1

Motivation and Basic Concepts

Sandra Gómez[1], Ignacio Fdez. Galván[2], Roland Lindh[2], and Leticia González[1]

[1]*Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Vienna, Austria*
[2]*Department of Chemistry – BMC, Uppsala University, SE-751 23 Uppsala, Sweden*

Abstract

This chapter describes what electronic excited states are and why they are important to study and therefore motivates the need for theoretical tools able to characterize them. Further and most importantly, in this introductory chapter, we put together in a comprehensive manner a collection of basic concepts that might be needed, depending on the background of the reader, to understand the remaining chapters of this book.

1.1 Mission and Motivation

When a photon of light strikes a molecule, the latter's electrons are promoted from the electronic ground state to higher electronic levels. Typically, the electronic ground state of a molecule is a singlet state, but depending on the number of electrons and their most favorable way of pairing, it can be a doublet, a triplet, or a state of higher multiplicity. Assuming the electronic ground state is a singlet, upon light absorption the molecule will be excited to another singlet state, as high in energy as the energy contained in the photon allows. Once excited, a number of radiative and non-radiative decay processes are possible. These are collected in the Jabłoński diagram shown in Figure 1.1(a), which assumes an electronic singlet ground state.

Radiative processes include fluorescence or phosphorescence, depending on whether the emission of light involves a transition between two states of the same multiplicity, for example from the lowest singlet S_1 to the S_0, or involves a change of spin, as shown in Figure 1.1, from the triplet T_1 to the S_0. Typically, as in the example depicted, the emitted light has a longer wavelength than the absorbed radiation because luminescence occurs from lower energy levels, and thus absorption and emission spectra are easy to identify from experimental data. In this example, the molecule returns to the original ground state from where it started and thus there was no photochemical reaction, one would say that a photophysical process has taken place.

Non-radiative processes can be much more complicated to observe experimentally, as they typically involve not only the bright or absorbing state defined by the wavelength employed to irradiate, but also dark states, i.e., states that do not have a significant oscillator strength but are populated from the bright states. A transition between electronic states of the same multiplicity is known as
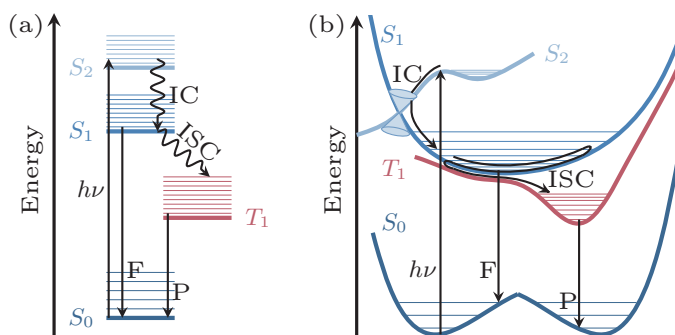
Figure 1.1 (a) Jabłoński diagram with levels. After absorption of a photon with energy $h\nu$, different processes can occur: radiative processes are fluorescence (F) and phosphorescence (P), non-radiative processes are internal conversion (IC) and intersystem crossing (ISC). (b) Jabłoński diagram with potential energy surfaces.

internal conversion, e.g., from S_2 to S_1. When two states of different multiplicities are involved, e.g., from the S_1 to T_1, one speaks of intersystem crossing.

The electronic levels of a molecule are defined through potential energy surfaces (PES) that extend along $3N - 6$ dimensions (with N the number of atoms contained in the molecule). PES are the direct consequence of invoking the Born–Oppenheimer approximation (BOA), see section 1.7. As comfortable as it might seem for a chemist to employ electronic states to envision the course of a chemical reaction from a reactant to a product, sticking to the BOA when talking about electronic excited states implies that the coupling between different PES is neglected. However, these so-called *non-adiabatic couplings* between PES are the "salt and pepper" of photochemistry, as they are essential to understand which states and geometrical conformations are populated after excitation. One key concept in this respect is the non-adiabatic transition around a *conical intersection*, see section 1.9. Named after the ideal topology two PES adopt when they intersect (see Figure 1.1(b)), a conical intersection is the molecular funnel that allows for internal conversion, and it can also be seen as the transition state in photochemistry, which connects a reactant with a product. Likewise, intersystem crossing is mediated by spin–orbit coupling, which is another form of vibronic or non-adiabatic coupling between electronic levels.

Figure 1.1(b) summarizes the radiative and non-radiative processes described before, now in terms of PES. If after the detour via the different PES, the molecule ends up at a different geometrical configuration from which it started after irradiation, one speaks of a photochemical reaction; if instead, it returns back to the electronic ground state of the reactant, the term photophysics is employed.

Be it photophysics or photochemistry, light-induced processes are all around us. As Ciamician already recognized in 1912[1], "reactions caused by light are so many, that it should not be difficult to find some of practical value". Indeed, just to give one representative example, the dream of using solar fuel to produce sustainable energy is keeping many scientists around the world busy. In an effort to mimic natural photosynthesis, one needs among others, to design efficient antenna complexes able to harvest the broad solar spectrum and direct the electrons towards the catalytic centers. This design requires a profound understanding of the underlying processes that take place in the molecules after light excitation. Theoretical modeling can help explain existing experiments and hopefully guide new ones. Which are the electronic states that are populated after

---

1 Giacomo Ciamician, "The photochemistry of the future", *Science* 36 (1912) 385–394.

excitation? How does the molecule evolve along the complicated PES associated to these electronic states? Often these two simple questions are not easy to answer. They imply a need to get an accurate solution of two key equations, the electronic time-independent Schrödinger equation and the time-dependent Schrödinger equation. Both equations are challenging to solve, except for very small molecules, and so approximations and numerical strategies are required. The solution of the first equation is the goal of electronic structure theory and the solution of the second, the target of chemical dynamics. Both fields have tremendously evolved in the last decades, with the emergence of many different methods that have a common objective.

The mission of this book is to keep up-to-date with the recent development in these two intertwined fields, setting the focus at solving electronic excited states and following their time evolution. Accordingly, Part I collects the most important electronic structure methods that can be used nowadays to calculate electronic excited states as well as associated PES and other electronic properties. Part II, in turn, covers the state of the art for solving molecular motion in the electronic excited states. The variety and extension of the methods collected in this book speaks for itself about how much progress has been achieved in this branch of theoretical chemistry, which undoubtedly has also massively profited in the last years from enormous advances in computational resources. It would not be fair, however, to pretend that theoretical photochemistry has reached its cusp. A deeper reading of the chapters will reveal to the reader not only how far we have come but also how much still remains to be done.

In an effort to make the contents of this book accessible to undergraduates and newcomers to the field, the rest of this chapter contains a number of basic concepts to ease the reading. All the chapters have been written in a fully consistent manner, so as to allow them to be studied independently from the others. The chapters are, nevertheless, organized such that they try to reflect a natural progression. In this respect, the chapters are grouped in two sections consisting of Part I and Part II – electronic structure theory and methods for molecular dynamics, respectively.

In the electronic structure section the selected order of the chapters tries, to some extent, to be in the order of sophistication. However, in some cases chapters are clustered together because of common grounds or methodology. In that sense, Part I starts with the chapters based on density functional theory (DFT) – the chapters on time-dependent DFT (TD-DFT) and multi-configurational DFT (MC-DFT). This is followed by chapters revolving around equation-of-motion coupled cluster theory (EOM-CC) and the algebraic-diagrammatic construction (ADC) scheme for the polarization propagator, which are grouped together due to the technical similarities of the methods. Finally, five chapters are grouped together based on the use of a configurational interaction (CI) type of wave function. Initially, the basics of the so-called complete active space SCF (CASSCF) and related methods – the foundation of multi-configurational quantum chemistry – is introduced. This is followed by two chapters on techniques describing how to solve the associated equations – the chapters on density matrix renormalization group (DMRG) and the quantum Monte-Carlo (QMC) approaches. To conclude Part I, two chapters about the inclusion of electronic dynamical correlation follow – the chapters on the multi-reference configuration interaction (MRCI) method and the multi-configurational reference perturbation theory (MRPT). A pictorial summary of the methods described is provided in Figure 1.2. Starting from Hartree–Fock (HF), different methods cover different degrees of dynamic and static correlation, all the way to the exact full-CI (FCI).

Part II, dealing with the time evolution of nuclear configurations, starts with three chapters that can be considered within the realm of quantum dynamics. The first one introduces the time-dependent Schrödinger equation and how to solve it exactly in a grid – what is known as wave packet dynamics. Due to the cost of obtaining PES, wave packet dynamics is typically done in reduced dimensionality. The multi-configuration time-dependent Hartree (MCTDH) family of
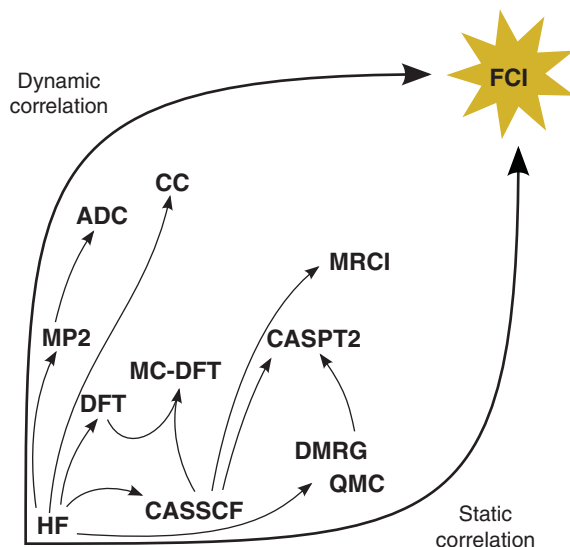
Figure 1.2 Scheme of quantum chemical methods for electronic structure. The lower left corner contains the most basic *ab initio* method, Hartree–Fock (HF), while the exact solution of the time-independent Schrödinger equation, full configuration interaction (FCI), lies, mostly unreachable, on the upper right corner. A panoply of methods described in Part I of this book, identified by their acronyms, try to "correct" HF, adding the missing *electronic correlation* and thus approximating the ideal FCI. The methods are arranged, qualitatively, based on their algorithmic relations and their prioritization of so-called *static* or *dynamic* correlation, which ultimately lead to the same end point.

methods is presented next, as a method that can alleviate in part the cost of grid-based wave packet methodologies. This chapter ends, bridging with the next block of four chapters that are based on quantum-mechanical and quantum-classical methods using on-the-fly computation of PES. These chapters are arranged in sort of going from more to less "quantum" – direct dynamics variational multi-configurational Gaussian (DD-vMCG) method, full and ab initio multiple spawning (FMS and AIMS), Ehrenfest methods, and surface hopping (SH). The next four chapters are based on alternative formulations of quantum dynamics. Exact factorization is based on an alternative way to express the electronic–nuclear wave function, Bohmian dynamics is based on wave theory, while semi-classical and path integral methods are based on Feynman's path integral formulation. Figure 1.3 illustrates pictorically the dynamical methods explained here.

Given the diversity of methods and authors it is unavoidable that every chapter follows its own writing style. For that reason, we considered it useful to collect here some underlying mathematical background, assuming basic knowledge of quantum mechanics, as well as a few photochemical concepts, that naturally arise in many chapters.

1.2 Atomic Units

A comment on atomic units is in order here. Hartree atomic units can elegantly simplify equations by setting to 1 the numerical value of some fundamental constants. Typical examples are the mass of the electron m_e, the electron charge e, the Coulomb or electric force constant $k_e = \frac{1}{4\pi\epsilon_0}$ and the reduced Plank constant $\hbar = \frac{h}{2\pi}$. Other useful constants used as units, derived from those fundamental quantities and used in this book are the bohr, $a_0 \approx 0.529$ Å, and the hartree, $E_h \approx 27.21$ eV.
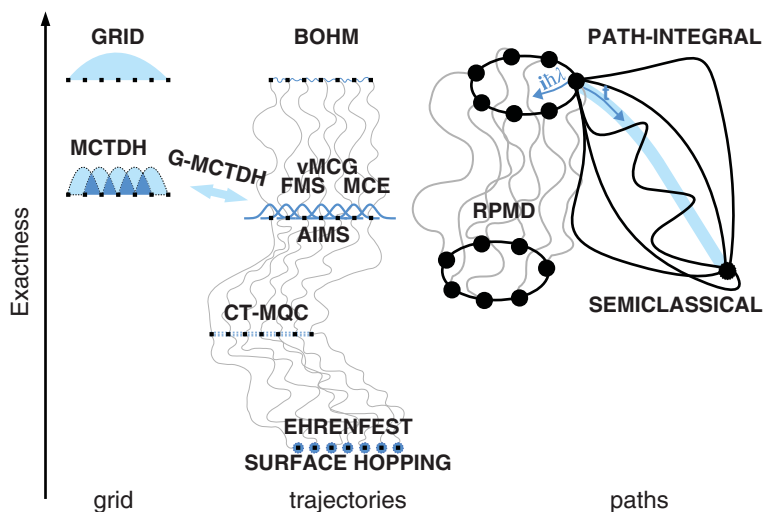
Figure 1.3 Grouping of dynamics methods by families and degree of exactness. Grid methods include the standard method to solve the time-dependent Schrödinger equation (GRID), the multi-configurational time-dependent Hartee method (MCTDH) and partially Gaussian MCTDH (G-MCTDH). From Bohmian trajectories, formally exact to frozen Gaussian methods, such as variational multi-configurational Gaussian (vMCG), full multiple spawning (FMS), multi-configurational Ehrenfest (MCE) and ab-initio multiple spawning (AIMS). Coupled trajectories mixed quantum classical (CT-MQC) is the trajectory method derived from exact factorization. Ehrenfest method and trajectory surface hopping (SH), follow next, since they are based on uncoupled trajectories. Derived from the formally exact path integral method, semi-classical and ring-polymer molecular dynamics (RPMD) arise.

However, using this notation forces readers to keep track of the omitted units, preventing a straightforward dimensionality analysis. For this reason, atomic units have been avoided as much as possible in most chapters, unless otherwise stated.

1.3 The Molecular Hamiltonian

The time evolution of a system is described by the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial\Psi(\boldsymbol{r},\boldsymbol{R},t)}{\partial t} = \hat{H}\Psi(\boldsymbol{r},\boldsymbol{R},t), \tag{1.1}$$

where $\hat{H}$ is the Hamiltonian of the system and $\Psi(\boldsymbol{r},\boldsymbol{R},t)$ is the wave function describing the molecule, with $\boldsymbol{r}$ and $\boldsymbol{R}$, the electronic and nuclear coordinates, respectively. When applied to the wave function, $\hat{H}$ yields the respective energy. If assumed as time-independent, $\hat{H}$ can be expressed as,

$$\hat{H}(\boldsymbol{r},\boldsymbol{R}) = \underbrace{-\sum_{i=1}^{N}\frac{\hbar^2}{2m_{\mathrm{e}}}\nabla_i^2}_{\hat{T}^{\mathrm{e}}} \underbrace{-\sum_{A=1}^{K}\frac{\hbar^2}{2M_A}\nabla_A^2}_{\hat{T}^{\mathrm{n}}} + \underbrace{\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{e^2}{4\pi\epsilon_0|\boldsymbol{r}_i-\boldsymbol{r}_j|}}_{\hat{V}^{\mathrm{ee}}}$$
$$+ \underbrace{\sum_{A=1}^{K}\sum_{B>A}^{K}\frac{e^2 Z_A Z_B}{4\pi\epsilon_0|\boldsymbol{R}_A-\boldsymbol{R}_B|}}_{\hat{V}^{\mathrm{nn}}} \underbrace{-\sum_{i=1}^{N}\sum_{A=1}^{K}\frac{e^2 Z_A}{4\pi\epsilon_0|\boldsymbol{r}_i-\boldsymbol{R}_A|}}_{\hat{V}^{\mathrm{ne}}}, \tag{1.2}$$

where the terms labeled as $\hat{T}$ are kinetic energy terms for K nuclei and N electrons, and the rest, labeled as $\hat{V}$ are the potential energy terms describing interactions between electrons or nuclei themselves, or between nuclei and electrons.

In atomic units, this equation reads simply as

$$\hat{H}(\boldsymbol{r}, \boldsymbol{R}) = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{A=1}^{K} \frac{1}{2M_A}\nabla_A^2 + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$
$$+ \sum_{A=1}^{K}\sum_{B>A}^{K} \frac{Z_A Z_B}{|\boldsymbol{R}_A - \boldsymbol{R}_B|} - \sum_{i=1}^{N}\sum_{A=1}^{K} \frac{Z_A}{|\boldsymbol{r}_i - \boldsymbol{R}_A|} . \tag{1.3}$$

1.4 Dirac or Bra-Ket Notation

The Dirac notation is a very compact way of describing quantum states and their inner products used in quantum mechanics, where the kets ($|\cdot\rangle$) are column vectors and the bras ($\langle\cdot|$) their Hermitian transpose row vectors, such as:

$$\langle\Psi| = |\Psi\rangle^* . \tag{1.4}$$

Ket vectors are normally used in this context to specify the state of a system in whatever space basis we are currently working on. Therefore, a wave function Ψ in x coordinates could be expressed as:

$$\Psi(x) \equiv \langle x|\Psi\rangle . \tag{1.5}$$

In the same way, applying an operator on this state would lead to:

$$\hat{A}\Psi(x) \equiv \langle x|\hat{A}|\Psi\rangle . \tag{1.6}$$

This notation can also be used to express *integrals* over products of wave functions – or rather a wave function and a complex-conjugate wave function. For example, $\langle\Psi|\Psi\rangle$ is nothing but a shorthand notation for

$$\int \Psi^*(\boldsymbol{r})\Psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \equiv \langle\Psi|\Psi\rangle . \tag{1.7}$$

where $\boldsymbol{r}$ symbolizes all the coordinates on which Ψ depends, and the integration is done over the whole domain. An operator can be included as in

$$\int \Psi^*(\boldsymbol{r})\hat{A}\Psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \equiv \langle\Psi|\hat{A}|\Psi\rangle , \tag{1.8}$$

In practical quantum chemistry calculations, one commonly uses a one-electron basis set to expand wave functions, i.e., a set of functions that depend on the coordinates of a single electron. In this context, a few particular forms of integrals are especially useful, and their usual notation will be introduced here. First, there is a term that collects the one-electron operators in the Hamiltonian, the kinetic energy and the nuclei–electron attraction (see section 1.3), and is expressed as

$$h_{pq} = \langle\phi_p|\hat{h}|\phi_q\rangle \tag{1.9}$$

$$= -\int \phi_p^*(\boldsymbol{r}) \left(\frac{\hbar^2}{2m_e}\nabla^2 + \frac{e}{4\pi\epsilon_0}\sum_{A=1}^{K}\frac{Z_A}{|\boldsymbol{r} - \boldsymbol{R}_A|} \right) \phi_q(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{1.10}$$

$$= -\frac{\hbar^2}{2m_e}\int \nabla\phi_p^*(\boldsymbol{r})\nabla\phi_q(\boldsymbol{r})\mathrm{d}\boldsymbol{r} - \frac{e}{4\pi\epsilon_0}\sum_{A=1}^{K}\int \frac{Z_A\phi_p^*(\boldsymbol{r})\phi_q(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{R}_A|}\mathrm{d}\boldsymbol{r} \tag{1.11}$$

where ϕ_p as ϕ_q are two basis functions. The other important term to note corresponds to the two-electron repulsion:

$$(pq|rs) = g_{pqrs} = \langle \phi_p \phi_r | \hat{g} | \phi_q \phi_s \rangle \tag{1.12}$$

$$= \frac{e^2}{4\pi\epsilon_0} \int \frac{\phi_p^*(\boldsymbol{r}_1)\phi_q(\boldsymbol{r}_1)\phi_r^*(\boldsymbol{r}_2)\phi_s(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \,. \tag{1.13}$$

Some alternative notations for these two-electron integrals are:

$$\langle pq|rs \rangle = (pr|qs) \tag{1.14}$$

$$\langle pq||rs \rangle = \langle pq|rs \rangle - \langle pq|sr \rangle. \tag{1.15}$$

1.5 Index Definitions

In several chapters of this book we will use the following convention with respect to the indexation of orbitals;

- $a, b, c, d, \dots$ to denote empty (virtual) orbitals;
- $i, j, k, l, \dots$ to denote doubly occupied (inactive) orbitals;
- $t, u, v, x, \dots$ to denote active orbitals; and
- $p, q, r, s, \dots$ as general indices to denote orbitals of unspecified type.

1.6 Second Quantization Formalism

We will now give a very brief introduction to the formalism of second quantization and how it is used to express the Hamiltonian. In the original formulation of quantum mechanics for a fixed number of particles, it was natural that the electronic Hamiltonian was expressed in terms of operators which are *sums over particles* – this was later called first quantization,

$$\hat{H}^{\mathrm{el}} = \sum_{i=1}^{N} (\hat{T}_i^{\mathrm{e}}(\boldsymbol{r}_i) + V^{\mathrm{ne}}(\boldsymbol{r}_i)) + \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \,, \tag{1.16}$$

where i is the index of an electron, $\hat{T}_i^{\mathrm{e}}$ is the kinetic energy operator of electron i, and

$$V^{\mathrm{ne}}(\boldsymbol{r}_i) = -\frac{e}{4\pi\epsilon_0} \sum_{A=1}^{K} \frac{Z_A}{|\boldsymbol{r}_i - \boldsymbol{R}_A|} \tag{1.17}$$

is the attraction experienced by electron i from all the nuclei in the system. The last term is the electron–electron repulsion term. However, with the onset of quantum field theory the notion of a system having a fixed number of particles was abandoned and a new formalism was introduced – second quantization – in which the *summations run over the orbital space* and the Hamiltonian operator is expressed in terms of operators that "probe" whether a particle (electron) is present in some orbital and if so, include the contribution of that particular orbital. In this formalism the electronic Hamiltonian is expressed as

$$\hat{H}^{\mathrm{el}} = \sum_{pq} \hat{E}_{pq} h_{pq} + \frac{1}{2} \sum_{pqrs} \hat{e}_{pqrs}(pq|rs), \tag{1.18}$$

where the summations are now in terms of the electronic orbitals[2], h_{pq} and $(pq|rs)$ are the one- and two-electron integrals introduced in Section 1.4, where ϕ are normalized molecular orbitals. The remaining operators are the "probing" operators in which the first operator

$$\hat{E}_{pq} = \sum_{\sigma=\{\alpha,\beta\}} \hat{a}_{p_\sigma}^\dagger \hat{a}_{q_\sigma} \tag{1.19}$$

is the spin-averaged electron replacement operator ($\hat{a}_{p_\sigma}^\dagger$ and $\hat{a}_{q_\sigma}$ are standard creation and annihilation operators for electrons of spin σ in orbitals p and q, respectively), which moves one electron from spatial orbital q to orbital p. The second operator is a two-electron replacement operator, which can be expressed in terms of the one-electron replacement operator as

$$\hat{e}_{pqrs} = \hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps} \,. \tag{1.20}$$

In this formalism the Hamiltonian is now invariant to the number of particles – in terms of calculations in a finite basis; however, the Hamiltonian is a function of the size of the basis set. This formalism has several advantages and is now the standard in multi-configurational electron structure theory. Let us now briefly explore the probing nature of the operator in Eq. (1.19). In the case $\hat{E}_{pp}$ operates on a closed-shell Slater determinant (SD), constructed from a set of orthonormal orbitals, we will have

$$\hat{E}_{pp}\psi_{\text{SD}} = \begin{cases} 2\psi_{\text{SD}} & \text{if } p \text{ is an occupied orbital} \\ 0\psi_{\text{SD}} & \text{if } p \text{ is an empty orbital,} \end{cases} \tag{1.21}$$

the operator will simply try to remove the electron and then try to put it back – this special case of the electron replacement operator is also called the *occupation number operator*. Since every occupied orbital in a closed-shell SD carries two electrons, we will get an occupation number of two, alternatively, if no electrons are found in orbital p the operator will be a null operator. In general we have that

$$\sum_p \hat{E}_{pp}\Psi = N\Psi, \tag{1.22}$$

where N is the number of particles (electrons) in the system. The following commutation relations apply to the one- and two-electron replacement operators:

$$[\hat{E}_{pq}, \hat{E}_{xy}] = \hat{E}_{py}\delta_{xq} - \hat{E}_{xq}\delta_{py} \tag{1.23}$$

$$[\hat{e}_{pqrs}, \hat{E}_{xy}] = \hat{e}_{pyrs}\delta_{xq} - \hat{e}_{xqrs}\delta_{py} + \hat{e}_{pqry}\delta_{xs} - \hat{e}_{pqxs}\delta_{ry} \,. \tag{1.24}$$

Finally we define the one- and two-particle density matrices as

$$D_{pq} = \langle\Psi|\hat{E}_{pq}|\Psi\rangle \,, \tag{1.25}$$

and

$$\Gamma_{pqrs} = \langle\Psi|\hat{e}_{pqrs}|\Psi\rangle \,. \tag{1.26}$$

It is important to note the four-fold permutational symmetry of the two-electron density matrix:

$$\Gamma_{pqrs} = \Gamma_{rspq} = \Gamma_{qpsr} = \Gamma_{srqp} \,. \tag{1.27}$$

---

2 We have used a shorthand notation to indicate multiple summations ($\sum_{pq} = \sum_p \sum_q$), and we leave the summation limits implicit

In this perspective we compute the electronic energy of a normalized wave function Ψ with the general expression

$$E = \sum_{pq} D_{pq} h_{pq} + \frac{1}{2} \sum_{pqrs} \Gamma_{pqrs} (pq|rs). \tag{1.28}$$

Finally, this expression can be transformed from a molecular orbital basis to any other basis. In particular, given that the orbitals ϕ are expressed as linear combinations of the one-particle basis functions χ as

$$\phi_p = \sum_{\mu} c_{p\mu} \chi_{\mu}, \tag{1.29}$$

we have that the one- and two-electron density matrices in the one-particle basis function expansion are generated by

$$D_{\mu\nu} = \sum_{pq} c_{p\mu} D_{pq} c_{q\nu} \tag{1.30}$$

and

$$\Gamma_{\mu\nu\gamma\delta} = \sum_{pqrs} c_{p\mu} c_{q\nu} \Gamma_{pqrs} c_{r\gamma} c_{s\delta}, \tag{1.31}$$

and we get

$$E = \sum_{\mu\nu} D_{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\gamma\delta} \Gamma_{\mu\nu\gamma\delta} (\mu\nu|\gamma\delta). \tag{1.32}$$

This expression has a special advantage in so-called direct methods, since the energy can be compiled directly from the integrals as they are generated in the one-particle basis set.

1.7 Born–Oppenheimer Approximation and Potential Energy Surfaces

The BOA is one of the most used approximations in quantum chemistry to solve the time-independent Schrödinger equation. Taking advantage of the fact that protons and neutrons are about 2000 times heavier than electrons, it neglects the kinetic energy of the nuclei. Therefore, at every nuclear position the electrons will feel an average potential depending on where the nuclei are located. This fact allows a separation of the Schrödinger equation into an electronic and a nuclear part. It is then possible to solve the electronic Schrödinger equation for every specific nuclear configuration, in which the Hamiltonian, eigenstates and eigenvalues depend parametrically on the nuclear position,

$$\hat{H}^{\text{el}} \Psi^{\text{el}}(\boldsymbol{r}; \boldsymbol{R}) = E^{\text{el}}(\boldsymbol{R}) \Psi^{\text{el}}(\boldsymbol{r}; \boldsymbol{R}). \tag{1.33}$$

Grouping the remaining terms of the molecular Hamiltonian (Eq. (1.2)), one arrives to the time-independent nuclear Schrödinger equation:

$$i\hbar \frac{\partial |\Psi^{\text{nuc}}(\boldsymbol{R})\rangle}{\partial t} = \hat{H} |\Psi^{\text{nuc}}(\boldsymbol{R})\rangle = [\hat{T}^{\text{n}}(\boldsymbol{R})) + E^{\text{el}}(\boldsymbol{R})] |\Psi^{\text{nuc}}(\boldsymbol{R})\rangle. \tag{1.34}$$

This equation represents nuclei that can move on effective potential surfaces represented by the electronic energies E^{el}. This representation of energies of electrons that depend parametrically on the nuclear coordinates is precisely what is called the potential energy surface (PES). This approximation will be valid whenever nuclei and electrons approximately decouple.

1.8 Adiabatic Versus Diabatic Representations

If the nuclei move extremely slowly, the electronic Hamiltonian will change very slowly with time, since it depends on the value of the nuclear coordinates. This means that if the starting electronic state was an eigenstate of the electronic Hamiltonian at the initial position, it will continue being an eigenstate during its time evolution. In this sense, the BOA is also known as the *adiabatic approximation*, since it assumes that the system behaves all the time "adiabatically", i.e., without changing its electronic wave function. However, there are some cases where the BOA breaks down.

Let us here express the total electronic wave function as a product of the electronic and nuclear ones using all electronic eigenstates (α indices):

$$|\Psi(\boldsymbol{r},\boldsymbol{R})\rangle = \sum_\alpha |\Psi_\alpha^{\mathrm{el}}(\boldsymbol{r};\boldsymbol{R})\rangle \cdot |\Psi_\alpha^{\mathrm{nuc}}(\boldsymbol{R})\rangle\,, \tag{1.35}$$

also known as the Born–Huang expansion. This expression can be inserted into the electronic Schrödinger equation to yield

$$\left(\hat{T}^{\mathrm{n}} + E_\alpha^{\mathrm{el}}\right)|\Psi_\alpha^{\mathrm{nuc}}(\boldsymbol{R})\rangle + \sum_\beta \hat{T}_{\beta\alpha}^{\mathrm{NAC}}|\Psi_\beta^{\mathrm{nuc}}(\boldsymbol{R})\rangle = E|\Psi_\alpha^{\mathrm{nuc}}(\boldsymbol{R})\rangle\,. \tag{1.36}$$

When comparing Eq. (1.36) and Eq. (1.34), one can see that the difference arises from the $\hat{T}_{\beta\alpha}^{\mathrm{NAC}}$ term, that can be expanded as

$$\hat{T}_{\beta\alpha}^{\mathrm{NAC}} = -\sum_{A=1}^{K} \frac{1}{2M_A}[\langle\Psi_\alpha^{\mathrm{el}}|\nabla_A^2|\Psi_\beta^{\mathrm{el}}\rangle + \langle\Psi_\alpha^{\mathrm{el}}|\nabla_A|\Psi_\beta^{\mathrm{el}}\rangle\nabla_A]\,. \tag{1.37}$$

Since neglecting these kinetic coupling terms is the core of the BOA, they can be seen as corrections. While the first term is known as BO diagonal coupling and is normally negligible, the second term – called derivative or non-adiabatic coupling (NAC) – can be rather large in regions where the electronic wave function changes fast with the nuclear coordinates. $\nabla_A|\Psi_\beta^{\mathrm{el}}\rangle$ is the gradient of the electronic wave function and gives us the direction where it changes fastest. After projecting it onto $\langle\Psi_\alpha^{\mathrm{el}}|$, i.e., calculating its overlap with it, the term can be seen as how much the change of the electronic wave function agrees with another electronic eigenstate. Its extent tells us how likely non-adiabatic events are, its direction the coordinate motions where this change is larger, always for a specific pair of electronic states. Note that this equation is still adiabatic, but corrected with terms corresponding to non-adiabatic events or the breakdown of the Born–Oppenheimer approximation. Thus, a total Hamiltonian might be composed of a Born–Oppenheimer one plus the NAC terms that generate transitions between BO states.

In contrast, we could define a basis where the electronic states do not depend on the nuclear coordinates (this labeling of the electronic wave function is normally called its *character*, so in this case we would say the electronic state keeps its electronic character). This basis can be defined at a particular geometry $\boldsymbol{R}_0$ where the electronic states were eigenstates of the electronic Hamiltonian. Those states are called *diabatic* states and do not diagonalize H^{el} at geometries different from $\boldsymbol{R}_0$,

$$|\Psi_\alpha^{\mathrm{el}}(\boldsymbol{R})\rangle = \sum_i c_{\alpha i}(\boldsymbol{R})|\Psi_\alpha^{\mathrm{el}}\rangle_{\mathrm{dia}}\,, \tag{1.38}$$

where there is no dependence of $|\Psi_\alpha^{\mathrm{el}}\rangle_{\mathrm{dia}}$ on the nuclear coordinates $\boldsymbol{R}$. Doing so, we can already neglect the NAC terms, since there is no change of the electronic wave function with the nuclear coordinates and therefore the coupling between electronic states is absorbed in the off-diagonal terms of the Hamiltonian matrix. A scheme depicting adiabatic and diabatic states can be seen in Figure 1.4.
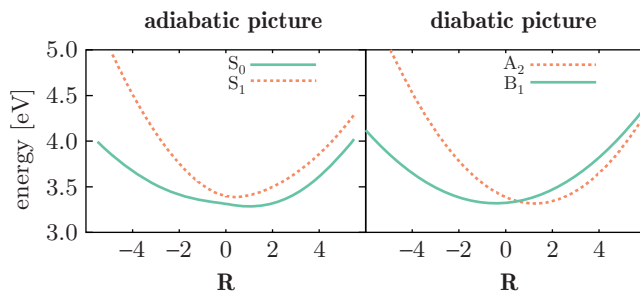
Figure 1.4 Schematic representation of adiabatic (states ordered by energy) and diabatic (states ordered by their symmetry label or character) potential energy curves.

For systems having more than two electronic states, it is usually not possible to find strictly diabatic states, so quasi-diabatic states are defined as a set of electronic states that minimize the NAC terms. In general, the diabatic representation is used whenever one needs to integrate in time domain over all the configurational space (see, for example, chapters 11 and 12) since the diabatic couplings are smoothly varying with the nuclear coordinates, making numerics easier. In contrast, dynamical methods based on local approaches (see e.g., chapters 14, 15 and 16), prefer the adiabatic picture due to the peaked localized NACs that will tell when the BOA breaks down.

1.9 Conical Intersections

The case depicted in Figure 1.4 is typical, where the adiabatic states display an *avoided crossing* along a particular coordinate: they become close in energy, but not exactly degenerate. Indeed, in systems with only one internal nuclear degree of freedom (diatomic molecules), and for electronic states of the same spin and spatial symmetry, this is almost always the case. In larger systems, however, the greater number of degrees of freedom allows for situations where the adiabatic states (as well as the diabatic states) are actually degenerate, these are known as *conical intersections*.

A conical intersection point is a particular geometry $R^\times$ at which two adiabatic electronic states are exactly degenerate. The degeneracy is lifted in two independent directions or nuclear displacements, any geometrical distortion in these directions causes the PES to split, creating a generic double cone shape that is the origin for the name (see Figure 1.1b). Conversely, distortions in orthogonal directions do not break the degeneracy, which indicates that $R^\times$ is not an isolated point, but is part of a connected $3N - 8$-dimensional subspace of geometrical configurations, known as intersection space or seam. The points where the energy of the degenerate states is a local minimum within the intersection space are called minimum energy conical intersections (MECI). The two dimensions that do lift the degeneracy form the branching space or branching plane, and are usually denoted as g (the difference between the gradients of the two states) and h (the derivative or non-adiabatic coupling vector). Since the two adiabatic states are exactly degenerate at $R^\times$, they are both eigenstates of the Hamiltonian with the same eigenvalue, and therefore any linear combination of them is also an eigenstate with the same eigenvalue. This means that the two states at the intersection are not uniquely defined, and neither are most state-specific properties or the g and h vectors. The branching plane, however – the space spanned by the two vectors – is uniquely defined and independent of which particular linear combinations of the two states is considered.

Conical intersections can be classified according to the topography of the PES in their vicinity. The most common distinction is between *peaked* and *sloped* intersections. Peaked intersections

are exemplified by the ideal shape displayed in Figure 1.1b: when the PES are represented in the branching plane, the intersection point is manifested as local maximum on the lower surface and a local minimum on the upper surface. This latter fact allows them to act as funnels or sinks from the upper to the lower surface. Sloped intersections, on the other hand, can be visualized by tilting the double cone's vertical axis until parts of the upper surface become lower in energy than the vertex (and parts of the lower surface higher than the vertex), at which point the intersection is neither a local maximum nor a local minimum, and its role as attractor is reduced in comparison to peaked intersections. An interesting property of sloped intersections is that they allow the existence of paths that go from the lower surface to the upper surface while continuously decreasing the potential energy.

1.10   Further Reading

For a deeper and more detailed discussion on the topics presented in this introductory chapter, the reader is referred to books on general computational or quantum chemistry, such as those listed below.

- *Modern Quantum Chemistry*. Attila Szabo and Neil S. Ostlund. McGraw–Hill, New York, 1989.
- *Molecular Electronic-Structure Theory*. Trygve Helgaker, Poul Jørgensen and Jeppe Olsen. Wiley, Chichester, 2000.
- *Essentials of Computational Chemistry: Theories and Models*. Christopher J. Cramer. Wiley, New York, 2002.
- *Multiconfigurational Quantum Chemistry*. Björn O. Roos, Roland Lindh, Per Åke Malmqvist, Valera Veryazov and Per-Olof Widmark. Wiley, Hoboken, 2016.
- *Introduction to Computational Chemistry*. Frank Jensen. 3rd ed. Wiley, Chichester, 2017.

1.11   Acknowledgments