} = E_{\text{HF}}$.³⁹ The MP2 energy reads

$$E_{\text{MP}2} = \frac{1}{4} \sum_{ij} \sum_{ab} \frac{|\langle ij||ab \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (19)$$

with $\langle pq||rs \rangle = \langle pq|rs \rangle - \langle pq|sr \rangle$, and where

$$\langle pq|rs \rangle = \iint d\mathbf{x}_1 d\mathbf{x}_2 \frac{\phi_p(\mathbf{x}_1)\phi_q(\mathbf{x}_2)\phi_r(\mathbf{x}_1)\phi_s(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (20)$$

are two-electron integral in the spin-orbital basis.⁴²

As mentioned earlier, there is, *a priori*, no guarantee that the MP m series converges to the exact energy when $m \rightarrow \infty$. In fact, it is known that when the HF wave function is a poor approximation to the exact wave function, for example in multi-reference systems, the MP method yields deceptive results.^{43–46} A convenient way to investigate the convergence properties of the MP series is to analytically continue the coupling parameter λ into the complex variable. By doing so, the Hamiltonian and the energy become complex-valued functions of λ , and the energy becomes a multivalued function on K Riemann sheets (where K is the number of basis functions). As mentioned above, by searching the singularities of the function $E(\lambda)$, one can get information on the convergence properties of the MP series. These singularities of the energy function are exactly the EPs connecting the electronic states as mentioned in Sec. I. The direct computation of the terms of the series is quite manageable up to fourth order in perturbation, while the fifth and sixth order in perturbation can still be obtained but at a rather high cost.⁴⁷ In order to better understand the behavior of the MP series and how it is connected to the singularity structure, we have to access high-order terms. For small systems, one can access the whole terms of the series using full configuration interaction (FCI). If the Hamiltonian $H(\lambda)$ is diagonalized in the FCI space, one gets the exact energies (in this finite Hilbert space) and the Taylor expansion with respect to λ allows to access the MP perturbation series at any order.

Obviously, although practically convenient for electronic structure calculations, the MP partitioning is not the only possibility, and alternative partitioning have been proposed in the literature: i) the Epstein-Nesbet (EN) partitioning which consists in taking the diagonal elements of \hat{H} as the zeroth-order Hamiltonian.^{48,49} Hence, the off-diagonal elements of \hat{H} are the perturbation operator, ii) the weak correlation partitioning in which the one-electron part is consider as the unperturbed Hamiltonian $\hat{H}^{(0)}$ and the two-electron part is the perturbation operator \hat{V} , and iii) the strong coupling partitioning where the two operators are inverted compared to the weak correlation partitioning.⁵⁰

III. HISTORICAL OVERVIEW

A. Behavior of the Møller-Plesset series

When one relies on MP perturbation theory (and more generally on any perturbative partitioning), it would be reasonable to ask for a systematic improvement of the energy with respect to the perturbative order, *i.e.*, one would expect that the more terms of the perturbative series one can compute, the closer the result from the exact energy. In other words, one would like a monotonic convergence of the MP series. Assuming this, the only limiting process to get the exact correlation energy (in a finite basis set) would be our ability to compute the terms of this perturbation series. Unfortunately this is not as easy as one might think because i) the terms of the perturbative series become rapidly computationally cumbersome, and ii) erratic behavior of the perturbative coefficients are not uncommon. For example, in the late 80's, Gill and Radom reported deceptive and slow convergences in stretched systems^{43,44} (see also Refs. 45 and 46). In Ref. 43, the authors showed that the RMP series is convergent, yet oscillatory which is far from being convenient if one is only able to compute the first few terms of the expansion (for example here RMP5 is worse than RMP4). On the other hand, the UMP series is monotonically convergent (except for the first few orders) but very slowly. Thus, one cannot practically use it for systems where only the first terms can be computed.

When a bond is stretched, in most cases the exact wave function becomes more and more of multi-reference nature. Yet the HF wave function is restricted to be a single Slater determinant. It is then inappropriate to model (even qualitatively) stretched systems. Nevertheless, the HF wave function can undergo symmetry breaking to lower its energy by sacrificing one of the symmetry of the exact wave function in the process (see for example the case of H₂ in Ref. 39). One could then potentially claim that the RMP series exhibits deceptive convergence properties as the RHF Slater determinant is a poor approximation of the exact wave function for stretched system. However, even in the unrestricted formalism which clearly represents a better description of a stretched system, the UMP series does not have the smooth and rapidly convergent behavior that one would wish for.

In the unrestricted framework the singlet ground state wave function is allowed to mix with triplet wave functions, leading to the so-called spin contamination issue. Gill *et al.* highlighted the link between slow convergence of the UMP series and spin contamination for H₂ in a minimal basis.⁴⁴ Handy and coworkers reported the same behavior of the series (oscillatory and slowly monotonically convergent) in stretched H₂O and NH₂.⁴⁵ Lepetit *et al.* analyzed the difference between the MP and EN partitioning for the UHF reference.⁴⁶ They concluded that the slow convergence is due to the coupling of the singly- and doubly-excited configurations. Cremer and He analyzed 29 atomic and molecular systems at the FCI level⁵¹ and grouped them in two classes: i) the *class A* systems where one observes a monotonic convergence to the FCI energy, and ii) the *class B* systems for which convergence is erratic after initial oscillations. Their system set contains stretched molecules as well as

molecules at their equilibrium geometry for various basis sets. They highlighted that⁵¹ “*Class A systems are characterized by electronic structures with well-separated electron pairs while class B systems are characterized by electronic structures with electron clustering in one or more regions.*” As one can only compute the first terms of the MP series, a smart way of getting more accurate results is to use extrapolation formula, *i.e.*, estimating the limit of the series with only few terms. Cremer and He proved that using specific extrapolation formulas of the MP series for class A and class B systems improves the precision of the results compared to the formula used without resorting to classes. The mean absolute deviation taking the FCI correlation energies as reference is 0.3 millihartree with the class-specific formula whereas the deviation increases to 12 millihartree using the general formula. Even if there were still shaded areas in their analysis and that their classification was incomplete, the work of Cremer and He clearly evidenced that understanding the origin of the different modes of convergence could potentially lead to a more rationalized use of MP perturbation theory and, hence, to more accurate correlation energy estimates.

B. Cases of divergence

In the late 90's, Olsen *et al.* discovered an even more pre-occupying behavior of the MP series.³³ They showed that the series could be divergent even in systems that they considered as well understood like Ne and HF.^{33,52} Cremer and He had already studied these two systems and classified them as *class B* systems. However, the analysis of Olsen and coworkers was performed in larger basis sets containing diffuse functions. In these basis sets, they found that the series become divergent at (very) high order.

The discovery of this divergent behavior is worrying as in order to get meaningful and accurate energies, calculations must be performed in large basis sets (as close as possible from the complete basis set limit). Including diffuse functions is particularly important in the case of anions and/or Rydberg excited states where the wave function is much more diffuse than the ground-state one. As a consequence, they investigated further the causes of these divergences as well as the reasons of the different types of convergence. To do so, they analyzed the relation between the dominant singularity (*i.e.*, the closest singularity to the origin) and the convergence behavior of the series.³⁴ 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). Their method consists in performing a scan of the real axis to detect the avoided crossing responsible

for the pair of dominant singularities. Then, by modeling this avoided crossing via a two-state Hamiltonian one can get an approximation of the dominant conjugate pair of singularities by finding the EPs of the following 2×2 matrix

$$\underbrace{\begin{pmatrix} \alpha & \delta \\ \delta & \beta \end{pmatrix}}_{\mathbf{H}} = \underbrace{\begin{pmatrix} \alpha + \alpha_s & 0 \\ 0 & \beta + \beta_s \end{pmatrix}}_{\mathbf{H}^{(0)}} + \underbrace{\begin{pmatrix} -\alpha_s & \delta \\ \delta & -\beta_s \end{pmatrix}}_{\mathbf{V}}, \quad (21)$$

where the diagonal matrix is the unperturbed Hamiltonian matrix $\mathbf{H}^{(0)}$ and the second matrix in the right-hand-side \mathbf{V} is the perturbation.

In Ref. 35, the simple 2×2 model proposed by Olsen *et al.* is generalized to a non-symmetric (i.e. non-Hermitian) Hamiltonian and various choice of perturbation (not only the MP partitioning). Interestingly, they showed that the convergence pattern of a given perturbation method can be characterized by its archetype which defines the overall “shape” of the energy convergence and can be subdivided in five classes for Hermitian Hamiltonians (zigzag, interspersed zigzag, triadic, ripples, and geometric), while two additional archetypes (zigzag-geometric and convex-geometric) are observed in non-Hermitian Hamiltonians. Other features characterizing the convergence behavior of a perturbation method are its rate of convergence, its length of recurring period, and its sign pattern.

They first studied molecules with low-lying doubly-excited states of the same spatial and spin symmetry. The exact wave function has a non-negligible contribution from the doubly-excited states, so these 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 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.

Moreover they proved that the extrapolation formulas of Cremer and He⁵¹ cannot be used for all systems, and that these formulas 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 10th order. For higher orders, the series is monotonically convergent. This surprising behavior is due to the fact that two pairs of singularities are approximately at the same distance from the origin.

C. The singularity structure

In the 2000’s, Sergeev and Goodson^{53,54} analyzed this problem from a more mathematical point of view by looking at the whole singularity structure where Olsen and collaborators were trying to find the dominant singularity causing the divergence.

They regrouped singularities in two classes: i) α singularities which have “large” imaginary parts, and ii) β singularities which have very small imaginary parts. Singularities of type α are related to large avoided crossing between the ground and low-lying excited states, whereas β singularities 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 following previous work of Stillinger.⁵⁵

To understand the convergence properties of the perturbation series at $\lambda = 1$, one must look at the whole complex plane, in particular, for negative (i.e., real) values of λ . If λ is negative, the Coulomb interaction becomes attractive but the mean field (which has been computed at $\lambda = 1$) remains repulsive as it is proportional to $(1 - \lambda)$:

$$\hat{H}(\lambda) = \sum_i^n \left[\overbrace{\left[-\frac{1}{2} \nabla_i^2 - \sum_A^N \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \right]}^{\text{independent of } \lambda} + \underbrace{(1 - \lambda) v^{\text{HF}}(\mathbf{x}_i)}_{\text{repulsive for } \lambda < 1} + \lambda \underbrace{\sum_{i < j}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{attractive for } \lambda < 0} \right]. \quad (22)$$

The major difference between these two terms is that the repulsive mean field is localized around the nuclei whereas the interelectronic interaction persist away from the nuclei. If λ becomes more and more negative the mean field becomes more and more repulsive so there exists a critical (negative) value of λ , λ_c , for which the Coulombic field created by the nuclei cannot bind the electrons anymore because of the λ -independent nature of the the electron-nucleus attraction. For $\lambda = \lambda_c$, the electrons dissociate from the nuclei and form a bound cluster which is infinitely separated from the nuclei. According to Baker,⁵⁶ this value is a critical point of the system and, by analogy with thermodynamics, the energy $E(\lambda)$ exhibits a singularity at λ_c . At this point the system undergo a phase transition and a symmetry breaking. Beyond λ_c there is a continuum of eigenstates thanks to which the electrons dissociated from the nuclei.

This reasoning is done on the exact Hamiltonian and energy, i.e., the Hamiltonian in the complete Hilbert space, this is the exact energy which exhibits this singularity on the negative real axis. However, in a finite basis set which does not span the complete Hilbert space, one can prove that, for a Hermitian Hamiltonian, the singularities of $E(\lambda)$ occurs in complex conjugate pairs with non-zero imaginary parts. Sergeev and Goodson proved,⁵³ as predicted by Stillinger,⁵⁵ 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. This explains that Olsen *et al.*, because they used a simple 2×2 model, only observed the first singularity of this cluster of singularities causing the divergence.³⁴

Finally, it was shown that β singularities are very sensitive to changes in the basis set 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,⁵⁷ the singularity structure of stretched molecules is difficult because there is more than one significant singularity. This is consistent with the observation of Olsen and coworkers³⁴ on the HF molecule at equilibrium geometry and stretched geometry. To the best of our knowledge, the effect of bond stretching on singularities, its link with spin contamination and symmetry breaking of the wave function has not been as well understood as the ionization phenomenon and its link with diffuse functions.

D. The physics of quantum phase transitions

In the previous section, we saw that a careful analysis of the structure of the Hamiltonian allows us to predict the existence of a critical point. In a finite basis set this critical point is model by a cluster of β singularities. It is now well known that this phenomenon is a special case of a more general phenomenon. Indeed, theoretical physicists proved that EPs close to the real axis are connected to *quantum phase transitions* (QPTs).^{23,58-63} In quantum mechanics, the Hamiltonian is almost always dependent of, at least, one parameter. In some cases the variation of a parameter can lead to abrupt changes at a critical point. These QPTs exist both for ground and excited states as shown by Cejnar and coworkers.^{61,64-68} A ground-state QPT is characterized by the derivatives of the ground-state energy with respect to a non-thermal control parameter.^{61,64} The transition is called discontinuous and of first order if the first derivative is discontinuous at the critical parameter value. Otherwise, it is called continuous and of m th order if the m th derivative is discontinuous. A QPT can also be identify by the discontinuity of an appropriate order parameter (or one of its derivatives).

The presence of an EP close to the real axis is characteristic of a sharp avoided crossing. Yet, at such an avoided crossing, eigenstates change abruptly. Although it is now well understood that EPs are closely related to QPTs, the link between the type of QPT (ground state or excited state, first or higher order) and EPs still need to be clarified. One of the major obstacles that one faces in order to achieve this resides in the ability to compute the distribution of EPs. The numerical assignment of an EP to two energies on the real axis is very difficult in large dimensions. Hence, the design of specific methods are required to get information on the location of EPs. Following this idea, Cejnar *et al.* developed a method based on a Coulomb analogy giving access to the density of EP close to the real axis.^{59,60} More recently Stransky and coworkers proved that the distribution of EPs is characteristic on the order of the QPT.⁶⁹ In the thermodynamic limit, some of the EPs converge towards a critical point λ_c on the real axis. They showed that, within the interaction boson model,⁷⁰ EPs associated to first- and second-order QPT behave differently when the number of particles increases. The position of these singularities converge towards the critical point on the real axis at different rates (exponentially and algebraically for the first and second orders, respectively) with respect to the number of particles.

It seems like our understanding of the physics of spatial and/or spin symmetry breaking in HF theory can be enlight-

ened by QPT theory. Indeed, the second derivative of the HF ground-state energy is discontinuous at the point of spin symmetry-breaking which means that the system undergo a second-order QPT. Moreover, the β singularities introduced by Sergeev and coworkers to describe the EPs modeling the formation of a bound cluster of electrons are actually a more general class of singularities. The EPs close to the real axis (the so-called β singularities) are connected to QPT because they result from a sharp avoided crossings at which the eigenstates change quickly. However, the α singularities arise from large avoided crossings. Thus, they cannot be connected to QPT. The avoided crossings generating α singularities generally involve the ground state and low-lying doubly-excited states. Those excited states have a non-negligible contribution to the exact FCI solution because they have (usually) the same spatial and spin symmetry as the ground state. We believe that α singularities are connected to states with non-negligible contribution in the CI expansion thus to the dynamical part of the correlation energy, while β singularities are linked to symmetry breaking and phase transitions of the wave function, *i.e.*, to the multi-reference nature of the wave function thus to the static part of the correlation energy.

IV. CONCLUSION

In order to model accurately chemical systems, one must choose, in a ever growing zoo of methods, which computational protocol is adapted to the system of interest. This choice can be, moreover, motivated by the type of properties that one is interested in. That means that one must understand the strengths and weaknesses of each method, *i.e.*, why one method might fail in some cases and work beautifully in others. We have seen that for methods relying on perturbation theory, their successes and failures are directly connected to the position of EPs in the complex plane. Exhaustive studies have been performed on the causes of failure of MP perturbation theory. First, it was understood that, for chemical systems for which the HF Slater determinant is a poor approximation to the exact wave function, MP perturbation theory fails too. Such systems can be, for example, molecules where the exact ground-state wave function is dominated by more than one configuration, *i.e.*, multi-reference systems. More preoccupying cases were also reported. For instance, it has been shown that systems considered as well-understood (*e.g.*, Ne) can exhibit divergent behavior when the basis set is augmented with diffuse functions. Later, these erratic behaviors of the perturbation series were investigated and rationalized in terms of avoided crossings and singularities in the complex plane. It was shown that the singularities can be classified in two families. The first family includes α singularities resulting from a large avoided crossing between the ground state and a low-lying doubly-excited states. The β singularities, which constitutes the second family, are artifacts generated by the incompleteness of the Hilbert space, and they are directly connected to an ionization phenomenon occurring in the complete Hilbert space. These singularities are close to the real axis and connected with sharp avoided crossing between the ground state and a highly diffuse state.

We have found that the β singularities modeling the ionization phenomenon described by Sergeev and Goodson are actually part of a more general class of singularities. Indeed, those singularities close to the real axis are connected to quantum phase transition and symmetry breaking, and theoretical physics have demonstrated that the behavior of the EPs depends of the type of transitions from which the EPs result (first or higher orders,

ground state or excited state transitions).

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