Quantum mechanical studies of ionization and electron transfer in diatomic systems: $O_2$ and $H^+ + H^-$

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Abstract

The present thesis is based upon two papers concerning the core-valence double ionization of molecular oxygen and mutual neutralization of H$^+$ and H$^-$ ions at low collision energies.

The former of these processes has been studied for the first time using a magnetic bottle time-of-flight electron coincidence spectrometer in combination with \textit{ab initio} electronic structure calculations. The core-valence photoelectron spectra have been interpreted by comparing with the calculated double ionization energies, as well as the conventional valence band spectrum. Based on this comparison, some general features of the process are discussed and assignments for several of the dicationic states proposed.

The latter process has been studied by means of a molecular close coupling approach in which both the nuclei and the electrons have been treated at a quantum mechanical level of theory. Accurate \textit{ab initio} potential energy curves and non-adiabatic couplings have been used to calculate the neutralization cross section in the collision energy region 0.001 to 100 eV. Special emphasis has been put on the energy region below a few eV from which the low temperature rate coefficient is evaluated. In this region, the calculated neutralization cross section is in good agreement with several other theoretical studies, but is a factor of two to three lower than the only published experimental data.
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Papers included in the thesis

Paper I.

*Single-photon core-valence double ionization of molecular oxygen,*

Paper II.

*Mutual neutralization in low energy $H^+ + H^-$ collisions,*
M. Stenrup, Å. Larson, and Nils Elander,
submit to Phys. Rev. A.

My contributions to the included papers

Paper I.

I carried out the electronic structure calculations, wrote the draft of the theoretical section, and took part in the discussion and analysis.

Paper 2.

I carried out the electronic structure and scattering calculations. I implemented computational methods for calculating the non-adiabatic couplings and inelastic cross sections. I carried out the analysis and wrote the paper.
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Chapter 1

Introduction

This thesis is a collection of two papers. The first is a joint experimental and theoretical study of the core-valence double ionization of O₂, the second a theoretical study of the mutual neutralization of H⁺ and H⁻ ions at low collision energies. Although the basic physical mechanisms behind these processes are inherently different, there are some important similarities to be emphasized; (i) both processes involve ionic species, (ii) both processes involve highly excited electronic states, and (iii) both processes involve systems in which electron correlation plays an important role. Consequently, the theoretical description of these processes must go well beyond the approaches routinely adopted for neutral species in their electronic ground state. These aspects will be considered in more detail later on in the thesis.

The organization is as follows: The remaining part of the present chapter is devoted to a short introduction of the two types of processes that have been studied. Chapter 2 contains a brief outline of the quantum mechanical framework within which molecular processes are described. Chapter 3 summarizes the computational methods that have been used. Chapter 4 concludes with some comments on the included papers.

1.1 Photoelectron spectroscopy

During the late 19th and early 20th century, discoveries by Hertz [1], Lenard [2] and others led to the conclusion that matter is able to emit electrons after absorption of light, a process referred to as the photoelectric effect. One of the most stunning observations was that the velocity of the photoelectrons depended on the type of radiation but not on its intensity. This was in sharp contrast to what was predicted by Maxwell’s wave theory of light. In 1905, the phenomena was explained by Einstein [3] as arising from the quantized nature of light. According to Einstein, electromagnetic radiation in some situations behave as particles, so called photons, which energies are given by the
relation \( E = hf \), where \( h \) is Planck’s constant and \( f \) is the frequency of the light. Therefore, increasing the intensity of the radiation increases the number of photons, and hence also the number of emitted photoelectrons, but not their individual energies, which depend exclusively on \( f \).

Photoelectron spectroscopy (PES) is the branch of spectroscopy that makes use of the photoelectric effect in order to gain knowledge about atomic and molecular properties. If the frequency of the incident radiation is denoted by \( f_{\text{in}} \) and the kinetic energy of the electron emitted from the sample by \( E_k \), the ionization potential, i.e., the energy required to remove an electron from the parent molecule, is given by

\[
E_{\text{IP}} = hf_{\text{in}} - E_k.
\]

In general, the ionized molecule can be left in several different excited states and several electrons can be ejected by each photon. Thus, Eq. (1.1) can be taken to define a whole set of ionization potentials. For monochromatic incident light, plotting the number of emitted electrons against \( hf_{\text{in}} - E_k \) defines the photoelectron spectrum.

As is illustrated in Fig. 1.1, PES techniques are traditionally divided into different sub branches depending on which source of radiation that is used [4]. Ultraviolet photoelectron spectroscopy (UPS) normally uses radiation in the region 10 to 45 eV and is suitable for exploring the valence structure of atoms and molecules. This is usually done according to the principle of one photon in – one electron out. In a similar way, X-ray photoelectron spectroscopy (XPS),
1.2. MUTUAL NEUTRALIZATION PROCESSES

with radiation ranging from around 100 eV up to a few thousand eV, is used to examine the more tightly bound core electrons. In Auger electron spectroscopy (AES), not only the ejected core electron but also possible secondary electrons resulting from internal relaxation due to the core hole vacancy are detected. Usually one secondary electron is emitted and a dicationic molecule is formed.

A more direct way to investigate double ionization processes is provided by the two electron analogues of UPS and XPS. Here, the emitted electrons are detected in coincidence and indirect processes of the Auger type can be excluded (the fast Auger electron can be used as a trigger to start each measurement). Whereas most studies in this field have concentrated on the ejection of two valence electrons, only a handful so far have included the removal of core electrons. In Paper I we report on such a study of the core-valence double ionization of molecular oxygen, where one of the electrons is taken from the $1\sigma_g$ or $1\sigma_u$ core orbital (essentially the 1s shell of atomic oxygen) and the other from a higher lying valence orbital. The physical process is schematically depicted in Fig. 1.2.

1.2 Mutual neutralization processes

Mutual neutralization (MN) is the process where two oppositely charged ions collide, transfer an electron and form neutral fragments. It is one of the key
reactions occurring in low temperature ionized environments. In particular, it
plays an important role in determining the fraction of negative ions that can
go on to take part in chemical reactions. Practical interest of MN arises in
atmospheric sciences [5, 6, 7, 8], astrophysics [9, 10, 11, 12, 13] and plasma
based technologies [14, 15].

The MN reaction can be schematically written as
\[ A^+ + B^- \rightarrow A + B, \]  
(1.2)

where A and B are either atomic or molecular species. If the ionization po-
tential of A is larger than the electron affinity of B, the energy of the ion-pair
will be greater than the energy of the corresponding neutral products in their
ground state. In this case, the reaction starts out in a quantum state which is
electronically excited. The products formed in MN processes can go either into
the electronic ground state, as in the Li$^+$ + F$^-$ system [16], or into a distribu-
tion of excited states as in the O$^+$ + O$^-$ system [17]. In the case of molecular
species, the situation is even more complicated since energy can be transferred
into the vibrational and rotational modes of the molecules.

The mutual neutralization of atomic species is often thought to take place
along a system of covalent potential energy curves crossed by an attractive ion-
pair potential. This is schematically depicted in Fig. 1.3. The system enters
the collision on the ion-pair potential and then sequentially passes through a
series of curve crossings. In the semi-classical Landau-Zener model [18, 19], the
possibility for the system to make a transition into a covalent state is assumed
to be localized to these curve crossings. The total reaction probability for

\[ A^+ + B^- \rightarrow A + B, \]  
(1.2)
the MN process can be determined by considering the compound effect of all crossings. As will be seen in Sec. 2.3, the "simplified" picture described above is related to the so called quasidiabatic representation of the ion-ion collision problem.

In order to improve on the Landau-Zener model, one should move to a fully quantum mechanical description of the collision process. This quantum approach is usually carried out in two steps. First the "electronic problem" is solved and a set of potential energy curves and dynamical couplings are obtained. Secondly, these quantities are entered into a set of coupled equations for the motion of the nuclei. From the solutions to these equations, the neutralization cross section and the corresponding reaction rate constant can be evaluated. In Paper II this approach has been applied to study the reaction

\[ \text{H}^+ + \text{H}^- \rightarrow \text{H}(1) + \text{H}(n), \]

where \( n \) is the main quantum number of the excited hydrogen atom. Due to the small number of particles involved, the collisional system consists of only two protons and two electrons, this reaction has served as a prototype ever since the semi-classical treatment of Bates and Lewis in the mid-fifties [20]. However, most studies since then have concentrated on the intermediate and high energy regions, whereas very little has been done at collision energies below a few eV. In addition, some puzzling discrepancies between experiment and theory exist, which have led to a considerable spread in the rates adopted for this reaction [11]. The aim of the present study has been to further investigate the low energy cross section from which this reaction rate is evaluated.
This chapter provides some theoretical background to the included papers. The purpose here is to set up a suitable formalism for treating molecular phenomena, and to introduce the relevant quantum mechanical equations, whereas the question of how to numerically solve these equations is postponed until Chap. 3. Unless stated otherwise, atomic units are used, i.e., $\hbar = k_e = m_e = e = 1$, where $\hbar$ is the reduced Planck constant, $k_e$ is the Coulomb constant, $m_e$ is the electron mass and $e$ is the elementary charge. Vector and matrix quantities are written in bold face and the gradient operator is denoted by $\nabla$. Furthermore, the notation $\langle A | B | C \rangle$ implies integration of the product $A^* B C$ over all electronic coordinates.

2.1 The molecular Hamiltonian

In analogy with classical mechanics, the energy of a quantum mechanical system is represented by its Hamiltonian operator. For the present purposes, this operator must account for the kinetic and potential energies of a molecular system composed of $N_{\text{nuc}}$ nuclei and $N_{\text{el}}$ electrons. The coordinates of the nuclei are denoted by $\mathbf{R}_k$, $k = 1, 2, 3, \ldots, N_{\text{nuc}}$, and those of the electrons by $\mathbf{r}_l$, $l = 1, 2, 3, \ldots, N_{\text{el}}$. All coordinates are measured in an inertial frame of reference (the laboratory system). The masses and charges of the nuclei are denoted by $M_k$ and $Z_k$, respectively. In this notation, the total non-relativistic Hamiltonian has the form

$$H = -\sum_{k=1}^{N_{\text{nuc}}} \frac{1}{2M_k} \nabla^2 \mathbf{R}_k + H_{\text{el}},$$

(2.1)
where $H_{el}$ is the electronic Hamiltonian
\[
H_{el} = -\frac{1}{2} \sum_{k=1}^{N_{el}} \nabla_{\mathbf{r}_k}^2 + \sum_{k=1}^{N_{el}} \sum_{l>k}^{N_{el}} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} \\
+ \sum_{k=1}^{N_{nuc}} \sum_{l>k}^{N_{nuc}} \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|} - \sum_{k=1}^{N_{nuc}} \sum_{l=1}^{N_{el}} \sum_{l>k}^{N_{el}} \frac{Z_k}{|\mathbf{R}_k - \mathbf{R}_l|}.
\] (2.2)

The sum in Eq. (2.1) and the first sum in Eq. (2.2) represent the kinetic energies of the nuclei and electrons, respectively. The second and third double sums in Eq. (2.2) represent the electron-electron and nucleus-nucleus repulsions, respectively, and the the final double sum in Eq. (2.2) the electron-nucleus attraction.

The total Hamiltonian is translationally invariant. It follows that the centre of mass (CM) motion of the total system is a constant and can be separated out. Equation (2.1) then reduces from $3(N_{nuc} + N_{el})$ to $3(N_{nuc} + N_{el} - 1)$ degrees of freedom. The general procedure that accomplish this separation is tedious and the explicit appearance of the new Hamiltonian will depend on the particular choice of relative coordinates. However, in the special case of a diatomic system, a simple transformation into centre of mass coordinates is given by
\[
\mathbf{R}_{12} = \mathbf{R}_2 - \mathbf{R}_1,
\]
\[
\mathbf{R}_{cm} = \frac{M_1 \mathbf{R}_1 + M_2 \mathbf{R}_2 + \sum_{k=1}^{N_{el}} r_k}{M_1 + M_2 + N},
\]
\[
\rho_k = \mathbf{r}_k - \frac{M_1 \mathbf{R}_1 + M_2 \mathbf{R}_2}{M_1 + M_2},
\]

where $\mathbf{R}_{12} = (R, \theta, \phi)$ is the internuclear separation vector, $\mathbf{R}_{cm}$ is the centre of mass of the total system, and $\rho_k$ the coordinates of the electrons measured relative to the centre of mass of the nuclei (CMN). Using the chain rule for derivatives and subsequently removing the CM motion yields the Hamiltonian [21]
\[
H = -\frac{1}{2\mu} \nabla_{\mathbf{R}_{12}}^2 + H_{el},
\] (2.4)

where
\[
H_{el} = -\frac{1}{2} \sum_{k=1}^{N_{el}} \nabla_{\rho_k}^2 + \frac{Z_1 Z_2}{R} + \sum_{k=1}^{N_{el}} \sum_{l>k}^{N_{el}} \frac{1}{|\rho_k - \rho_l|} \\
- \sum_{k=1}^{N_{el}} \left( \frac{\mu}{M_1} \mathbf{R}_{12} + \rho_k \right) + \left( \frac{\mu}{M_2} \mathbf{R}_{12} - \rho_k \right) \\
- \frac{1}{2(M_1 + M_2)} \sum_{k=1}^{N_{el}} \sum_{l=1}^{N_{el}} \nabla_{\rho_k} \cdot \nabla_{\rho_l}.
\] (2.5)
2.2. THE COUPLED SCHRÖDINGER EQUATION

The reduced mass \( \mu \) is defined by

\[
\mu = \frac{M_1 M_2}{M_1 + M_2}.
\]  

(2.6)

The interpretation of most of the above terms should be clear. The first term in Eq. (2.4) represents the kinetic energy associated with the relative motion of the nuclei, and the first sum in Eq. (2.5) the kinetic energies of the electrons measured relative to CMN. The potential energy terms in Eq. (2.5) are expressed in relative coordinates, but otherwise are identical to those in Eq. (2.2). The only surprise is the appearance of the final sum in Eq. (2.5), which contains the so-called mass polarization operators. These arise as a consequence of separating out the centre of mass motion for a system of more than two particles. For the vast majority of molecular applications, the mass polarization terms are small and can be neglected.

2.2 The coupled Schrödinger equation

Using the Hamiltonian (2.1) for an arbitrary molecular system measured in the laboratory frame of reference, we wish to find solutions \( \psi(R, r) \) with energy \( E \) to the time-independent Schrödinger equation

\[
H \psi(R, r) = E \psi(R, r).
\]

(2.7)

Here, \( R \) and \( r \) collectively denote the nuclear and electronic degrees of freedom, respectively. The direct solution of Eq. (2.7), which is a partial differential equation in \( 3(N_{\text{nuc}} + N_{\text{el}}) \) variables, offers a computational problem of monumental complexity. It is therefore natural to start by looking at the situation where the nuclei can be considered as fixed in space. In this case, the kinetic energy operators for the nuclear motion do not enter the problem and \( H_{\text{el}} \) alone is the appropriate Hamiltonian. The corresponding electronic Schrödinger equation is given by

\[
H_{\text{el}} \phi_{ai}(R, r) = E_{ai}(R) \phi_{ai}(R, r),
\]

(2.8)

where the electronic wave functions \( \phi_{ai}(R, r) \) and energies \( E_{ai}(R) \) depend parametrically on the positions of the nuclei. The superscript \( a \) is an abbreviation for adiabatic, indicating that these quantities are obtained under the assumption that the nuclei move "infinitely slow".

The solutions to Eq. (2.8) can be taken as orthogonal and normalized. Furthermore, they provide a complete basis for functions defined over the electronic space. Assuming that Eq. (2.8) has been successfully solved for all values of \( R \) and a full set of electronic states has been obtained, it is therefore justified to write the total wave function as

\[
\psi(R, r) = \sum_{i}^{\infty} \chi_{i}(R) \phi_{ai}(R, r),
\]

(2.9)
where the nuclear wave functions $\chi^a(R)$ are included in order to span the full configuration space, even when the velocities of the nuclei are finite. A simple interpretation of Eq. (2.9) is that each wave function $\chi^a_i(R)$ describes how the nuclei "move" in the particular electronic state $\phi^a_i(R, r)$. Inserting the expansion (2.9) into Eq. (2.7), multiplying from the left with $\phi^a_j(R, r)$ and integrating over the electronic coordinates yields a set of coupled equations for the motion of the nuclei:

$$
\left[ \sum_{k=1}^{N_{\text{nuc}}} \left( \frac{1}{2M_k} 1 \nabla^2_{\mathbf{R}_k} - \frac{1}{M_k} \mathbf{F}^a_k \cdot \nabla_{\mathbf{R}_k} - \frac{1}{2M_k} \mathbf{G}^a_k \right) + \mathbf{V}^a \right] \chi^a = E^a \chi^a, \quad (2.10)
$$

with

$$
F^a_{k,ij}(R) = \langle \phi^a_i | \nabla_{\mathbf{R}_k} | \phi^a_j \rangle, \quad (2.11)
$$

$$
G^a_{k,ij}(R) = \langle \phi^a_i | \nabla^2_{\mathbf{R}_k} | \phi^a_j \rangle, \quad (2.12)
$$

$$
V^a_{ij}(R) = \langle \phi^a_i | H_{\text{el}} | \phi^a_j \rangle = \delta_{ij} E^a_i(R). \quad (2.13)
$$

Here, $\chi^a$ is a colon vector made up of the wave functions $\chi^a_i(R)$. Since the adiabatic electronic states are eigenstates of $H_{\text{el}}$, the matrix $\mathbf{V}^a$ by definition is diagonal. Comparing with the standard form of the Schrödinger equation, we are led to interpret the diagonal elements of this matrix, i.e., the electronic energies $E^a_i(R)$, as the potential energy surfaces upon which the nuclei move. It is clear that nuclei moving in different electronic states will experience different interaction potentials. The matrix vectors $\mathbf{F}^a_k$ and the matrices $\mathbf{G}^a_k$ both have off-diagonal elements, which act as couplings between different electronic states. The former of these are referred to as first derivative and the latter as second derivative non-adiabatic couplings. Under normal circumstances, the elements of $\mathbf{F}^a_k$ are of the order of $1/\sqrt{M_k}$ times larger than those of $\mathbf{G}^a_k$ when acting on the nuclear states [22]. Furthermore, $\mathbf{G}^a_k$ has diagonal elements usually referred to as adiabatic corrections, whereas $\mathbf{F}^a_k$ can be shown to be antisymmetric and thus to be purely off-diagonal. The physical relevance of the potential energy curves and non-adiabatic couplings will be discussed in more detail in the next section.

The coupled equations (2.10) in their present form are exact. However, in practical applications the expansion (2.9) has to be truncated and an approximate set of coupled equations is obtained. Nevertheless, the computational effort of solving these equations even for the smallest molecules is significant (and it grows violently with the size of $N_{\text{nuc}}$). A great simplification is achieved by noting that the coupling terms in Eq. (2.10) in many situations are small, and that only one term in the expansion (2.9) contributes significantly to each solution $\psi(R, r)$. A more thorough analysis reveals that this is true for regions of $\mathbf{R}$-space where the potential energy surfaces stay well separated. In such regions, the total wave function can be approximated with the single product

$$
\psi(R, r) = \chi^a_i(R) \phi^a_i(R, r), \quad (2.14)
$$
2.2. THE COUPLED SCHröDINGER EQUATION

and the non-adiabatic coupling matrices $F_{ak}^a$ and $G_{ak}^a$ set to zero. This procedure is recognized as the well-known Born-Oppenheimer (BO) approximation [23, 24], resulting in the "uncoupled" Schrödinger equations

$$\left[-\sum_{k=1}^{N_{\text{nucl}}} \frac{1}{2M_k} \nabla_R^2 + E_i^a(R)\right] \chi_i^a(R) = E \chi_i^a(R), \quad i = 1, 2, 3, \ldots, \tag{2.15}$$

where the nuclear motion is confined to the single potential energy surface $E_i^a(R)$. The BO approximation is often motivated from the fact that electrons and nuclei in a molecule, on one hand, experience a great mass difference, but on the other hand have similar momenta. Consequently, the kinetic energies of the electrons under normal circumstances are much larger than those of the nuclei. Since this also implies a larger spacing between the electronic energy levels (compared to the nuclear ones), the two type of motions can to a good approximation be considered as uncoupled. Although the BO approximation under many situation performs extremely well, in particular for near equilibrium and ground state calculations, there are important situations where a break down of this approximation can be observed. The reasons for this breakdown will be further discussed in the next section.

The derivation of the coupled Schrödinger equation (2.10) was carried out for an arbitrary number of nuclei measured in a laboratory fixed coordinate system. The procedure in the case of a diatomic system described by relative coordinates is almost completely analogous. The total wave function $\psi(R_{12}, \rho)$ is expanded as

$$\psi(R_{12}, \rho) = \sum_{i=1}^{\infty} \chi_i^a(R_{12}) \phi_i^a(R_{12}, \rho), \tag{2.16}$$

where $\rho$ collectively denote the electronic coordinates (measured relative to CMN) and $\phi_i^a(R_{12}, \rho)$ are solutions to the electronic Schrödinger equation

$$H_{el} \phi_i^a(R_{12}, \rho) = E_i^a(R) \phi_i^a(R_{12}, \rho). \tag{2.17}$$

Since the energy of a molecule can not depend on its orientation in field-free space, $E_i^a(R)$ is a function of the internuclear distance $R$ but not the angles $\theta$ and $\varphi$. Inserting Eq. (2.16) into the Schrödinger equation (2.7) and again projecting with the electronic states from the left leads to the coupled equations

$$\left(-\frac{1}{2\mu} \nabla_{R_{12}}^2 - \frac{1}{\mu} F^a \cdot \nabla_{R_{12}} - \frac{1}{2\mu} G^a + V^a\right) \chi^a = E^a \chi^a, \tag{2.18}$$

with

$$F_{ij}^a(R) = \langle \phi_i^a | \nabla_{R_{12}} | \phi_j^a \rangle, \tag{2.19}$$

$$G_{ij}^a(R) = \langle \phi_i^a | \nabla_{R_{12}}^2 | \phi_j^a \rangle, \tag{2.20}$$

$$V_{ij}^a(R) = \langle \phi_i^a | H_{el} | \phi_j^a \rangle = \delta_{ij} E_i^a(R). \tag{2.21}$$
2.3 Adiabatic vs. diabatic representations

The discussion of the preceding section led to some very important concepts such as the adiabatic electronic energies $E_a^1$ and the non-adiabatic couplings $F_{ij}^a$ and $G_{ij}^a$. The former of these determine the potential energy of the nuclei when moving in a certain electronic state $\phi_i^a$, and the latter the coupling between this electronic state and all the others. There is in fact two different ways to interpret this coupling. If the interest is in bound states of the nuclei, the non-adiabatic couplings emerge as corrections to the BO approximation and may for instance be included in order to carry out very accurate calculations of rovibrational frequencies and other spectroscopic properties. However, more direct is the role played by the non-adiabatic couplings in the dynamics of molecular systems, in which they are responsible for determining the rate of transition between different electronic states, and thus are able to drastically alter the outcome of chemical and physical processes.

In order to illustrate the above concepts, Fig. 2.1 shows the adiabatic potential energy curves for the ground and first excited electronic states of a diatomic molecule AB. The potential energy diagram is schematic but indeed resembles many of the features possessed by the so called alkali halides, e.g., LiF, LiCl and NaI [25, 26, 27], which are often taken as model examples for the breakdown of the BO approximation. The potential energy curve for the electronic ground state is denoted by $E_a^1(R)$ and that for the first excited state by $E_a^2(R)$. Also

![Figure 2.1: Schematic representation of the adiabatic potential energy curves for the ground ($E_a^1$) and first excited ($E_a^2$) electronic states of the diatomic molecule AB. The ionic and covalent characters of the corresponding electronic wave functions are also indicated in the figure.](image-url)
2.3. ADIABATIC VS. DIABATIC REPRESENTATIONS

![Graph showing the first derivative radial coupling](image)

**Figure 2.2**: The first derivative radial coupling $f_{12}(R)$ between the ground and first excited states of AB.

indicated in the figure are the characteristics of the corresponding electronic wave functions $\phi_1^a(R_{AB})$ and $\phi_2^a(R_{AB})$. For internuclear distances smaller than $R_c$, the wave function $\phi_1^a(R_{AB})$ is mainly ionic and for internuclear distances larger than $R_c$ mainly covalent. The situation for $\phi_2^a(R_{AB})$ is reversed.

Near the equilibrium distance $R_e$, the two potential energy curves stay well separated and the mixing of the electronic states is expected to be small. Thus, the BO-approximation can be invoked and the lowest bound states of the nuclei be obtained by solving Eq. (2.15). Conversely, if the system has enough energy to freely move along the potential energy curves, it may eventually reach to the point $R_c$. Here, the energy splitting between $E_1^a$ and $E_2^a$ is small enough for a breakdown of the BO-approximation to occur. As illustrated by Fig. 2.2, this is accompanied by a rapid increase in the radial component

$$f_{12}(R) = \left\langle \phi_1^a \left| \frac{\partial}{\partial R} \right| \phi_2^a \right\rangle,$$

(2.22)

of the first derivative coupling $F_{12}^a$. It is due to this coupling that a system which enters a collision on the ionic part of $E_2^a$ is able to make a transition down to $E_1^a$ and dissociate into neutral fragments. If this mechanism would be absent, the reaction

$$A^+ + B^- \rightarrow A + B$$

(2.23)

would indeed be forbidden.

It is no coincidence that the adiabatic potential energy curves in Fig. 2.1 come close to each other but never cross. Rather, this is a consequence of the
so called non-crossing rule [28], which in the case of a diatomic system states that two potential energy curves belonging to the same symmetry species are not allowed to cross. Therefore, regions such as that around \( R_c \) are commonly known as avoided crossings. Near an avoided crossing, the electronic wave functions experience a rapid change of character and the derivatives with respect to the nuclear coordinates may become large, thus resulting in a rapid increase of the corresponding non-adiabatic couplings.

For polyatomic molecules, there exist a generalized version of the non-crossing rule, stating that potential energy surfaces depending on \( N \) relative coordinates are allowed to intersect only in \( N - 2 \) dimensions [29]. Consequently, a set of potential energy surfaces which depend on two coordinates can become degenerate in one or several isolated points in nuclear configuration space. Such degeneracies are commonly known as conical intersections. In the neighbourhood of a conical intersection, the non-adiabatic couplings may become very large, and in fact, at the degeneracy point may become infinite.

The violent behaviour of the first derivative coupling terms near an avoided crossing or conical intersection may lead to severe difficulties when trying to solve the coupled equations (2.10). Moreover, the bare presence of these couplings leads to differential equations which contain both first and second order derivatives. It is therefore desirable to find a formulation of the theory in which the first derivative non-adiabatic couplings are absent; what is commonly referred to as a diabatic representation.

The concept of diabatic states goes all the way back to the early works of Landau [18] and Zener [19], and were intuitively defined as electronic states \( \phi^d_i \) which preserve their character through a region of avoided crossing. By employing electronic wave functions which are smooth functions of the nuclear coordinates, the non-adiabatic couplings can be expected to reduce in magnitude and in best cases be neglected. Because of this rather approximate approach, such states are sometimes referred to as quasidiabatic. Since the diabatic states in general are no eigenstates of the electronic Hamiltonian \( H_{el} \), the potential matrix \( V^d \) can have both diagonal and off-diagonal elements. The former of these are referred to as diabatic potential energy curves and the latter as electronic couplings. The diabatic potential energy curves do not obey the non-crossing rule. Figure 2.3 illustrates the quasidiabatic potential energy curves corresponding to the two lowest electronic states of the molecule AB (compare with Fig. 2.1).

A more formal approach to the concept of diabatic states is the so called strictly diabatic representation, defined as a representation of the electronic states in which the first derivative non-adiabatic couplings vanish identically [30]. The existence of such states in general has been a subject of controversy (see for example Refs. [30, 31, 32, 33]). However, in the special case of a diatomic molecule where all electronic states belong to the same symmetry species, a strictly diabatic representation can be shown to trivially exist [30]. We thus conform to this special case and assert that the strictly diabatic states can be
2.3. ADIABATIC VS. DIABATIC REPRESENTATIONS

![Quasidiabatic potential energy curves](image)

Figure 2.3: Quasidiabatic potential energy curves corresponding to the two lowest electronic states of AB.

Expressed as

\[ \phi^d_i(R_{12}, \rho) = \sum_{j=1}^{M} \phi^a_j(R_{12}, \rho) T^T_{ij}(R_{12}) , \quad (2.24) \]

where \( T_{ij} \) is the orthogonal adiabatic to diabatic transformation (ATDT) matrix and \( M \) is the number of adiabatic states which are to be transformed. Inserting the transformation (2.24) into the strictly diabatic condition

\[ F^d_{ij}(R) = \langle \phi^d_i | \nabla R_{12} | \phi^d_j \rangle = 0 , \quad (2.25) \]

yields after some manipulations a differential equation for the ATDT matrix:

\[ (\nabla R + F^a) T = 0 . \quad (2.26) \]

Assuming that this equation has been successfully solved, and furthermore, that the first derivative couplings between the adiabatic states with \( i < M \) and those with \( i \geq M \) are zero, it can also be shown that [34]

\[ G^d_{ij}(R) = \langle \phi^d_i | \nabla^2 R_{12} | \phi^d_j \rangle = 0 . \quad (2.27) \]

The coupled Schrödinger equation in the strictly diabatic representation then reduces to:

\[ \left( -\frac{1}{2\mu} \nabla^2_R + V^d \right) \chi^d = E \chi^d , \quad (2.28) \]

where

\[ V^d = T^T V^a T . \quad (2.29) \]
2.4 Scattering theory

This chapter is concluded by reviewing how the inelastic collision of two atoms (ions) can be described within the molecular framework developed in the previous sections. Starting from the fact that the electronic states $\phi_i(R_{12})$ approximately correlate with the separated atomic limits, we wish to answer the question "how large is the probability for the two atoms (ions) to enter a collision in state $j$ and emerge in state $i$". In the time-independent Schrödinger formalism developed above, this is related to the incoming and outgoing fluxes of the corresponding nuclear wave functions, $\chi^+_a(R_{12})$ and $\chi^+_j(R_{12})$, evaluated in the asymptotic region where the separated atomic limits are reached. Since we wish to carry out the calculations in a strictly diabatic representation, it is assumed that the ATDT matrix has been obtained under the boundary condition

$$\lim_{R \to \infty} T(R) = 1,$$

which makes the adiabatic and diabatic representations coincide in the region where the scattering wave function is evaluated.

In scattering theory, a product of the form $\chi^+_a(R_{12}) \phi_i(R_{12})$ is usually referred to as a channel. At large internuclear distances, the scattering wave function must behave as an incoming plane wave in some entrance channel $j$ and outgoing spherical waves in all channels which are energetically available. Provided that the interaction potential falls off reasonably fast [35], this leads to the asymptotic boundary conditions

$$\chi^+_i(R_{12}) \sim R \to \infty \delta_{ij} e^{ik_jz} + \frac{f_{ij}(\theta) e^{ik_i R}}{R},$$

where the incoming plane wave has been taken along the z-axis. The angular function $f_{ij}(\theta)$ is the amplitude for scattering from channel $j$ to channel $i$. Due to cylindrical symmetry around the z-axis, $f_{ij}(\theta)$ can be taken as independent of the azimuthal angle $\phi$. The asymptotic wave number $k_i$ is defined as

$$k_i = \left\{ 2\mu \left[ E - V^d_i(\infty) \right] \right\}^{1/2}.$$

Although it is theoretically meaningful to speak about both transition and reaction probabilities, these are not convenient quantities to compare with experiment. More suitable is the related integral cross section $\sigma_{ij}$, which is defined as the total amount of outgoing flux in channel $i$ divided by the incoming flux per unit area in channel $j$. By evaluating the probability fluxes associated with each term in Eq. (2.31), we arrive at the expression [21]

$$\sigma_{ij} = \frac{2\pi k_i}{k_j} \int_0^{\pi} |f_{ij}(\theta)|^2 \sin \theta d\theta,$$
2.4. SCATTERING THEORY

for the integral cross section in terms of the scattering amplitude. In order to
determine \( f_{ij}(\theta) \), it is conventional to expand \( \chi_i^d(\mathbf{R}_{12}) \) in terms of the familiar
Legendre polynomials \( P_l(\cos \theta) \) according to

\[
\chi_i^d(\mathbf{R}_{12}) = \frac{1}{R} \sum_{l=0}^{\infty} A_l u_{i,l}(R) P_l(\cos \theta) ,
\]

(2.34)

where \( u_{i,l}(R) \) are radial wave functions and \( A_l \) are constants which should be
chosen such that the boundary conditions (2.31) are satisfied. Inserting this
expansion into the diabatic Schrödinger equation (2.28) yields a set of coupled
equations for the radial motion:

\[
\left( \frac{d^2}{dR^2} + Q_l \right) \tilde{u}_l = 0 ,
\]

(2.35)

with

\[
Q_l = 2\mu \left( E_1 - V^d \right) - \frac{l(l+1)}{R^2} - 1 .
\]

(2.36)

The square matrix \( \tilde{u}_l \) is the made up of the column vectors \( u_l^{(1)}, u_l^{(2)}, \ldots, u_l^{(M)} \),
which themselves are linearly independent solutions to Eq. (2.35).

For large internuclear distances, say \( R \) larger than some point \( R_a \), the in-
teraction between the two atoms (ions) can be approximated as being either
Coulombic or covalent. If it can be further assumed that the off-diagonal
elements of the potential matrix are zero, the solutions to the radial Schrödinger
equation (2.35) have well known analytical forms. We can exploit this fact by
writing the radial wave functions as [35, 36]

\[
\tilde{u}_l(R) = \begin{cases} \alpha_l(R) - \beta_l(R)S_l, & R \geq R_a \\ \end{cases}
\]

(2.37)

where \( \alpha_l \) and \( \beta_l \) are diagonal square matrices which contain the incoming and
outgoing wave solutions to Eq. (2.35), respectively, and \( S_l \) is the so called
scattering matrix. In order to determine the scattering amplitude \( f_{ij}(\theta) \) we
now insert this expression into the partial wave expansion (2.34) and compare
with the boundary conditions (2.31). The result is

\[
f_{ij}(\theta) = \frac{1}{2i(k_ik_j)^{1/2}} \sum_{l=0}^{\infty} \left( 2l + 1 \right) \left( S_{ij,l}^o - \delta_{ij} \right) P_l(\cos \theta) ,
\]

(2.38)

where \( S_{ij,l}^o \) is the open-open partition of \( S_l \), i.e., the partition of \( S_l \) which
connects the energetically available channels. Inserting the expression (2.38)
into Eq. (2.33), and using the properties of the Legendre polynomials finally
gives

\[
\sigma_{ij} = \sum_{l=0}^{\infty} \sigma_{ij,l} ,
\]

(2.39)
where

$$\sigma_{ij,l} = \frac{\pi}{k^2_j} (2l + 1) \left| S_{ij,l}^* - \delta_{ij} \right|^2 .$$  \hfill (2.40)

In principle, our scattering theory is now complete. Provided that the potential matrix $V^d$ is known, the radial Schrödinger equation (2.35) is numerically integrated from the origin out to the point $R_a$ and the scattering matrix $S_l$ is extracted from Eq. (2.37). Inserting $S_l$ into Eq. (2.40) and summing up according to Eq. (2.39) yields the integral cross section $\sigma_{ij}$. From a numerical point of view, however, it is still desirable to make some slight adjustments of the theory. The first one is the introduction of the so called reaction matrix $K_l$, defined by [35, 36]

$$\tilde{u}_l(R) = a_l(R) - b_l(R) K_l ,$$  \hfill (2.41)

where $a_l$ and $b_l$ are regular and irregular solutions to Eq. (2.35). Clearly, these must be linear combinations of the incoming and outgoing wave solutions $\alpha_l$ and $\beta_l$. By an appropriate choice of normalization factors, we can derive the relationship [36]

$$S_l^o = (1 + iK_l^o)^{-1} (1 - iK_l^o) ,$$  \hfill (2.42)

between the open-open partitions of $S_l$ and $K_l$. This expression is identical to the so called Cayley transform, and since $S_l^o$ can be shown to be unitary, this implies that $K_l^o$ is real [35]. The opposite is also true, and thus the unitarity of $S_l^o$ is guaranteed by keeping $K_l^o$ real.

The second and final modification is to introduce the logarithmic derivative

$$y_l = \tilde{u}_l' \tilde{u}_l^{-1} ,$$  \hfill (2.43)

which transforms the radial Schrödinger equation (2.35) into the numerically more stable matrix Riccati equation [37, 38]

$$y_l' + Q_l + y_l^2 = 0 .$$  \hfill (2.44)

The relation to $K_l$ is seen to be [36]:

$$K_l = \left[ y_l(R_a) b_l(R_a) - b_l'(R_a) \right]^{-1} \times \left[ y_l(R_a) a_l(R_a) - a_l'(R_a) \right] .$$  \hfill (2.45)
Chapter 3

Computational methods

In the previous chapter it was seen how the "molecular problem", whether the BO approximation was invoked or not, could be approached by separately considering (i) the motion of the electrons in the field of the fixed nuclei and (ii) the motion of the nuclei on the (coupled) potential energy surfaces generated by the electrons. Part (i) requires the solution of the electronic Schrödinger equation (2.8). This is almost universally carried out using the variational principle in combination with a basis set expansion of the electronic wave functions (possibly also followed by some perturbative treatment). Examples of methods that use this approach, and which are of interest for the present work, are the Hartree-Fock (HF), configuration interaction (CI) and multi configuration self-consistent field (MCSCF) methods, which are summarized in Secs. 3.1, 3.2 and 3.3. Having successfully obtained the electronic wave functions, these can be used to evaluate the first derivative non-adiabatic couplings (2.11). Here, the conceptually simplest and probably most popular technique is the finite difference method outlined in Sec. 3.4. Part (ii) requires the solution of a set of (coupled) Schrödinger equations for the motion of the nuclei. In the present case, these come in the shape of the matrix Riccati equation (2.44), which is in a convenient form for numerical integration. How this is done is summarized in Sec. 3.5.

3.1 Hartree-Fock

One of the landmarks of modern chemistry is the molecular orbital (MO) concept, i.e., the idea that the electrons in a molecule can be described by one particle wave functions, and the total electronic wave function written as a product of such one particle functions. This turns out to be not only a great simplification computational wise, but also provide a way how to think about molecular structure, bonding and reactivity. In addition to describing the spatial distribution of the electrons, the one particle wave functions must also
account for the electron spin. This is most easily done by taking each orbital
to be a product of a spatial wave function and a spin function; a so called
spin orbital. For electrons, the spin function is either \( \uparrow \) or \( \downarrow \) corresponding
to the spin projection quantum numbers \( 1/2 \) and \( -1/2 \), respectively. Finally,
since electrons are fermions, their wave function must be antisymmetric under
exchange of any two particles. The above criteria can be met by writing the
electronic wave function as a Slater determinant,

\[
\phi_{SD} = \frac{1}{\sqrt{N_{el}}} \left| \begin{array}{cccc}
\xi_1(1) & \xi_2(1) & \cdots & \xi_{N_{el}}(1) \\
\xi_1(2) & \xi_2(2) & \cdots & \xi_{N_{el}}(2) \\
\vdots & \vdots & \ddots & \vdots \\
\xi_1(N_{el}) & \xi_2(N_{el}) & \cdots & \xi_{N_{el}}(N_{el})
\end{array} \right|, \tag{3.1}
\]

where \( \xi_i(j) \) denotes the \( j \)-th electron in the \( i \)-th spin orbital. The functions \( \xi_i(j) \)
are assumed to be orthogonal and normalized. The energy of the approximate
wave function (3.1) is given by [39, 40]

\[
E_{SD} = \langle \phi_{SD} | H_{el} | \phi_{SD} \rangle = \sum_{i=1}^{N_{el}} h_i + \sum_{i=1}^{N_{el}} \sum_{j>i} (J_{ij} - K_{ij}) + V_{nuc}, \tag{3.2}
\]

where

\[
\begin{align*}
h_i &= \left\langle \xi_i(1) \right| \hat{h}_i \left| \xi_i(1) \right\rangle, \tag{3.3} \\
J_{ij} &= \left\langle \xi_i(1)\xi_j(2) \right| \hat{g}_{12} \left| \xi_i(1)\xi_j(2) \right\rangle, \tag{3.4} \\
K_{ij} &= \left\langle \xi_i(1)\xi_j(2) \right| \hat{g}_{12} \left| \xi_i(2)\xi_j(1) \right\rangle, \tag{3.5} \\
V_{nuc} &= \sum_{k=1}^{N_{nuc}} \sum_{l>k} Z_k Z_l \left| \mathbf{R}_k - \mathbf{R}_l \right|, \tag{3.6}
\end{align*}
\]

and

\[
\begin{align*}
\hat{h}_i &= -\frac{1}{2} \nabla_i^2 - \sum_{k=1}^{N_{nuc}} \frac{Z_k}{\left| \mathbf{R}_k - \mathbf{r}_i \right|}, \tag{3.7} \\
\hat{g}_{ij} &= \frac{1}{\left| \mathbf{r}_i - \mathbf{r}_j \right|}. \tag{3.8}
\end{align*}
\]

The term \( h_i \) represents the energy of an electron occupying orbital \( i \) in the
field of all the nuclei, \( J_{ij} \) the Coulomb repulsion between two electrons in
the orbitals \( i \) and \( j \), and \( V_{nuc} \) the Coulomb repulsion among the nuclei. If
we think of the molecular orbitals in terms of charge distributions, all of the
above mentioned terms have classical analogues. This is not the case for the
exchange term \( K_{ij} \), which is identical to \( J_{ij} \) except for the fact the two electrons
on the right hand side of \( \hat{g}_{12} \) have been interchanged. This term arises from the
antisymmetry of the electronic wave function and is purely quantum mechanical
in its origin.
According to the variational principle, the best determinantal wave function (in an energetical sense) is that which minimizes the expression (3.2). Taking the variation of this expression and equating it to zero leads after some manipulations to the Hartree-Fock (HF) equations

\[ \hat{F}_i \xi_i = \epsilon_i \xi_i , \] (3.9)

where \( \epsilon_i \) are orbital energies and \( \hat{F}_i \) the so called Fock operators defined by

\[ \hat{F}_i = \hat{h}_i + \sum_{j=1}^{N_{el}} (\hat{J}_j - \hat{K}_j) . \] (3.10)

The Coulomb and exchange operators, \( \hat{J}_j \) and \( \hat{K}_j \), are defined in terms of their actions upon the spin orbitals according to

\[ \hat{J}_j |\xi_i(2)\rangle = \langle \xi_j(1) | \hat{g}_{12} | \xi_j(1) \rangle |\xi_i(2)\rangle \] (3.11)

and

\[ \hat{K}_j |\xi_i(2)\rangle = \langle \xi_j(1) | \hat{g}_{12} | \xi_j(1) \rangle |\xi_j(2)\rangle . \] (3.12)

The Hartree-Fock equations (3.9) constitute a pseudo eigenvalue problem since the \( \hat{J}_j \) and \( \hat{K}_j \) operators themselves depend on the molecular orbitals that need to be solved for. Therefore, these equations must be approached in a self consistent manner using an initial "guess" of the molecular orbitals and then iterating the solution procedure until convergence is obtained.

In most practical situations, the Hartree-Fock equations are not directly solved. Instead the molecular orbitals are expanded in terms of a set of atomic orbitals (AO:s) \( \alpha_k \) according to

\[ \xi_i = \sum_k a_{ik} \alpha_k , \] (3.13)

which reduces Eq. (3.9) to the Roothan-Hall equations

\[ \hat{F} a = \hat{S} a \epsilon . \] (3.14)

Here, \( \mathbf{F} \) is the Fock matrix expressed in the AO basis, \( \mathbf{S} \) is the overlap matrix, \( \epsilon \) is a diagonal matrix containing the orbital energies, and \( \mathbf{a} \) is a vector containing the coefficients \( a_{ik} \). Equation (3.14) can, although self consistently, be solved by standard methods of linear algebra. If there are \( N_{AO} \) atomic orbitals, this will give rise to equally many spin orbitals. However, only the \( N_{cl} \) lowest of these will be occupied and contribute to the Hartree-Fock energy (3.2). The unoccupied orbitals are named virtual and play an important role in post Hartree-Fock methods such as those discussed in the next section.
3.2 Configuration interaction

The approximation made by expressing the electronic wave function as a single
Slater determinant is associated with some serious limitations; the electron-
electron interaction is only taken care of in an average fashion, whereas the more
explicit electron correlation is to a large extent ignored. Furthermore, single
determinant wave functions are not in general eigenfunctions of the \( S^2 \) operator
and thus are no pure spin states. Both of these issues can be resolved by
introducing more flexibility into the wave function. The most obvious way to do
this is to use linear combinations of several Slater determinants. Accordingly,
the electronic wave function is written as

\[
\phi_{\text{CI}} = \phi_{\text{SD}} + \sum_i c_i \phi_i ,
\]

where \( \phi_{\text{SD}} \) is the single determinant Hartree-Fock wave function and \( \phi_i \) are
Slater determinants which are obtained by exciting one or several electrons
from the \( N_{\text{el}} \) occupied spin orbitals to the \( N_{\text{ao}} - N_{\text{el}} \) unoccupied (virtual) ones.
This procedure is known as configuration interaction.

Applying the variational principle to the wave function (3.15) and using the
orthonormality of the Slater determinants yields the secular equations [39, 40]

\[
Hc = E_{\text{CI}}c ,
\]

where \( E_{\text{CI}} \) is a diagonal matrix containing the CI energies, \( c \) is a vector con-
taining the coefficients \( c_i \), and \( H \) is the Hamiltonian matrix

\[
H_{ij} = \langle \phi_i | H_{\text{el}} | \phi_j \rangle .
\]

Equation (3.16) has the same number of solutions as there are configurations in
the CI expansion. The solution with the lowest energy is the electronic ground
state, that with the second lowest energy the first excited state, etc.

The size of the CI expansion is determined by both the number of spin or-
bital and the type of excitations out of the HF wave function that are allowed.
In CI singles (CIS) only single electron excitations are allowed, in CI singles
and doubles (CISD) only single and double excitations, etc. In the full CI (FCI)
approach an arbitrary number of electrons are allowed to be excited out of the
HF wave function. It can be shown that the FCI limit is equivalent to the exact
solution of the electronic Schrödinger equation in the particular atomic basis
that is used. However, the computational price one has to pay for this accuracy
is high; the full CI scales factorially with the number of electrons and orbitals
and therefore the FCI approach is feasible only for the smallest molecules.

An alternative to the expansion in terms of Slater determinants is the use of
so called configuration state functions (CSF:s), which are designed to be
eigenfunctions of the \( S^2 \) operator, i.e., singlets, doublets, triplets, etc. In general,
these are constructed as linear combinations of Slater determinants with
the same set of occupied spatial orbitals but with some of the $\uparrow$ and $\downarrow$ spin functions interchanged. A nice example is the provided by the $S_z = 0$ component of the lowest triplet state of H$_2$. Here, the leading configuration has one electron in the $1\sigma_g$ and the other in the $1\sigma_u$ orbital. The corresponding CSF can be written as

$$\phi_{1,0} = \frac{1}{2} \left[ \begin{array}{c} \uparrow 1\sigma_g(1) & \downarrow 1\sigma_u(1) \\ \uparrow 1\sigma_g(2) & \downarrow 1\sigma_u(2) \end{array} \right] + \left[ \begin{array}{c} \downarrow 1\sigma_g(1) & \uparrow 1\sigma_u(1) \\ \downarrow 1\sigma_g(2) & \uparrow 1\sigma_u(2) \end{array} \right]$$

(3.18)

$$= \frac{1}{2} \left[ \uparrow (1) \downarrow (2) + \downarrow (1) \uparrow (2) \right] \left[ 1\sigma_g(1)1\sigma_u(2) - 1\sigma_u(1)1\sigma_g(2) \right].$$

Since the electronic Hamiltonian is spin independent, matrix elements between CSF:s of different spin will be zero. In a similar way, since the electronic Hamiltonian belongs to the totally symmetric representation, matrix elements between CSF:s of different spatial symmetry will be zero. This leads to a Hamiltonian matrix which is block diagonal with respect to both spin and spatial symmetries.

### 3.3 Multi configuration self-consistent field

The energy lowering that results from the correlated motion of the electrons is sometimes quantified as the difference between the HF and the FCI energies, i.e.,

$$E_{\text{corr}} = E_{\text{HF}} - E_{\text{CI}}.$$  \hspace{1cm} (3.19)

This energy contribution can be further divided into static correlation, which is associated with near degeneracies of the orbitals/configurations, and dynamic correlation, which is associated with the reluctance of the electrons to be found in the same region of space [40]. Sometimes only the former of these may need to be recovered in order to give a qualitatively correct description of the wave function. In these cases, the multi configuration self-consistent field (MCSCF) method may be a good choice. The MCSCF approach can be considered as an intermediate between HF and CI where both the MO:s and CI coefficients are optimized simultaneously. In fact, both HF and CI can be regarded as special cases of MCSCF.

The most common schemes for constructing the MCSCF wave function is the complete active space (CASSCF) and restricted active space (RASSCF) self consistent field approaches. These are schematically illustrated in Fig 3.1. The CASSCF method uses a partitioning of the molecular orbitals into three different spaces; an inactive space, in which all orbitals are kept fully occupied during the optimization, a complete active space, within which a full CI is performed, and a secondary space, which is kept empty during the optimization. For computational reasons, the size of the MCSCF expansion is usually restricted to about 10 - 14 active orbitals/electrons.
In the RASSCF approach, the complete active space is further divided into RAS1, RAS2 and RAS3 subspaces. The definition on these varies, but usually the RAS1 space is taken to consist of orbitals which are doubly occupied in the HF wave function and RAS3 of orbitals that are unoccupied. The RAS2 space is constructed from both occupied and unoccupied orbitals and within this space a full CI is performed. Additional configurations is generated by specifying a certain number of electrons that can be excited from RAS1 (to RAS2 and RAS3) and a certain number of electrons that can be excited into RAS3 (from RAS1 and RAS2). By a proper choice of RAS spaces this type of wave function can recover much of the static correlation of CASSCF without having to perform a full CI within the complete active space. In addition, the RASSCF scheme allows for some special type of wave functions such as those describing core exited states to be constructed (as has been utilized in Paper I).

### 3.4 The finite difference method for non-adiabatic couplings

Several different methods for evaluating non-adiabatic couplings have been proposed in the literature. Some of these, like the Hellmann-Feynman [41] and Sidis [42] approaches, are computationally rather cheap, but have the drawback that they are derived under assumption of exact electronic states and
3.4. THE FINITE DIFFERENCE METHOD FOR NON-ADIABATIC COUPLINGS

that the error introduced by applying them to approximate wave functions is
difficult to estimate. Conversely, the finite difference method for evaluating
non-adiabatic couplings [43] provides a straightforward way to converge the
calculations toward the exact result for the particular type of wave functions
being used.

In the present case we consider two multi-configuration wave functions \( \phi_A \) and \( \phi_B \):

\[
\phi_A(R) = \sum_i c_i^A(R) \phi_i(R) \tag{3.20}
\]

and

\[
\phi_B(R) = \sum_i c_i^B(R) \phi_i(R), \tag{3.21}
\]

where \( c_i^A \) are \( c_i^B \) are CI coefficients, \( \phi_i \) is a set of orthogonal and normalized
CSF:s, and \( R \) is the nuclear coordinate which is to be differentiated (the de-
pendence on all other coordinates is suppressed). We wish to calculate the first
derivative coupling matrix element

\[
f_{AB} = \left\langle \phi_A(R) \left| \frac{\partial}{\partial R} \right| \phi_B(R) \right\rangle. \tag{3.22}
\]

By using the product rule for derivatives and exploiting the orthonormality of
the CFS:s, it is readily seen that

\[
f_{AB} = \sum_i c_i^A(R) \frac{\partial}{\partial R} c_i^B(R) + \sum_i \sum_j c_i^A(R) c_j^B(R) \left\langle \phi_i(R) \left| \frac{\partial}{\partial R} \right| \phi_j(R) \right\rangle \equiv f_{AB}^{\text{CI}} + f_{AB}^{\text{MO}} \tag{3.23}
\]

The first part of this expression is related to the change of the CI coefficients
as functions of \( R \), and the second part to the change of the molecular orbitals.
However, while this division is mathematically clear-cut, its physical interpre-
tation is somewhat arbitrary since there are transformations that change the
CI coefficients and MO:s, but leave the electronic wave function invariant [40].

The CI part is already in a form suitable for numerical differentiation. Taking
the finite difference yields

\[
f_{AB} \approx \frac{1}{\Delta R} \sum_i c_i^A(R) \left[ c_i^B(R + \Delta R) - c_i^B(R) \right] \tag{3.24}
\]

where \( \Delta R \) is the step length over which the derivative is calculated.

The MO part can be simplified by noting that matrix elements in the double
sum in Eq. (3.23) vanish unless \( \phi_i \) and \( \phi_j \) differ in exactly two spatial orbitals,
\( \xi_m \) and \( \xi_n \) say. In this case we have

\[
\left\langle \phi_i(R) \left| \frac{\partial}{\partial R} \right| \phi_j(R) \right\rangle = \lambda \left\langle \xi_m(R) \left| \frac{\partial}{\partial R} \right| \xi_n(R) \right\rangle \tag{3.25}
\]
where $\lambda$ is a constant that depends on the construction of $\phi_i$ and $\phi_j$. Taking the finite difference of Eq. (3.25), using the orthonormality of the MO:s and expanding them in terms of atomic basis functions,

$$\xi_m(R) = \sum_k a_{mk}(R)\alpha_k(R),$$

(3.26)

yields

$$\left\langle \phi_i(R) \left| \frac{\partial}{\partial R} \right| \phi_j(R) \right\rangle \approx \frac{\lambda}{\Delta R} \sum_k \sum_l a_{mk}(R)a_{nl}(R+\Delta R) \langle \alpha_k(R)|\alpha_l(R+\Delta R) \rangle.$$  

(3.27)

As can be expected for a finite difference type of approach, there is a delicate balance between the choice of step length $\Delta R$, and the numerical accuracy with which the electronic wave functions are calculated. On one hand, $\Delta R$ must be small enough for a good approximation of the true derivative to be obtained, on the other hand it must not be too small, in which case the variation in the wave function (over $\Delta R$) may become of the same order as the numerical error. These type of effects can to some degree be stabilized by introducing left and right derivatives and calculating the final coupling element as the mean value of these.

### 3.5 The log-derivative method

In Sec. (2.4) it was seen how the atom-atom scattering problem could be reduced to solving the matrix-Riccati equation

$$y'_l + Q_l + y^2_l = 0 ,$$

(3.28)

where

$$Q_l = 2\mu \left( E_1 - V^d \right) - \frac{l(l+1)}{R^2} \mathbf{1} .$$

(3.29)

It was also seen that in order to calculate the cross section, we only need to know the logarithmic derivative $y_l$ in the single point $R_a$ in which the S-matrix is evaluated. An efficient and stable algorithm for this purpose has been developed by Johnson [37, 38].

Before the algorithm can be applied, the solution to Eq. (3.28) need to be fixed with a boundary condition. This can be deduced from the corresponding boundary conditions on the solutions to the radial Schrödinger equation (2.35). On physical grounds, the radial wave functions must vanish at the origin and thus we have $\tilde{u}_l(0) = 0$. The derivative of $\tilde{u}_l$ can be chosen arbitrarily as long as it leads to linearly independent solutions. For simplicity we choose $\tilde{u}'_l(0) = 1$. From the definition (2.43) it then follows that $y_l(0)$ is a diagonal matrix with infinitely large elements. In practice, the boundary condition on $y_l$ is imposed at some point close to the origin and is taken to be large but finite.
3.5. THE LOG-DERIVATIVE METHOD

Now, let $y_{l,n}$ be the value of the logarithmic derivative in the point $R_n$ ($n = 0, 1, 2, \ldots, N$), and $h$ the distance between two neighbouring points $R_n$ and $R_{n-1}$. Furthermore, let $R_0$ be the point where the boundary condition is imposed and $R_N = R_a$ the point in which the logarithmic derivative is to be evaluated. The algorithm of Johnson is then given by:

$$y_{l,n} = (1 + hy_{l,n-1})^{-1} y_{l,n-1} - \frac{h}{3} w_n q_{l,n},$$ \hspace{1cm} (3.30)

where

$$q_{l,n} = \begin{cases} Q_l(R_n) & n = 0, 2, 4, \ldots, N \\ \left[1 + \frac{h^2}{6} Q_l(R_n)\right]^{-1} Q_l(R_n) & n = 1, 3, 5, \ldots, N - 1 \end{cases}$$ \hspace{1cm} (3.31)

and

$$w_n = \begin{cases} 1 & n = 0, N \\ 4 & n = 1, 3, 5, \ldots, N - 1 \\ 2 & n = 2, 4, 6, \ldots, N - 2 \end{cases}$$ \hspace{1cm} (3.32)

As is emphasized in Ref. [37], it is only in the final integration point $n = N$ that $y_{l,n}$ is a good approximation to the true logarithmic derivative $y_l(R_n)$. Here, the error is given by

$$y_l(R_N) = y_{l,N} + Ch^4 + O(h^6)$$ \hspace{1cm} (3.33)

where $C$ is a constant matrix and $O(h^6)$ is a matrix of sixth order in $h$. 
Chapter 4

Comments on the included papers

4.1 Paper I

Here we present results from a joint experimental and theoretical study of the core-valence double ionization of molecular oxygen (see fig. 1.2). Photoelectron spectra were recorded at three different photon energies; 605, 620, and 650 eV, using a magnetic bottle time-of-flight electron coincidence spectrometer described in Ref. [44]. Due to the increased number of unpaired electrons in the dication formed, double ionization spectra in general are more complicated than their single ionization analogues. In the present case, this is partly due to the different spin couplings that can arise when the two electrons are removed, i.e., singlets, triplets, quintets, and partly due to the gerade-ungerade splitting of the energy levels caused by the fact that the core electron can be taken from either the $1\sigma_g$ or $1\sigma_u$ orbital. In addition to the g-u splitting, which is not resolved in the present experiment, the spectral lines are also broadened by the short life time of the core hole states.

The interpretation of the photoelectron spectra has been done by comparing with the conventional valence band spectrum of O$_2$ [45, 46], as well as the vertical double ionization energies obtained from \textit{ab initio} electronic structure calculations. These calculation were carried out using the RASSCF approach described in Sec. 3.3 together with the aug-cc-pVQZ basis set. For the dicaticonic states, the RAS1 space was taken to consist of the $1\sigma_g$ and $1\sigma_u$ orbitals and was restricted to have three electrons and one hole. The RAS2 space, was taken to consist of the $(2-4)\sigma_g$, $(2-3)\sigma_u$, $(1-2)\pi_u$ and $(1-2)\pi_g$ orbitals. Within this subspace a full CI of the remaining 13 electrons were performed. Singlet, triplet and quintet states of all spatial symmetries were considered in the calculations. The ground state of the neutral molecule was optimized using the
CHAPTER 4. COMMENTS ON THE INCLUDED PAPERS

Figure 4.1: Core-valence double ionization spectra of O$_2$ measured at 560 eV photon energy. Also shown are the calculated double ionization energies associated with singlet (S), triplet (T) and quintet (Q) dicationic states. The larger bars correspond to dicationic states that are formed through pure double ionization without any further excitations or spin-flips. The calculated double ionization energies have been shifted by a constant value of +1.9 eV.

In this paper we report on a study of the mutual neutralization of H$^+$ and H$^-$ ions at low collision energies (0.001-100 eV). The main objective has been
to investigate the neutralization cross section for collision energies below a few eV, whereas the extension to higher energies has been done in order to facilitate comparison with available experiments. Our theoretical approach made use of accurate \textit{ab initio} potential energy curves and radial couplings, and both the nuclei and electrons were treated on a quantum mechanical level of theory. Because of the prototypical nature of this reaction, we decided to also investigate some more subtle effects such as those arising from the identity of the nuclei.

The negative hydrogen ion is unusual in the sense that it has only one bound state; this is the $^1S_e$ ground state \cite{47}. As a consequence, the compound $\text{H}^+ + \text{H}^-$ system is initially in either a $^1\Sigma_g^+$ or $^1\Sigma_u^+$ electronic state (there is one of each symmetry). In principle, these states have significant couplings to an infinite number of other electronic states. However, with only a few exceptions these couplings occur at small internuclear distances and therefore are shielded by the centrifugal barrier term in Eq. (2.36). This reduces the set of electronic states that need to be considered to the seven lowest $^1\Sigma_g^+$ states and the six lowest $^1\Sigma_u^+$ states.

Electron transfer reactions like the present one often are notoriously sensitive to the quality of the electronic wave functions, in particular in regions of avoided crossing. Fortunately, the $\text{H}_2$ quasi molecule is one of the few systems for which the full CI approach is feasible, and therefore the quality of the wave function is entirely determined by the choice of atomic basis set. On one hand, this basis set must be large enough to accurately describe all the excited states, including the highly correlated character of the $\text{H}^-$ ion. On the other hand, since the calculations are carried out for a wide range of internuclear distances, the basis set may not be too large, in which case severe linear dependencies may be encountered. In fact, in the present study this aspect turned out to be a limitation of the same magnitude as the miserable scaling of the FCI method with the number of basis functions. The basis set finally adopted was constructed starting from the aug-cc-pVQZ basis set of Dunning and co-workers \cite{48, 49}, adding a set of (4s, 4p, 4d) Gaussian basis functions and then manually optimizing the exponents of the diffuse functions in order to satisfy the above conditions. This procedure was highly facilitated by the possibility to compare with the analytical solutions for the separated atomic limits, as well as the very accurate \textit{ab initio} calculations reported by Wolniewicz and co-workers \cite{50, 51, 52, 53, 54}. The calculated adiabatic potential energy curves for the $(2-7)^1\Sigma_g^+$ states of $\text{H}_2$ are shown in Fig. 4.2

The non-adiabatic radial couplings were initially evaluated using the Sidis method described in detail in Ref. \cite{42}. This method has the advantage of being easy to implement, to require only one wave function calculation for each point on the potential energy curve, and to make use of integrals over the electronic angular momenta and kinetic energy operators, which are quantities readily obtained in many standard quantum chemistry programs. However, some of the coupling elements calculated in this way showed a suspiciously
Figure 4.2: Adiabatic potential energy curves for the \((2-7)^1\Sigma_g^+\) states of \(\text{H}_2\). The separated atomic limits are indicated at the far right of the figure.

Figure 4.3: Total cross section for the mutual neutralization of \(\text{H}^+\) and \(\text{H}^-\). The present results are compared with the measurements by Moseley et al. [57], Szucs et al. [58], and Peart and Hayton [59], and the calculations by Bates and Lewis [20], Fussen and Kubach [55], and Eerden et al. [56].
strange behaviour and the Sidis method where abandoned in favour of the finite difference method described in Sec. 2.1. To assure stable and accurate results, the convergence with respect to both the step length $\Delta R$ and the numerical accuracy of the HF and CI calculations were examined carefully. As is shown in the paper, the resulting coupling elements are in very good agreement with those calculated by Wolniewicz and co-workers [51].

After a transformation into a strictly diabatic basis had been performed, the scattering calculations were carried out using the Johnson log-derivative method described in Sec. 2.1 and 2.2. This yielded two sets of inelastic cross sections, one for the gerade and one for the ungerade manifold of states. The fully symmetrized cross-section, taking into account the identity of the nuclei, was obtained by properly combining the gerade and ungerade results as described in Paper II.

Our calculated total neutralization cross section is shown in Fig. 4.3. The present results are in good agreement with several of the previous theoretical studies [20, 55, 56], but is a factor of two to three higher than the only experimental cross section [57] that has been reported for collision energies below a few eV. However, this cross section has for a long time been suspected to be overestimated. Recently, new measurements of the neutralization cross section in the energy region 0.001 to 0.2 eV were performed by the group of Urbain [60] at the Université Catholique de Louvain, Belgium. Although the analysis of their experimental data is not complete, preliminary results seem to support the neutralization cross section obtained from the various theoretical treatments.
Bibliography


[60] X. Urbain, (private communication).