Theoretical Studies on Magnetic and Photochemical Properties of Organic Molecules

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(陈星)

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To my parents
Abstract

The present thesis is concerned with the theoretical studies on magnetic and photochemical properties of organic molecules. The \textit{ab initio} and first principles theories were employed to investigate the vibrational effects on the isotropic hyperfine coupling constant (HFCC) known as the critical parameter in electron paramagnetic resonance spectrum, the theoretical simulations of the vibronically resolved molecular spectra, the photo-induced reaction mechanism of \(\alpha\)-santonin and the spin-forbidden reaction of triplet-state dioxygen with cofactor-free enzyme. The theoretical predictions shed light on the interpretation of experimental observations, the understanding of reaction mechanism, and importantly the guideline and perspective in respect of the popularized applications.

We focused on the vibrational corrections to the isotropic HFCCs of hydrogen and carbon atoms in organic radicals. The calculations indicate that the vibrational contributions induce or enhance the effect of spin polarization. A set of rules were stated to guide experimentalist and theoretician in identification of the contributions from the molecular vibrations to HFCCs. And the coupling of spin density with vibrational modes in the backbone is significant and provides the insight into the spin density transfer mechanism in organic \(\pi\) radicals.

The spectral characters of the intermediates in solid-state photoarrangement of \(\alpha\)-santonin were investigated in order to well understand the underlying experimental spectra. The molecular spectra simulated with Franck-Condon principle show that the positions of the absorption and emission bands of photosantonic acid well match with the experimental observations and the absorption spectrum has a vibrationally resolved character.

\(\alpha\)-Santonin is the first found organic molecule that has the photoreaction activities. The photorearrangement mechanism is theoretically predicted that the low-lying excited state \(^1(n\pi^*)\) undergoing an intersystem crossing process decays to \(^3(\pi\pi^*)\) state in the Franck-Condon region. A pathway which is favored in the solid-state reaction requires less space and dynamic advantage on the excited-state potential energy surface (PES). And the other pathway is predominant in the weak polar solvent due to the thermodynamical and dynamical preferences. Lumisantonin is a critical intermediate derived from \(\alpha\)-santonin photoreaction. The \(^3(\pi\pi^*)\) state plays a key role in lumisantonin photolysis. The photolytic pathway is in advantage of dynamics and thermodynamics on the triplet-state PES. In contrast, the other reaction pathway is facile for pyrolysis ascribed to a stable intermediate formed on the ground-state PES.
The mechanism of the oxidation reaction involving cofactor-free enzyme and triplet-state dioxygen were studied. The theoretical calculations show that the charge-transfer mechanism is not a sole way to make a spin-forbidden oxidation allowed. It is more likely to take place in the reactant consisting of a non-conjugated substrate. The other mechanism involving the surface hopping between the triplet- and singlet-state PESs via a minimum energy crossing point (MECP) without a significant charge migration. The electronic state of MECP exhibits a mixed characteristic of the singlet and triplet states. The enhanced conjugation of the substrate slows down the spin-flip rate, and this step can in fact control the rate of the reaction that a dioxygen attaches to a substrate.
Preface

All works presented in the thesis were completed in the past three years, 2008.09 – 2011.12, at the Department of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, Stockholm, Sweden, and Department of Chemistry and State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China.

List of papers included in the thesis

Paper 1. Zero-point Vibrational Corrections to Isotropic Hydrogen Hyperfine Constants in Polyatomic Molecules,


Paper 2. Vibrationally induced carbon hyperfine coupling constants: a reinterpretation of the McConnell relation

Z. Rinkevicius, X. Chen, H. Ågren, K. Ruud, Submitted for publication.


X. Chen, G. Tian, Z. Rinkevicius, O. Vahtras, H. Ågren, Z. Cao, Y. Luo, Submitted for publication.

Paper 4. Theoretical Studies on the Mechanism of α-Santonin Photo-Induced Reaction


Paper 5. Role of the $^3(\pi\pi^*)$ State in Photolysis of Lumisantonin: Insight from ab Initio Studies


Paper 6. Theoretical Studies on Reaction of Cofactor-Free Enzyme with Triplet Oxygen Molecule

List of related papers not included in the thesis

Paper 1. Theoretical Studies on the Interactions of Cations with Diazine,

X. Chen, W. Wu, J. Zhang and Z. Cao,


Paper 2. Theoretical Study on the Singlet Excited State of Pterin and Its Deactivation Pathway,

X. Chen, X. Xu and Z. Cao,


Paper 3. Theoretical Study on the Dual Fluorescence of 2-(4-cyanophenyl)-N,N-dimethyl-aminoethane and Its Deactivation pathway,

X. Chen, Y. Zhao and Z. Cao,


Paper 4. DFT Study on Polydiacetylenes and Their Derivatives,

B. Huang, X. Chen and Z. Cao,


Comments on my contributions to the papers included

I was responsible for the calculations, discussion and writing the first drafts of Papers 1, 3, 4, 5, 6

I took partly responsibility for the calculations, discussion and writing of Paper 2.
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How time flies! The slice of life that I was making effort to prepare my licentiate thesis in the last year arising in my mind looks like a vivid episode that just happened. I have spent about three years in Stockholm, and it draws to an end by now. The feeling at this moment can not be described by any simple word. It indeed is not a long time from the viewpoint of a whole academic career, however, the rememberable and precious experience I have learned a lot from in these years will be treasured up forever in my life. On the occasion of the thesis coming to the end, I would like to express my sincere gratitude to many people, who support me, inspire me and stand beside me always.

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Xing Chen
Fall 2011, Stockholm
# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>BO</td>
<td>Born-Oppenheimier</td>
</tr>
<tr>
<td>CASSCF</td>
<td>complete active space self-consistent-field</td>
</tr>
<tr>
<td>CSF</td>
<td>configuration state function</td>
</tr>
<tr>
<td>CI</td>
<td>conical intersection</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DFT-RU</td>
<td>restricted-unrestricted density functional theory</td>
</tr>
<tr>
<td>EPR</td>
<td>electron paramagnetic resonance</td>
</tr>
<tr>
<td>ESR</td>
<td>electron spin resonance</td>
</tr>
<tr>
<td>FC</td>
<td>Franck-Condon</td>
</tr>
<tr>
<td>GGA</td>
<td>generalized gradient approximations</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree-Fock</td>
</tr>
<tr>
<td>HK</td>
<td>Hohenberg-Kohn</td>
</tr>
<tr>
<td>HFCC</td>
<td>hyperfine coupling constant</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>IC</td>
<td>internal conversion</td>
</tr>
<tr>
<td>ISC</td>
<td>intersystem crossing</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>LCAO</td>
<td>linear combination of atomic orbitals</td>
</tr>
<tr>
<td>L(S)DA</td>
<td>Local (spin) density approximations</td>
</tr>
<tr>
<td>LR-TDDFT</td>
<td>linear response TDDFT</td>
</tr>
<tr>
<td>LCM</td>
<td>linear coupling model</td>
</tr>
<tr>
<td>MCSCF</td>
<td>Multi-configurational self-consistent field</td>
</tr>
<tr>
<td>MRCI</td>
<td>multireference configuration interaction</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>PES</td>
<td>potential energy surface</td>
</tr>
<tr>
<td>RASSCF</td>
<td>restricted active space self-consistent-field</td>
</tr>
<tr>
<td>RG</td>
<td>Runge-Gross</td>
</tr>
<tr>
<td>SCF</td>
<td>self-consistent-field</td>
</tr>
<tr>
<td>SOC</td>
<td>spin-orbit coupling</td>
</tr>
<tr>
<td>TDDFT</td>
<td>Time-depend density functional theory</td>
</tr>
<tr>
<td>TS</td>
<td>transition state</td>
</tr>
<tr>
<td>UKS</td>
<td>unrestricted Kohn-Sham</td>
</tr>
<tr>
<td>VR</td>
<td>vibrational relaxation</td>
</tr>
<tr>
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Chapter 1

Introduction

Organic molecules with peculiar magnetic or optical properties have attracted much scientific attention in many fields, including medicine, industry and material science. Spectroscopy is a measurement of the system in response to an external perturbation of, for example, light or magnetic field. Molecular structures can be identified from the magnetic resonance spectroscopies and/or the visible, ultraviolet, and the fluorescence spectroscopies. Magnetic resonance phenomena illustrate an intrinsic property of magnetic molecules in an external magnetic field. They can be divided into two types depending on the particles that interact with the magnetic field: electron paramagnetic resonance (EPR), also referred to as electron spin resonance (ESR), and nuclear magnetic resonance (NMR). EPR spectroscopy is a technology adopted to describe the spatial distribution of paramagnetic species\textsuperscript{1}. The underlying physics is that the unpaired electrons with spin magnetic moments can absorb or emit electromagnetic radiation depending on the strength of the external magnetic field. Nowadays, with the development of EPR technology, it has been widely used to monitor the presence of radicals in chemical reactions, as well as to investigate biological and medical molecules with non-vanishing total electron spins and magnetic materials\textsuperscript{2}.

It’s a challenging and complicated task to extract useful and significant information from EPR spectroscopy in order to make assignments of molecular electronic and geometrical structures. A way to understand the experimental observations is by theoretical calculation of the effective spin Hamiltonian which gives a relation between experimental data and predictions of quantum mechanics. Nowadays, \textit{ab initio} calculations play an important role in the prediction of EPR parameters. These are calculations with high accuracy but which have the disadvantage of high computational cost which limits their applicability to small-
sized molecules. With the development of the density functional theory (DFT), theoretical calculations of the EPR parameters can shed light on moderate- and large-sized molecules with reasonable computational cost and accuracy.

Electronic absorption/emission spectroscopy is an important tool in analytical chemistry, where matter-radiation interaction between a sample and photons is measured. These spectra contain important information about the excited-state properties of molecules. The position and shape of a band in an electronic spectrum are determined by the nature of the molecular electronic structure. Accordingly, the comparison between the simulated and the experimental spectra provides accurate assignment of the transitions, the molecular electronic structure and the excited-state properties.

As stated by the Grotthuss-Draper law, a photochemical reaction takes place when a photon is absorbed by a molecule. Photochemistry is tied up with our daily life, for instance, photosynthesis takes place every moment in organisms. In fact, the first organic molecule to be discovered with a photo-induced reactivity was α-santonin, in the 1830s. Since then, many researchers have been attracted to study of photoreaction and the photochemical techniques have been widely used in industrial synthesis and other fields\[3\]. The photochemical reaction, chemical reaction induced by light, is quite different from the conventional thermal reactions on the ground-state potential energy surface (PES). As usually more than two PESs are involved, investigations of the mechanism for a photochemical reaction is challenging both in computations and experiments.

This thesis is devoted to the quantum mechanical simulations of two kinds of spectra, the EPR and the electronic spectra, and two types of reactions, the photochemical and spin-forbidden reactions. Special attention is payed to one of the EPR parameters, the isotropic hyperfine coupling constant (HFCC). In the following chapters, the basic computational approaches employed in the investigations is first introduced in Chapter 2. Then, the essential concepts and basic principles in molecular spectroscopy are represented in Chapter 3. Next, Chapter 4 discusses the photochemical process and spin-forbidden reactions. Finally, a summary of included papers is provided in Chapter 5.
Chapter 2

Basic computational methods

*Ab initio* and density functional theory are the basic methodologies to investigate electronic structures of molecules. In molecular quantum mechanics, the calculations of the energy and the wavefunction in a specific electronic state of a medium-sized molecule are feasible under the Born-Oppenheimer (BO) approximation. Owing to the large ratio of nuclear mass to electronic mass, the nuclear coordinates are regarded as constants in the potential energy term, and the total wavefunctions are successfully divided into electronic and nuclear (vibrational, rotational) parts. Accordingly, the molecular wavefunction is represented by

$$
\Psi_t(r, R) = \Psi_N(R)\Psi_e(r, R).
$$

(2.1)

Although the BO approximation introduces some errors, the errors still can be acceptable for the many-electron systems. The basic computational methods summarized below are in the framework of the BO approximation.

An *ab initio* method is a parameter-free method to solve Schrödinger equation. The Hartree-Fock (HF) approximation is the simplest of *ab initio* theories. It is based on the approximation that each electron moves separately in the average potential field arising from the remaining electrons, which means that the electron-electron interaction is approximately described by a mean-field approach. Thereby the many-body Schrödinger equation turns into an effective one-electron equation, and the Coulomb interaction is treated in an averaged way. A consequence of this approximation is that the probability of two close electrons is overestimated, and the strength of coulomb interaction is enhanced. In quantum mechanics, the correlation energy ($E_{\text{cor}}$) is defined by

$$
E_{\text{cor}} = E^0 - E^{\text{HF}},
$$

(2.2)
where $E^0$ is the exact lowest electronic energy in a given basis set in the BO approximation. The $E_{\text{cor}}$ consists of two parts: dynamical (short-ranged) originating from the instantaneous repulsion of electrons and static (long-ranged) arising from the near-degeneracy of different electronic configurations in energy. The $E_{\text{cor}}$ gives much more contributions to some specific cases, such as molecular dissociation reactions and excited state calculations, which are poorly described by HF method. The post-Hartree-Fock methods use the HF calculation as starting point and further improve the HF result by taking account of $E_{\text{cor}}$, but are computationally more expensive. The post-HF methods include configuration interaction (CI)\cite{10,11}, coupled cluster (CC)\cite{12-14}, Møller-Plesset perturbation theory (MP2\cite{15}, MP3, MP4\cite{16}, etc.), quadratic configuration interaction (QCI\cite{17}) and quantum chemistry composite methods (G2\cite{18}, G3\cite{19}, CBS, T1, etc). Other post-HF methods include multiconfigurational self-consistent field (MCSCF)\cite{8,20,21}, and as a special case, the complete active space SCF (CASSCF)\cite{22,23}. The multireference methods taking $E_{\text{cor}}$ into account, are extensions of single reference methods (HF or CI methods), which take multi-configurational wave functions as starting points for higher order approximations – multireference perturbation theory (MRPT, CASPT2\cite{24,25}) as well as multireference configuration interaction (MRCI)\cite{26} belong to these types. Density functional theory (DFT) differing from \textit{ab initio} methods is an alternative methodology in quantum mechanics, and also considers the $E_{\text{cor}}$.

In our previous works summarized in this thesis, we used the popular computational methods (CASSCF and CASPT2) in the excited-state studies of the photolysis mechanisms of santonin and lumisantonin. Time-dependent DFT (DFT) was also used in the excited-state optimizations in our studies.

For the evaluation of isotropic HFCCs, we used the restricted-unrestricted DFT (DFT-RU) approach\cite{27,28} to avoid the spin-contamination problems introduced by unrestricted Kohn-Sham (UKS) formalism. The details in DFT-RU is given in the following section.
2.1 *Ab Initio* theory

2.1.1 Hartree-Fock

As mentioned above, in the HF approximation many-body wavefunctions are represented by an antisymmetrized product, the Slater determinant given by\[^{[29]}\],

\[
\Psi(\chi_1, \chi_2, \ldots, \chi_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\phi_1(\chi_1) & \phi_2(\chi_1) & \cdots & \phi_N(\chi_1) \\
\phi_1(\chi_2) & \phi_2(\chi_2) & \cdots & \phi_N(\chi_2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_1(\chi_N) & \phi_2(\chi_N) & \cdots & \phi_N(\chi_N)
\end{vmatrix},
\]

(2.3)

where \(\phi_i\) is a set of orthonormal orbitals - single electron wave functions. The total electronic Hamiltonian of a molecule with \(M\) nuclei \(N\) electrons at fixed nuclear geometry is written as\[^{[6]}\],

\[
\mathcal{H}_e = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{a=1}^{M} \sum_{i=1}^{N} \frac{Z_a}{r_{ia}} + \sum_{i<j} \frac{1}{r_{ij}}.
\]

(2.4)

The HF energy is given by,

\[
E_{HF} = -\frac{1}{2} \sum_{i=1}^{N} \langle \phi_i | \nabla^2 | \phi_i \rangle - \sum_{a=1}^{M} \sum_{i=1}^{N} \langle \phi_i | \frac{Z_a}{r_{ia}} | \phi_i \rangle \\
+ \sum_{i<j} \langle \phi_i(1) \phi_j(2) | \frac{1}{r_{12}} | \phi_i(1) \phi_j(2) \rangle - \sum_{i<j} \langle \phi_i(1) \phi_j(2) | \frac{1}{r_{12}} | \phi_i(2) \phi_j(1) \rangle \\
= \sum_{i=1}^{N} \mathcal{H}_{ii}^{\text{core}} + \sum_{i=1}^{N} \sum_{j>i}^{N} (J_{ij} - K_{ij}),
\]

(2.5)

\[
\mathcal{H}_{ii}^{\text{core}} \equiv \langle \phi_i | \mathcal{H} | \phi_i \rangle,
\]

(2.6)

where \(\mathcal{H} = -\frac{1}{2} \nabla_i^2 + \sum_{a=1}^{M} \frac{Z_a}{r_{ia}}\) is one-electron operator, \(J_{ij}\) and \(K_{ij}\) are Coulomb and exchange integrals, respectively.

To solve the HF problem is to find the single Slater determinant which yields the lowest energy by means of the variational principle. This leads to the canonical HF equations\[^{[21,30,31]}\]

\[
\hat{f}(1) \phi_i(1) = \varepsilon_i \phi_i(1),
\]

(2.7)
where $\varepsilon_i$ represents the orbital energy, and Fock operator is defined by

$$ f_i(1) \equiv \mathcal{H}(1) + \sum_{j \neq i} (J_j(1) - K_j(1)), $$

(2.8)

where $J_j$ and $K_j$ are Coulomb operator and exchange operator, respectively. They are defined by\textsuperscript{[32]},

$$ J_j\varphi(1) = \int \frac{\phi_j^*(2)\phi_j(2)}{r_{12}} d\tau_2 \varphi(1), $$

$$ K_j\varphi(1) = \int \frac{\phi_j^*(2)\varphi(2)}{r_{12}} d\tau_2 \phi_j(1). $$

(2.9)

The Coulomb operator $J_j$ stands for the potential energy of the interaction between electron 1 and the remaining electrons, and the exchange operator $K_j$ arising from the antisymmetric property of wavefunction has no counterpart in classical physics. Finally, the total energy is calculated by\textsuperscript{[6]},

$$ E_{\text{HF}} = \sum_i \varepsilon_{ii} - \frac{1}{2} \sum_{ij} (J_{ij} - K_{ij}), $$

(2.10)

where,

$$ J_{ij} = \langle \phi_i(1)\phi_j(2)|r_{12}^{-1}|\phi_i(1)\phi_j(2)\rangle, $$

$$ K_{ij} = \langle \phi_i(1)\phi_j(2)|r_{12}^{-1}|\phi_i(2)\phi_j(1)\rangle. $$

(2.11)

### 2.1.2 Configuration interaction

Configuration interaction (CI) is the oldest approach which accounts for $E_{\text{cor}}$. The trial wavefunction in the HF method is represented by a single Slater determinant, whereas the total CI wavefunction is written as a linear combination of the HF determinant and Slater determinants corresponding to excited-state configurations, and the expansion coefficients are determined to give the lowest total energy\textsuperscript{[33]}. The CI wavefunction is given by\textsuperscript{[6,8]},

$$ |\Psi\rangle = c_0|\Psi_0\rangle + \sum_{a} c_a^i|\Psi_a^i\rangle + \sum_{a < b} c_{ab}^j|\Psi_{ab}^j\rangle + \sum_{a < b < c} c_{abc}^k|\Psi_{abc}^k\rangle + \sum_{a < b < c < d} c_{abcd}^{ijkl}|\Psi_{abcd}^{ijkl}\rangle + \cdots, $$

(2.12)

where the coefficients may be chosen to normalize the total wave function, or to satisfy $c_0 = 1$ in the case of intermediate normalization $\langle \Psi_0 | \Psi \rangle = 1$. $abcd$ etc. stand for the occupied HF orbitals, $ijkl$ etc. represent virtual orbitals. $|\Psi_a^i\rangle$ is
singly excited determinant, which differs from $|\Psi_0\rangle$ by orbital $\phi_a$ replacing $\phi_i$. $|\Psi_{ab}\rangle$ is doubly excited determinant, which means two electrons are promoted from $ab$ to $ij$, and so on. The combination coefficients, $c_0, c_\alpha^i, c_{ij}^k, c_{ijk}^l, \ldots$, represent the contribution of each configuration to the total CI wavefunction.

The CI wave function consisting of all possible configurations is named full CI, which gives the exact nonrelativistic ground state energy of the system within the BO approximation for a given basis set. According to Brillouin’s theorem\cite{8} and Slater-Condon rules\cite{29,34}, the total energy is given by\cite{6},

$$E = \langle \Psi_0|H_e|\Psi_0 \rangle + \sum_{a<b}^{i<j} c_{ij}^{ab} \langle \Psi_0|H_e|\Psi_{ij}^{ab} \rangle = E_{HF} + \sum_{a<b}^{i<j} c_{ij}^{ab} \langle \Psi_0|H_e|\Psi_{ij}^{ab} \rangle.$$\hspace{1cm} (2.13)

From the definition of $E_{cor}$, it can be calculated by,

$$E_{cor} = E - E_{HF} = \sum_{a<b}^{i<j} c_{ij}^{ab} \langle \Psi_0|H_e|\Psi_{ij}^{ab} \rangle.$$\hspace{1cm} (2.14)

Evidently, the main contribution to $E_{cor}$ is solely arising from the doubly excited configuration. The determination of $E_c$ requires the values of all configuration coefficients, because $c_{ij}^{ab}$ is coupled with all the other coefficients. In other words, the eigenvector of full CI matrix should be known. It is a time consuming method, accordingly confined to the systems with few electrons using very small basis sets. There are approximate methods taking account of the most important configurations in the electron wavefunctions, such as CISD\cite{35}, which means the wavefunction is truncated after the doubly excited configurations. The singly excited CI (CIS) - truncation of the series after singly excited configurations\cite{36} is the simplest of CI methods to compute excited states.

### 2.1.3 Multiconfiguration self-consistent field method

In some cases, single configuration and single reference methods poorly describe the electronic states of system with near-degenerate configuration state functions (CSFs)\cite{36}. One popular approach employed to research the excited states is the multiconfiguration self-consistent field method (MCSCF)\cite{8,20,21}. The MCSCF
wavefunction is given by a linear combination of CSFs, as shown in (2.15)\(^6,8\),

$$\Psi_{MCSCF} = \sum_i C_i \Phi_i, \quad (2.15)$$

where \(\Phi_i\) is a CSF, and it can be expressed as a determinant constructed by molecular orbitals, see (2.16)

$$\Phi_i = \frac{1}{\sqrt{N!}} Det \left[ \prod_{j \in i} \phi_j \right]. \quad (2.16)$$

and the molecular orbital is a linear combination of atomic basis functions,

$$\phi_j = \sum_{\nu} C_{\nu j} \chi_{\nu}. \quad (2.17)$$

In the MCSCF method, the total energy is a functional of expansion coefficients, \(C_i\) and orbital coefficients \(C_{\nu j}\), which are simultaneously optimized to obtain the lowest energy.

The MCSCF approach provides a valid tool to give an accurate static correlation energy considering a relatively small number of CSFs. Moreover, MCSCF is free of the spin contamination problem for the open-shell systems. An essential task in an MCSCF calculation is the choice of configurations which is dependent on the nature of studied problem, i.e. it is not a ‘black box’ method. Usually, the configurations originate from the lowest electronic excitations the orbitals of which define an active space. A special case is called CASSCF\(^{37}\) which considers all possible configurations within the active space. In the CASSCF approach, the molecular orbital space is divided into three subspaces: inactive, active and external orbitals. All the orbitals are doubly occupied in the inactive space, the remaining electrons occupy in the active space, and the external orbitals are virtual orbitals in all configurations. Once the electrons distributed into the active space is defined, the number of CSFs regardless of molecular symmetry is determined by the Weyl-Robinson equation\(^{38}\),

$$K(n, N, S) = \frac{2S + 1}{n + 1} \left( \frac{n + 1}{\frac{1}{2}N - S} \right) \left( \frac{n + 1}{\frac{1}{2}N + S + 1} \right), \quad (2.18)$$

where \(n\) is the number of electrons distributed into the active space, \(m\) is the number of active orbitals where \(S\) is the total spin of electronic state. The key problem in CASSCF calculations is the choice of active space. The selected rules
can not easily be generalized because of the specific problems in different systems. The rule of thumb is that all orbitals related to the excited states we are concerned about or are involved in the chemical reactions should belong to the active space. For the small conjugated organics, the active space usually includes π-type orbitals in order to obtain the ππ* state. In some cases, the nπ* state is quite significant, therefore, lone pairs should be taken into account. An extension to the CASSCF approach is restricted active space SCF (RASSCF) method\cite{39}. The active space is further divided into three subspaces: RAS1, RAS2 and RAS3. In RAS1, the orbitals are doubly occupied, but a limited number of electrons allowed to be promoted from the RAS1 to RAS2 or RAS3 subspace. A given number of electrons are distributed into RAS2 subspace, where the CSFs generated from full CI method. In RAS3, only limited number of electrons is allowed, and the excited electrons either come from the RAS1 or RAS2 subspace. If the orbitals in RAS1 are fully occupied and RAS3 is totally empty, the RASSCF is equal to CASSCF. The orbital partitioning is schematically illustrated in Fig. 2.1. The advantage of RASSCF method is to enlarge the active space without exploding the CI expansion. Therefore, it has the potential to be applied to systems where the CASSCF method is not possible to use.

Figure 2.1 The partition of orbital space in MCSCF approach
2.1.4 Perturbation theory

As mentioned previously, in CASSCF the CSFs are composed of the near-degenerate configurations, so that static correlation is sufficiently taken into account. However, a lack of dynamic correlation gives inaccurate energies at equilibrium geometries of excited states and surface intersections. An efficient way to improve the CASSCF approach with dynamic correlation is based on perturbation theory, namely CASPT2\cite{25}. The spirit of this method is to calculate the second-order energy with CASSCF wavefunction as zeroth-order approximation. The zeroth-order Hamiltonian is defined by one-electron Hamiltonian in a convenient way. However, the CASPT2 method is inappropriate when the electronic states with same symmetry are near-degenerate. As an extension of CASPT2, multi-state perturbative methods developed by Nakano and Finley et al\cite{40,41} can handle such problem well. Nowadays, CASPT2 is employed to explore the stationary points or surface intersections in potential energy surfaces (PES). In our previous work included in this thesis, the CASPT2 method was used to evaluate the energies of the CASSCF-optimized key points along the reaction pathways on the PESs.

2.2 First principles theory

2.2.1 Density functional theory

Density Functional Theory (DFT) stems from the work by Thomas and Fermi in the early 1920s\cite{42,43}, and has made a significant impact in quantum chemistry. Because of moderate computational cost and high accuracy compared with ab initio methods, it is widely used in many fields, such as computational chemistry, solid state physics, and computational biology. It has grown to be one of the brilliant and glamorous stars in the vast galaxy of numerous computational methods by now. The inherent advantages of efficient scaling with the size of system and an accurate description of ground-state properties by using an appropriate exchange-correlation functional, it is a popular tool for exploring many interesting properties of large-sized systems.

Kohn-Sham approach

The corner stone of the Kohn-Sham (KS) approach is the Hohenberg-Kohn (HK) theorem\cite{44} proposed by Hohenberg and Kohn in 1964. They provided a solid proof
2.2 First principles theory

to verify that DFT is an exact theory for the description of electronic structure of matter. The remarkable theorem is stated

There exists a variational principle in terms of the electron density which determines the ground state energy and electron density. Further, the ground state electron density determines the external potential, within an additive constant.

It indicates the ground state energy $E$ is a functional of electron density $\rho(\mathbf{r})$ and external potential $v$, that is $E = E[\rho(\mathbf{r}), v]$, and a trial well-behaved density corresponds to an energy which is higher or equal to the exact energy ($E_0$). Accordingly, the energy of ground state is given by\cite{44,45},

$$E_0[\rho] = F[\rho] + \int v_{\text{ext}}\rho d\mathbf{r}, \quad (2.19)$$

where $F[\rho]$ is the universal functional consisting of electron kinetic energy and electron-electron repulsion energy. Using Lagrange’s method with undetermined multipliers, there is

$$\delta \left( E(\rho) - \mu \left( \int \rho d\mathbf{r} - N \right) \right) = 0. \quad (2.20)$$

Eq. (2.20) is rewritten as an Euler equation,

$$\frac{\delta F[\rho]}{\delta \rho} + v_{\text{ext}} = \mu. \quad (2.21)$$

Here $\mu$ is a Lagrange multiplier, implying the change in chemical potential arising from different electron densities, and $N$ is the total number of electrons. However, the HK theorem doesn’t point out how to calculate $E$ from $\rho$ because of the form of $F[\rho]$ unknown or how to find $\rho$.

Nowadays, the most popular methods of DFT are based on KS scheme\cite{46}. It introduces a reference system with $N$ noninteracting electrons moving in an effective potential $v_s$, the Hamiltonian is written as\cite{46},

$$\mathcal{H}_s = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i v_s(\mathbf{r}_i). \quad (2.22)$$

The energy is given by

$$E_s = T_s[\rho] + \int v_s \rho d\mathbf{r}. \quad (2.23)$$

Here $T_s[\rho]$ is kinetic functional of reference system. Derived from Eq. (2.21) and (2.23), there is

$$\frac{\delta T_s[\rho]}{\delta \rho} + v_s = \mu_s. \quad (2.24)$$
For a real system, \( F[\rho] \) is expressed as,

\[
\]

(2.25)

where \( J[\rho] \) is coulomb repulsion represented as, \( \frac{1}{2} \int \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)r_{12}^{-1}d\mathbf{r}_1d\mathbf{r}_2 \), and \( E_{xc}[\rho] \) is exchange and correlation functionals. Eq. (2.21) is rewritten as,

\[
\frac{\delta T_s[\rho]}{\delta \rho} + \int \frac{\rho(\mathbf{r}_2)}{r_{12}}d\mathbf{r}_2 + v_{xc} + v_{ext} = \mu.
\]

(2.26)

According to HK theorem, the same electron density yields the same external potential. Compared Eq. (2.26) with Eq. (2.24), KS effective potential is represented as,

\[
v_s = \int \frac{\rho(\mathbf{r}_2)}{r_{12}}d\mathbf{r}_2 + v_{xc} + v_{ext}.
\]

(2.27)

The spirit of the KS method is to search for the density which minimizes the energy for an approximate \( E_{xc}[\rho] \)\textsuperscript{[45,47]}. Given \( E_{xc}[\rho] \), the exchange-correlation potential \( v_{xc} \) is determined, which is used for the construction of the KS potential \( v_s \). The solution of the KS equations gives the KS orbitals, which are used to construct electron density, and the ground-state energy. An iterative method must be applied because the construction of \( v_s \) requires the electron density. A convenient way to obtain the KS orbitals is by employment of the linear combination of atomic orbitals (LCAO) method, in analogy to Hartree-Fock-Roothan theory. Therefore, the KS orbitals are represented in terms of basis functions \( \chi_\mu \),

\[
|\phi_irangle = \sum_\mu M \chi_\mu c_{\mu i}.
\]

(2.28)

where \( M \) is the number of basis functions. The KS equations are written as

\[
\hat{f}|\phi_irangle = \epsilon_i|\phi_irangle,
\]

\[
\hat{f} = -\frac{1}{2}\nabla^2 + v_s.
\]

(2.29)

Spin-restricted Kohn-Sham approach

In an paramagnetic molecules, i.e. open-shell system, the spin orbitals require additional care, as the \( \alpha \) and \( \beta \) densities are different. In an open-shell molecule,
2.2 First principles theory

The energy is rewritten as,

$$E[\rho_\alpha, \rho_\beta] = T[\rho_\alpha, \rho_\beta] + J[\rho_\alpha, \rho_\beta]$$

$$+ E_{xc}[\rho_\alpha, \rho_\beta] + \int (\rho_\alpha, \rho_\beta) v_{\text{ext}} dr,$$

(2.30)

where $\rho_\alpha$ and $\rho_\beta$ are $\alpha$ and $\beta$ spin densities, respectively, which are defined by,

$$\rho_\alpha = \sum_i n_{\alpha i} |\phi_\alpha^i|^2,$$

$$\rho_\beta = \sum_i n_{\beta i} |\phi_\beta^i|^2.$$

(2.31)

$n_{\alpha i}$ represents an occupation number in spin orbital $\phi_\alpha^i$. And the Kohn-Sham equations for $\alpha$ and $\beta$ spin orbitals are given by,

$$\hat{f}_\alpha \phi_\alpha^i = \frac{\epsilon_{\alpha i}}{n_{\alpha i}} \phi_\alpha^i,$$

$$\hat{f}_\beta \phi_\beta^j = \frac{\epsilon_{\beta j}}{n_{\beta j}} \phi_\beta^j.$$

(2.32)

where, $i$ and $j$ run over all the $\alpha$ and $\beta$ orbitals, respectively. The operators are defined,

$$\hat{f}_\alpha = -\frac{1}{2} \nabla^2 + v_\alpha^\alpha = -\frac{1}{2} \nabla^2 + v_{\text{ext}} + \sum \frac{\rho_\alpha(r_2) + \rho_\beta(r_2)}{r_{12}} dr_2$$

$$+ \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha},$$

(2.33)

$$\hat{f}_\beta = -\frac{1}{2} \nabla^2 + v_\beta^\beta = -\frac{1}{2} \nabla^2 + v_{\text{ext}} + \sum \frac{\rho_\alpha(r_2) + \rho_\beta(r_2)}{r_{12}} dr_2$$

$$+ \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta},$$

(2.34)

By using the variational method, the minimization of energy is performed with respect to $\alpha$ and $\beta$ spin densities, respectively. There are two solutions in this procedure differing by the variational constraints. One is the unrestricted KS approach dealing with the $\alpha$ and $\beta$ orbitals separately. In this method, two KS matrixes are generated and diagonalized in each iteration for the exploration of the lowest energy. The disadvantage of this method is the introduction of spin contamination. The other is spin-restricted KS approach, which divides orbitals into double-occupied and single-occupied types. This solution avoids the spin contamination problem, but it leads to the off-diagonal Lagrangian multipliers.
There exist two methods to cope with this difficulty: one is handle the equations of double-occupied and single-occupied orbitals individually, and the other is a construction of ‘effective equation’ with off-diagonal Lagrangian multipliers. In our previous works, we adopted the latter to treat the open-shell molecules to calculate the magnetic properties. I give a brief introduction of spin-restricted KS approach with the latter solution in this section.

In the spin-restricted approach, the KS equations are given by,

\[
\hat{f}_d \phi_k = \sum_j^{N_d+N_s} \epsilon_{kj} \phi_j,
\]

\[
\frac{1}{2} \hat{f}_s \phi_l = \sum_j^{N_d+N_s} \epsilon_{lj} \phi_j,
\]

where \(N_d\) and \(N_s\) are the total number of doubly-occupied and singly-occupied orbitals, respectively. \(k\) runs over the doubly occupied orbitals and \(l\) runs over the singly occupied orbitals. The KS operators are represented as,

\[
\hat{f}_d = -\frac{1}{2} \nabla^2 + v^d + \frac{1}{2} \nabla^2 + v_{\text{ext}} + \int \frac{\rho_\alpha(r_2) + \rho_\beta(r_2)}{r_{12}} dr_2
\]

\[
+ \frac{1}{2} \frac{\delta E_{\text{xc}}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha} + \frac{1}{2} \frac{\delta E_{\text{xc}}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta},
\]

\[
\hat{f}_s = -\frac{1}{2} \nabla^2 + v^s + \frac{1}{2} \nabla^2 + v_{\text{ext}} + \int \frac{\rho_\alpha(r_2) + \rho_\beta(r_2)}{r_{12}} dr_2
\]

\[
+ \frac{\delta E_{\text{xc}}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha},
\]

where the \(\alpha\) and \(\beta\) spin densities are written as

\[
\rho_\alpha = \sum_{i=1}^{N_d} |\phi^\alpha_i|^2 + \sum_{j=1}^{N_s} |\phi^\alpha_j|^2,
\]

\[
\rho_\beta = \sum_{i=1}^{N_d} |\phi^\beta_i|^2.
\]

Accordingly, the effective KS matrix is defined by,

\[
\mathcal{H} = \begin{pmatrix}
F_d & F_{ds} & F_s \\
F_{ds} & F_s & F_{sv} \\
F_s & F_{sv} & F_d
\end{pmatrix}.
\]
The \( F_{\mu\nu} \) are defined by,

\[
\begin{align*}
F_d &= \frac{1}{2}(f_\alpha + f_\beta), \\
F_{ds} &= f_\beta, \\
F_{sv} &= f_\alpha,
\end{align*}
\]  

(2.40)

where \( f_\alpha \) and \( f_\beta \) stand for the matrix elements which are defined in Eq. (2.32). It should be mentioned that the eigenvalues of the effective matrix have no physical meaning, it is only a construction for minimizing the energy in spin-restricted calculations.

**Exchange-correlation functional**

As the exact exchange-correlation functional is unknown, approximations are required, generally fittings of appropriately parameterized functionals in order to describe the total energy within the framework of the KS approach. The exchange-correlation functionals are mainly composed of the following types:

**Local (spin) density approximations (L(S)DA)** It is a coarse approximation to the real functional. The energy volume density is solely dependent on the electron density at a given position\(^\text{[48]}\),

\[
E_{xc}[\rho_\alpha, \rho_\beta] = \int \rho(\mathbf{r}) \varepsilon_{xc}(\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r})) d\tau.
\]  

(2.41)

where \( \rho_\alpha \) and \( \rho_\beta \) are \( \alpha \) and \( \beta \) spin densities, respectively. \( \varepsilon_{xc} \) is the exchange-correlation energy per particle in the uniform electron gas approximation.

**Generalized gradient approximations (GGA)** The density and the gradient of density \( \nabla \rho(\mathbf{r}) \) are the variables in the exchange-correlation functional. It has better performance in regions of the highly varying electron density\(^\text{[49,50]}\).

\[
E_{xc}[\rho_\alpha, \rho_\beta] = \int f(\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r}); \nabla \rho_\alpha(\mathbf{r}) \nabla \rho_\beta(\mathbf{r})) d\tau.
\]  

(2.42)

**Hybrid functional** This functional has in addition to GGA contributions, a fraction of the Hartree-Fock exchange term\(^\text{[51]}\). The most common hybrid functional B3LYP\(^\text{[52]}\) was first proposed by Becke, and is well suited for predictions of energetics with in the KS framework,

\[
E_{xc} = E_{xc}^{LDA} + 0.72(E_x^{B88} - E_x^{LDA}) + 0.81(E_c^{LYP} - E_c^{LDA}) + 0.2(E_x^{HF} - E_x^{LDA})
\]  

(2.43)
2.3 Response theory

The interaction between a molecule and an external electric field can be described with response theory, i.e. a formalism for time-dependent perturbation theory which has time-independent perturbation theory as a special case.

The molecular properties are computed as response functions\[^{[53]}\]. Under a time-dependent perturbation field, the Hamiltonian ($H$) can be written as a combination of the unperturbed Hamiltonian $H_0$ and the time-dependent perturbation $\mathcal{V}(t)$,

$$H = H_0 + \mathcal{V}(t). \quad (2.44)$$

The perturbation operator can be expressed by Fourier transform in the frequency domain,

$$\mathcal{V}(t) = \int_{-\infty}^{+\infty} \mathcal{V}^\omega \exp\left[\left(-i\omega + \varepsilon\right)t\right]d\omega. \quad (2.45)$$

The perturbation field contains a positive infinitesimal $\varepsilon$, such that $\mathcal{V}(t)$ is zero at $t = -\infty$. $\mathcal{V}^\omega$ satisfies the hermiticity condition,

$$(\mathcal{V}^\omega)^\dagger = \mathcal{V}(-\omega). \quad (2.46)$$

The perturbed wavefunction can be rewritten as,

$$|\tilde{0}(t)\rangle = |0\rangle + \int_{-\infty}^{+\infty} |0_1^{(\omega_1)}\rangle \exp\left[\left(-i\omega + \varepsilon\right)t\right]d\omega_1$$

$$+ \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} |0_2^{(\omega_1, \omega_2)}\rangle \exp\left[\left(-i(\omega_1 + \omega_2) + 2\varepsilon\right)t\right]d\omega_1 d\omega_2 + \cdots. \quad (2.47)$$

Here the second and third terms describe the wavefunction changes in linear and quadratic response to a perturbation, respectively. The expectation value can be derived at the time-dependent perturbation,

$$\langle 0(t)|\hat{A}|\tilde{0}(t)\rangle = \langle 0|\hat{A}|0\rangle + \int_{-\infty}^{+\infty} \langle \langle \hat{A}; \mathcal{V}^{\omega_1}\rangle \rangle \omega_1 \exp\left[\left(-i\omega + \varepsilon\right)t\right]d\omega_1$$

$$+ \frac{1}{2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \langle \langle \hat{A}; \mathcal{V}^{\omega_1}, \mathcal{V}^{\omega_2}\rangle \rangle \exp\left[\left(-i(\omega_1 + \omega_2) + 2\varepsilon\right)t\right]d\omega_1 d\omega_2 + \cdots. \quad (2.48)$$

Here, the first term on the right-hand of the equation is the expectation value of the operator $\hat{A}$ without a perturbation. The second and third terms corresponds to the linear and quadratic response functions, respectively.
2.3 Response theory

2.3.1 Time-dependent density functional theory

Time-dependent density functional theory (TDDFT) is based on the Runge-Gross (RG) theorem\cite{54}, which states that the potential is a functional of the time-dependent density. The time-dependent KS (TDKS) equations are written as,

\[ \frac{i}{\hbar} \frac{\partial}{\partial t} \phi_i(r, t) = \left( -\frac{1}{2} \nabla^2 + v_s(r, t) \right) \phi_i(r, t), \]  

(2.49)

with the density

\[ \rho(r, t) = \sum_i |\phi_i(r, t)|^2. \]  

(2.50)

$v_s(r, t)$ is represented as,

\[ v_s(r, t) = v_{\text{ext}}(r, t) + v_J(r, t) + v_{xc}(r, t), \]  

(2.51)

where $v_J(r, t)$ is time-dependent Coulomb potential, written as $v_J(r, t) = \int d^3r' \frac{\rho(r', t)}{|r-r'|}$.

$v_{xc}$ is exchange-correlation potential.

The most common method to solve the TDDFT equations is the linear response TDDFT (LR-TDDFT); assuming a weak perturbing field, perturbation theory is applied. $v_{xc}$ depends on the change of densities ($\rho(r, t) = \rho_{gs}(r, t) + \delta\rho(r, t)$)\cite{55},

\[ v_{xc}[\rho_{gs} + \delta\rho](r, t) = v_{xc}[\rho_{gs}](r) + \int dt' \int d^3r' f_{xc}[\rho_{gs}](r, r', t - t') \delta\rho(r', t'), \]  

(2.52)

Here an important definition of $f_{xc}$ kernel is introduced\cite{56}

\[ f_{xc}[\rho_{gs}](r, r', t - t') = \frac{\delta v_{xc}(r, t)}{\delta \rho(r', t')} |_{\rho = \rho_{gs}}. \]  

(2.53)

As a functional of the ground state density solely, it simplifies the full time-dependent exchange-correlation potential. Here, we give another definition of point-wise susceptibility $\chi[\rho_{gs}](r, r', t - t')$, in order to show the importance of $f_{xc}$,

\[ \delta\rho(r, t) = \int dt' \int d^3r' \chi[\rho_{gs}](r, r', t - t') \delta v_{\text{ext}}(r', t'), \]  

(2.54)

where $\chi$ is the linear density-density response functional of the ground-state density. It tells us how the density changes at position $r$ and later time $t$ in response to a tiny change in the external potential field at position $r'$. By analogy to
ground-state KS system, it also has $\chi_{KS}$ and the density response is given by,

$$
\delta \rho(\mathbf{r}, t) = \int dt' \int d^3 \mathbf{r}' \chi_{KS}[\rho_{gs}](\mathbf{r}, \mathbf{r}', t - t') \delta v_b(\mathbf{r}', t').
$$

(2.55)

Accordingly, derived from Eq.(2.54) as well as using Fourier transform in frequency domain, $\chi$ of the interacting system can be described as\textsuperscript{[55–58]},

$$
\chi(\mathbf{r}, \mathbf{r}', \omega) = \chi_{KS}(\mathbf{r}, \mathbf{r}', \omega) + \int d^3 \mathbf{r}_1 \int d^3 \mathbf{r}_2 \chi_{KS}(\mathbf{r}, \mathbf{r}_1, \omega)\left\{ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega) \right\} \chi(\mathbf{r}_2, \mathbf{r}', \omega).
$$

(2.56)

The equation carries information about the electronic excitations in TDDFT. As $\omega$ is equal to a transition frequency, $\chi$ has a pole. By analogy, $\chi_{KS}$ has a series of poles, the one-particle excitation in KS system\textsuperscript{[55]},

$$
\chi_{KS}(\mathbf{r}, \mathbf{r}', \omega) = 2 \lim_{\eta \to 0^+} \sum_q \left( \frac{\xi_q(\mathbf{r})\xi^*_q(\mathbf{r}')}{(\omega - \omega_q + i\eta)} - \frac{\xi^*_q(\mathbf{r})\xi_q(\mathbf{r}')}{(\omega + \omega_q - i\eta)} \right),
$$

(2.57)

where, $\xi_q(\mathbf{r}) = \varphi_i^*(\mathbf{r})\varphi_q(\mathbf{r})$. When the electron is promoted from the occupied KS orbital $\varphi_i$ to an unoccupied KS orbital $\varphi_q$, it is represented as,

$$
\omega_q = \varepsilon_q - \varepsilon_i,
$$

(2.58)

where $\varepsilon$ is the energy of KS orbital. As frequency equals $\omega$, the excitation energy corresponds to the pole of the linear susceptibility $\chi_{KS}$ for the ground-state potential.
Chapter 3

Molecular spectroscopy

With the development of accurate and efficient computational methods in recent decades, theoretical investigations in molecular spectroscopy have become more feasible. Various spectroscopies are widely used in many research fields, such as clinical inspection, atmospheric monitoring and photochemical synthesis. In this work we focus on magnetic resonance spectroscopy and vibrationally resolved electronic spectroscopy.

3.1 Magnetic resonance spectroscopy

Magnetic resonance spectroscopy measures the irradiation absorption in response to the strength of external magnetic field. The magnetic resonance phenomenon includes two types: nuclear magnetic resonance and electron paramagnetic resonance, referring to nuclear spin and electronic spin, respectively, which interact with the magnetic field\(^{59}\). EPR spectroscopy is adopted for studying systems with one or more unpaired electrons, which are capable of absorbing microwave radiation in the presence of an external static magnetic field. The first experiment on magnetic resonance can be traced back to 1945\(^{60}\), and the first report about hyperfine structure of EPR spectrum was in 1949\(^{61}\). However, the progress of the EPR technique was not significant until the 1980s, the golden age of EPR development. Then commercial pulsed spectrometers were developed and employed in large scale and high-field EPR spectroscopy developed rapidly\(^{62}\). It is worthy to mention that the first high-frequency pulsed EPR, produced by J. Schmidt et al., came out in 1988\(^{63}\). The advanced EPR spectrometers provide high quality spectra providing accurate analysis of experimental data. Nowadays, EPR has been widely used in many fields to identify the structure of paramagnetic molecules.
A magnetic resonance spectrometer is schematically illustrated in Fig. 3.1. An electronic spin magnetic moment aligns itself parallel or antiparallel along the external magnetic field, leading to a split of the original energy level. The unpaired electron undergoes a transition between the levels by absorption or emission of a photon with a frequency which matches the energy gap between the split levels\[^{[64]}\]. The most common photon frequency used in the EPR spectrometer is in the range of 9000-10000 MHZ, with a magnetic field of about 3500 G, and a relaxation with characteristic time scale from $10^{-4}$ to $10^{-8}$ s. In the following subsections, I give an outline of the general theory of the spin Hamiltonian approach and its applications in EPR.

### 3.1.1 Spin Hamiltonian approach

The spin Hamiltonian is like a bridge which connects the magnetic resonance phenomenon calculated by using theoretical methods with experimental spectroscopy\[^{[1,59]}\]. A reasonable assignment of the observed molecular electronic structure is derived from a comparison of the computed magnetic resonance parameters, such as the g-tensor and the hyperfine coupling constants, with the experimental data.

The spin Hamiltonian can be constructed in two ways, one roots in the experimental data, namely the effective spin Hamiltonian and the other is true quantum mechanical spin Hamiltonian, originating from relativistic quantum mechanics in description of the particle mechanics and electromagnetic interactions. The effective spin Hamiltonian contains the parametric matrices fitted from experimental...
spectroscopy, while the true spin Hamiltonian is composed of differential operators coming from relativistic quantum mechanics in expression of physical effects underlying the magnetic resonance spectra\textsuperscript{[59]}. Taking advantage of both methodologies is significant to give an accurate estimate of the quantitative influence of the magnetic field compared with the experimental observations.

The effective spin Hamiltonian is defined as a Hermitian operator in terms of spin operators and parameters\textsuperscript{[1,59,65]}. Generally, the effective spin Hamiltonian is given by,

$$
\mathcal{H}_S = \beta_B \vec{S} \cdot \vec{g}_e \cdot \vec{B} + \sum_N \vec{S} \cdot \vec{A}_N \cdot \vec{I}_N + \vec{S} \cdot \vec{D} \cdot \vec{S} \\
- \sum_N \beta_N \vec{B} \cdot \vec{g}_N \cdot (1 - \sigma_N) \vec{I}_N + \sum_{i<j} \vec{I}_i \cdot \left( \vec{G}_{ij} + \vec{K}_{ij} \right) \cdot \vec{I}_j.
$$

(3.1)

Here $\beta_B$ and $\beta_N$ stand for Bohr and nuclear magnetons, respectively. $\vec{g}_e$ and $\vec{g}_N$ represent the electronic and nuclear $g$-tensors, respectively. $\vec{A}$, the A-tensor, predicts the hyperfine interaction arising from the electronic spin and the magnetic field generated from the magnetic nuclei, and $\vec{D}$ and $\sigma_N$ are called zero field splitting tensor and the $n$th nuclear shielding tensor, respectively. The first and forth terms in Eq. (3.1) represent the Zeeman effect on the resonance energy for electronic and nuclear spin states, respectively. The second term is related to the hyperfine structure in EPR. The third term refers to the spin-spin interactions arising from the unpaired electrons. The last term describes the nuclear spin-spin interaction including the classical ($\vec{G}$) and indirect ($\vec{K}$) nuclear dipolar spin-spin coupling tensors.

### 3.1.2 EPR spin Hamiltonian

The EPR phenomenon is the response of a molecule with non-vanishing electronic spin angular momentum to an external static magnetic field and a radiation field and is recorded by the EPR spectroscopy. The Zeeman effect removes the originally degenerate levels of the electron spin states, and the transition energy between the two splitted levels is identified. Although a molecule studied by EPR may have the non-vanishing nuclear magnetic moments, the nuclear magnetic dipole is only two parts per thousand in magnitude of the electronic magnetic dipole; therefore, the chemical shifts and the nuclear spin-spin interactions do not appear on the same energy scale as the electronic interactions. Consequently, the terms related to nuclear magnetic dipole interactions in Eq. (3.1) can be discarded in the
construction of EPR spin Hamiltonian. Accordingly, the basic and conventional effective spin Hamiltonian is defined as,

$$\mathcal{H}_S(\text{EPR}) = \beta_B \vec{S} \cdot \vec{g}_e \cdot \vec{B} + \sum_N \vec{S} \cdot \vec{A}_N \cdot \vec{I}_N + \vec{S} \cdot \vec{D} \cdot \vec{S}. \quad (3.2)$$

The first term is the electronic Zeeman effect governing the position of the peaks in the EPR spectra, the second term corresponds to hyperfine splitting term originating from the interaction of electronic spin with nuclear spin moment. The third term stands for the high spin paramagnetism ($S > \frac{1}{2}$) arising from the dipole-dipole field-independent interaction between the electronic spins, namely the zero-field splitting.

Fig. 3.2 illustrates an isotropic energy level split of a paramagnetic molecule with one magnetic nucleus and one unpaired electron in the presence of an external magnetic field of strength $B_0$. Without the perturbation from the external static magnetic field, all the spin states are degenerate. As the strength of external magnetic field increases, the degenerate spin states are split into two sublevels regardless of the coupling between the electronic and nuclear spins. Taking the hyperfine coupling effects into account, each energy level is further split into two sublevels. The electronic transition between different energy levels is required to satisfy a selection rule concerned with a single excitation process in EPR, where $\Delta m_S = \pm 1$ and $\Delta m_I = 0$. The transition strengths are equal, which is reflected in the EPR spectrum by two splitted peaks with same intensity, and their distance is the isotropic hyperfine coupling constant.

### 3.1.3 Hyperfine coupling tensor

As mentioned above, the hyperfine coupling tensor, which represents the interaction between the unpaired electronic spin and the nuclear magnetic moment gives rise to a hyperfine structure in EPR spectroscopy. Essential information about the chemical environment surrounding a given nucleus and the spin density distribution can be obtained from the hyperfine coupling tensors.[66,67]

Ab initio studies on the hyperfine coupling interaction can be traced back to 1960s[68]. The estimation derived from Hartree-Fock theory greatly deviates from experiment due to lack of electron correlation. Accordingly, the post-Hartree-Fock approaches with electron correlation give the significantly improved results. However, correlated ab initio calculations of high-accuracy are expensive and confined to light main group systems and small-sized organic radicals. The development
3.1 Magnetic resonance spectroscopy

Energy

\[ m_s = \pm \frac{1}{2} \]

\[ E_1 \]

\[ E_2 \]

Figure 3.2  Splitted energy level in magnetic field for a molecule with \( S = \frac{1}{2} \) and \( I = \frac{1}{2} \), where \( E_1 = \mu_B g^{iso} B + \frac{1}{2} A \) and \( E_2 = \mu_B g^{iso} B - \frac{1}{2} A \).

of density functional theory (DFT) has enabled hyperfine coupling tensor calculations for large-sized systems as well\(^{69–71}\). By including electron correlation with moderate computational cost, DFT is a good alternative for the prediction of hyperfine coupling tensors. The unrestricted Kohn-Sham formalism gives rise to spin contamination leading to an unreliable results\(^{72,73}\). However, density functional restricted-unrestricted approach avoids this in magnetic property calculations. The isotropic hyperfine coupling constant calculations displayed in this thesis are carried out by DFT-RU methodology\(^{27,28,74}\).

The spin Hamiltonian representing the hyperfine coupling interaction between the electronic and nuclear magnetic moments is given by,

\[ \mathcal{H}_{\text{HFC}} = \sum_N \vec{S} \cdot \vec{A}_N \cdot \vec{I}_N. \]  (3.3)
The hyperfine tensor $\mathbf{A}_N$ consists of two contributions from the isotropic and anisotropic (dipolar) interactions, differing by their physical origins and how they are observed in experiment\cite{59}. The former contribution is equal to the average value of non-classic Fermi contact interaction, measured in the gas phase or solution by experimental means. The anisotropic contribution arises from the magnetic dipolar interaction between the nuclear and electronic spins, and it should be considered in ordered samples, meaning that the molecules are oriented under the external magnetic field. The isotropic interaction term is given by\cite{75},

$$A_{iso}^N = \frac{4}{3\hbar} g_e g_N \beta_e \beta_N \langle S_Z \rangle^{-1} \langle \Psi | \delta(r) | \Psi \rangle.$$  \hspace{1cm} (3.4)

Here $g_e$ represents the g-value (2.002 319 31) of the free electron and $g_N$ the nuclear $g$-value, which are the fundamental parameters responsible for the Zeeman effect. $\langle S_Z \rangle$ is the expectation value of total electron spin along z-axis. $\langle \Psi | \delta(r) | \Psi \rangle$ is the spin density at a given nucleus. Generally, the electron spin density is highly influenced by $s$ orbital of nucleus. Consequently, the basis sets chosen for the $A_{iso}^N$ calculations should be good at describing a flexible inner core with a series of tight $s$ functions. The classical electron-nuclear dipole-dipole interaction term is given by\cite{75},

$$A_{dip}^{N,ij} = g_e g_N \beta_e \beta_N \langle S_Z \rangle^{-1} \langle \Psi | \delta_{ij} r^2 - 3 r_i r_j r^5 | \Psi \rangle,$$  \hspace{1cm} (3.5)

and the dipolar coupling tensor $\mathbf{A}_{dip}^N$ is traceless and symmetric. The hyperfine coupling tensor can be defined as the second-order derivative of the total electronic energy with respect to electronic and nuclear spins given by,

$$\mathbf{A} = \frac{\partial^2 E}{\partial S \partial I_N} |_{S=0, I_N=0}.$$  \hspace{1cm} (3.6)

**Isotropic hyperfine coupling constant by the restricted-unrestricted DFT approach**

The isotropic HFCC, namely the Fermi contact interaction, represents the interaction between magnetic moments of the nuclear and electronic spins in a paramagnetic molecule\cite{76,77}, and can be calculated by first order perturbation theory. In the KS-DFT scheme, a triplet perturbation can be taken into account in different ways. The unrestricted KS (UKS) formalism\cite{78–81} is commonly employed to evaluate HFCCs. It has the advantage of a simple formalism, but introduces spin contamination. A spin-unrestricted formalism is not feasible because doubly
occupied core orbitals give zero spin density on the nucleus. Fortunately, the DFT-RU approach avoids the shortcomings and inherits the advantages of UKS\cite{27,28,74}. This approach is derived from the open-shell spin-restricted KS method for the ground state and unrestricted approach to treat the triplet properties by perturbations\cite{27,28,74}. The isotropic HFCC of the $n$-th nucleus within the framework of DFT-RU approach is written as,

$$A_{N}^{\text{iso}} = \langle 0 | \frac{\partial^2 \mathcal{H}_{\text{FC}}}{\partial S_z \partial I^N_z} | 0 \rangle \bigg|_{S_z=0, I^N_z=0} + \langle \langle \frac{\partial^2 \mathcal{H}_{\text{FC}}}{\partial S_z \partial I^N_z}; \mathcal{H}_0 \rangle \rangle_{0,0} \bigg|_{S_z=0, I^N_z=0}, \quad (3.7)$$

where $S_z$ and $I^N_z$ are the Cartesian $z$ component of the effective electronic spin and the nuclear spin of the $n$-th magnetic nucleus, respectively. $\mathcal{H}_{\text{FC}}$ stands for the FC operator, and $\mathcal{H}_0$ represents the zeroth-order KS Hamiltonian without perturbation. The Fermi contact interaction arising from spin-density contribution is calculated from the first term in the right-hand side of Eq. (3.7), and the second term is the spin polarized correction to the Fermi contact interaction in terms of a triplet linear response function\cite{27,28}. In this way, the isotropic HFCC is rigorously divided into two types: the direct spin density and spin polarized contributions.

**Zero-point vibrational correction to isotropic hyperfine coupling constant**

The zero-point vibrational corrections (ZPVC) usually make a significant contribution to the HFCC of semi-rigid paramagnetic species with several small frequencies in the ground state. There exists some approaches for investigating ZPVC effects. They are mainly divided into two types: perturbation theory and variational methodology. The earlier attempts were to fit the higher potential energy derivatives to a potential energy functional at different geometries\cite{82-85}, which need a large number of suitable energy sampling points. Furthermore, there is no universal solution to all fitting problems. Due to its high cost, the application of this method is obviously confined to small-sized systems, usually with no more than four atoms. The perturbation approach employs a Taylor expansion of the potential energy around the equilibrium geometry or so-called effective geometry\cite{86-89}. The former takes account of the harmonic and anharmonic vibrational corrections simultaneously in a perturbative manner, which could cause the convergence problem arising from the existent higher derivative terms for large-sized molecules. In this thesis, I concentrate on the latter approach where the harmonic correction is computed at the effective geometry, and the anharmonic correction
Molecular spectroscopy is derived from the difference between the property estimated at both the equilibrium and the effective geometries\cite{87,90–92}. The effective geometry optimization satisfy the following condition:

\begin{equation}
V_{\text{eff},j}^{(1)} + \frac{1}{4} \sum_{i=1}^{N} \frac{V_{\text{eff},iij}}{\omega_{\text{eff},i}} = 0. \tag{3.8}
\end{equation}

Here $i$ and $j$ denote vibrational modes, $V_{\text{eff},j}^{(1)}$ and $V_{\text{eff},iij}$ are the first- and third-order derivatives of the potential with respect to the normal coordinates, respectively. $\omega_{\text{eff},i}$ stands for the harmonic frequency at the effective geometry for normal mode $i$, and $N$ is the total number of vibrational modes. The molecular effective geometry is derived from the equilibrium geometry \{$R_{\text{eq},K}$\} following a manner

\begin{equation}
\{R_{\text{eff},K}\} = \{R_{\text{eq},K}\} - \frac{1}{4\omega_{K}^{2}} \sum_{L} V_{\text{eq},KLL}^{(3)} \omega_{L}, \tag{3.9}
\end{equation}

where $V_{\text{eq},KLL}^{(3)}$ represents the semi-diagonal elements of the cubic force field at the equilibrium geometry. Accordingly, the effective geometry is related to the cubic force with $6K-11$ molecular hessian gradient along the normal coordinates, where $K$ is the total number of atoms in the concerned molecule. And HFCC including ZPVC is given by,

\begin{equation}
A_{\text{iso}}^{\text{vib}} = A_{\text{eff}}^{\text{iso}} + \frac{1}{4} \sum_{i=1}^{N} \frac{A_{\text{eff},ii}^{(2)\text{iso}}}{\omega_{\text{eff},i}}, \tag{3.10}
\end{equation}

where the first term on the right-hand side of the Eq. (3.10) is the HFCC obtained at the effective geometry, the second term describes the harmonic vibrational contribution, in the form of the second derivative with respect to the normal mode $i$. The anharmonic vibrational contribution is derived from the effective geometry. The ZVPC is given by,

\begin{equation}
A_{\text{ZPV}}^{\text{iso}} = A_{\text{eff}}^{\text{iso}} - A_{\text{eq}}^{\text{iso}} + A_{\text{har}}^{\text{iso}} = A_{\text{anh}}^{\text{iso}} + A_{\text{har}}^{\text{iso}}, \tag{3.11}
\end{equation}

with

\begin{equation}
A_{\text{har}}^{\text{iso}} = A_{\text{vib}}^{\text{iso}} - A_{\text{eff}}^{\text{iso}}, \tag{3.12}
\end{equation}

\begin{equation}
A_{\text{anh}}^{\text{iso}} = A_{\text{eff}}^{\text{iso}} - A_{\text{eq}}^{\text{iso}}. \tag{3.13}
\end{equation}
3.2 Vibrationally resolved electronic spectroscopy

Electronic spectroscopy measures the transition energy between different electronic states by irradiation of ultraviolet (UV) or visible light. With the aid of electronic spectra electronic state properties can be studied. However, experiment alone may not be sufficient for studying excited states properties. Fortunately, quantum mechanics methodologies can be used to complement experiment, and help the experimentalists to make correct assignments from the spectra.

In theoretical investigations of electronic spectra, the Born-Oppenheimer approximation is assumed, that is the electrons and nuclei can be treated separately. In this way, the electronic spectra with vibronic resolution is divided into two main contributions; electron promotion and nuclear motion. The position of spectral bands is determined by the transition energy and the shape of spectral profile is determined by the band intensity, which can be calculated according to the Franck-Condon (FC) principle.

The molecule from excited state to the ground state may emit the excessive energy by luminescence. Based on the so-called Kasha rule\(^9\), the fluorescence and the phosphorescence involve mainly the first singlet/triplet excited state \((S_1/T_1)\) and the singlet ground state \(S_0\), and can be expressed by,

\[
\begin{align*}
S_1 &\rightarrow S_0 + \hbar \nu \text{(Fluorescence)}, \\
T_1 &\rightarrow S_0 + \hbar \nu \text{(Phosphorescence)}.
\end{align*}
\]

Due to that a part of excess energy is lost via radiationless processes, the emission energy is lower than the absorption energy. This energy shift, the so-called Stockes shift, exists in absorption and emission spectra, and are schematically represented in Fig. 3.3. The characteristic lifetime of fluorescence is on a quite short time scale \((10^{-9} \sim 10^{-6} \text{ s})\), as compared to phosphorescence where it is five orders of magnitude larger. The lifetime of spontaneous luminescence is estimated by,

\[
\tau = \frac{1.5003}{f \Delta E},
\]

\[
f = \frac{2}{3} \Delta E \mu^2.
\]

Here \(f\) is the dimensionless oscillator strength related to the transition dipole moment \(\mu\).
3.2.1 Fermi’s golden rule

Fermi’s golden rule describes the transition rate (transition probability per unit time) from an initial eigenstate (Ψᵢ) to a continuum final eigenstate (Ψᶠ) as a result of a perturbation. Simply, in a time-independent interaction potential, the Fermi’s golden rule is expressed as

\[ W_{f \to i} = \frac{2\pi}{\hbar} |\langle \Psi_f | \mathcal{H}' | \Psi_i \rangle|^2 \delta(E_f - E_i). \]  

(3.16)

It is assumed that \( \mathcal{H}' \) is a time-dependent perturbation Hamiltonian with an angular frequency of \( \omega \). The perturbation operator has the form

\[ \mathcal{H}' = \mathcal{V} e^{i\omega t} + \mathcal{V}^\dagger e^{-i\omega t}. \]  

(3.17)

Here \( \mathcal{V} \) is time-independent operator and \( \omega \) is the photon frequency.

Within the dipole approximation, the state-to-state form of Fermi’s golden rule yields

\[ W_{\text{stim}} = \frac{2\pi}{\hbar} |\langle \Psi_f | \mu | \Psi_i \rangle|^2 \delta(E_f - E_i \mp \hbar \omega), \]  

(3.18)

Here, the negative and positive signs correspond to the stimulated one-photon absorption and emission, respectively.

There are two essential concepts in the description of vibrationally resolved
electronic spectra, the cross section and oscillator strength. The absorption cross section represents the transition rate per unit photon flux, and it is written as \[^{[96-98]}\]

\[
\sigma_{\text{abs}}(\omega) \propto \omega |\langle \Psi_f|\mu|\Psi_i \rangle|^2 \delta(\omega_{if} - \omega), \tag{3.19}
\]

where \(\omega_{if}\) represents the absorbed/emitted photon frequency, \(\omega_{if} = E_f - E_i\). The optical oscillator strength is derived from the integration over all frequencies of Eq. (3.19)\[^{[96]}\]

\[
f \propto \omega_{if} |\langle \Psi_f|\mu|\Psi_i \rangle|^2. \tag{3.20}
\]

Additionally, fluorescence belongs to the spontaneous emission, whose transition rate is represented as \[^{[99]}\]

\[
W_{\text{spont}} = \frac{4}{3\hbar} \left(\frac{\omega_{if}}{c}\right) |\langle \Psi_f|\mu|\Psi_i \rangle|^2, \tag{3.21}
\]

where the emission intensity is proportional to the cube of \(\omega_{if}\),

\[
I_{\text{spont}} \propto \omega_{if}^3 |\langle \Psi_f|\mu|\Psi_i \rangle|^2. \tag{3.22}
\]

### 3.2.2 Franck-Condon principle

The Franck-Condon principle states that an intensity of vibronic transition from one vibronic energy level to another is related to the overlap between their vibrational wave functions\[^{[100]}\]. Classically, the vertical transition originating from the lowest vibronic level of the equilibrium geometry of the ground state to a vibronic level of an excited state without the geometrical changes is responsible for the peak with a significant intensity in vibronically resolved spectra\[^{[101]}\], as shown in Fig. 3.3. The final state is named as the FC state. According to Eq. (3.20), the intensity of the vibronic transition is proportional to the square of the transition dipole moment given by\[^{[6,102]}\]

\[
I \propto |\langle \Psi_f|\mu|\Psi_i \rangle|^2; \tag{3.23}
\]

\[
\mu = -e \sum_i r_i + e \sum_j Z_j R_j = \mu_e + \mu_N. \tag{3.24}
\]

Here \(\mu\) represents the dipole moment operator. \(r\) and \(R\) stand for the electron and nuclear coordinates, respectively, and \(Z_j\) the nuclear charges. Within the BO-approximation\[^{[4]}\], the overall wave function is a product of the electronic and the nuclear wave functions \((\Psi = \Psi_e \Psi_N)\), where \(\Psi_e\) consists of electronic space and
spin wave functions and $\Psi_N$ is separated into transitional ($\Psi_t$), rotational ($\Psi_r$), and vibrational ($\Psi_v$) modes which are represented by a series of eigenfunctions of harmonic oscillators within the harmonic approximation. Accordingly, transition dipole moment arising from a vibronic transition is given by\textsuperscript{[103]},

$$
\mu_{i\rightarrow f} = \langle \Psi'_e \Psi'_N | \mu_e + \mu_N | \Psi_e \Psi_N \rangle \\
= \int \psi'^*_e \mu_e(\mathbf{Q}) \psi_e d\tau_e \int \psi'^*_N \psi_N d\tau_v \\
= \int \psi'^*_e \mu_e \psi_e d\tau_e \int \psi'^*_s \psi_s d\tau_s \int \psi'^*_v \psi_v d\tau_v. 
$$

(3.25)

The allowed vibronic transitions satisfy the condition that $\mu_{i\rightarrow f}$ is non-zero. Therefore, the three integrals in the Eq. (3.25) should have non-vanishing values. $\int \psi'^*_e \mu_e \psi_e d\tau_e$ and $\int \psi'^*_s \psi_s d\tau_s$ are named by orbital and spin selection rules, and the third integral, $\langle \Psi'_e | \psi_v \rangle$ is called the FC overlap. The FC factor is defined by the square of the FC overlap\textsuperscript{[104]}. There is no selection rules for the vibrational quantum numbers, due to the non-orthogonal properties of two different electronic states with vibronic energy levels $v$ and $v'$.

The critical issue in theoretical simulations of vibrationally resolved absorption and emission spectra is the calculation of FC factors\textsuperscript{[105]}. Normally, the vibrational normal modes between the ground and excited state are not identical overall. Therefore, the Duschinsky transformation connecting two normal modes of ground and excited states is adapted to well describe this situation as given by\textsuperscript{[106–109]},

$$
\mathbf{Q}' = \mathbf{JQ} + \mathbf{K}, \\
\mathbf{J} = \mathbf{LL}'^T, \\
\mathbf{K} = \mathbf{LM}^{1/2} \Delta \mathbf{R}.
$$

(3.26)

In the above expression, $\mathbf{Q}$ and $\mathbf{Q}'$ denote the vibrational normal coordinates of the ground and excited states, respectively. $\mathbf{J}$ is named as the Duschinsky rotation and $\mathbf{L}$ and $\mathbf{L}'$ represent the mass-weighted normal modes in Cartesian coordinates of the ground and excited states, respectively. $\mathbf{M}$ is the diagonal matrix of atomic masses and $\Delta \mathbf{R}$ is the displacement of two equilibrium geometries. In the limit that the normal modes of two electron states are completely identical, $\mathbf{J}$ turns out to be the identity matrix, leading to simplified calculations of FC factors. This simplified model is called the linear coupling model (LCM). By using LCM, the vibrationally resolved absorption and emission spectra have a mirror-symmetry.
relationship around the 0-0 band, as schematically shown in Fig. 3.3.
Chapter 4

Photochemical processes

When a molecule absorbs photon energy, successive photophysical and photochemical processes can take place\textsuperscript{[110]}. A molecule in a high-energy level of an excited state releases the excess energy to revert to the ground state. The whole process is called excited-state deactivation, which can be classified as two types: chemical and physical deactivation\textsuperscript{[111]}.

Photophysical deactivation does not yield new molecules, and can be divided into intramolecular and intermolecular deactivation, according to the type of energy transfer process. Intramolecular deactivation is an energy relaxation process by two means: radiative transition and radiationless decay. The two essential processes differ by the transformations of electronic energy: the former emits energy by photos and the latter converts the excessive electronic energy into rotational/vibrational energy. As mentioned in the Section 3.2, the radiative transitions include the emissions of fluorescence (F) and phosphorescence (P), arising from the preservation and alteration of the spin state occurs along with the electronic transition, respectively. On the other hand, a ‘hot’ molecule in an unstable excited state undergoes radiationless decay involving intramolecular vibrational relaxation (VR), internal conversion (IC) and intersystem crossing (ISC)\textsuperscript{[112]}. VR is a process where the energy transfers from high-energy to low-energy vibronic states. IC process is featured by the electronic-state conversion with spin-state preservation. On the contrary, the ISC process leads to a change of the spin state\textsuperscript{[113]}. Owing to the spin-orbit coupling originating from the coupling of the electron spin with the orbital angular momentum, the spin-forbidden decay is allowed. IC and ISC processes may take place in the region of surface crossings. Accordingly, the study of radiative decay means to explore the nature of surface intersections and electronic state properties. All the photophysical intermolecu-
lar deactivation processes are described by the Jablonski diagram, as shown in Fig. 4.1.

Figure 4.1 Jablonski diagram.

A competing deactivation process a ‘hot’ molecule undergoes, another way to release the extra energy, is chemical deactivation. This involves bond cleavage and formation, molecular rearrangement and isomerization yielding new molecules.

Taking a simple example to illustrate chemical deactivation, consider Fig. 4.2. The reactant \((R)\) in the ground state is promoted to the excited state \((R^*)\), the following reaction would proceed either via a surface intersection back to the
ground state yields a product (P) (as the left side of Fig. 4.2 shows), or on the excited-state potential energy surface to the formation of product (P''), which decays to P' by emission.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.2}
\caption{Schematic view of the photochemical reaction pathways.}
\end{figure}

4.1 Potential energy surface

A correct description of the PES along the reaction coordinates is critical to investigate the mechanism of a photochemical reaction. For an N-atomic system, the ‘real’ PES is 3N-6 (N > 2) dimensional. It is difficult to represent the reaction pathway of a polyatomic molecule. In actual computations, a popular and favorable way to describe a chemical reaction is to construct a pathway along the reaction coordinates, which are determined by the changes in structural parameters of the key species of the reaction. This method is called the pathway approach, suggested by Fuss et al\cite{114}. For the ground-state reaction, these critical points refer to reactant, product and a transition state connecting the reactant and the product, and the ground-state PES where the reaction takes place does not interact with any other electronic state PESs. Accordingly, under the BO approximation, the PES is called an adiabatic PES, which is schematically represented Fig. 4.3. In comparison to a thermal reaction, the photochemical reaction pathway on the excited-state PES is much more complicated to describe, due to the interplay of excited-state and ground-state PESs. The reactant, product and transition states are not adequate to describe the photochemical reaction pathway along the reaction coordinates, as the surface intersection leading to the electronic
state conversion via a radiationless decay process plays a critical role in the photoinduced reaction. The surface intersection actually stands for a crossing of PESs in terms of non-adiabatic surface where the BO approximation breaks down (see the left side of Fig. 4.2). However, surface intersection does not always represent a real crossing between two PESs, for instance, the avoided crossing which is typical of adiabatic PES, as shown in Fig. 4.3. The transition rate of radiationless decay occurring in the vicinity of real surface intersection is on a timescale of $10^{-15}$ to $10^{-12}$ s, which could be estimated by the non-adiabatic transition state theory. In the region of an avoided crossing surface intersection, the transition rate is quite slow as compared to the decay at a real surface intersection. In this case, the rate constant is determined by the Franck-Condon factors and density of vibrational states, which are predicted by Fermi’s golden rule as mentioned previously.

Figure 4.3  Schematic presentation of the reaction pathways along reaction coordinates on adiabatic PESs.

### 4.2 Surface intersection

Since essential nonadiabatic processes are related to PES intersection which governs the photo-induced reaction pathway, the search for a surface intersection is a central task to investigate the photochemical reaction mechanism. As early as 1930s, von Neumann and Wigner\cite{115} proposed the existence of conical intersection (CI) between two PESs of electronic states from a mathematical point of view. However, it was not employed in the explanation of photochemical reaction mechanisms at that time. In 1969, Teller\cite{116} pointed out that the noncrossing rule of
diatomics is invalid to a polyatomic molecule, which means two electronic states could intersect in CI even if they have the same symmetry and spin multiplicity. Zimmerman\textsuperscript{[117]} and Michl\textsuperscript{[118–120]} independently stated IC process takes place in the region of CI leading to the photoproduct formation, and they first used ‘funnel’ to describe the characteristic of CI. In quantum mechanics, the intersecting adiabatic electronic state ($\Psi$) could be represented by the linear combination of two orthonormal diabatic states ($\phi_1$ and $\phi_2$)\textsuperscript{[121]}.

$$\Psi = C_1\phi_1 + C_2\phi_2.$$  \hfill (4.1)

According to the variational principle, the secular equation is derived\textsuperscript{[122]},

\[
\begin{bmatrix}
H_{11} - E & H_{12} \\
H_{21} & H_{22} - E
\end{bmatrix}
\times
\begin{bmatrix}
C_1 \\
C_2
\end{bmatrix}
= 0,
\]  \hfill (4.2)

where, $H_{11} = \langle\phi_1|\mathcal{H}|\phi_1\rangle$, $H_{22} = \langle\phi_2|\mathcal{H}|\phi_2\rangle$, and $H_{12} = H_{21} = \langle\phi_1|\mathcal{H}|\phi_2\rangle$. Derived from the secular equation, the energies of two states are given by\textsuperscript{[123]},

\[
E_1 = \frac{1}{2} \left( H_{11} + H_{22} - \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2} \right),
\]

\[
E_2 = \frac{1}{2} \left( H_{11} + H_{22} + \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2} \right).
\]  \hfill (4.3)

At a surface intersection where $E_1=E_2$, it is required that

$$H_{11} = H_{22},$$

$$H_{12} = H_{21} = 0.$$  \hfill (4.4)

In order to satisfy the above conditions, at least two independent variable nuclear coordinates are needed. For the diatomic molecule, there is only one variable (i.e. the distance of atoms). Therefore, $H_{11}=H_{22}$ is satisfied at an appropriate value of variable, and the condition of $H_{12}=H_{21}=0$ requires that the symmetries of two states differ by either the spatial or the spin. However, for a $N$-atomic system ($N>2$), it is feasible to satisfy these conditions simultaneously.

At the origin where $H_{11} = H_{22} = W$ is satisfied and $H_{12} = H_{21} = 0$, we use two independent coordinates denoted as $x_1$ and $x_2$ and three parameters ($m$, $n$, and $l$) to rewrite secular equation in the first-order approximation\textsuperscript{[122,124]},

\[
\begin{bmatrix}
W + (m+n)x_1 - E & lx_2 \\
lx_2 & W + (m-n)x_1 - E
\end{bmatrix}
\times
\begin{bmatrix}
C_1 \\
C_2
\end{bmatrix}
= 0,
\]  \hfill (4.5)
where,

\[ m = \frac{1}{2}(h_1 + h_2), \]
\[ n = \frac{1}{2}(h_1 - h_2), \]

with the energy expressed as,

\[ E = W + mx_1 \pm \sqrt{n^2x_1^2 + l^2x_2^2}. \]  

It’s an equation of an elliptic double cone, and the vertex is at the origin. In the surface intersection, the energies of the diabatic states \((H_{11} \text{ and } H_{22})\) are equal, accordingly, the adiabatic energies is derived from Eq. 4.3,

\[ E_1 = H_{11} - H_{12}, \]
\[ E_2 = H_{11} + H_{12}. \]

Evidently, the energy gap between the two states is expressed as,

\[ \Delta E = E_2 - E_1 = 2H_{12}. \]

If \(H_{12} = 0\), there exists a real intersection, otherwise, the intersection is split, namely avoided crossing. As mentioned previously, the conditions for a real crossing should be satisfied in the proper values of two independent variables \((x_1 \text{ and } x_2)\), which are represented mathematically as\(^{[125]}\)

\[ x_1 = \frac{\partial(E_1 - E_2)}{\partial Q}, \]
\[ x_2 = \langle C_1 | \frac{\partial \mathcal{H}}{\partial Q} | C_2 \rangle. \]

Here \(\mathcal{H}\) represents configuration interaction Hamiltonian, \(C_1\) and \(C_2\) are eigenvectors, \(Q\) stands for the nuclear configuration vector, \(x_1\) is the gradient difference vector and \(x_2\) is the derivative coupling vector. In the so-called branching space (the plane spanned by the two vectors), the degeneracy is lifted, while the energy is still degenerate in the intersection space (the rest \(n-2\) dimensions), which is a hyperline consisting of an infinite number of conical intersections, as shown in the right side of Fig. 4.4. A comparison between the surface intersection and the transition state are made to feasibly understand the critical role a surface intersection plays in a photochemical reaction. As Fig. 4.4 shows, the transition
Figure 4.4  Schematic description of (a) transition state and (b) conical intersection.

state (TS) is a highest energy point connecting two potential wells of reactant and product along the reaction path, which is determined by a sole vector denoted as $x_1$, and in the remaining $(n-1)$-dimensional space, it is the lowest energy point. In the reaction kinetics, TS is a bottleneck the reaction channel go through. In contrast, the conical intersection (CI) does not connect the reactant and product via one reaction path, however, the intersection separates the excited-state and the ground-state PESs along reaction path. Based on the nature of the double cone, two or more products will be yielded, due to the different reaction pathways in the branching space via CI, as shown in the right side of Fig. 4.4.

Taking account of the spin flip in electronic state conversion, the crossings are divided into two types: conical intersection with $(n-2)$-dimensional intersection space, describing the crossing derived from two electronic state in the same spin multiplicity, and surface crossing featured by $(n-1)$-dimensional intersection hyperline as the result of the interstate coupling vector vanishing. And in this intersection, two electronic states have the different spin multiplicities. The characteristics of these two type of intersections are illustrated in Fig. 4.5. The spin-orbit coupling (SOC), leading to the forbidden reaction and intersystem crossing processes allowed, should be taken into account at surface crossings. In my previous work included in this thesis, the SOC constant of surface crossing between the singlet and triplet state PESs are calculated by using a one-electron approximate spin-orbit Hamiltonian, and its value elucidates the magnitude of energy splitting in a surface crossing.
Figure 4.5 Topological surface intersections (a) \((n-2)\)-dimensional conical intersection (b) \((n-1)\)-dimensional surface crossing.

### 4.3 Nonadiabatic transition state theory

Theoretical studies on thermal rate constants of nonadiabatic reactions including photochemical reactions or spin-forbidden reactions, where a couple of electronic states are involved, are carried out with the aid of nonadiabatic transition state theory. Derived from Miller’s general formula of the flux-side correlation function\[^{126}\] incorporated with Zhu-Nakamura theory\[^{127–129}\], the semiclassical expression of rate constants is given by\[^{130}\],

\[
k = \frac{kT}{Z_r \hbar} \left( \frac{2 \pi}{\hbar^2 \beta} \right)^{(3N-1)/2} \int P|\nabla S(Q)|dQ \cdot \delta[S(Q)]\exp(-\beta V[S(Q)]) \tag{4.12}
\]

where \(Q\) represents the mass-reduced Cartesian coordinates of \(N\)-atomic system, \(S(Q)\) denotes the crossing seam surface, \(Z_r\) and \(P\) are the partition function of reactant and the transmission probability at a crossing point, respectively. In our previous work, the one-dimensional model was employed to calculate the rate constant of nonadiabatic reaction, where \(S(Q)=s-s_0\) (\(s_0\) is crossing point), accordingly, Eq. \((4.12)\) is rewritten as\[^{130}\],

\[
k = \frac{1}{2 \pi Z_r} \int_0^\infty \exp(-\beta E) P_{sh}(E, s_0) dE, \tag{4.13}
\]
where we use Landau-Zener equation\textsuperscript{[131,132]} to treat the hopping probability ($P_{LZ}$) from one diabatic PES to another, which is expressed as,

$$P_{LZ} = \exp \left( -\frac{2\pi V_{12}^2}{\hbar \Delta F} \sqrt{\frac{\mu}{2E}} \right),$$

(4.14)

where $V_{12}$ is the coupling element of crossing diabatic PESs. To investigate forbidden reactions between singlet and triplet electronic states particularly, $V_{12}$ corresponds to the spin-orbit coupling constant. $\Delta F$ denotes the magnitude of the gradient difference between two intersecting PESs at the crossing point along reaction coordinate, $\mu$ represents the reduced mass of a normal mode in the direction of the reaction coordinate normal to the crossing seam. The transmission probability ($P_{sh}$) is closely related to $P_{LZ}$. Depending on the shape of the crossing point, the expressions of $P_{sh}$ are of various kinds. In normal crossing, the product of slopes of two diabatic PESs along reaction coordinate is negative, $P_{sh}$ is given by\textsuperscript{[130]},

$$P_{sh} = \frac{1 - P_{LZ}}{1 - \frac{1}{2}P_{LZ}},$$

(4.15)

On the contrary, the product is positive for an inverted crossing, $P_{sh}$ is expressed as,

$$P_{sh} = \frac{1 - P_{LZ}}{1 + \frac{1}{2}P_{LZ}}.$$

(4.16)

Incorporating with Eq. (4.13), (4.13) and (4.15) or (4.16), the rate constant of nonadiabatic reaction is estimated in the 1D-model approximation.
Chapter 5

Summary of included papers

5.1 Molecular spectroscopy

Molecular spectroscopies are crucial implements for extracting molecular intrinsic properties. In this thesis, I am concerned with isotropic hyperfine coupling constants, which determine the shape of electron paramagnetic resonance spectrum, and the molecular electronic spectrum. Accordingly, I make a brief summary of my previous works on these topics.

5.1.1 Hydrogen hyperfine coupling tensor in organic radicals, Papers 1-2

Density functional theory provides a useful and efficient theoretical tool to evaluate spin Hamiltonian parameters. These works involve the application of response theory within the framework of the spin restricted-unrestricted DFT (DFT-RU) formalism\textsuperscript{[27,28,74]}, which avoids spin contamination in isotropic HFCC calculations of $\pi$ conjugated organic radicals.

We evaluated the zero-point vibrational corrections to isotropic HFCCs in the allyl radical and four of its derivatives: the cyclobutenyl radical, the cyclopentenyl radical, the bicyclo[3.1.0]hexenyl radical and the 1-hydronaphtyl radical (see Fig. 5.1). The effect of ZPVC on the HFCCs cannot be estimated by an experimental measurement directly, and what’s more, only sparse results from previous calculations are available. Accordingly, to know how important the ZPVCs are to HFCCs in the allyl radicals and its derivatives are, a systematical analysis is required by means of an accurate and efficient theoretical approach. We adopted the DFT-RU approach with a strategy featured by a solving the property expanded
around the effective geometry as mentioned in Chapter 3 in an attempt to explore the answers. For a good description of the spin density in the inner core and valence region which is important for accurate HFCCs, an appropriate basis set, HIII-su\textsuperscript{[133,134]}, was chosen in the HFCC calculations. According to the molecular symmetry, there are 22 unique hydrogens, where 19 hydrogens have isotropic HFCCs determined by the spin-polarization effects and 3 hydrogens have isotropic HFCCs controlled by not only the spin-polarization but also the direct spin-density contribution arising from the singly occupied molecular orbital (SOMO). Including the ZPV contributions, not all the isotropic HFCCs are in accordance with the experimental data\textsuperscript{[135]}. It implies that the B3LYP exchange-correlation functional systematically overestimates the isotropic HFCCs.

Based on the results from theoretical predictions, we summarized a set of rules to guide how to make an estimate of vibrational contributions to HFCCs. When the magnitude of HFCC is larger than 20 G, we do not need to consider ZPVCs. Otherwise, they should be further investigated. When the isotropic HFCC is smaller than 3 G and the distance between a hydrogen of interest and SOMO is less than 2.5 Å, we should consider if the HFCC are controlled by spin polarization effects or the combined contributions from direct spin-density and spin-polarization, and identify which vibrational modes make the significant contributions.

The McConnell relation is used to describe spin density distributions in the carbon backbone of organic π radicals from the hydrogen HFCCs measured by electron paramagnetic resonance experiments. It is represented by \( \rho = Q_{\text{H}} \), where \( Q \) is an empirical spin-transfer parameter given by -22.5 G\textsuperscript{[136–138]}. Although the McConnell relation is widely used in the analysis of EPR data, its origin has not been investigated by using modern quantum chemistry. Accordingly, we further explore the physical origin and limitations of the McConnell relation in Paper 2. The vibrational corrections to carbon HFCCs influence not only the

![Figure 5.1](https://example.com/figure5.1.png) The five allylic radicals. Selected from Paper 1, reprinted with permission from The Royal Society of Chemistry.
molecular spectroscopy

5.1 Molecular spectroscopy

magnitude but also the sign. The model molecules chosen in our studies are schematically plotted in Fig. 5.2. The calculations indicate that the ZPVCs

\[ \delta_{H_3} \]
methyl

\[ \text{Benzyl} \]

\[ \text{Fulvalene anion} \]

\[ \text{Tropone anion} \]

\[ \text{\( \sigma \)-Benoquinone anion} \]

\[ \text{\( p \)-Benoquinone anion} \]

Figure 5.2 Organic \( \pi \) radicals for which isotropic carbon and hydrogen HFCCs has been computed with zero-point vibrational corrections.

Figure 5.3 Dependence between hydrogen and carbon HFCCs in organic \( \pi \) radical anions: (a) computed at equilibrium geometry (b) with zero-point vibrational corrections added. Greenand blue denotes \( C_2 \) positions for which in \( p \)-benzoquinone and fulvalene anions McConnell relation predict different sign for the carbon HFCC.

overall improve the accuracy of carbon HFCCs as compared with the experimental data. In particular, the ZPV contribution changes the sign of HFCCs of the \( C_2 \) atom in \( p \)-benzoquinone anion. It suggests that the static picture is invalid for the description of spin density and the dynamic picture with the coupling of nuclear motion with spin density should be considered. In our studied molecules, the non-varnishing HFCC of hydrogen atom is ascribed to the spin polarization which leads to a rather small spin transfer constant \( Q \) and a disagreement between the computed result and the value based on the McConnell relation. As shown
in Fig. 5.3, the linear dependence of the spin density of hydrogen and carbon atoms represented by HFCCs is deficient without ZPVCs. In consideration of the effects, the correct behavior is restored, especially for \( p \)-benzoquinone anion. Thus the coupling between spin density and vibrational degrees of freedom in the backbone is important and holds the key for understanding the spin density transfer mechanism in such systems.

5.1.2 Vibronically resolved spectroscopy of \( \alpha \)-santonin derivatives, Paper 3

\( \alpha \)-Santonin was the organic molecule that was first found to have a photo-induced activity. Many experimentalists carried out systematical studies on \( \alpha \)-santonin photorearrangement reactions\(^{139-141}\). Recently, Natarjan and his co-workers identified the intermediates and products in solid-state reaction, moreover, recorded the changes of molecular spectra with the time increase\(^{142}\). We carried out computational simulations of vibronically resolved spectra to investigate the spectral characters of the molecules formed in the reaction (see Fig. 5.4), in order to well understand the molecular spectra observed in the experiment. The computational results show that the emission energies of photosantonic acid and the topochemical product are within the visible light range. Consequently, we studied the vibronic spectra of photosantonic acid and the topochemical product by using the Franck-Condon principle. The absorption spectrum of photosantonic acid has the vibrationally resolved character consistent with experimental observations, as

![Figure 5.4](image-url)
5.2 Nonadiabatic reactions

Compared with adiabatic reactions, nonadiabatic reactions are more complicated, due to the involvement of surface intersections in the multiple electronic-state PESs and the competitions in a diversity of products along the various reaction channels. The challenges of exploring a nonadiabatic reaction mechanism are to search for the surface intersection playing a key role along reaction pathway and further study its character governing the radiationless decay channels, and all attempts require the appropriate calculation method and sufficient computer resources. Fortunately, with the rapid development of computational methodology and technology in recent years, the theoretical studies on nonadiabatic reactions

Figure 5.5  Vibronically resolved spectra of photosantonic acid simulated at the CASSCF and TDDFT levels in comparison with the experimental spectra.

shown in Fig. 5.5. Moreover, the positions of the emission and absorption bands well match with the experimental spectra. However, the absorption band of the topochemical product without vibrational resolution deviates considerably from the experiment, indicating that it is not responsible for the spectra measured by Natarjan et al\textsuperscript{[142]}.  

5.2 Nonadiabatic reactions
make exciting achievements, which provide reasonable explanations and predictions to experimental observations. In this section, I will give a brief summary of my previous studies on the photochemical reactions originating from α-santonin and forbidden reaction between cofactor-free enzyme and triplet oxygen molecule with the aid of quantum mechanics incorporated with reaction kinetics.

5.2.1 α-Santonin photo-induced reactions, Papers 4-5

Under UV irradiation, α-Santonin undergoes various photorearrangement reactions\cite{143,144}. Since Kahler\cite{145} and Alms\cite{146} successfully isolated α-santonin in 1830s, the experimental explorations of reaction mechanisms\cite{147,148,148–153} have never ceased. The early works were only concerned with phenomena happening in a photoreaction, due to limited knowledge about photochemistry and immature measurement technology. The structure of photosantonic acid in aqueous ethanol was not reported by van Tamelen et al\cite{154,155} until 1958. Consequently, the structures of several intermediates appearing in solution reactions were identified, and gradually the reaction pathways were approximately estimated in experiment\cite{141,156,157}. Compared with the reaction taking place in solution, the work on solid-state reaction of α-santonin progressed slowly. In 1968, a metastable intermediate appeared and a cycloadditional product were found in solid state\cite{158}.

The critical intermediate, called cyclopentadienone, was characterized by Garcia-Garibay et al in 2007\cite{142}.

The photo-induced reaction pathways derived from α-santonin are illustrated schematically in Fig. 5.6. α-Santonin undergoes a ring closed reaction leading to a intermediate designated as INT, the following reactions face two choices: C4-C5 or C3-C4 bond cleavages, respectively. It is proposed that C4-C5 bond breaking is feasible in solid state, due to less hindrance arising from steric effects, while C3-C4 bond breaking is favorable in solvent reaction. If the reaction starting from the rupture of the C4-C5 bond, designated by path A\cite{141,157}, it leads to the formation of the intermediate, A-INT. The subsequent reaction is featured by 1,2-hydrogen immigration. Both C2 and C4 are suitable to accommodating the hydrogen atom. The C4-H bond formation yields cyclopentadienone, labeled as A-P-I, and the other way leads to photosantoic acid (A-P-II)\cite{159}. As the reaction originates from the cleavage of C3-C4 bond, named by path B\cite{139,140}, an intermediate (B-INT) is generated. B-INT undergoing a configurational rotation of cyclopropylcarbinyl yields lumisantonin, which can be irradiated by UV light leading to the successive photorearrangement reactions\cite{139,140,157,160–167}. Lumisantonin undergoes a bond
cleavage taking place in three-membered ring, resulting in two possible reaction pathways, denoted as path C and path D, respectively. Along path C, the reaction generates an intermediate via the cleavage of C5-C6, namely C-INT, and the subsequent reaction with a characteristic of methyl migration yields a product (C-P).

Along path D, the reaction undergoing a breakage of C4-C5 bond leads to an intermediate (D-INT) formation. The following reaction featured by intramolecular hydrogen immigration generates another intermediate, labeled as D-INT-I. Due to its enol configuration, a ketonization reaction is favorably taken place yielding an isomer of pyrolumisantonin, namely, D-P-I. And the ratio of C-P to D-P-I is 8:1 estimated by the experiment[162]. The reaction pathways provide a general

![Diagram of reaction pathways]

Figure 5.6  Photochemical reaction pathways of α-santonin and lumisantonin suggested by experiments.

picture of α-santonin photorearrangement. However, there still exist several questions. Why does the reaction depend on media? How many excited states are involved in the photorearrangement under the experimental condition, and which excited state governs the reaction? How does the reaction decay along radiationless channel via surface crossing between excited-state and ground-state PESs? Moreover, are there any other reaction paths except for those from experimental suggestions? All these questions are troublesome to solve by experiments; while theoretical calculations can fill the gaps[168]. Based on the results from theoretical calculations, we found that the $^1(n\pi)$ state is the solely accessible singlet-excited state under the given wavelength of irradiation light. Subsequently, the $^1(n\pi)$ state decays to the low-lying $^3(\pi\pi^*)$ state via a surface crossing $^1(n\pi^*)/^3(\pi\pi^*)$-SC-1 with a remarkable SOC as large as 55.70 cm$^{-1}$ in the FC region leading to the initiation of photorearrangement. The excited-state radiationless decays of α-santonin in the FC region are illustrated in Fig. 5.7. The initial reaction from the C3-C5 bond form taking place on $^3(\pi\pi^*)$ state PES leads to INT, where around a surface crossing $^3(\pi\pi^*)/S_0$-SC-1 exists, indicating the possible transition from $^3(\pi\pi^*)$ to the ground state. The subsequent reaction pathway is divided into two
channels. Path A is more favorable in a solid-state reaction not only due to the involvement of the planar intermediate with a reduced space requirement but also the advantage of the dynamic performance on the $\tilde{3}(\pi\pi^\star)$ state PES. The cleavage of C4-C5 bond undergoing a transition state (A-TS) leads to the formation of A-INT, and in the vicinity of it, there is a surface crossing $\tilde{3}(\pi\pi^\star)/S_0$-A-SC. If the SC point is accessible, the reaction prefers yielding A-P-II on the ground state PES in thermodynamics and dynamics, compared to the reaction path in respect of A-P-I. In the dioxane reaction, path B is the preferential ascribed to the thermodynamical preference of the biradical B-INT and lower energy barrier leading to C3-C4 bond breakage on both PESs as well as smaller energy barrier overcome resulting in lumisantonin formation on ground-state PES, in comparison with reactions along path A. Around B-INT, a state conversion would happen via a surface crossing $\tilde{3}(\pi\pi^\star)/S_0$-B-SC, and finally lumisantonin is yielded via
5.2 Nonadiabatic reactions

almost barrier free process. Exposed to UV light with a wavelength of 320nm, lumisantonin is excited to $^1(n\pi^*)$ state with a notable oscillator strength and subsequently decays to $^3(\pi\pi^*)$ state via a surface crossing $(^1(n\pi^*)/^3(\pi\pi^*)$-SC-2) in the FC region. The photophysical processes are quite analogous to the decay channels of $\alpha$-santonin in the FC region. Interestingly, the $^3(\pi\pi^*)$ state originates from the electronic promotion from $\pi$-type orbital featured by a mixture of $\pi$-type orbital coupling with $\sigma$-type orbital of C-C bond in the three-membered carbon ring to $\pi^*$ orbital. Due to the nature of the $^3(\pi\pi^*)$ state, the C-C bond breaks. Along path C, starting from C5-C6 bond cleavage, the reaction undergoes a barrier-free channel on the ground- and $^3(\pi\pi^*)$-state PESs. Particularly, it is preferential both dynamically and thermodynamically on $^3(\pi\pi^*)$-state PES. In the vicinity of C-INT, a surface crossing $^3(\pi\pi^*)/S_0$-C-SC makes the deactivation decay from $^3(\pi\pi^*)$ to the ground state possible, leading to the recovery of B-P with C5-C6 bond reformed in the ground state. Otherwise, an energy barrier should be overcome to fulfill the reaction yielding C-P in the $^3(\pi\pi^*)$ state. Along path D, arising from C5-C4 bond rupture, the reaction is characteristic of a concerted reaction consisting of two stages: bond rupture and a hydrogen or methyl migration on the ground-state PES. The reaction involving a hydrogen shift is labeled as path D-I and a methyl migration is called as path D-II. Compared with the reaction along path C, the channel proceeding along path D on the ground state PES is more favorable due to a stable intermediate separated from B-P by a transition state. Moreover, the energy barrier corresponding to the bond rupture and hydrogen shift is much lower than that of the reaction assigned to bond rupture and methyl migration. Accordingly, the formation of D-INT-I is overwhelming on the ground state PES. On the $^3(\pi\pi^*)$ state PES, a surface crossing $^3(\pi\pi^*)/S_0$-D-SC adjacent to the D-INT indicates the intersystem crossing may take place. The successive stage should surmount much higher energy barrier to complete the reaction than its counterpart in path C. Overall, photolytic reaction along path C is more favorable dynamically and thermodynamically on the $^3(\pi\pi^*)$-state PES, while the pyrolytic reaction along path D is facile owing to a stable intermediate generated. These results provide a further insight into the experimental observations.
5.2.2 Reaction of Cofactor-Free Enzyme with Triplet Oxygen Molecule, Paper 6

Oxidation reactions catalyzed by a wide variety of enzymes are the most common chemical reactions occurring in the primary and secondary metabolism of organisms. Many oxygenation enzymes with the help of transition metal ions or organic cofactors active substrate and/or dioxygen\cite{169,170}. There are some exceptions that they are independent of cofactors, such as the quinone-forming monooxygenases, the bacterial dioxygenases and the vancomycin biosynthetic dioxygenases\cite{171–173}.

For cofactor-free dioxygenase, the amino acid residue plays a key role in the oxidation catalyzed reaction. It is a ‘spin-forbidden’ reaction, due to the interplay of triplet-state dioxygen and singlet-state substrate. Accordingly, how the spin state of dioxygen changes is an essential question concerned with the reaction mechanism. As experimentalists suggested, the common mechanism of oxidation reaction catalyzed by cofactor-independent enzyme could be described that a proton of substrate is firstly abstracted by an amino acid residue, subsequently, the anionic substrate feasibly transfers one electron to oxygen molecule leading to the formation of caged radical pair\cite{169}, which is a critical precursor for the subsequent reaction. The proposed general reaction mechanism is derived from crystal structure, however, the static picture is limited in description of the underlying reaction mechanism. The theoretical studies can provide useful information about the electronic structures and the reaction energies. In this paper, we regard the vancomycin biosynthetic enzyme DpgC as the original model to study the spin-forbidden reaction. We expect the calculations will provide an insight into understanding spin flip of dioxygen in the oxidation.

As shown in Fig. 5.8, we design three models under investigation: anionic sulfidomethyl propanethioate, anionic sulfidomethyl but-3-enethioate and anionic sulfidomethyl 2-(3,5-dihydroxyphenyl) ethanethioate, respectively, for the exploration in the substituent effects on the reaction mechanism. The theoretical studies show that the electron-transfer mechanism is not a sole way to make the spin-forbidden oxidation allowed. Only the reaction of anionic sulfidomethyl propanethioate with dioxygen shows a significant charge migration, and the rest models obey another reaction mechanism, which involves the surface hopping between the singlet- and triplet-state PESs via surface crossing, where the electronic configuration is mixed with the singlet- and triplet-state character, and no significant charge migration occurs from the substrate to the molecular oxygen.

As shown in fig. 5.9. The frontier orbitals of \((S/T)_{SC-I}\) are quite similar
5.2 Nonadiabatic reactions

\[
\begin{align*}
\text{I. } & \quad [^1\text{O}_2 + \text{CH}_3\text{C}^\alpha \text{HCOSCH}_3]^\cdot \rightarrow [^1\text{CH}_3\text{HC}^\alpha \text{CHO}_{\text{SCH}_3}]^\cdot \\
\text{O} \cdot \text{O} \\
\text{II. } & \quad [^1\text{O}_2 + \text{C}_2\text{H}_3\text{C}^\alpha \text{HCOSCH}_3]^\cdot \rightarrow [^1\text{C}_2\text{H}_3\text{HC}^\alpha \text{CHO}_{\text{SCH}_3}]^\cdot \\
\text{O} \cdot \text{O} \\
\text{III. } & \quad [^1\text{O}_2 + \text{C}_6\text{H}_6\text{O}_2\text{C}^\alpha \text{HCOSCH}_3]^\cdot \rightarrow [^1\text{C}_6\text{H}_6\text{O}_2\text{C}^\alpha \text{CHO}_{\text{SCH}_3}]^\cdot \\
\text{O} \cdot \text{O} \\
\end{align*}
\]

Figure 5.8 Oxidation reaction of the computational models from the reactants to the first intermediates.

Figure 5.9 Schematic view of molecular orbitals and the electron occupancies of minimum energy crossing points (a) (\textit{S}/\textit{T})sc-I, (b) (\textit{S}/\textit{T})sc-II and (c) (\textit{S}/\textit{T})sc-III.

except that the orbital phases on the substrate are reversed. The electron occupancies are 1.116 and 0.910, respectively, indicating that (\textit{S}/\textit{T})sc-I is a biradical. In contrast, the plotted frontier orbitals of (\textit{S}/\textit{T})sc-II are quite different, one is dioxygen $\pi^*$ orbital with the electron occupancies of 1.490, and the other is $\pi$-type orbital localized on the dioxygen and the substrate with the electron occupancies of 0.612. The character of the frontier orbitals of (\textit{S}/\textit{T})sc-III has some analogy to that of (\textit{S}/\textit{T})sc-II. The electron occupancies are shown as 1.500 and 0.621 in these two orbitals, respectively. It should be mentioned that the newly formed O-C$^\alpha$ bond removes the degenerate highest occupied molecular orbitals localized on the dioxygen. However, the interaction between the $\pi$-type frontier orbitals localized in the conjugated substituents (i.e. vinyl and resorcinol) and the $\pi^*$ orbital of dioxygen gives rise to the dioxygen away from the substrates.

The conjugated substrate can stabilize the dioxygen at a long distance away from it, and the charge-transfer mechanism does not manipulate this kind of oxidation. With the size of conjugated substrate increasing, the SOC constant at a minimum of energy crossing point gets larger, indicating the interplay between the single- and triplet-state PESs is enhanced. However, the rate of the spin-flip process becomes lower and determines the whole stage rate of the oxidation, since the energy barrier of the spin-state conversion is increased.

The energies of an $\alpha$-hydrogen abstracted from the substrates indicate that the non-conjugated conformation is relatively unfavorable to the loss of a proton
from $\alpha$-carbon, however, the conjugated substrate is propitious for the stabilization of the negative charge after a hydrogen abstracted, which is cardinal reason why the spin flip appears without the significant charge migration. The design of cofactor-free enzyme with a good performance is required to take all factors into consideration. Generally speaking, a strongly conjugated cofactor-free substrate is in favor of the oxidation catalysis.
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