

4-2020

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Mathematical and Physical Description of Conical Intersections

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Honors College Senior Project

Introduction

One of the most powerful features in computational chemistry is the ability to predict reaction mechanisms. This is typically done by an examination of the potential energy surface (PES) for the reaction, which is a function that yields the energy of a molecule given a particular geometry. However, molecules have multiple electronic states, so there are many PESs at each geometry. If the molecule is excited into an energy level above the ground state, more PESs are introduced into the system. Therefore, there is a possibility for the ground state and excited state PESs to cross and share the same energy. When these PESs take the form of a double cone, the point of intersection in the nuclear coordinate system is known as a conical intersection (CI).¹ Due to the intersection point, it is much easier for molecules to transition their electronic, vibrational, and rotational energies between the two surfaces. Therefore, CIs are critical to the study of excited states, particularly in the context of photochemistry.² This has manifested in the emergence of photoexcited states in organic and inorganic chemistry.³⁻⁴ For example, chemists now have the ability to induce long-lasting photoexcited states in certain molecules, allowing for reactions to occur that were otherwise unattainable.⁵ CIs are important in other applications as well, including nonradiative recombination, solar energy conversion, and nanomaterials.⁶⁻⁸

However, CIs are difficult to study because they interfere with traditional adiabatic processes in thermodynamics and deviate from the Born-Oppenheimer approximation, the assumption that the motion of nuclei and electrons can be treated separately.⁹ This approximation is foundational to all traditional calculations performed by quantum chemists so deviating from it is not a simple task and requires new mathematical models. These new mathematical models are required in the study of CIs because the dynamics of both potential energy surfaces involved in the intersections are important, leading to the region where the Born-Oppenheimer

approximation is no longer valid (*i.e.*, the nonadiabatic region). These excited state electronic wave functions require expanded basis sets and a thorough treatment of the active space in configuration interaction calculations.¹⁰ It also means that specialized methods are needed to couple the two potential energy surfaces that occupy different electronic states.

This review lays the foundation for the mathematics and physics behind CIs. Its primary purpose is to teach undergraduate students who have taken CHM 356 (an introduction course to quantum mechanics) some of the basics of CIs. The first section derives the Born-Oppenheimer equation and expands on it to include non-adiabatic coupling terms that are necessary when considering nucleus-electron attractions. The second section discusses the non-crossing rule and its importance on mapping the local topology of the PESs close to the CI. The third section develops an understanding of one method for locating a CI. Finally, this review concludes with an application on silicon nanocrystals to demonstrate the importance of CIs on real systems that undergo chemical reactions in their excited states. Also included in this application is a brief introduction to how physical defects in a molecule can drive CIs.

Theory of the Non-Adiabatic Process

In general, the Schrödinger equation,

$$\hat{H}\psi = i\hbar \frac{d}{dt}\psi, \quad (1)$$

is a sufficient model for describing chemical systems, where \hat{H} is the Hamiltonian, or the total energy operator. Thus, the Hamiltonian is defined as

$$\hat{H} = K_n + K_e + U(\vec{R}, \vec{r}), \quad (2)$$

where K_n is the kinetic energy of the nuclei, K_e is the kinetic energy of the electrons, and $U(\vec{R}, \vec{r})$ is the potential energy between all atoms in the system in terms of the nuclear \vec{R} and electronic coordinates \vec{r} . As such, $U(\vec{R}, \vec{r})$ includes nuclear and electronic repulsions as well as nucleus-electron attractions.

One way to simplify the Schrödinger equation is to utilize the Born-Oppenheimer approximation, where the motion of the electrons and nuclei are treated separately. This is because nuclei are about three orders of magnitude heavier than electrons and thus move significantly slower. For that reason, the Born-Oppenheimer approximation assumes that the nuclei are stationary compared to the fast-moving electrons. This eliminates the K_n term, reducing the Hamiltonian to

$$\hat{H}_e = K_e + U(\vec{R}, \vec{r}), \quad (3)$$

where the nuclear repulsion term is not present because it can be computed exactly when the nuclei are treated as parameters. Re-writing the electronic Hamiltonian in this way provides a basis for the most direct way to solve the Schrödinger equation: by manipulating the Hilbert space, which is defined as the vector space of solutions to the Schrödinger equation and can be represented by all possible wavefunctions built from their atomic orbitals. The Hilbert space consists of two subspaces that represent the nuclear and electronic parts of the Schrödinger equation. These subspaces are separated via the tensor product

$$\mathcal{H} = \mathcal{H}_n \otimes \mathcal{H}_e, \quad (4)$$

where \mathcal{H}_n is the subspace represented by the slow motion of the nuclei and \mathcal{H}_e is the quicker electronic motion.¹¹

The electronic Schrödinger equation can also be written in the form,

$$\hat{H}\phi_n = E(\vec{R})\phi_n, \quad (5)$$

where the total energy of the system is only dependent on the nuclear coordinates. This is due to the Born-Oppenheimer approximation, where the electronic coordinates do not affect the nuclear wavefunction, allowing for the simplification that the energy only depends on the nuclear coordinates. The eigenvalues $E(\vec{R})$ of the Hamiltonian operator can also be written as the expectation value,

$$\int_{-\infty}^{\infty} \phi_n^* H \phi_n dx. \quad (6)$$

In addition, the Hamiltonian commutes with the nuclear position operator,

$$\begin{aligned} [\hat{p}, \hat{H}] &= \hat{p}\hat{H}\psi - \hat{H}\hat{p}\psi \\ &= -i\hbar \frac{d}{dx} \left[i\hbar \frac{d}{dx} \psi \right] - i\hbar \frac{d}{dx} \left[-i\hbar \frac{d}{dx} \psi \right] \\ &= \hbar^2 \frac{d^2}{dx^2} \psi - \hbar^2 \frac{d^2}{dx^2} \psi = 0, \end{aligned} \quad (7)$$

such that the arbitrary ψ can be expanded via the resolution of the identity. The matrix multiplication of the identity matrix leads to the projection of the original, complicated ψ onto a set of electronic and nuclear states that are more easily understandable. In conventional wavefunction notation, this can be written, as expressed in Malhado, et. al, in terms of the real-valued functions,

$$\psi(\vec{R}, \vec{r}) = \sum_n \phi_n(\vec{R}, \vec{r}) \chi_n(\vec{R}), \quad (8)$$

where ϕ_n are the nuclear wavefunctions with eigenvalues of the Hamiltonian from eq. 3, and χ_n are the nuclear wavefunctions projected onto \mathcal{H}_e .¹¹ Eq. 8 is known as the Born-Oppenheimer expansion.

Next, it is imperative to determine how the Schrödinger equation changes over time (evolution of the time-dependent Schrödinger equation). This can be accomplished using the electronic wavefunctions for the chemical systems with nuclear coordinates \vec{R} and performing the dot product with the Schrödinger equation, where the left product is

$$\langle \phi_n(\vec{R}) | i\hbar \frac{d}{dt} | \psi \rangle = i\hbar \frac{d}{dt} \langle \phi_n(\vec{R}) | \psi \rangle. \quad (9)$$

The reason why this works is because $\phi_n(\vec{R})$ does not depend on time. In fact, the left product shows that time dependence can only be expressed in terms of the coefficients for ϕ_n . This time dependence can be expanded, as in Malhado, et. al, as

$$\begin{aligned} i\hbar \frac{d}{dt} \langle \phi_n(\vec{R}) | \psi \rangle &= \sum_{c,m} -\frac{\hbar}{2m_c} \langle \phi_n(\vec{R}) | \nabla^2 | \phi_m(\vec{R}) \rangle + 2 \langle \phi_n(\vec{R}) | \nabla | \phi_m(\vec{R}) \rangle \langle \phi_m(\vec{R}) | \psi \rangle \\ &+ \sum_c -\frac{\hbar}{2m_c} \nabla^2 + U(\vec{R}) \langle \phi_n(\vec{R}) | \psi \rangle \end{aligned} \quad (10)$$

where c is the index over \vec{R} and m is the index over the mass.¹¹ In eq. 10, the first term is electronic, and the second term is nuclear, which combine to equate to the non-adiabatic coupling terms because of the dependence on the nuclear coordinates. The last term is the time-dependent Schrödinger equation. Altogether, eq. 10 offers a complete depiction of the non-adiabatic dynamics of chemical systems.

The non-crossing rule and the local topology around CIs

The potential energy surfaces involved in CIs have unique shapes near the point of intersection. These shapes are defined by the non-crossing rule, which says that surfaces with electronic states with the same symmetry are not allowed to cross.¹ However, CIs are points where two surfaces are degenerate, which is justified by a stipulation in the non-crossing rule that says that crossings are allowed for polyatomic molecules because they have more than two degrees of freedom. One way to illustrate this is by writing a matrix of the electronic Hamiltonian that spans the intersecting surfaces,

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{12} & H_{22} \end{bmatrix}, \quad (11)$$

where the subscript “1” is assigned to functions in the primary subspace, the subscript “2” is assigned to functions in the secondary subspace, and \vec{R} is suppressed for simplicity. The eigenvalues of these Hamiltonians are potential energies for the surfaces, $V_+(\vec{R})$ and $V_-(\vec{R})$, where

$$V_{\pm}(\vec{R}) = \frac{H_{11} + H_{22}}{2} \pm \frac{1}{2} \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2}, \quad (12)$$

as expressed in Malhado, et. al.¹¹ It is important to focus on the case when $V_+(\vec{R}) = V_-(\vec{R})$ for applications in CIs. In order to meet this condition, $H_{11} = H_{22}$ and $H_{12} = 0$ so that the PESs meet. For this to occur, two different components of \vec{R} , \vec{u} and \vec{v} , must occupy the branching space, or area of the nuclear coordinate where the PESs converge onto one intersecting point.¹¹ These components are physically interpreted as displacements in \vec{R} from the intersection point and are defined along the intersecting PESs. The space in the nuclear coordinate system that is

perpendicular to \vec{u} and \vec{v} is called the intersection space because it is the point where the converging surfaces cross.

When the distance to the CI is small, it is convenient to break up the matrix eq. 11, as expressed in Malhado, et. al, as follows,

$$\begin{bmatrix} 0.5(H_{11} + H_{22}) & 0 \\ 0 & 0.5(H_{11} + H_{22}) \end{bmatrix} + \begin{bmatrix} 0.5(H_{11} - H_{22}) & H_{12} \\ H_{12} & -0.5(H_{11} - H_{22}) \end{bmatrix}, \quad (13)$$

because it explicitly describes the impact of the above conditions on the electronic Hamiltonian near the CI.¹¹ Based on the formal directions of the vectors \vec{u} and \vec{v} , the Hamiltonian matrix can be rewritten as,

$$\begin{bmatrix} \nabla_{u,v}[0.5(H_{11} + H_{22})] + f(\vec{R}) & 0 \\ 0 & \nabla_{u,v}[0.5(H_{11} + H_{22})] + f(\vec{R}) \end{bmatrix} + \begin{bmatrix} u & v \\ v & -u \end{bmatrix}, \quad (14)$$

where $f(\vec{R})$ is an arbitrary function of the nuclear coordinates, as shown in Malhado, et. al.¹¹ The gradient ($\nabla_{u,v}$) physically represents the point of maximum change in \vec{u} and \vec{v} close to the CI.

The potential energy of the system also describes the topology around a CI. When moving in small increments in the intersection space, the energy gaps between the potentials of each surface do not change. However, when moving along the branching space the two PESs have a conical shape where the energy gap decreases until it reaches a common point, leading to a CI.¹¹

Locating CIs between two potential energy surfaces

The location of a CI is especially important because it describes where on the PES the energy crossing occurs. A direct method for determining this location involves the wavefunction itself; it changes sign as it adiabatically travels through a closed loop near the intersection, being

that there is a single point inside the loop where the two PESs meet. This test was derived by Longuet-Higgins in 1975.¹² Later, the sign change in the wavefunction was called the geometric, or Berry, phase effect. The geometric phase shows up when the CI is low enough in energy to be accessible, no matter the energy of the two PESs involved.

The geometric phase can be illustrated by transforming eq. 11 via the rotation matrix,

$$T(\varphi) = \begin{bmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{bmatrix}. \quad (15)$$

For this example, suppose the CI is at the origin $(x, y) = (0,0)$. Surrounding the origin is a closed loop that is defined in polar coordinates (ρ, θ) , where $x = \rho\cos\theta$ and $y = \rho\sin\theta$.

Evaluating the transformation matrix (eq. 15) in terms of the polar coordinates yields,

$$T(\varphi[\rho, \theta]) = T(\rho, \theta) = -T(\rho, \theta + 2\pi), \quad (16)$$

where $\theta \rightarrow \theta + 2\pi$ demonstrates the phase difference that is acquired as the molecule traverses the closed loop.² This phase difference occurs because of the evolution of the Hamiltonian as the eigenstates change when the wavefunction adiabatically moves around the loop. While it takes several steps to reach eq. 16 from eq. 15, it should be obvious by seeing the result of the matrix transformation that the sign does change at the CI.

Application to a real chemical system

In a paper recently published in *Chemical Science*, Levine and co-workers studied the effects of CIs in silicon nanocrystals (SiNCs) with dangling bond defects.¹³ A dangling bond is an unsatisfied valence on an atom in the solid state (*i.e.*, when the atom is immobilized). Figure 1 shows the dangling bond defect sites in the silicon clusters studied in this work.¹³ These defect sites are problematic because they limit the performance of silicon-based photovoltaic cells and

light emitting diodes by consuming the electronic excitations that are critical for their operation and converting the energy to useless heat.¹⁴ Therefore, the defect sites are known as nonradiative centers, which means that they undergo nonradiative recombination. During this process, the energy of electrons is converted to the vibrational energy of phonons, or the excitation of lattice atoms in the crystal. The current mechanism for recombination involves the capture of an electron and hole (particles that take the place of missing electrons that have the same property as those electrons but with a positive charge) into the non-bonding orbital of a defect site. This causes a change in the oxidation state of the defect site that results in nuclear relaxation of the bending mode that maintains the symmetry of the molecule. While it generally explains the recombination process, it ignores important physical properties of SiNCs, such as the known and non-instantaneous interactions between electrons, holes, and defect sites. However, the theory of CIs takes these into consideration, so the authors investigated whether CIs of the ground and first excited state contribute to the recombination process.

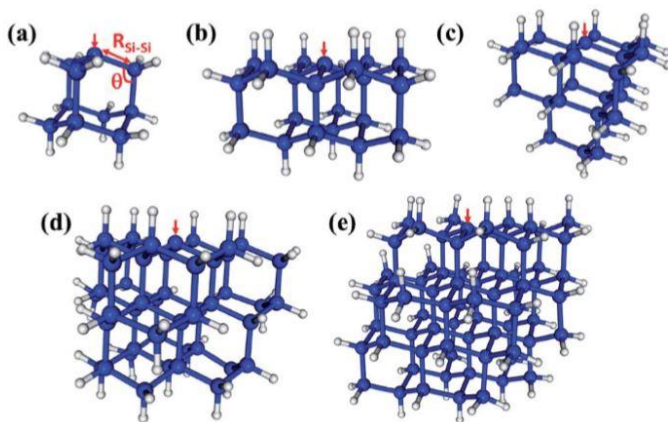


Figure 1. SiNCs with dangling bond defects that were studied in the Levine et. al. paper. (a) $\text{Si}_{10}\text{H}_{15}$, (b) $\text{Si}_{22}\text{H}_{27}$, (c) $\text{Si}_{26}\text{H}_{31}$, (d) $\text{Si}_{47}\text{H}_{49}$, and (e) $\text{Si}_{72}\text{H}_{63}$. The red arrows indicate the positions of the defect sites. This figure and caption were reproduced, with permission, from Figure 1 of ref. 13. It was originally published by the Royal Society of Chemistry.

They used *ab initio* molecular dynamics (AIMD) simulations and high-level electronic structure calculations to determine how the potential energy and length (with corresponding angles) of bonds adjacent to the defect site of SiNCs change over time (Figure 2).¹³ This data shows that the PES of SiNCs with dangling bond defects converge on a CI within 40 – 60 fs after excitation to the first excited state.¹³ Interestingly, they found that the bond stretching is asymmetric close to the defect site at the 40 – 60 fs timescale, meaning that the symmetry breaks at the CI. They also saw that the bond angle generally increases around the same time as the excited/ground state energy gap approaches zero. Another important finding is that the defect site remains close to the CI for another 40 – 60 fs after the initial crossing, indicating that it may pass over the intersection multiple times, leading to nonradiative recombination.¹³

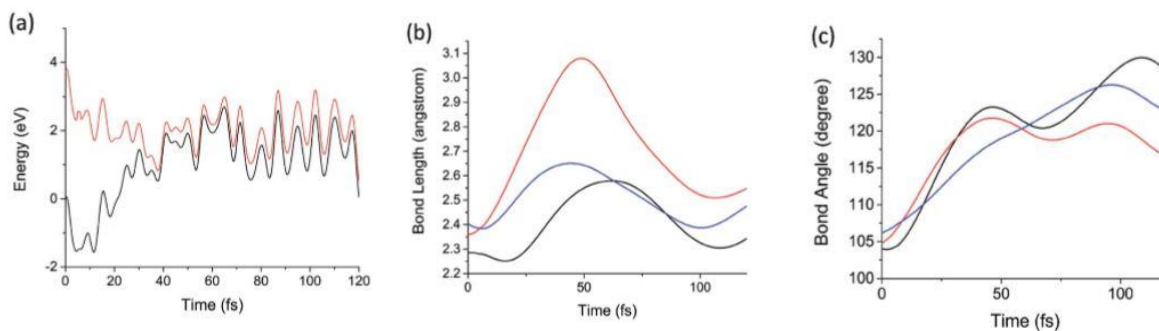


Figure 2. (a) Potential energies of the excited (red) and ground (black) electronic states as a function of time from the excited state AIMD simulation of $\text{Si}_{72}\text{H}_{63}$. (b) The three Si-Si bond lengths and corresponding bond angles (c) adjacent to the bond defect site as a function of time from the same simulation. This figure and caption were reproduced, with permission, from Figure 3 of ref. 13. It was originally published by the Royal Society of Chemistry.

Then, they investigated why symmetry breaks at the CI by performing an analysis of the orbitals involved with the excitation in SiNCs. The excitation promotes an electron from the $\sigma_{\text{Si-Si}}$ orbital to the non-bonding orbital, which reduces the bond order of the Si-Si bond and elongates one of the Si-Si bonds. Therefore, the motions described in Figure 2 breaks the double degeneracy in the excited state orbitals and causes a distortion in the PES. This distortion leads to a CI.

The key finding in this paper is that the mechanism for nonradiative recombination in SiNCs proceeds via a CI. Therefore, they concluded that it would be important to use protocols developed in this review to investigate similar mechanisms in other systems. However, the authors say early on in the paper that they used the Born-Oppenheimer approximation for their simulations. This does not make much sense, as it is well known that CIs are non-adiabatic. I was hoping to clear this up with the principal investigator (Levine) during a visit to Michigan State University but was unable to due to the unforeseen circumstances of the COVID-19 pandemic.

Conclusions

This review explained the basics of CIs from a mathematical and physical perspective. The first section described the theory of non-adiabatic processes by examining the Born-

Oppenheimer approximation and concluded that it is not enough when considering CIs. It should be clear now that corrections are required to account for nuclear dependencies. Next, the local geometry around CIs were considered and how the non-crossing rule played a role. The process of locating CIs was also discussed. It was found, surprisingly, that simply observing the negative sign of the wavefunction by the geometric phase effect is enough to locate a CI between two PESs. Finally, an application of defect sites on silicon nanocrystals showed why the contents of this review are important and that it is crucial to study CIs in nonradiative recombination.

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