MASTER THESIS

Non-adiabatic effects in one-dimensional one and two electron systems:
The cases of the one-dimensional $H_2^+$ and $H_2$ molecules

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Introduction and motivations

This work has been developed to answer questions raised in the context of recent techniques employed in molecular spectroscopy such as attosecond time-resolved spectroscopy.

Molecular spectroscopy deals with the response of molecules interacting with an external electromagnetic source. The response provides structural as well as compositional information about the molecules.

In practice, the experimental analysis of spectroscopic properties is a complex task in many cases. This is specially the case when we want to understand the response of coupled electrons and ions to an external electromagnetic source.

Up until now, attosecond time-resolved and ultrashort pump-probe pulse experiments [18], [9], [4], [12], [8], [7], [13], [14], [6], [11], [3], [15] have been performed in order to try to investigate these complex coupled physical processes. Studying the inner transformations of atoms and molecules on the electronic timescale has become possible only with the recent development of isolated attosecond (10^{-18} s) laser pulses.

Thanks to advances in computer performance, computer simulations allow us to interpret with a reasonable degree of accuracy, many physical processes that occur for molecular systems when they are exposed to an external electromagnetic source [20], [23], [22], [2], [16].

However, there are still unfeasible computational tasks, such as e.g., that the electron-ion diagonalisation and time propagation processes can only be solved exactly for small molecules like H_2 [12].

In order to be able to theoretically interpret the experimental results for larger more realistic systems, the complicated electron-ion process is simplified by using various techniques such as the Born Oppenheimer Approximation (BOA), Time Dependent Density Functional Theory (TDDFT) [10] and Ehrenfest dynamics. The Born Oppenheimer Approximation assumes rigid or very slow moving ions. Time Dependent Density Functional Theory, typically used in its adiabatic approximation, may be used to describe the correlated motion of the electrons, and Ehrenfest dynamics is used for the coupled evolution of electrons and ions.

The aim of this project is a comparison among the exact electron-ion and BOA approaches to describe coupled electronic and ionic processes for small interacting systems of electrons and ions, for which the numerical exact solution of the coupled electron-ion system is feasible.

In particular, we assess the validity of the BOA with respect to the exact electron-ion solution, to quantify non-adiabatic contributions as we ficticiously vary the electron-ion mass ratio R_m = m_e/m_I [24] by means of computer simulations. The mass ratio analysis provides us with a useful check of the validity of the BOA which is based on the idea of decoupling the fast electronic and the much slower ionic motion.

This BOA assessment with respect to the exact electron-ion solution, is performed both for the static eigenvalue spectra and for the linear response spectra obtained by time propagation of an initial state exposed to an impulsive perturbation, i.e. a “kick”, which provides the initial state a finite momentum. Both spectra provide useful information about the coupled electron-ion problem. However, time propagation is somewhat closer to the
experimental situation and allows for simulation of more realistic time dependent fields (e.g., shaped ultrashort pulses).

The results of our work will help us to determine the domain of applicability of the simplified BOA, TDDFT and Ehrenfest numerical approaches and to interpret coupled electron-ion attosecond time-resolved and ultrashort pump-probe pulse experiments for more realistic systems.

The rest of the thesis is organised as follows: in the first chapter we introduce the theoretical methods used to simulate the coupled electronic and ionic processes; in the second and third chapters we use these theoretical methods to analyse the $H_2^+$ and $H_2$ molecules in 1D, respectively (during this analysis we have also provided some appendices to which the reader can refer to for more details; these appear at the end of the thesis); and finally, we summarise the main conclusions and relevant results of our work.
CHAPTER 1

Theoretical background

In this chapter we discuss the main theoretical concepts used throughout this thesis. We will also introduce the specific model systems used which are the $H_2^+$ and $H_2$ molecules in 1D.

1.1. Introducing the electron-ion Hamiltonian

The quantum mechanical motion of a many-body system composed of a collection of $N$ ions and $n$ electrons is governed by the total electron-ion time-dependent Hamiltonian (atomic units a.u. are used throughout this thesis) which in 3D can be written as:

$$\hat{H}(t) = \hat{T}_I + \hat{T}_e + \hat{V}_{II} + \hat{V}_{Ie} + \hat{V}_{ee}(t).$$  \hspace{1cm} (1.1)

Here

$$\hat{T}_I = \sum_{\alpha=1}^{N} -\frac{1}{2M_\alpha} \nabla^2 \alpha,$$ \hspace{1cm} (1.2)

with the mass $M_\alpha$ of ion $\alpha$ and

$$\hat{T}_e = \sum_{i=1}^{n} -\frac{1}{2} \nabla^2 i,$$ \hspace{1cm} (1.3)

are the ionic and electronic kinetic energy operators, respectively. The interaction between the ions is given by:

$$\hat{V}_{II} = \frac{1}{2} \sum_{\alpha,\beta=1}^{N} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|},$$ \hspace{1cm} (1.4)

where $Z_\alpha$, $Z_\beta$, $\mathbf{R}_\alpha$, and $\mathbf{R}_\beta$ are the corresponding positive charges and positions of ion $\alpha$ and $\beta$. Similarly the electron-electron repulsion is:

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i,j=1}^{n} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$ \hspace{1cm} (1.5)

where $\mathbf{r}_i$ and $\mathbf{r}_j$ are the positions of electrons $i$ and $j$, while the attraction between electrons and ions is:

$$\hat{V}_{Ie} = -\sum_{\alpha=1}^{N} \sum_{i=1}^{n} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|}.$$ \hspace{1cm} (1.6)

Finally, $\hat{V}_{ext}(t)$ describes the interaction of the system of electrons and ions with an external electromagnetic time-dependent field.
The time-dependent Schrödinger Equation then reads:

$$\frac{i}{\hbar} \frac{\partial}{\partial t} \psi(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N; r_1 s_1, r_2 s_2 \ldots r_n s_n, t) =$$

$$= \hat{H}(t) \psi(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N; r_1 s_1, r_2 s_2 \ldots r_n s_n, t),$$

(1.7)

where \(\psi\) is the total time-dependent electron-ion wavefunction which depends on the ionic and electronic position coordiantes defined previously and on the spin coordiantes \(S_\alpha\) and \(s_i\) of ion \(\alpha\) and electron \(i\), respectively.

For time-independent problems \((\hat{V}_{ext}(t) = 0)\), the general solution of the time-dependent Schrödinger Equation can be written as:

$$\psi(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N; r_1 s_1, r_2 s_2 \ldots r_n s_n, t) =$$

$$= \sum_k \epsilon_k e^{-i\epsilon_k t} \psi_k(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N; r_1 s_1, r_2 s_2 \ldots r_n s_n)$$

(1.8)

where \(\epsilon_k\) and \(\psi_k\) are the \(k^{th}\) eigenvalue and eigenstate of the stationary Schrödinger Equation

$$\hat{H} \psi_k(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N; r_1 s_1, r_2 s_2 \ldots r_n s_n) =$$

$$= \epsilon_k \psi_k(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N; r_1 s_1, r_2 s_2 \ldots r_n s_n),$$

(1.9)

with:

$$\hat{H} = \hat{T}_I + \hat{T}_e + \hat{V}_{II} + \hat{V}_{Ie} + \hat{V}_{ee}. \tag{1.10}$$

In quantum mechanics there are two basic types of particles; particles with half-integer spin which are called fermions and particles with integer spin which are called bosons. For electrons the spin is equal to \(\frac{1}{2}\) and they are therefore fermions, whereas ions can be both fermions or bosons. The many-body wavefunction must be odd under the exchange of any two identical fermions and even under the exchange of any two identical bosons. In other words, when one swaps two identical fermions, the wavefunction of the system changes sign, whereas if one swaps two identical bosons, the wavefunction of the system remains unchanged.

As an example for Eq. 1.7, we have that if ions 1 and 2 are identical fermions:

$$\psi(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N; r_1 s_1, r_2 s_2 \ldots r_n s_n, t) =$$

$$= -\psi(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N; r_1 s_1, r_2 s_2 \ldots r_n s_n, t),$$

(1.11)

and similarly for other ions which are identical fermions, whereas if ions 1 and 2 are identical bosons:

$$\psi(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N; r_1 s_1, r_2 s_2 \ldots r_n s_n, t) =$$

$$= \psi(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N; r_1 s_1, r_2 s_2 \ldots r_n s_n, t),$$

(1.12)

and similarly for other ions which are identical bosons, and for electrons 1 and 2 we have:

$$\psi(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N; r_1 s_1, r_2 s_2 \ldots r_n s_n, t) =$$

$$= -\psi(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N; r_1 s_1, r_2 s_2 \ldots r_n s_n, t),$$

(1.13)

and similarly for all other electrons as they are fermions.
1.2. The Born Oppenheimer Approximation (BOA)

In order to simplify the complicated total electron-ion many body problem, we now introduce the so called Born Oppenheimer Approximation (BOA) which is used in the vast majority of electronic structure calculations. Physically, the BOA is motivated by the fact that the mass of the ions is much larger than the electronic mass.

We specialize to the time-independent case and make a product ansatz for the solution \( \psi_k \) of the electron-ion stationary Schrödinger Equation as:

\[
\psi_k(R_1S_1, R_2S_2, \ldots R_NS_N; r_1s_1, r_2s_2 \ldots r_ns_n) = \\
= \chi(R_1S_1, R_2S_2, \ldots R_NS_N)\varphi(R_1, R_2, \ldots R_N)(r_1s_1, r_2s_2 \ldots r_ns_n), \tag{1.14}
\]

where \( \chi \) depends on the ionic coordinates only and \( \varphi \) depends on both the electronic coordinates and on the ionic coordinates which, however, only enter in the electronic wavefunctions as parameters.

Inserting Eq. 1.14 into Eq. 1.9 we obtain:

\[
\chi \hat{H}_e \varphi + \varphi \hat{T}_I \chi + \chi \sum^{N}_{\alpha=1}(-\frac{1}{M_\alpha}\nabla_{\alpha}\chi \nabla_{\alpha}\varphi) = \varepsilon_k \chi \varphi, \tag{1.15}
\]

where we have defined the electronic Hamiltonian as:

\[
\hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{II}.
\]  

We now define the BOA wavefunction in the following way: take \( \varphi_i^{(R_1, R_2, \ldots R_N)} \) to be the \( i^{th} \) eigenfunction of the “frozen ion” (with ionic coordinate \( R_\alpha \) fixed as parameters) Schrödinger Equation:

\[
\hat{H}_e \varphi_i^{(R_1, R_2, \ldots R_N)}(R_1s_1, R_2s_2 \ldots r_ns_n) = \\
= \varepsilon_i^{(R_1, R_2, \ldots R_N)} \varphi_i^{(R_1, R_2, \ldots R_N)}(R_1s_1, R_2s_2 \ldots r_ns_n). \tag{1.17}
\]

Here we solve for the electronic motion at fixed ionic coordinates to find the so called \( i^{th} \) potential energy surfaces \( \varepsilon_i^{(R_1, R_2, \ldots R_N)} \) (PES's) which are hypersurfaces in the \( 3N \) dimensional space of the ionic coordinates. \( \chi_{i,j}(R_1S_1, R_2S_2, \ldots R_NS_N) \) is the \( j^{th} \) eigenfunction of the ionic Schrödinger Equation:

\[
\hat{H}_I \chi_{i,j}(R_1S_1, R_2S_2, \ldots R_NS_N) = \\
= \varepsilon_{i,j}^{(R_1S_1, R_2S_2, \ldots R_NS_N)}, \tag{1.18}
\]

where

\[
\hat{H}_I = \sum^{N}_{\alpha=1} -\frac{1}{2M_\alpha} \nabla_{\alpha}^2 + \varepsilon_i(R_1, R_2, \ldots R_N). \tag{1.19}
\]

Note that the spin coordinates do not enter into the Hamiltonians and that now the potential for the ionic or vibrational excitations \( j \) depends on the electronic excitations, \( i \).

Then the wavefunction of the electron-ion system in the BOA is defined as:

\[
\psi_{BOA}^{i,j}(R_1S_1, R_2S_2, \ldots R_NS_N; r_1s_1, r_2s_2 \ldots r_ns_n) = \\
= \chi_{i,j}(R_1S_1, R_2S_2, \ldots R_NS_N)\varphi_i^{(R_1, R_2, \ldots R_N)}(r_1s_1, r_2s_2 \ldots r_ns_n). \tag{1.20}
\]

Comparing Eq. 1.20 with Eq. 1.15 we realize that the last two terms of the left hand side of Eq. 1.15 are neglected in the BOA.

Physically, this means that we neglect that the movement of the ions can excite or affect the electronic state of the molecule. Due to the large difference between the electron and a generic ion mass, \( m_I \geq 1836 m_e \) the electrons move much faster than the ions so
that the movement due to the kinetic energy of the ions does not cause the excitation of the electrons to another electronic state (adiabatic approximation).

In Sec. 1.4.1 we will give a more quantitative argument based on time-independent perturbation theory to justify the BOA.

1.3. Model systems: the \( H_2^+ \) and \( H_2 \) molecules in 1D

In this section we will introduce the model systems that we have used which correspond to the \( H_2^+ \) and \( H_2 \) molecules in 1D.

As we want to understand in an easy way what happens when we go beyond the BOA, i.e., when we cannot neglect the coupling of ionic and electronic motion, we use small and simple systems such as the \( H_2^+ \) and \( H_2 \) molecules in 1D. Using small and simple systems has the advantage that the computational effort to carry out the calculations is significantly reduced and one can in fact solve exactly the numerical problem. On the other hand, the qualitative features of the PES’s in 1D (see the first four PES’s in Fig. 2.8 for \( H_2^+ \) and in Fig. 3.8 for \( H_2 \)) are the same as in 3D for diatomic molecules.

Instead of using the bare Coulomb interaction in 1D we model the interactions between any type of particles by the so called “Soft Coulomb interaction” which for particles \( i \) and \( j \) with charges \( q_i \) and \( q_j \) takes the form:

\[
V_{int}(x_i - x_j) = \frac{q_i q_j}{\sqrt{(x_i - x_j)^2 + a^2}},
\]

where \( a \) is the Soft Coulomb parameter. This parameter \( a \) is a length scale that does not appear in the bare Coulomb potential. The reason for using this modified interaction is that the bare Coulomb interaction is too singular in 1D. This may lead to physically pathological features such as, e.g., an infinite ground state energy of the 1D \( H \) atom as \( a \to 0 \). [19].

1.3.1. \( H_2^+ \) model system in 1-D. \( H_2^+ \) is a diatomic molecule which consists of three particles: two protons and one electron (Fig. 1.1).

The classical energy of the one-dimesional \( H_2^+ \) molecule (Fig. 1.1) is given by:

\[
E = \frac{1}{2} M V_1^2 + \frac{1}{2} M V_2^2 + \frac{1}{2} v^2 - \frac{1}{\sqrt{(r - R_1)^2 + a^2}} + \frac{1}{\sqrt{(R_2 - r)^2 + a^2}} + \frac{1}{\sqrt{(R_2 - R_1)^2 + a^2}},
\]

where \( M \) is the proton mass; \( V_1 \) and \( V_2 \) are the proton velocities; \( R_1 \) and \( R_2 \) are the proton positions; \( v \) is the electron velocity; and \( r \) is the electron position.

The first three terms of Eq. 1.22 represent the kinetic energy of the two protons and the electron, respectively. The last three terms represent the potential energy, i.e., the electrostatic attraction between each proton and the electron, and the corresponding repulsion between the two protons, respectively.
1.3.3. Model systems: The $H_2^+$ and $H_2$ molecules in 1D

1.3.2. Centre of mass transformation of the $H_2^+$ model system in 1D. The spatial configuration of the $H_2^+$ molecule in 1D is described by three variables: $R_1$, $r$ and $R_2$ (see Fig. 1.1). However, the geometry of the molecule does not change if the particle positions are translated uniformly (i.e., if every particle is translated in the same way). Therefore, there are two internal degrees of freedom.

To rewrite the classical energy in Eq. 1.22 in terms of the uniform translation and the internal degrees of freedom of the molecule, we use the centre-of-mass transformation. The quantum momentum operators are used instead of the correspondent classical momenta to obtain the following Hamiltonian:

$$\hat{H} = -\frac{1}{2(2M + 1)} \frac{\partial^2}{\partial R_{CM}^2} + \hat{H}_{int}(R, \xi),$$

where $\hat{H}_{int}$ is the internal Hamiltonian, which depends only on the internal coordinates $R$ and $\xi$:

$$\hat{H}_{int}(R, \xi) = -\frac{1}{2\mu_I} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_e} \frac{\partial^2}{\partial \xi^2} + \frac{1}{\sqrt{(\frac{R}{2} + \xi)^2 + a^2}} - \frac{1}{\sqrt{(\frac{R}{2} - \xi)^2 + a^2}} + \frac{1}{\sqrt{R^2 + a^2}}.$$ (1.24)

Here, the reduced ion mass is:

$$\mu_I = \frac{M}{2},$$ (1.25)

the reduced electron mass is:

$$\mu_e = \frac{2M}{2M + 1},$$ (1.26)

and:

$$R_{CM} = \frac{M(R_1 + R_2) + r}{2M + 1},$$ (1.27)

$$R = R_2 - R_1,$$ (1.28)

$$\xi = r - \frac{R_1 + R_2}{2},$$ (1.29)

where $R_{CM}$ is the global centre of mass, $R$ is the distance between the ions and $\xi$ is the distance between the centre of mass of the ions and $r$.

We are now interested in a solution of the time-independent Schrödinger Equation:

$$\hat{H}\Psi(R_{CM}, R, \xi) = \varepsilon_{tot}\Psi(R_{CM}, R, \xi).$$ (1.30)

We can factorise the centre-of-mass motion by using the following ansatz for the wavefunction:

$$\Psi(R_{CM}, R, \xi) = e^{ikR_{CM}}\psi(R, \xi),$$ (1.31)

which is a solution of Eq. 1.30 if $\psi(R, \xi)$ is a solution of:

$$\hat{H}_{int}(R, \xi)\psi(R, \xi) = \varepsilon_{int}\psi(R, \xi),$$ (1.32)

and the total energy eigenvalue is:

$$\varepsilon_{tot} = \frac{k^2}{2(2M + 1)} + \varepsilon_{int}.$$ (1.33)

---

1 The internal degrees of freedom are given in 1D by $N - 1$, where $N$ is the number of particles which constitute the molecule.
The first term in Eq. 1.33 is the translational energy of the total system of mass $2M + 1$ moving with constant momentum $k$.

### 1.3.3. $H_2$ model system in 1-D

$H_2$ is a diatomic molecule which consists of four particles: two protons and two electrons (Fig. 1.2).

![Diagram of H2 molecule](image)

**Figure 1.2.** Schematic representation of the $H_2$ molecule in 1-D: $V_1$ and $V_2$ are the proton velocities; $R_1$ and $R_2$ are the proton positions; $v_1$ and $v_2$ are the electron velocities; and $r_1$ and $r_2$ are the electron positions.

The classical energy of the one-dimensional $H_2$ molecule (Fig. 1.2) is:

$$E = \frac{1}{2} MV_1^2 + \frac{1}{2} MV_2^2 + \frac{1}{2} v_1^2 + \frac{1}{2} v_2^2 + \frac{1}{\sqrt{(r_1 - R_1)^2 + a^2}} + \frac{1}{\sqrt{(R_2 - R_1)^2 + a^2}} + \frac{1}{\sqrt{(r_2 - r_1)^2 + a^2}} + \frac{1}{\sqrt{(R_2 - r_2)^2 + a^2}}$$  \hspace{1cm} (1.34)

where $M$ is the proton mass; $V_1$ and $V_2$ are the proton velocities; $R_1$ and $R_2$ are the proton positions; $v_1$ and $v_2$ are the electron velocities; and $r_1$ and $r_2$ are the electron positions.

The first four terms of Eq. 1.34 represent the kinetic energies of the two protons and the two electrons, respectively. The last six terms represent the potential energies, i.e., the electrostatic attraction between each proton and each electron, and the corresponding repulsion between the two protons and the two electrons, respectively.

### 1.3.4. Centre of mass transformation of the $H_2$ model system in 1-D

The spatial configuration of the $H_2$ molecule in 1D is described by four variables: $R_1$, $r_1$, $r_2$, and $R_2$ (see Fig. 1.2). In this case, there are three internal degrees of freedom.

As before, in order to rewrite the classical energy in Eq. 1.34 in terms of the uniform translation and the internal degrees of freedom of the molecule, we use the centre-of-mass transformation (see details in Appendix A.2). Note that in Appendix A.2 we have performed the centre of mass transformation with respect to the centre of mass of the protons and the centre of mass of the electrons. This transformation has the advantage that for two identical fermions (both electrons and protons are fermions) the fermionic symmetry can be mapped in the wavefunction parity (see Sec. 1.3.5). This is not as clear if we choose other possible transformations. Again, we replace the classical momenta by the quantum momentum operators to obtain the following Hamiltonian:

$$\hat{H} = -\frac{1}{2(2M + 2)} \frac{\partial^2}{\partial R_{CM}^2} + \hat{H}_{int}(R, r, \xi),$$  \hspace{1cm} (1.35)

where $\hat{H}_{int}$ is the internal Hamiltonian, which depends only on the internal coordinates $R$, $r$ and $\xi$. 

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1.3. MODEL SYSTEMS: THE $H_2^+$ AND $H_2$ MOLECULES IN 1D

\[ \hat{H}_{\text{int}}(R, r, \xi) = -\frac{1}{2\mu_I} \frac{\partial^2}{\partial R^2} - \frac{1}{2\tilde{\mu}_e} \frac{\partial^2}{\partial r^2} - \frac{1}{2\mu_{eI}} \frac{\partial^2}{\partial \xi^2} + \]
\[ -\frac{1}{\sqrt{R_2^2 - \xi^2 + a^2}} - \frac{1}{\sqrt{(R/2 - \xi/2 + \xi/2)^2 + a^2}} + \]
\[ -\frac{1}{\sqrt{(R/2 + \xi/2 + \xi/2)^2 + a^2}} + \frac{1}{\sqrt{R^2 + a^2}} + \frac{1}{\sqrt{r^2 + a^2}}, \]  
(1.36)

Here, $\mu_I$ was defined in Eq. 1.25, the reduced mass of the electrons is:
\[ \tilde{\mu}_e = \frac{1}{2}, \]  
(1.37)

the reduced mass of a combined particle formed by the protons and electrons is:
\[ \mu_{eI} = \frac{2M}{1 + M}, \]  
(1.38)

and:
\[ R_{CM} = \frac{M(R_1 + R_2) + 2(r_1 + r_2)}{2M + 2}, \]  
(1.39)
\[ R = R_2 - R_1, \]  
(1.40)
\[ r = r_2 - r_1, \]  
(1.41)
\[ \xi = \frac{r_1 + r_2}{2} - \frac{R_1 + R_2}{2}, \]  
(1.42)

where $R_{CM}$ is the global centre of mass, $R$ is the distance between the ions and $\xi$ is the distance between the centre of mass of the ions and the centre of mass of the electrons.

As before, we are now interested in a solution of the time-independent Schrödinger Equation:
\[ \hat{H}_{\text{int}}(R, r, \xi) = \epsilon_{\text{tot}} \Psi(R_{CM}, R, r, \xi). \]  
(1.43)

We can factorise the centre-of-mass motion by using the following ansatz for the wavefunction:
\[ \Psi(R_{CM}, R, r, \xi) = e^{ikR_{CM}} \psi(R, r, \xi), \]  
(1.44)

which is a solution of Eq. 1.43 if $\psi(R, r, \xi)$ is a solution of:
\[ \hat{H}_{\text{int}}(R, r, \xi) \psi(R, r, \xi) = \epsilon_{\text{int}} \psi(R, r, \xi), \]  
(1.45)

and the total energy eigenvalue is:
\[ \epsilon_{\text{tot}} = \frac{k^2}{2(2M + 2)} + \epsilon_{\text{int}}. \]  
(1.46)

The first term in Eq. 1.46 is the translational energy of the total system of mass $2M + 2$ moving with constant momentum $k$. 
1.3.5. Symmetries of the wavefunction for the $H_2^+$ and $H_2$ molecules in 1-D. The total wavefunction $\Psi_{H_2^+}$ for $H_2^+$ and $\Psi_{H_2}$ for $H_2$ in the original coordinates (see Figs. 1.1 and 1.2) can be written as:

$$\Psi_{H_2^+}(R_1S_1, R_2S_2, rs), \quad (1.47)$$

and

$$\Psi_{H_2}(R_1S_1, R_2S_2, r_1s_1, r_2s_2), \quad (1.48)$$

where $r$ and $s$ represent the position of the electron and its spin for the $H_2^+$ molecule, $r_1, r_2$ and $s_1, s_2$ represent the positions and the spins of the two electrons for the $H_2$ molecule, and $R_1, R_2$ and $S_1, S_2$ represent the positions and the spins of the two protons for both molecules.

Since in the $H_2^+$ molecule there are one electron and two protons (which are fermions), the antisymmetry of the many-body wavefunction must be enforced for the protons only as:

$$\Psi_{H_2^+}(R_1S_1, R_2S_2, rs) = -\Psi_{H_2^+}(R_2S_2, R_1S_1, rs). \quad (1.49)$$

For the $H_2$ molecule there are two electrons and two protons, therefore, the antisymmetry of the many-body wavefunction must be enforced both for the protons and the electrons as:

$$\Psi_{H_2}(R_1S_1, R_2S_2, r_1s_1, r_2s_2) = -\Psi_{H_2}(R_2S_2, R_1S_1, r_1s_1, r_2s_2), \quad (1.50)$$

and

$$\Psi_{H_2}(R_1S_1, R_2S_2, r_1s_1, r_2s_2) = -\Psi_{H_2}(R_1S_1, R_2S_2, r_2s_2, r_1s_1), \quad (1.51)$$

respectively.

For two identical particles the many-body wavefunction can be factorised into a spin and spatial part as:

$$\Psi_{H_2^+}(R_1S_1, R_2S_2, rs) = \Phi_{H_2^+}(R_1R_2, r)|s\rangle_e|SM\rangle_I, \quad (1.52)$$

and

$$\Psi_{H_2}(R_1S_1, R_2S_2, r_1s_1, r_2s_2) = \Phi_{H_2}(R_1R_2, r_1r_2)|sm\rangle_e|SM\rangle_I. \quad (1.53)$$

where the subscripts “e” and “I” refer to electronic and ionic spin coordinates, respectively.

For spin $\frac{1}{2}$ fermions, the single particle spin basis functions are denoted as $|\uparrow\rangle_\gamma, |\downarrow\rangle_\gamma$ with $\gamma \in [e, I]$.

The total spin quantum number of the ionic wavefunction for $H_2^+$ and of the ionic and electronic wavefunction for $H_2$ can be zero (singlet state) or one (triplet state).

The singlet state is given by:

$$|0, 0\rangle_\gamma = \frac{1}{\sqrt{2}}(|\uparrow\rangle_\gamma - |\downarrow\rangle_\gamma) \quad S = 0 \text{ (singlet)}, \quad (1.54)$$

while the three triplet states are:

$$|1, -1\rangle_\gamma = |\downarrow\rangle_\gamma \quad |1, 0\rangle_\gamma = \frac{1}{\sqrt{2}}(|\uparrow\rangle_\gamma + |\downarrow\rangle_\gamma) \quad S = 1 \text{ (triplet)}, \quad (1.55)$$

If the particles are exchanged, the singlet state changes sign (antisymmetric) while the sign of the triplet state remains unchanged (symmetric). Therefore, in order to have a
total antisymmetric many-body wavefunction, the spatial part of the ionic and electronic wavefunction must be antisymmetric for the triplet state and symmetric for the singlet state. As a consequence, we will only be concerned with the spatial part of the wavefunction, the spin part already being separated off due to the exchange symmetry of the many-body wavefunction.

The antisymmetry in the ionic coordinates requires that the spatial part in the centre of mass frame of the $H^+_2$ wavefunction in the singlet state:

$$\Psi_{H^+_2}(R, \xi) = \Psi_{H^+_2}(-R, \xi),$$

and similarly for the $H_2$ molecule:

$$\Psi_{H_2}(R, r, \xi) = \Psi_{H_2}(-R, r, \xi).$$

For $H_2$, the antisymmetry in the electronic coordinates requires that the spatial part in the centre of mass frame of the $H_2$ wavefunction in the singlet state:

$$\Psi_{H_2}(R, r, \xi) = \Psi_{H_2}(R, -r, \xi).$$

Similarly, in the triplet state we have with respect to the antisymmetry of the ionic coordinates:

$$\Psi_{H^+_2}(R, \xi) = -\Psi_{H^+_2}(-R, \xi),$$

and

$$\Psi_{H_2}(R, r, \xi) = -\Psi_{H_2}(-R, r, \xi),$$

and for the antisymmetry in the electronic coordinates:

$$\Psi_{H_2}(R, r, \xi) = -\Psi_{H_2}(R, -r, \xi).$$

1.4. The BOA in 1D for the $H_2^+$ and $H_2$ molecules

Within the BOA we search for a solution of Eqs. 1.32 and 1.45 in the form of a wavefunction factorised or decoupled in ionic and electronic parts as:

$$\psi(R, \xi) = \psi_{i,j}(R, \xi) = \chi_{i,j}(R)\varphi_i(R, \xi),$$

for $H_2^+$ and

$$\psi(R, r, \xi) = \psi_{i,j}(R, r, \xi) = \chi_{i,j}(R)\varphi_i(R, r, \xi),$$

for $H_2$ where $\varphi_i(R, \xi)$ and $\varphi_i(R, r, \xi)$ are the $i^{th}$ eigenfunctions of the “frozen ion” ($R$ is fixed as a parameter) Schrödinger Equations:

$$\hat{H}_e(R, \xi)\varphi_i(R, \xi) = \epsilon_i(R)\varphi_i(R, \xi),$$

and

$$\hat{H}_e(R, r, \xi)\varphi_i(R, r, \xi) = \epsilon_i(R)\varphi_i(R, r, \xi),$$

from which we solve for the electronic motion at fixed interionic distances $R$ to obtain the PES $\epsilon_i(R)$.

Here, we have defined the electronic “frozen ion” Hamiltonian for $H_2^+$ as:

$$\hat{H}_e(R, \xi) = \frac{1}{2\mu\epsilon} \frac{\partial^2}{\partial \xi^2} - \frac{1}{\sqrt{(\frac{R}{2} + \xi)^2 + a^2}} - \frac{1}{\sqrt{(\frac{R}{2} - \xi)^2 + a^2}} + \frac{1}{\sqrt{R^2 + a^2}},$$

and for $H_2$ as:
\begin{equation}
\hat{H}_e(R, r, \xi) = -\frac{1}{2\mu_e \frac{\partial^2}{\partial r^2}} - \frac{1}{2\mu_e \frac{\partial^2}{\partial \xi^2}} - \frac{1}{\sqrt{\left(\frac{R}{2} - \frac{r}{2} + \frac{\xi}{2}\right)^2 + a^2}} + \frac{1}{\sqrt{\left(\frac{R}{2} + \frac{r}{2} + \frac{\xi}{2}\right)^2 + a^2}} + \frac{1}{\sqrt{R^2 + a^2}} + \frac{1}{\sqrt{r^2 + a^2}},
\end{equation}

and \(\chi_{i,j}(R)\) is the \(j\)th eigenfunction of the effective ionic Schrödinger Equation:

\begin{equation}
\hat{H}_I^i(R)\chi_{i,j}(R) = \varepsilon_{i,j}\chi_{i,j}(R),
\end{equation}

where

\begin{equation}
\hat{H}_I^i(R) = -\frac{1}{2\mu_I \frac{\partial^2}{\partial R^2}} + \varepsilon_i(R).
\end{equation}

Note that now the potential for the ionic or vibrational excitations \(j\) depends on the electronic excitations, \(i\).

### 1.4.1. Perturbative argument to justify the BOA for the \(H_2^+\) and \(H_2\) molecules in 1D

The accuracy of the static BOA calculations can be understood from a perturbation theory argument in terms of the small parameter \((\frac{m_e}{m_I})^{\frac{1}{4}}\) [1], [24].

We illustrate this in more detail for the 1D \(H_2^+\) molecule whose internal Hamiltonian (see Eq. 1.24) is given by:

\begin{equation}
\hat{H}_{\text{int}}(R, \xi) = -\frac{1}{2\mu_I \frac{\partial^2}{\partial \xi^2}} + V(R, \xi),
\end{equation}

where we have defined:

\begin{equation}
V(R, \xi) = -\frac{1}{\sqrt{\left(\frac{R}{2} + \frac{\xi}{2}\right)^2 + a^2}} - \frac{1}{\sqrt{\left(\frac{R}{2} - \frac{\xi}{2}\right)^2 + a^2}} + \frac{1}{\sqrt{R^2 + a^2}} + \frac{1}{\sqrt{R^2 + a^2}}.
\end{equation}

We write the interionic coordinate as:

\begin{equation}
R = R_{eq} + \kappa \zeta,
\end{equation}

where \(R_{eq}\) is the interionic equilibrium distance of the BOA PES for the electronic ground state and:

\begin{equation}
\kappa = \left(\frac{m_e}{m_I}\right)^{\frac{1}{4}},
\end{equation}

is the small parameter used for the perturbation expansion shown below.

Expansion of Eq. 1.70 in terms of \(\kappa\) using Eq. 1.72 leads to:

\begin{align}
\hat{H}_{\text{int}}(R_{eq} + \kappa \zeta, \xi) &\approx -\frac{1}{2\mu_I} \kappa^2 \frac{\partial^2}{\partial \zeta^2} - \frac{1}{2\mu_e} \frac{\partial^2}{\partial \xi^2} + V(R_{eq}, \xi) + \\
&+ \kappa \frac{\partial}{\partial R} V(R, \xi)|_{R=R_{eq}} \zeta + \frac{1}{2!} \kappa^2 \frac{\partial^2}{\partial R^2} V(R, \xi)|_{R=R_{eq}} \zeta^2 + \\
&+ \frac{1}{3!} \kappa^3 \frac{\partial^3}{\partial R^3} V(R, \xi)|_{R=R_{eq}} \zeta^3 + O(\kappa^4).
\end{align}

We sort the Hamiltonian in different powers of \(\kappa\). The zeroth order term is the electronic frozen ion Hamiltonian:
\[ \hat{H}^{(0)} = -\frac{1}{2\mu_e} \frac{\partial^2}{\partial \kappa^2} + V(R_{eq}, \xi). \] (1.75)

The first, second and third order terms are given by:

\[ \hat{H}^{(1)} = \frac{\partial}{\partial R} V(R, \xi)_{R=R_{eq}} \xi, \] (1.76)

\[ \hat{H}^{(2)} = -\frac{1}{2\mu_e} \frac{\partial^2}{\partial \kappa^2} + \frac{1}{2!} \frac{\partial^2}{\partial R^2} V(R, \xi)_{R=R_{eq}} \xi^2, \] (1.77)

\[ \hat{H}^{(3)} = \frac{1}{3!} \frac{\partial^3}{\partial R^3} V(R, \xi)_{R=R_{eq}} \xi^3. \] (1.78)

Expanding the time-independent internal Schrödinger Equation Eq.1.32 in powers of \( \kappa \), we obtain:

\[ (\hat{H}^{(0)} + \kappa^1 \hat{H}^{(1)} + \kappa^2 \hat{H}^{(2)} + \kappa^3 \hat{H}^{(3)})[\psi^{(0)}] + \kappa^1 [\psi^{(1)}] + \kappa^2 [\psi^{(2)}] + \kappa^3 [\psi^{(3)}] = 0. \]

(1.79)

We decompose this equation order by order to obtain the following four equations:

\[ O(\kappa^0) : \hat{H}^{(0)} \psi^{(0)} = \epsilon^{(0)} \psi^{(0)} \] (1.80)

\[ O(\kappa^1) : \hat{H}^{(0)} \psi^{(1)} + \hat{H}^{(1)} \psi^{(0)} = \epsilon^{(0)} \psi^{(1)} + \epsilon^{(1)} \psi^{(0)} \] (1.81)

\[ O(\kappa^2) : \hat{H}^{(0)} \psi^{(2)} + \hat{H}^{(1)} \psi^{(1)} + \hat{H}^{(2)} \psi^{(0)} = \epsilon^{(0)} \psi^{(2)} + \epsilon^{(1)} \psi^{(1)} + \epsilon^{(2)} \psi^{(0)} \] (1.82)

\[ O(\kappa^3) : \hat{H}^{(0)} \psi^{(3)} + \hat{H}^{(1)} \psi^{(2)} + \hat{H}^{(2)} \psi^{(1)} + \hat{H}^{(3)} \psi^{(0)} = \epsilon^{(0)} \psi^{(3)} + \epsilon^{(1)} \psi^{(2)} + \epsilon^{(2)} \psi^{(1)} + \epsilon^{(3)} \psi^{(0)} \] (1.83)

We note that \( \hat{H}^{(0)} \) is a purely electronic operator depending on a parameter \( R_{eq} \) (see Eq. 1.75) and \( \epsilon^{(0)} \) is the zeroth-order energy which corresponds to the electronic motion. Therefore, we choose the zeroth-order wavefunction as:

\[ \psi^{(0)}(R_{eq}, \xi, \zeta) = \chi(\zeta) \varphi^{(0)}(R_{eq}, \xi), \] (1.84)

where \( \varphi^{(0)} \) is the electronic ground state wavefunction of \( \hat{H}^{(0)} \) and \( \chi(\zeta) \) is the ionic wavefunction which will be specified later.

Multiplying Eq. 1.81 times [\( \psi^{(0)} \)] and integrating over both electronic and ionic coordinates we obtain for the first-order correction to the energy:

\[ \epsilon^{(1)} = \langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(0)} \rangle = \langle \varphi^{(0)} | \frac{\partial}{\partial R} V(R, \xi)_{R=R_{eq}} | \varphi^{(0)} \rangle \langle \chi(\zeta) | \chi \rangle. \] (1.85)

By virtue of the Hellmann-Feynman Theorem (see Appendix B), \( \epsilon^{(1)} \) has to vanish.

\[ \epsilon^{(1)} = \langle \varphi^{(0)} | \frac{\partial}{\partial R} V(R, \xi)_{R=R_{eq}} | \varphi^{(0)} \rangle \langle \chi(\zeta) | \chi \rangle = 0. \] (1.86)
The absence of the first order term is related to the existence of an equilibrium position of the ions, in which the electronic energy for frozen ions is at a minimum and therefore the first derivative with respect to the energy is zero.

The first order correction to the wavefunction from Eqs. 1.81, 1.84 and 1.86 is:

$$|\psi^{(1)}\rangle = -\sum_{n>0} \frac{\langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_0^{(0)} \rangle}{\varepsilon_n^{(0)} - \varepsilon_0^{(0)}} |\psi_0^{(0)}\rangle$$

$$= -\sum_{n>0} \frac{\langle \psi_n^{(0)} | \frac{\partial}{\partial R} V(R, \xi) | R = R_{eq} \rangle \chi |\psi_n^{(0)}\rangle}{\varepsilon_n^{(0)} - \varepsilon_0^{(0)}}$$

$$= -\sum_{n>0} \frac{\langle \psi_n^{(0)} | \frac{\partial}{\partial R} V(R, \xi) | R = R_{eq} \rangle |\psi_n^{(0)}\rangle \chi}{\varepsilon_n^{(0)} - \varepsilon_0^{(0)}} \zeta \chi,$$

where \(\varepsilon_n^{(0)}\) and \(|\psi_n^{(0)}\rangle\) are the \(n^{th}\) electronic eigenvalue and eigenstate of the Hamiltonian \(\hat{H}^{(0)}\).

Multiplying Eq. 1.82 times \(\langle \psi^{(0)}|\) and integrating over both electronic and ionic coordinates we obtain the second-order correction to the energy:

$$\varepsilon^{(2)} = \langle \psi^{(0)} | \hat{H}^{(2)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(1)} \rangle =$$

$$= \langle \chi | -\frac{1}{2\mu_I} \frac{\partial^2}{\partial \zeta^2} |\chi\rangle + \langle \varphi^{(0)} | \frac{1}{2\mu_I} \frac{\partial^2}{\partial R^2} V(R, \xi) | R = R_{eq} \rangle |\varphi^{(0)}\rangle \langle \chi | \zeta^2 |\chi\rangle +$$

$$- \sum_{n>0} \frac{|\langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_0^{(0)} \rangle|^2}{\varepsilon_n^{(0)} - \varepsilon_0^{(0)}} =$$

$$= \langle \chi | -\frac{1}{2\mu_I} \frac{\partial^2}{\partial \zeta^2} |\chi\rangle + \langle \varphi^{(0)} | \frac{1}{2\mu_I} \frac{\partial^2}{\partial R^2} V(R, \xi) | R = R_{eq} \rangle |\varphi^{(0)}\rangle \langle \chi | \zeta^2 |\chi\rangle +$$

$$- \sum_{n>0} \frac{|\langle \varphi_n^{(0)} | \frac{\partial}{\partial R} V(R, \xi) | R = R_{eq} \rangle |\varphi_n^{(0)}\rangle|^2}{\varepsilon_n^{(0)} - \varepsilon_0^{(0)}} \langle \chi | \zeta^2 |\chi\rangle.$$

We now choose \(\chi(\zeta)\) (see Eq. 1.84) to be the lowest eigenfunction of the harmonic oscillator problem so that we can write:

$$\varepsilon^{(2)} = \langle \chi | -\frac{1}{2\mu_I} \frac{\partial^2}{\partial \zeta^2} |\chi\rangle + \frac{1}{2\mu_I} k \langle \chi | \zeta^2 |\chi\rangle = \frac{1}{2} \omega_I$$

(1.89)

where:

$$k = \langle \varphi^{(0)} | \frac{\partial^2}{\partial R^2} V(R, \xi) | R = R_{eq} \rangle +$$

$$- 2 \sum_{n>0} \frac{|\langle \varphi_n^{(0)} | \frac{\partial}{\partial R} V(R, \xi) | R = R_{eq} \rangle |\varphi_n^{(0)}\rangle|^2}{\varepsilon_n^{(0)} - \varepsilon_0^{(0)}},$$

(1.90)

and:

$$\omega_I = \sqrt{\frac{k}{\mu_I}}.$$  

(1.91)

Therefore the ionic zero-point vibrations correspond to second-order corrections to the energy.

Finally, from Eq. 1.83 times \(\langle \psi^{(0)}|\) and integrating over both electronic and ionic coordinates we obtain for the third-order correction to the energy:
where the second-order correction to the wavefunction is from Eqs. 1.82, 1.86 and 1.87:

\[ |\psi^{(0)}\rangle = \langle \psi^{(0)}| \hat{H}^{(1)}|\psi^{(0)}\rangle + \langle \psi^{(0)}| \hat{H}^{(2)}|\psi^{(1)}\rangle + \langle \psi^{(0)}| \hat{H}^{(3)}|\psi^{(0)}\rangle = \]

\[ = \langle \varphi^{(0)}| \frac{\partial}{\partial R} V(R, \xi)|_{R=R_{eq}}|\varphi^{(2)}\rangle \langle \chi|\xi^2|\chi\rangle + \]

\[ + \langle \chi| - \frac{1}{2\mu_I} \frac{\partial^2}{\partial \xi^2} |\chi\rangle + \langle \varphi^{(0)}| \frac{1}{2!} \frac{\partial^2}{\partial R^2} V(R, \xi)|_{R=R_{eq}}|\varphi^{(1)}\rangle \langle \chi|\xi^2|\chi\rangle + \]

\[ + \langle \varphi^{(0)}| \frac{1}{3!} \frac{\partial^3}{\partial R^3} V(R, \xi)|_{R=R_{eq}}|\varphi^{(0)}\rangle \langle \chi|\xi^3|\chi\rangle, \]

where the second-order correction to the wavefunction is from Eqs. 1.82, 1.86 and 1.87:

\[ |\psi^{(2)}_0\rangle = \sum_{n>0} \frac{\langle \psi^{(0)}_n| \hat{H}^{(1)}|\psi^{(0)}_n\rangle |\psi^{(0)}_n\rangle}{\varepsilon^{(0)}_n - \varepsilon^{(0)}_0} + \]

\[ + \sum_{n>0} \frac{\langle \psi^{(0)}_n| (\hat{H}^{(2)} - \hat{H}^{(1)})|\psi^{(0)}_n\rangle |\psi^{(0)}_n\rangle}{\varepsilon^{(0)}_n - \varepsilon^{(0)}_0}. \]

All the terms from Eq. 1.92 using Eqs. 1.87 and 1.93 vanish by symmetry, as they are all proportional to \( \langle \psi^{(0)}| \hat{H}^{(3)}|\psi^{(0)}\rangle \) where \( \hat{H}^{(3)} \) is odd in \( \zeta \) and \( \psi^{(0)} \) is even in \( \zeta \) leading to \( \varepsilon^{(3)} = 0 \).

Therefore the total energy in 1-D is given by

\[ \varepsilon^{BOA} = \varepsilon^{(0)} + \varepsilon^{(2)} + O(\kappa^4), \]

i.e., the BOA energy expression gives the correct total ground state energy of the full electron-ion problem up to the fourth order in \( \kappa \).

For the \( H_2 \) molecule we follow the same procedure as for \( H_2^{+} \) using Eq. 1.36.

\[ \hat{H}_{int}(R, r, \xi) = -\frac{1}{2\mu_I} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_e} \frac{\partial^2}{\partial r^2} - \frac{1}{2\mu_{eI}} \frac{\partial^2}{\partial \xi^2} + V(R, r, \xi), \]

where we have defined:

\[ V(R, r, \xi) = -\frac{1}{\sqrt{\left(\frac{R}{2} - \frac{r}{2} + \xi\right)^2 + a^2}} - \frac{1}{\sqrt{\left(\frac{R}{2} - \frac{r}{2} - \xi\right)^2 + a^2}} + \]

\[ -\frac{1}{\sqrt{\left(\frac{R}{2} + \frac{r}{2} + \xi\right)^2 + a^2}} - \frac{1}{\sqrt{\left(\frac{R}{2} + \frac{r}{2} - \xi\right)^2 + a^2}} + \frac{1}{\sqrt{R^2 + a^2}} + \frac{1}{\sqrt{r^2 + a^2}}. \]

In this case the electronic motion is given by:

\[ \hat{H}^{(0)} = -\frac{1}{2\mu_e} \frac{\partial^2}{\partial r^2} - \frac{1}{2\mu_{eI}} \frac{\partial^2}{\partial \xi^2} + V(R_{eq}, r, \xi), \]

All the other terms remain the same as for \( H_2^{+} \), we just have to consider that now the potential also depends on \( r \).

Therefore, we conclude that in 1D, as we have no rotations, the first order correction to the ground state energy for the full electron-ion problem using the BOA is the term of fourth order in \( \kappa \), whereas in 3D this correction corresponds to the sixth order term.
1.5. Linear response spectra from time-propagation

In this section, we show how we calculate the optical spectra of the \( H_2^+ \) and \( H_2 \) molecules within linear response. For the moment we have only calculated the optical spectra for \( H_2^+ \) and it is currently in progress for \( H_2 \).

To calculate the optical spectra we solve the time-dependent Schrödinger Equation for an initial state which is obtained from the ground state \( |\psi_{gs}\rangle \) by applying an instantaneous “kick” with momentum \( k \). This kicked initial electronic state is given by [25]:

\[
|\psi(t = 0)\rangle = e^{ikt}|\psi_{gs}\rangle.
\]  

This initial electronic state can be expressed as a linear combination of eigenvectors \( m \):

\[
|\psi(t = 0)\rangle = \sum_m |\psi_m\rangle\langle \psi_m |\psi(t = 0)\rangle = \sum_m c_m |\psi_m\rangle.
\]  

Note that here we have introduced the completeness relation using \( 1 = \sum_m |\psi_m\rangle\langle \psi_m |\).

Then the time-dependent Schrödinger equation with this initial non-stationary electronic state is solved by propagating:

\[
|\psi(t)\rangle = e^{-iH_0\Delta t}|\psi(t = 0)\rangle = \sum_m c_m e^{-i\varepsilon_m t}|\psi_m\rangle.
\]  

If \( k^{-1} \) is small compared to the extension of the system, then we can use the dipole approximation and expand Eq. 1.100 as:

\[
|\psi(t)\rangle \approx e^{-i\varepsilon_{gs} t}|\psi_{gs}\rangle + ik \sum_m e^{-i\varepsilon_m t}\langle \psi_m |\hat{\mathbf{x}}|\psi_{gs}\rangle|\psi_m\rangle.
\]  

The expectation value of the dipole moment \( d(t) \) at time \( t \):

\[
d(t) = \langle \psi(t) |\hat{\mathbf{x}}| \psi(t)\rangle,
\]  

which by using Eq. 1.101 can be written as:

\[
d(t) = \langle \psi_{gs} |e^{i\varepsilon_{gs} t} - ik \sum_m e^{i\varepsilon_m t}\langle \psi_m |\hat{\mathbf{x}}|\psi_{gs}\rangle|\psi_m\rangle
\[
= ik \sum_m e^{i(\varepsilon_m - \varepsilon_{gs}) t}\langle \psi_m |\hat{\mathbf{x}}|\psi_{gs}\rangle|\psi_m\rangle +
\]

\[
= -ik \sum_m e^{i(\varepsilon_m - \varepsilon_{gs}) t}\langle \psi_m |\hat{\mathbf{x}}|\psi_{gs}\rangle|\psi_m\rangle +
\]

\[
= -ik \sum_m e^{i(\varepsilon_m - \varepsilon_{gs}) t}\langle \psi_m |\hat{\mathbf{x}}|\psi_{gs}\rangle|\psi_m\rangle + e^{i(\varepsilon_{gs} - \varepsilon_m) t}|\psi_m\rangle^2
\]

Using the euler formula \( e^{i\omega_m t} = \cos(\omega_m t) + i \sin(\omega_m t) \) we obtain from Eq. 1.103 using the definition \( \omega_m = (\varepsilon_m - \varepsilon_{gs}) \):

\[
d(t) = -ik \sum_m \cos(\omega_m t) + i \sin(\omega_m t) +
\]

\[
= 2k \sum_m \sin(\omega_m t)|\psi_m\rangle^2
\]
1.6. DISCRETISATION OF THE CONFIGURATION SPACE

Note that as the strength of the impulse $k$ is weak we can use the dipole approximation and expand Eq. 1.100 to obtain a dipole moment response which depends linearly on $k$.

The optical photoabsorption cross section spectra $\sigma_{abs}$ can be obtained by Fourier Transformation of $d(t)$ as \[^\[\text{'1.105}][\]

\[
\sigma_{abs} = 4\pi\alpha\omega\mathbb{I}m\left[\frac{1}{k} \int_0^t dt e^{-i\omega t} f(t) (d(t) - d(0))\right],
\]

where

\[
f(x) = 1 - 3x^2 + 2x^3,
\]

is a damping third order polynomial to improve the resolution of the photoabsorption peaks in the optical cross section spectra (see Fig. 2.13 as an example),

\[
\alpha = \frac{1}{137},
\]

is the fine structure constant, $t$ is the propagation time, $d(t)$ is the dipole evolution, $T = \frac{2\pi}{\omega}$ is the period of the oscillations of $d(t)$ and $k$ is the kick strength.

1.6. Discretisation of the configuration space

In order to numerically solve Eqs. 1.32, 1.45, 1.104 and 1.105 which are infinite dimensional Hilbert space eigenvalue and time-propagation problems we discretise the configuration space of the $H^+_2$ and $H_2$ molecules (see Figs. 1.1 and 1.2), using a finite set of values (i.e. a so-called grid) for values of $R$, $r$ and $\xi$ in the following box intervals:

\[
R \in [-L_R, L_R],
\]

\[
r \in [-L_r, L_r],
\]

\[
\xi \in [-L_\xi, L_\xi],
\]

which are discretised as:

\[
R_i = -L_R + i\Delta R \text{ for } i = 0, 1, 2...N_R
\]

\[
r_j = -L_r + j\Delta r \text{ for } j = 0, 1, 2...N_r
\]

and

\[
\xi_k = -L_\xi + k\Delta \xi \text{ for } k = 0, 1, 2...N_\xi
\]

by using $N_R$, $N_r$ and $N_\xi$ equispaced points, respectively. The spacing between two adjacent points in the $R$, $r$ and $\xi$ directions are:

\[
\Delta R = \frac{2L_R}{N_R},
\]

\[
\Delta r = \frac{2L_r}{N_r},
\]

and

\[
\Delta \xi = \frac{2L_\xi}{N_\xi}.
\]

Note that within the BOA, only the coordinates $\xi$ and $r$ need to be discretised as the $R$ coordinate is fixed being a parameter.

Therefore, $N_{H^+_2} = (N_R + 1)(N_\xi + 1) \approx (N_R)(N_\xi)$ points for the $H^+_2$ molecule and $N_{H_2} = (N_R + 1)(N_r + 1)(N_\xi + 1) \approx (N_R)(N_r)(N_\xi)$ points for the $H_2$ molecule in 1D as $N_R, N_r, N_\xi \gg 1$ are needed in the discretised configuration space. Using this discretised configuration space, the infinite dimensional Hilbert space problems become finite dimensional space problems where the wavefunctions are represented by complex...
vectors and the operators such as the Hamiltonians by Hermitian matrices with a dimension given by \( N_{H_2^+} \) for \( H_2^+ \) and by \( N_{H_2} \) for \( H_2 \).

The Hamiltonians are observables (Hermitian operators, \( \hat{H} = \hat{H}^\dagger \)) which we diagonalise to obtain the real eigenvalues which give the energy levels. The solutions of the Schrödinger Equation are the wavefunctions.

To numerically diagonalise the Hamiltonian we must consider that the dimensions of the discretised Hilbert spaces \( N_{H_2^+} \) and \( N_{H_2} \) grow exponentially with the number of internal coordinates.

One expects that as \( L_R, L_r, L_\xi \to \infty \) and \( N_R, N_r, N_\xi \to \infty \) the numerically diagonalised eigenvalues in a finite dimensional space should converge to the “real ones” in an infinite dimensional Hilbert space.

To achieve a good convergence of the numerically diagonalised eigenvalues we must consider that:

- As the wavefunctions are oscillating in space, one wants \( \Delta R \ll \Delta R_{\text{oscillation}} \), \( \Delta r \ll \Delta r_{\text{oscillation}} \) and \( \Delta \xi \ll \Delta \xi_{\text{oscillation}} \) to reproduce these oscillations.
- Moreover, if the wavefunction is localised, one wants \( L_R \gg L_R(\text{localisation}) \), \( L_r \gg L_r(\text{localisation}) \) and \( L_\xi \gg L_\xi(\text{localisation}) \). Note that if the eigenvalues are unbound, their energy will depend on the simulation box because the walls of the box act as infinite potential barriers.

Numerical propagation is computationally more convenient than numerical diagonalisation because it requires less operations. In the worst case, the memory needed to diagonalise the Hamiltonian for \( H_2^+ \) is of the order of \( [(N_R)(N_\xi)]^2 \) and for \( H_2 \) as \( [(N_R)(N_\xi)(N_r)]^2 \), i.e. it depends on the number of internal coordinates and on the “quality” of the discretised space we use for each internal coordinate. Therefore, the computational effort to carry out the diagonalisation process would require \( [(N_R)(N_\xi)]^3 \) operations for \( H_2^+ \) and \( [(N_R)(N_\xi)(N_r)]^3 \) operations for \( H_2 \). As a consequence, achieving a good convergence when we perform exact numerical calculations is only feasible for very small molecules like \( H_2^+ \) or \( H_2 \).

To perform the numerical tasks of diagonalising the molecular Hamiltonians and performing the time propagation we have used the real space electronic structure code Octopus [5].
CHAPTER 2

The accuracy of the BOA in computing the electron-ion spectrum of $H_2^+$

In this chapter the results obtained from the numerical real-space approach to solve the time-independent and time-dependent Schrödinger Equations for $H_2^+$ (Eqs. 1.32, 1.104 and 1.105) are shown.

The purpose of this chapter is to determine the accuracy of the BOA versus the exact solution of the electron-ion diagonalisation and propagation. For the static diagonalisation we compare the ground state eigenvalue obtained from the BOA and the exact diagonalisation of the electron-ion Hamiltonian. For the time propagation we compare the main “harmonic” transition from frozen-ion and exact electron-ion propagation in the linear response spectra.

According to the BOA we first diagonalise Eq. 1.64 at fixed ionic positions $R$ to find the electronic PES’s. We fit the bottom of the PES’s and then numerically diagonalise the fitted PES’s using Eqs. 1.68 and 2.11 to get the BOA electron-ion eigenvalues. We have used a fitting function to describe the PES’s because, for the moment with the code Octopus $^5$, we are not able to perform an interpolation for large interionic distances $R$ (see this feature for the gs PES in Fig. 2.4 as an example). Fitting the bottom of the PES’s is enough for our purpose, as we only want to compare ground state eigenvalues to determine the accuracy of the BOA. However, as we will show in Chapter 3 this is not enough for $H_2$, as $H_2$ is more tightly bound than $H_2^+$. This leads to less bound states for the $H_2$ molecule than for the $H_2^+$ molecule because as the potential is more localized the eigenvalues shift to higher energies. For bound states that are higher in energy, the fitted PES’s used to calculate the BOA electron-ion eigenvalues are not as accurate (see Fig. 3.6).

For the exact numerical solution, we diagonalise the electron-ion Hamiltonian in Eq. 1.32. To obtain the linear response spectra we employed the evolution of the “kicked” wave-function in Eq. 1.101.

The BOA is motivated by the fact that $m_I \geq 1836 m_e$, or that the electron-ion mass ratio $R_m = \frac{m_I}{m_e}$ is small.

Therefore, in order to check the accuracy of the BOA we fictitiously vary the electron-ion mass ratio $R_m$ by changing the ion mass. If this ratio increases, by decreasing the ion mass, the BOA can break down (see Secs. 1.2 and 1.4).

We are going to use four different types of electron-ion mass ratios, the first one corresponding to the proton mass where $R_m \approx 5.45 \times 10^{-4}$, the second one to the muon mass where $R_m \approx 4.84 \times 10^{-3}$, the third one to ten times the electron mass where $R_m = 0.1$ and the fourth one to the electron mass where $R_m = 1$. These values of $R_m$ have been choosen to have an almost homogeneous logarithmic sampling of the mass ratios, using the mass of existing particles whenever it was possible.

To perform these numerical approaches we have used for our model $a = 1$ as the Soft Coulomb parameter (see Eq. 1.21). This value has been used because we can see the PES’s features that we are interested in, such as the repulsive barrier, the attractive minimum and the molecular dissociation limit for large $R$ values (see Fig. 2.4 as an example).
Boa vs exact electron-ion diagonalisation and propagation

\[ \varepsilon \left( H^{+} \right) (\text{gs}) \text{[eV]} \]

\[ \varepsilon \left( \text{H} \cdots H^{+} \right) (\text{gs}) \text{[eV]} \]

\[ \varepsilon_{\text{b(exact)}} \left( H^{+} \right) \text{[eV]} \]

<table>
<thead>
<tr>
<th>( R_{m} \approx )</th>
<th>( \varepsilon_{H^{+}} ) (gs) [eV]</th>
<th>( \varepsilon_{\text{H} \cdots H^{+}} ) (gs) [eV]</th>
<th>( \varepsilon_{\text{b(exact)}} \left( H^{+} \right) ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 5.45 \times 10^{-4} )</td>
<td>-21.9702 (3)</td>
<td>-18.2248 (2)</td>
<td>3.7454 (3)</td>
</tr>
<tr>
<td>( 4.84 \times 10^{-4} )</td>
<td>-21.7035 (2)</td>
<td>-18.2183 (2)</td>
<td>3.4852 (2)</td>
</tr>
<tr>
<td>( 0.1 )</td>
<td>-20.3296 (3)</td>
<td>-18.0771 (2)</td>
<td>2.2525 (3)</td>
</tr>
<tr>
<td>( 1 )</td>
<td>-17.5579 (3)</td>
<td>-16.9527 (2)</td>
<td>0.6052 (3)</td>
</tr>
</tbody>
</table>

TABLE 2.1. \( H^{+} \) and \( H \cdots H^{+} \) ground state (gs) eigenvalues with the corresponding binding energies \( \varepsilon_{\text{b(exact)}} \left( H^{+} \right) \) for \( R_{m} \approx 5.45 \times 10^{-4} \), \( R_{m} \approx 4.84 \times 10^{-4} \), \( R_{m} = 0.1 \) and \( R_{m} = 1 \) obtained by exact numerical diagonalisation of the electron-ion Hamiltonian in Eqs. 1.32 and 2.3.

2.1. Exact numerical diagonalisation of the electron-ion Hamiltonian

In this section, we present the exact numerical diagonalisation of the electron-ion Hamiltonian of the time-independent internal Schrödinger Equation (Eq. 1.32) using the code Octopus [5].

We just consider the discrete electron-ion energy levels up to the molecular dissociation, that we take as a reference energy and so we set to zero. This molecular dissociation reference energy corresponds to the energy of a proton and a 1D \( H \) atom in its ground state very far apart.

The positive binding energy is then defined as:

\[ \varepsilon_{\text{b(exact)}} \left( H^{+} \right) = \varepsilon_{\text{H} \cdots H^{+}} (\text{ground state}) - \varepsilon_{H^{+}} (\text{ground state}) \] (2.1)

Therefore, we have solved the exact problem for a proton and a 1D \( H \) atom in its ground state very far apart for each value of the mass ratio, \( R_{m} \).

Eq. 1.24 for \( H^{+} \) for large \( R \) is reduced to:

\[ \hat{H}_{\text{int}}(\xi) = -\frac{1}{2\mu_{e}} \frac{\partial^{2}}{\partial \xi^{2}} - \frac{1}{\sqrt{\xi^{2} + 1}} \] (2.2)

The ground state energy of the dissociated \( H^{+} \) molecule is then calculated as the lowest energy eigenvalue of the Schrödinger Equation:

\[ \hat{H}_{\text{int}}(\xi)\psi(\xi) = \varepsilon_{\text{int}}(\xi)\psi(\xi) \] (2.3)

where \( \varepsilon_{\text{int}} \) corresponds to the energy eigenvalues obtained by diagonalisation of the Hamiltonian \( \hat{H}_{\text{int}} \) which depends only on the internal coordinate \( \xi \) which measures the distance between the centre of mass of the two protons and the electron for the dissociated \( H^{+} \) molecule.

The eigenvalues for the ground state obtained by the exact numerical diagonalisation of the electron-ion Hamiltonian of the \( H^{+} \) molecule (Eq. 1.32) and the dissociated \( H^{+} \) molecule (Eq. 2.3) with the corresponding binding energies (Eq. 2.1) are shown in Table 2.1 for the four types of electron-ion mass ratios \( R_{m} \) considered.

Since in the \( H^{+} \) molecule there are one electron and two protons (which are fermions), the antisymmetry of the many-body wave function must be enforced for the protons only (see Sec. 1.3.5). The internal coordinate for the protons is \( \xi \).

The code Octopus only calculates the spatial part of the total wavefunction. However, due to the exchange symmetry of the total wavefunction when we have two identical fermions, the spin part of the total wavefunction can be directly determined if we know the spatial part of the wavefunction.

From Eq. 1.24 we see that the potential for the \( H^{+} \) molecule is invariant under the interionic distance coordinate transformation \( R \rightarrow -R \). This means that the resulting ionic eigenfunctions will either be even or odd under the same transformation. Physically
the even ionic eigenfunctions correspond to the singlet state while the odd ones correspond to the triplet state.

In order to visualise the effect of the different electron-ion mass ratios in Eq. 1.24 we use the following transformation for the internal coordinate $R$:

$$R = \sqrt{\frac{\mu_I}{\mu_e}} X,$$ \hspace{1cm} (2.4)

and for the internal coordinate $\xi$:

$$\xi = \sqrt{\frac{\mu_I}{\mu_e}} Y.$$ \hspace{1cm} (2.5)

Using these coordinate transformations the internal Hamiltonian of Eq. 1.24 reads:

$$\hat{H}_{\text{int}}(X,Y) = -\frac{\partial^2}{\partial X^2} - \frac{\partial^2}{\partial Y^2} - \frac{1}{\sqrt{\left(\frac{1}{4\mu_I} X + \frac{1}{\mu_e} Y\right)^2 + 1}} + \frac{1}{\sqrt{\left(\frac{1}{4\mu_I} X - \frac{1}{\mu_e} Y\right)^2 + 1}} + \frac{1}{\sqrt{\left(\frac{1}{\mu_I} X\right)^2 + 1}}.$$ \hspace{1cm} (2.6)

Now in Eq. 2.6 the reflection symmetry of the interionic distance coordinate transformation $R \rightarrow -R$ manifests itself through the invariance of $\hat{H}_{\text{int}}$ under the coordinate transformation $X \rightarrow -X$.

In Fig. 2.1 we plot the potential energy landscape, i.e, the last three terms in Eq. 2.6, for each electron-ion mass ratio.

**FIGURE 2.1.** a) Potential energy landscapes obtained from Eq. 2.6 for $H_2^+$ for $R_m \approx 5.45 \times 10^{-4}$ b) As in a) for $R_m \approx 4.84 \times 10^{-3}$ c) As in a) for $R_m = 0.1$ d) As in a) for $R_m = 1$. The colour scale represents the potential energy. Note that as $R_m$ increases, the potential minima get closer with respect to the X axis (see the scale).
Due to the inversion symmetry with respect to the X axis of the potential in Fig. 2.1 the ionic eigenfunctions have a given parity. Due to our particular choice of internal coordinate \( R \), where the fermionic symmetry can be mapped in the wavefunction parity, it turns out that the even and the odd ionic eigenfunctions are associated to a singlet and a triplet, respectively. Therefore, the odd eigenfunctions are antibonding \( \psi_A \) and the even eigenfunctions are bonding \( \psi_B \). These are defined as a function of the internal coordinate \( R \) by:

\[
\psi_A(R) = \frac{1}{\sqrt{2}}(\psi_L(R) - \psi_R(R)); \quad \psi_B(R) = \frac{1}{\sqrt{2}}(\psi_L(R) + \psi_R(R)),
\]

where \( \psi_L(R) \) and \( \psi_R(R) \) are the left and right eigenfunction components of the even and odd ionic eigenfunction in each of the symmetric potentials in Fig. 2.1 with respect to the X axis. Note, as mentioned previously, the relation between \( R \) and \( X \) in Eq. 2.4. In Fig. 2.1 there is also a clear symmetry \( Y \rightarrow -Y \). However, this is not related to the statistics of the ions, but to the symmetry of the electronic molecular orbital.

The eigenvalues of the even and odd wavefunctions will be degenerate (singlet-triplet degeneracy) if the left and right eigenfunction components in the potentials in Fig. 2.1 do not overlap, i.e., if they are confined in the left and right potentials. As the wavefunctions components overlap, the degeneracy will break (singlet-triplet splitting).

From Fig. 2.1 we see that as the electron-ion mass ratio increases, i.e., for lighter ions, the potential minima get closer with respect to the X axis (note that the X axis scale decreases as \( R_m \) increases), so the corresponding left and right wavefunction components that lie in this potential minima can overlap leading to a lifting of the singlet-triplet degeneracy.

In Fig. 2.2, we show the electron-ion energy spectrum below the molecular dissociation energy for the different electron-ion mass ratios. Numerical parameters such as the simulation box \((L_R, L_\xi)\) and the grid spacing \((\Delta R, \Delta \xi)\) introduced in Sec. 1.6 are varied till convergence of all the eigenvalues below molecular dissociation has been achieved by visual inspection. From numerical inspection, the convergence of the eigenvalues is of the order of \( 0.1 - 1 \text{meV} \).

For \( R_m \approx 5.45 \times 10^{-4} \) and \( R_m \approx 4.84 \times 10^{-3} \) the convergence of the discrete electron-ion energy levels is good below the molecular dissociation energy for \( \Delta \xi = 0.053; \Delta R = 0.0265 \) and \( L_R = L_\xi = 15.9 \text{Å} \). For \( R_m = 0.1 \) we need \( \Delta \xi = \Delta R = 0.106 \) and \( L_R = L_\xi = 13.225 \text{Å} \), while for \( R_m = 1 \) we need \( \Delta \xi = \Delta R = 0.106 \) and \( L_R = L_\xi = 18.52 \text{Å} \) to achieve a good convergence of the discrete electron-ion energy levels below the molecular dissociation energy. If we increase the box size and/or decrease the spacing the electron-ion energy spectra are not going to change as shown with the blue and red lines in Fig. 2.2.

We have 62, 18, 4 and 1 bound electron-ion energy lines below the molecular dissociation energy for \( R_m \approx 5.45 \times 10^{-4} \), \( R_m \approx 4.84 \times 10^{-3} \), \( R_m = 0.1 \) and \( R_m = 1 \), respectively. For \( R_m \approx 5.45 \times 10^{-4} \) and \( R_m \approx 4.84 \times 10^{-3} \) the number of electron-ion energy lines we see in Fig. 2.2 correspond to half the amount of bound electron-ion energy lines which is due to a singlet-triplet degeneracy. However, this is not the case for \( R_m = 0.1 \) and \( R_m = 1 \). The number of bound electron-ion energy lines decreases as we increase the electron-ion mass ratio. This will be explained in Sec. 2.3.

### 2.2. BOA numerical diagonalisation of the electron-ion Hamiltonian

In this section, we solve the time-independent internal Schrödinger Equation (Eq. 1.32) using the BOA for each \( R_m \) we have selected.

We first diagonalise Eq. 1.64 at fixed ionic positions \( R \) to find the first four electronic PES’s. We fit the bottom of the PES’s and then numerically diagonalise the fitted PES’s using Eq. 1.68 to get the BOA electron-ion eigenvalues.
In the BOA the molecular dissociation energy corresponds to the ground state PES dissociation limit of the molecule for very large interionic distances \( R \). We refer all the electronic PES energies to this gs PES dissociation limit which has been set to zero.

The positive binding energy with respect to the gs PES dissociation limit is then defined as:

\[
\epsilon_b(BOA)(H^+_2) = \epsilon(H\cdots H^+) - \epsilon_{gs}(BOA),
\]

where \( \epsilon_{gs}(BOA) \) is the energy of the first vibrational energy level calculated from the BOA.

We have used \( \Delta \xi = 0.053 \) and \( L_\xi = 26.45 \text{Å} \) for the calculations as a larger simulation box is needed to reach the gs PES dissociation energy limit for large \( R \) values.

To see the qualitative behaviour of the PES’s, we plot the first four adiabatic PES’s for each \( R_m \) in Fig. 2.3.

According to Fig. 2.3, the BOA electronic excitation energies in the dissociation limit are equal for the second excited PES and the third excited PES, and also for the gs PES and 1Ex PES. The gs PES corresponds to an even electronic eigenfunction and the 1Ex PES to an odd electronic eigenfunction. The existence of these even/odd electronic eigenfunctions is due to the invariance of Eq. 1.24 under exchange of \( \xi \rightarrow -\xi \). The even and odd electronic eigenfunctions are degenerate in the dissociation limit for large values of \( R \):

\[
\langle \psi_B(R)|\psi_B(R)\rangle = \frac{1}{2} \int \left[ |\psi_R^2(R)| + |\psi_L^2(R)| + 2|\psi_R(R)\psi_L(R)| \right] dR;
\]

(2.9)
FIGURE 2.3. a) First four adiabatic PES’s for \( R_m \approx 5.45 \times 10^{-4} \) using the BOA with a soft coulomb potential in 1-D where \( \Delta \xi = 0.053 \) and \( L_\xi = 26.45 \AA \), where we have used fixed values of \( R \) up to 21.16 \( \AA \) for \( H_2^+ \). b) As a) but for \( R_m \approx 4.84 \times 10^{-3} \). c) As a) but for \( R_m = 0.1 \). d) As a) but for \( R_m = 1 \).

<table>
<thead>
<tr>
<th>( R_m \approx 5.45 \times 10^{-4} )</th>
<th>2Ex/3Ex PES ( \varepsilon_{dl(BOA)} ) [eV]</th>
<th>( H \cdots H^+(gs \rightarrow 1Ex) \varepsilon_x(H \cdots H^+) ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.74601 (2)</td>
<td>10.7457 (2)</td>
<td></td>
</tr>
<tr>
<td>( R_m \approx 4.84 \times 10^{-3} )</td>
<td>10.74839 (1)</td>
<td>10.7481 (3)</td>
</tr>
<tr>
<td>( R_m = 0.1 )</td>
<td>10.79855 (5)</td>
<td>10.7982 (2)</td>
</tr>
<tr>
<td>( R_m = 1 )</td>
<td>11.07503 (4)</td>
<td>11.0741 (2)</td>
</tr>
</tbody>
</table>

TABLE 2.2. BOA electronic excitation energies \( \varepsilon_{dl(BOA)} \) for the second excited (2Ex) PES and third excited (3Ex) PES in the dissociation limit and \( H \cdots H^+ \) excitation energies \( \varepsilon_x(H \cdots H^+) \) for each \( R_m \). The BOA electronic excitation energies in the dissociation limit have been obtained by fitting the PES’s for large values of \( R \) (see below). These BOA electronic excitation energies in the dissociation limit correspond to the excitation energies of the dissociated \( H_2^+ \) molecule, as for very large frozen-ion interionic distances \( R \) in the gs BOA dissociation limit, we have a proton and a 1D \( H \) atom in its ground state very far apart.

\[
(\psi_A(R)|\psi_A(R)) = \frac{1}{2} \int [\psi_R^2(R) + \psi_L^2(R) - 2\psi_L(R)\psi_R(R)]dR, \tag{2.10}
\]

because the mixed terms \( 2\psi_L(R)\psi_R(R) \) and \(-2\psi_L(R)\psi_R(R) \) do not contribute in this limit. The left and right eigenfunction components in the potentials in Fig.2.1 do not overlap for large \( R \). At the same time, the qualitative features of the PES’s are similar as we change the electron-ion mass ratio \( R_m \) (see Fig.2.3).

In Table 2.2 we show the BOA electronic excitation energies for the second excited (2Ex) PES and third excited (3Ex) PES given with respect to the molecular dissociation energy limit, and the dissociated \( H_2^+ \) excitation energies for each \( R_m \).
We plot (Fig. 2.4) the electronic ground state potential energy surface for the frozen ion calculation as a function of the fixed values of $R$ for each $R_m$.

**FIGURE 2.4.** a) Electronic ground state PES for $R_m \approx 5.45 \times 10^{-4}$ using the BOA with a soft coulomb potential in 1-D where $\Delta \xi = 0.053$ and $L_\xi = 26.45 \AA$, where we have used fixed values of $R$ up to 21.16 $\AA$. The 62 exact electron-ion energy levels of $H_2^+$ (horizontal black lines) from Fig. 2.2 a) have been added. b) As a) but for $R_m \approx 4.84 \times 10^{-3}$, adding the 18 exact electron-ion energy levels from Fig. 2.2 b). c) As a) but for $R_m = 0.1$, adding the 4 exact electron-ion energy levels from Fig. 2.2 c). d) As a) but for $R_m = 1$, adding the 1 exact electron-ion energy level from Fig. 2.2 d).

We do not show electron-ion energy levels above the molecular dissociation energy limit because they are in the continuum. We find a single minimum.

From Fig. 2.4 a) and b) we see that the energy difference between two subsequent electron-ion energy levels decreases as their energy increases. At low energies around the minimum of the PES of the electronic ground state, the BOA is expected to be accurate and the exact eigenvalues of the electron-ion problem can be interpreted in terms of the anharmonic ionic vibrational levels for the electronic ground state PES (the BOA picture). For larger energies, however, this simple interpretation of the exact energies is no longer possible because the total electron-ion wavefunction is no longer factorisable, as in the BOA. For small mass ratios, the electronic transitions will require more energy than ionic transitions and therefore there will be little coupling between electrons and ions. However, as the mass ratio increases, the energy required for electronic and ionic transitions will become comparable, therefore leading to a larger electron-ion coupling. For energies closer but below the molecular dissociation energy, the electron-ion energy spectrum is still discrete but the separation between the levels becomes very small and the black lines become indistinguishable.

As the gs PES (Fig. 2.5 a)) is anharmonic we approximate the gs PES around its classical minimum $R_{eq}$ by a fourth order polynomial (Fig. 2.5 c)) for $R_m \approx 4.84 \times 10^{-3}$ as an example of one of the $R_m$.

To calculate the vibrational or ionic structure we diagonalise Eq. 1.68 where:
where $k_1 = \omega^2 \mu_I$ is the harmonic fitting parameter and $k_2$ and $k_3$ are higher order fitting parameters. The energy eigenvalues of this anharmonic fit of the BOA gs PES are shown in Fig. 2.5 (c).

The gs PES (Fig. 2.5 (a)) can also be approximated by a harmonic potential (Fig. 2.5 (b)), for $R_m \approx 4.84 \times 10^{-3}$. Note that for the harmonic fit, we only approximate the gs PES around its classical minimum $R_{eq}$ by a second order polynomial.

The eigenvalues in a harmonic potential correspond to $\varepsilon_n = (n + \frac{1}{2})\hbar\omega$ where $n$ is the index of the ionic eigenvalues for a certain electronic PES, $\omega$ is the angular frequency (from which we obtain the vibrational frequency in wave numbers $\lambda = \frac{\omega}{2\pi c}$ where $c$ is the velocity of light in vacuum), and $\hbar = \frac{h}{2\pi}$ where $h$ is Planck’s constant. These eigenvalues have been plotted in Fig. 2.5 (b).

As the harmonic fit is appropriate to fit the PES’s around the minimum $R_{eq}$ we have obtained the “strength” of the harmonic fit from the corresponding vibrational frequencies $\lambda$ in wavenumbers for each $R_m$ using the harmonic fitting parameter $k_1$ from Eq. 2.11. The $\lambda$ results for each PES and $R_m$ are given in Table 2.3.
2.2. $H_2^+$ BOA ELECTRON-ION DIAGONALISATION

<table>
<thead>
<tr>
<th>$\lambda$ (cm$^{-1}$)</th>
<th>$R_m \approx 5.45 \times 10^{-4}$</th>
<th>$R_m \approx 4.84 \times 10^{-4}$</th>
<th>$R_m = 0.1$</th>
<th>$R_m = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>gs PES</td>
<td>2172 (2)</td>
<td>6470 (6)</td>
<td>29069 (31)</td>
<td>83350 (95)</td>
</tr>
<tr>
<td>1Ex PES</td>
<td>136 (2)</td>
<td>404 (7)</td>
<td>1757 (34)</td>
<td>3576 (111)</td>
</tr>
<tr>
<td>2Ex PES</td>
<td>743 (1)</td>
<td>2213 (30)</td>
<td>9707 (20)</td>
<td>22652 (9)</td>
</tr>
<tr>
<td>3Ex PES</td>
<td>95.2 (6)</td>
<td>281 (2)</td>
<td>1186 (17)</td>
<td>2479 (12)</td>
</tr>
</tbody>
</table>

Table 2.3. $H_2^+$ vibrational frequencies in wavenumbers for the first four PES for each $R_m$ obtained by a harmonic fit around the PES’s minima.

We have also used the Morse potential to describe the adiabatic ground state PES (Fig. 2.5 d)) for $R_m \approx 4.84 \times 10^{-3}$. In Fig. 2.7 we see that the Morse potential is qualitatively similar to the gs PES.

The Morse potential is given by:

$$\varepsilon(R) = (\varepsilon_{dl}(BOA) - \varepsilon_0)(1 - e^{-a(R-R_{eq})})^2 + \varepsilon_0,$$

(2.12)

where:

$$a = \sqrt{\frac{k_1}{2(\varepsilon_{dl}(BOA) - \varepsilon_0)}},$$

(2.13)

where $\varepsilon_{dl}(BOA)$ is given in Table 2.2, $k_1$ is given by Eq. 2.11 and $\varepsilon_0$ is the energy that corresponds to the minimum of the gs PES at the equilibrium interionic distance $R_{eq}$. The values for these last two parameters are given in Table 2.4.

The Morse corresponding eigenvalues are shown in Fig. 2.5 d) for $R_m \approx 4.84 \times 10^{-3}$ are:

$$\varepsilon_n = -(\beta - n - \frac{1}{2})^2,$$

(2.14)

where

$$\beta = \frac{\sqrt{2\mu_e(\varepsilon_{dl}(BOA) - \varepsilon_0)}}{a\hbar}.$$

(2.15)

We have only shown Fig. 2.5 for the $R_m \approx 4.84 \times 10^{-3}$ case because we can see the following ideas in a clearer way.

In Fig. 2.5 b) we see that only the harmonic oscillator ground state vibrational energy is similar in energy to the exact ground state electron-ion energy level. However this only happens for the $R_m \approx 5.45 \times 10^{-4}$ and $R_m \approx 4.84 \times 10^{-3}$ cases as the BOA is only expected to work when $R_m$ is small.

As the eigenvalues energy increases, the separation between the exact electron-ion levels decreases. In the BOA picture these levels are better described by the fourth order anharmonic and Morse potentials, as is shown in Fig. 2.5 than for the harmonic oscillator levels which are evenly spaced by $\hbar\omega$.

For the anharmonic potential in Fig. 2.5 e) the energy spacing increases with respect to the exact diagonalised eigenvalues while the opposite occurs for the Morse potential as the energy increases as shown in Fig. 2.5 d).

As shown in Fig. 2.7, the Morse potential is similar to the exact ground state PES. If we calculate the first correction to the harmonic energy relative to a fourth order expansion of the Morse potential using time-independent perturbation theory (see Appendix B for details) which gives:

$$\varepsilon_n = \hbar\omega[(n + \frac{1}{2}) - \frac{a^2\hbar}{2\mu_1\omega}(n + \frac{1}{2})^2],$$

(2.16)
the anharmonic correction improves the harmonic approximation (see Fig. 2.6).

Using this correction from Eq. 2.16 the harmonic spacing $\hbar \omega$ decreases as $n$ increases by:

$$\varepsilon_{n+1} - \varepsilon_n = \hbar \omega [1 - \frac{a^2 \hbar}{\mu \omega}(n + 1)]$$  \hspace{1cm} (2.17)

Therefore, the anharmonic correction introduced in Eq. 2.16 is only valid for positive energy differences $\varepsilon_{n+1} - \varepsilon_n$, i.e., when $\frac{a^2 \hbar}{\mu \omega}(n + 1) < 1$.

![Figure 2.6](image)

**Figure 2.6.** As Fig. 2.5 b) using the first correction to the harmonic energy relative to a fourth order expansion of the morse potential. The eigenvalues in this case are then given by Eq. 2.16

Table 2.4 summarizes the results obtained for the parameters in Fig. 2.5 b) and c) for $R_m \approx 4.84 \times 10^{-3}$.

In this table we also show the corresponding results that have been obtained for the other mass ratios $R_m \approx 5.45 \times 10^{-4}$, $R_m = 0.1$ and $R_m = 1$ for which we have not shown a figure like Fig. 2.5.

In Fig. 2.8 we show for $R_m \approx 5.45 \times 10^{-4}$ the first three electronic excited PES’s together with the electronic ground state PES. These PES’s are similar for the other electron-ion mass ratios.

The first, second and third excited electronic states have a very shallow minimum. We can clearly see this minimum for the second excited state in Fig. 2.8, but it is not so clear for the first and third excited state in the original scale but the corresponding minima are clearly recognizable in the insets of Fig. 2.8 b) and c).

Some of the exact electron-ion diagonalised eigenvalues in Fig. 2.4 a) lie inside the BOA 1Ex PES minimum below the BOA dissociation energy limit in Fig. 2.8 for $R_m \approx 5.45 \times 10^{-4}$ although this is not the case for the other $R_m$. However, as mentioned previously, the BOA is not accurate in this situation for larger energies close to the dissociation...
TABLE 2.4. $H_2^+$ ground state fitted PES parameters for each $R_m$ using the fourth order anharmonic fit around the minimum where: $\varepsilon_0$ is the energy that corresponds to the minimum of the gs PES at the equilibrium interionic distance $R_{eq}$; $\varepsilon_{gs(\text{exact})}$ is the energy for the ground state eigenvalue obtained by exact electron-ion diagonalisation of $H_2^+$; $\varepsilon_{gs(BOA)}$ is the ground state energy of the first vibrational state calculated from the minimum of the BOA gs PES; $\varepsilon_{b(BOA)}$ is the binding energy in the BOA picture; $\varepsilon_{zp}$ is the zero point energy of the harmonic oscillator $\frac{1}{2} \hbar \omega$ from the minimum $\varepsilon_0$ of the gs PES; $R_{eq}$ is the equilibrium interionic distance that corresponds to the minimum of the gs PES; $k_1$, $k_2$ and $k_3$ are the fitting parameters used in Eq. 2.11. Note that the binding energy is negative for the $R_m = 1$ case using the BOA, i.e., the BOA does not predict the only bound state we have for $R_m = 1$.

<table>
<thead>
<tr>
<th>$R_m$ (Å)</th>
<th>$\varepsilon_0$ (eV)</th>
<th>$k_1$ (eV Å)</th>
<th>$k_2$ (eV Å)</th>
<th>$k_3$ (eV Å)</th>
<th>$\varepsilon_{gs(BOA)}$ (eV)</th>
<th>$\varepsilon_{gs(exact)}$ (eV)</th>
<th>$\varepsilon_{b(BOA)}$ (eV)</th>
<th>$\varepsilon_{zp}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.45 \times 10^{-4}$</td>
<td>-3.8793 (1)</td>
<td>8.740 (8)</td>
<td>-24.84 (7)</td>
<td>43.5 (9)</td>
<td>-3.7447 (7)</td>
<td>-3.7454 (3)</td>
<td>3.7447 (7)</td>
<td>0.1346 (7)</td>
</tr>
<tr>
<td>$4.84 \times 10^{-5}$</td>
<td>-3.8801 (1)</td>
<td>8.731 (8)</td>
<td>-24.81 (7)</td>
<td>43.5 (8)</td>
<td>-3.4851 (3)</td>
<td>-2.2525 (2)</td>
<td>3.4851 (3)</td>
<td>0.401 (2)</td>
</tr>
<tr>
<td>0.1</td>
<td>-3.8956 (1)</td>
<td>-24.18 (6)</td>
<td>-3.6052 (2)</td>
<td>3.4851 (3)</td>
<td>-2.2525 (2)</td>
<td>-2.2525 (2)</td>
<td>3.4851 (3)</td>
<td>0.401 (2)</td>
</tr>
<tr>
<td>1</td>
<td>-4.0016 (1)</td>
<td>-19.28 (5)</td>
<td>3.165 (3)</td>
<td>0.6052 (2)</td>
<td>-2.2525 (2)</td>
<td>-2.2525 (2)</td>
<td>3.4851 (3)</td>
<td>0.401 (2)</td>
</tr>
</tbody>
</table>
42 2. $H_2^+$ BOA VS EXACT ELECTRON-ION DIAGONALISATION AND PROPAGATION

<table>
<thead>
<tr>
<th>$R_m \approx 5.45 \times 10^{-4}$</th>
<th>1Ex PES</th>
<th>2Ex PES</th>
<th>3Ex PES</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{eq} (\text{A})$</td>
<td>4.949 (7)</td>
<td>3.5626 (3)</td>
<td>8.470 (2)</td>
</tr>
<tr>
<td>$\varepsilon_0 (\text{eV})$</td>
<td>-0.03318 (7)</td>
<td>9.1085 (1)</td>
<td>10.69389 (2)</td>
</tr>
<tr>
<td>$k_1 (\frac{A}{\text{eV}})$</td>
<td>0.0342 (6)</td>
<td>1.024 (2)</td>
<td>0.0168 (1)</td>
</tr>
<tr>
<td>$k_2 (\frac{A}{\text{eV}})$</td>
<td>-0.079 (3)</td>
<td>-1.372 (3)</td>
<td>-0.0233 (2)</td>
</tr>
<tr>
<td>$k_3 (\frac{A}{\text{eV}})$</td>
<td>0.089 (7)</td>
<td>0.94 (2)</td>
<td>0.0218 (9)</td>
</tr>
<tr>
<td>$\varepsilon_{gs(BOA)} (\text{eV})$</td>
<td>-0.0248 (1)</td>
<td>9.1546 (1)</td>
<td>10.6998 (2)</td>
</tr>
<tr>
<td>$\varepsilon_{zp} (\text{eV})$</td>
<td>0.0084 (1)</td>
<td>0.0461 (4)</td>
<td>0.0059 (2)</td>
</tr>
<tr>
<td>$\varepsilon_b(BOA) (\text{eV})$</td>
<td>0.0248 (1)</td>
<td>1.5914 (1)</td>
<td>0.0462 (2)</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>$R_m \approx 4.84 \times 10^{-4}$</th>
<th>1Ex PES</th>
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<th>3Ex PES</th>
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<tr>
<td>$R_{eq} (\text{A})$</td>
<td>4.955 (7)</td>
<td>3.5667 (3)</td>
<td>8.489 (2)</td>
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<td>$\varepsilon_0 (\text{eV})$</td>
<td>-0.03314 (7)</td>
<td>9.1121 (1)</td>
<td>10.69628 (2)</td>
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<tr>
<td>$k_1 (\frac{A}{\text{eV}})$</td>
<td>0.0340 (6)</td>
<td>1.021 (2)</td>
<td>0.0165 (1)</td>
</tr>
<tr>
<td>$k_2 (\frac{A}{\text{eV}})$</td>
<td>-0.079 (3)</td>
<td>-1.366 (3)</td>
<td>-0.0231 (2)</td>
</tr>
<tr>
<td>$k_3 (\frac{A}{\text{eV}})$</td>
<td>0.089 (8)</td>
<td>0.93 (2)</td>
<td>0.0214 (9)</td>
</tr>
<tr>
<td>$\varepsilon_{gs(BOA)} (\text{eV})$</td>
<td>-0.0081 (2)</td>
<td>9.249 (2)</td>
<td>10.71370 (5)</td>
</tr>
<tr>
<td>$\varepsilon_{zp} (\text{eV})$</td>
<td>0.0250 (2)</td>
<td>0.137 (2)</td>
<td>0.01742 (5)</td>
</tr>
<tr>
<td>$\varepsilon_b(BOA) (\text{eV})$</td>
<td>0.0081 (2)</td>
<td>1.499 (2)</td>
<td>0.03469 (5)</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>$R_m = 0.1$</th>
<th>1Ex PES</th>
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<th>3Ex PES</th>
</tr>
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<tbody>
<tr>
<td>$R_{eq} (\text{A})$</td>
<td>5.076 (6)</td>
<td>3.6573 (4)</td>
<td>8.785 (3)</td>
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<tr>
<td>$\varepsilon_0 (\text{eV})$</td>
<td>-0.03178 (7)</td>
<td>9.1903 (2)</td>
<td>10.74859 (2)</td>
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<tr>
<td>$k_1 (\frac{A}{\text{eV}})$</td>
<td>0.0340 (6)</td>
<td>1.021 (2)</td>
<td>0.0165 (1)</td>
</tr>
<tr>
<td>$k_2 (\frac{A}{\text{eV}})$</td>
<td>-0.079 (3)</td>
<td>-1.366 (3)</td>
<td>-0.0231 (2)</td>
</tr>
<tr>
<td>$k_3 (\frac{A}{\text{eV}})$</td>
<td>0.089 (8)</td>
<td>0.93 (2)</td>
<td>0.0214 (9)</td>
</tr>
<tr>
<td>$\varepsilon_{gs(BOA)} (\text{eV})$</td>
<td>0.077 (1)</td>
<td>9.7920 (6)</td>
<td>10.8221 (5)</td>
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<tr>
<td>$\varepsilon_{zp} (\text{eV})$</td>
<td>0.109 (1)</td>
<td>0.6017 (4)</td>
<td>0.0735 (5)</td>
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<tr>
<td>$\varepsilon_b(BOA) (\text{eV})$</td>
<td>-0.077 (1)</td>
<td>1.0062 (6)</td>
<td>-0.0239 (5)</td>
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<table>
<thead>
<tr>
<th>$R_m = 1$</th>
<th>1Ex PES</th>
<th>2Ex PES</th>
<th>3Ex PES</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{eq} (\text{A})$</td>
<td>6.251 (7)</td>
<td>4.49016 (5)</td>
<td>11.490 (1)</td>
</tr>
<tr>
<td>$\varepsilon_0 (\text{eV})$</td>
<td>-0.02287 (3)</td>
<td>9.68970 (1)</td>
<td>11.038722 (3)</td>
</tr>
<tr>
<td>$k_1 (\frac{A}{\text{eV}})$</td>
<td>0.0129 (4)</td>
<td>0.5179 (2)</td>
<td>0.00620 (3)</td>
</tr>
<tr>
<td>$k_2 (\frac{A}{\text{eV}})$</td>
<td>-0.027 (2)</td>
<td>-0.5824 (3)</td>
<td>-0.00594 (6)</td>
</tr>
<tr>
<td>$k_3 (\frac{A}{\text{eV}})$</td>
<td>0.066 (5)</td>
<td>0.392 (3)</td>
<td>0.0035 (4)</td>
</tr>
<tr>
<td>$\varepsilon_{gs(BOA)} (\text{eV})$</td>
<td>0.199 (3)</td>
<td>11.0939 (2)</td>
<td>11.1924 (4)</td>
</tr>
<tr>
<td>$\varepsilon_{zp} (\text{eV})$</td>
<td>0.222 (3)</td>
<td>1.4042 (2)</td>
<td>0.1537 (4)</td>
</tr>
<tr>
<td>$\varepsilon_b(BOA) (\text{eV})$</td>
<td>-0.199 (3)</td>
<td>-0.0189 (2)</td>
<td>-0.1174 (4)</td>
</tr>
</tbody>
</table>

**Table 2.5.** $H_2^+$ first three excited state fitted PES parameters for each $R_m$ obtained by a fourth order anharmonic fit around the minimum using Eq. 2.11 where for each PES: $R_{eq}$ is the equilibrium separation; $\varepsilon_0$ is the energy minimum; $k_1, k_2$ and $k_3$ are the fitting parameters $\varepsilon_{gs(BOA)}$ is the energy of the first ionic excitation; $\varepsilon_b(BOA)$ is the binding energy in the BOA picture (see Eq. 2.8); $\varepsilon_{dp(BOA)}$ is the BOA energy in the dissociation limit, the values are given in Table 2.2) and $\varepsilon_{zp}$ is the zero-point energy.
perturbed by the presence of a second proton $H^+$ very far apart as we are going to fit the gs PES around the asymptotic part (see new reference frame coordinates in Fig. 2.9). The electronic Hamiltonian in Eq. 1.66 in the new reference frame reads:

$$\hat{H} = -\frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{1}{\sqrt{r^2 + a^2}} - \frac{1}{\sqrt{(|R - r|)^2 + a^2}} + \frac{1}{\sqrt{R^2 + a^2}} = \hat{H}^{(0)} + \hat{H}^{(1)}, \quad (2.19)$$

where $\hat{H}^{(0)}$ is the Hamiltonian of the isolated $H$ atom which was defined in Eq. 2.2 and:

$$\hat{H}^{(1)} = -\frac{1}{\sqrt{(|R - r|)^2 + 1}} + \frac{1}{\sqrt{R^2 + 1}}, \quad (2.20)$$

will be treated as perturbation, i.e., a small correction to $\hat{H}^{(0)}$. For large interionic separations $R >> r, 1$, $\hat{H}^{(1)}$ reads:

$$\hat{H}^{(1)} = -\frac{1}{R} \left( \frac{1}{1 - \frac{r}{R}} \right) + \frac{1}{R} = \frac{1}{R} \left( 1 - \frac{1}{1 - \frac{r}{R}} \right), \quad (2.21)$$

which we can expand:

$$\hat{H}^{(1)} = \frac{1}{R} \left( 1 - (1 + \frac{r}{R} + \frac{r^2}{R^2} + \frac{r^3}{R^3} + \cdots) \right) = -\frac{r}{R^2} - \frac{r^2}{R^3} - O(\frac{r^3}{R^4}). \quad (2.22)$$

Using first order time-independent perturbation theory we find the first-order energy correction:

$$\varepsilon^{(1)} = \langle \varphi^{(0)} | \hat{H}^{(1)} | \varphi^{(0)} \rangle, \quad (2.23)$$
2. $H_2^+$ BOA VS EXACT ELECTRON-ION DIAGONALISATION AND PROPAGATION

**Figure 2.8.** a) First four adiabatic potential energy surfaces for $R_m \approx 5.45 \times 10^{-4}$ obtained by the BOA with the soft coulomb potential in 1-D using $\Delta \xi = 0.053$ and $L_\xi = 20.45 \, \text{Å}$, where we have used fixed values of $R$ up to 21.16 Å for $H_2^+$. b) Zoom of the minimum for the first excited electronic state from a). c) Zoom of the minimum for the third excited electronic state from a).

**Figure 2.9.** Schematic representation of the new reference frame coordinates of $H_2^+$ to determine the interaction decaying order $b$ of the tail of the PES’s

i.e.,:

\[ \varepsilon^{(1)} = -\frac{\langle \varphi^{(0)} | \hat{r} | \varphi^{(0)} \rangle}{R^2} - \frac{\langle \varphi^{(0)} | \hat{r}^2 | \varphi^{(0)} \rangle}{R^3}. \]  

(2.24)

Note that $\varphi^{(0)}$ is the ground state electronic wavefunction. Due to selection rules, the first term (dipole) is zero because $r$ is an odd function and $\varphi^{(0)}$ is even with respect to $r$ (see Eq. 2.24) so the dominant term is in our case the “quadrupole” term so that $b = 3$. At variance with the numerator of the first term in Eq. 2.24, the numerator of second term does not necessarily have to vanish because $r^2$ is an even function. By comparison, in 3D the second term in Eq. 2.24 also vanishes because we have rotations so this exponent should correspond to $b = 4$ or higher orders.

The results for the dissociation energies in Eq. 2.18 were shown in Table 2.2 for each $R_{m}$ that we have selected.
2.3. Validity of the BOA numerical diagonalisation of the electron-ion Hamiltonian

In the previous section we have seen that the ground state BOA anharmonic, Morse and harmonic levels do not agree as well to the exact ground electron-ion energy level as the ion mass decreases or the electron-ion mass ratio increases (see Table 2.4). This is expected as the BOA breaks down when we increase the electron-ion mass ratio. However, these levels are better described by the anharmonic and Morse potentials (see Fig. 2.5).

With respect to the binding energies in Table 2.6 for the first four PES with respect to each electron-ion mass ratio we see that they increase as the electron-ion mass increases. We can relate this to an increase in the vibrational frequency $\lambda$ or $k_1$ as the electron-ion mass increases (see Tables 2.3 and 2.4). Moreover, as the potentials are narrower as $R_m$ increases, the exact electron-ion energy levels will increase in energy leading to less bound exact electron-ion energy levels (see Fig. 2.2).

To determine the accuracy of the BOA for the gs PES for each electron-ion mass ratio (see Sec. 1.4.1) we compare the BOA ground state energy level $\varepsilon_{gs}^{(BOA)}$ obtained using

<table>
<thead>
<tr>
<th>$\varepsilon_{b(DOA)}$ [eV]</th>
<th>$R_m \approx 5.45 \times 10^{-4}$</th>
<th>$R_m \approx 4.84 \times 10^{-3}$</th>
<th>$R_m = 0.1$</th>
<th>$R_m = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>gs PES</td>
<td>3.7447 (7)</td>
<td>3.4791 (4)</td>
<td>2.0936 (9)</td>
<td>-1.165 (3)</td>
</tr>
<tr>
<td>1Ex PES</td>
<td>0.0248 (1)</td>
<td>0.0081 (2)</td>
<td>-0.077 (1)</td>
<td>-0.199 (3)</td>
</tr>
<tr>
<td>2Ex PES</td>
<td>1.5914 (1)</td>
<td>1.499 (2)</td>
<td>1.0062 (6)</td>
<td>-0.0189 (2)</td>
</tr>
<tr>
<td>3Ex PES</td>
<td>0.0462 (2)</td>
<td>0.03469 (5)</td>
<td>-0.0239 (5)</td>
<td>-0.1174 (4)</td>
</tr>
</tbody>
</table>

TABLE 2.6. Binding energies for the first four adiabatic PES for $H_2^+$ using the BOA for the four electron ion mass ratios considered $R_m \approx 5.45 \times 10^{-4}$, $R_m \approx 4.84 \times 10^{-3}$, $R_m = 0.1$ and $R_m = 1$, which have been defined with respect to the first vibrational state for each PES and electron-ion mass ratio.
the harmonic approximation with respect to the ground state diagonalised exact electron-ion eigenvalue \( \varepsilon_{gs(exact)} \), by calculating the difference between them \( \Delta \varepsilon = \varepsilon_{gs(BOA)} - \varepsilon_{gs(exact)} \) for \( H_4^+ \) (see Table 2.7). Note that the anharmonic approximation is better than the harmonic one. Even though, there is little difference between the BOA energy levels obtained using the anharmonic and harmonic approximation. Moreover, the anharmonic BOA energy levels lie below the exact electron-ion energy levels. We expect that the BOA is accurate around the minimum of the gs PES as the exact eigenvalues of the electron-ion problem can be interpreted in terms of the ionic vibrational levels for the electronic ground state PES (the BOA picture). For small mass ratios, the electronic transitions will require more energy than ionic transitions and therefore there will be little coupling between electrons and ions. However, as the mass ratio increases, the energy required for electronic and ionic transitions will become comparable, therefore leading to a larger electron-ion coupling.

To check the accuracy of the BOA we use the following power law relation:

\[
\varepsilon_{gs(BOA)} - \varepsilon_{gs(exact)} = a(R_m)^b = a \kappa^b
\]

where \( \kappa \) is the perturbation parameter of the BOA (see Sec. 1.4.1).

We verify this power law behaviour of the BOA error (Eq. 2.25) as a function of the four types of electron-ion mass ratios \( R_m \) in Fig. 2.11 using the logarithmic scale where we obtain \( b = 1.047 \) (1). As \( b \approx 1 \), we obtain as we expected that the first term neglected in the BOA correction to the energy in 1D is the fourth order term in \( \kappa \) as we have no rotations (see Sec. 1.4.1). In 3D, \( b \approx 1.5 \), as the first term neglected in the BOA correction to the energy is the sixth order term in \( \kappa \). Rotations give a fourth order in \( \kappa \) correction and the fifth order in \( \kappa \) is zero [24].

2.4. Linear response spectra from numerical frozen-ion approximation

In this section we perform the frozen-ion approximation to obtain the optical photoabsorption spectra within linear response using Eqs. 1.32, 1.104 and 1.105 for the four different types of electron-ion mass ratios considered \( R_m \approx 5.45 \times 10^{-4}, R_m \approx 4.84 \times 10^{-3}, R_m = 0.1 \) and \( R_m = 1 \).

In this approximation we freeze the ions at a fixed interionic separation \( R \) and initially “kick” the electron to a non-stationary state, which we then propagate in time. Note that this time propagation is performed using the electronic coordinate \( \xi \) to calculate the dipole transitions. The ions are frozen at a given \( R \) position and do not propagate. We follow the time evolution of this initial state from the dipole moment \( d(t) \) defined in Eq. 1.104.

From the time propagation in this initial “kicked” state we obtain the linear response photoabsorption spectra by Fourier Transformation of the dipole moment \( d(t) \) using Eq. 1.105.

In the photoabsorption spectra we have all the allowed electronic transitions that are present. These electronic transitions will have a given photoabsorption frequency that

<table>
<thead>
<tr>
<th>( R_m \approx 5.45 \times 10^{-4} )</th>
<th>( \varepsilon_{gs(exact)} ) [eV]</th>
<th>( \varepsilon_{gs(BOA)} ) [eV]</th>
<th>( \Delta \varepsilon = \varepsilon_{gs(BOA)} - \varepsilon_{gs(exact)} ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.7454 (3)</td>
<td>-3.7447 (7)</td>
<td>0.0007 (5)</td>
<td></td>
</tr>
<tr>
<td>( R_m \approx 4.84 \times 10^{-4} )</td>
<td>-3.4851 (3)</td>
<td>-3.4791 (4)</td>
<td>0.0060 (4)</td>
</tr>
<tr>
<td>( R_m = 0.1 )</td>
<td>-2.0936 (9)</td>
<td>-2.0936 (9)</td>
<td>0.0000 (1)</td>
</tr>
<tr>
<td>( R_m = 1 )</td>
<td>-0.6052 (2)</td>
<td>1.165 (3)</td>
<td>1.770 (3)</td>
</tr>
</tbody>
</table>

TABLE 2.7. \( H_4^+ \) ground state eigenvalues obtained by exact electron-ion diagonalisation \( \varepsilon_{gs(exact)} \) and ground state BOA vibration levels obtained from each PES using the harmonic approximation \( \varepsilon_{gs(BOA)} \) for the different electron-ion mass ratios where \( \Delta \varepsilon = \varepsilon_{gs(BOA)} - \varepsilon_{gs(exact)} \) has been calculated.
2.4. \( H_2^+ \) FROZEN-ION PROPAGATION

FIGURE 2.11. Power law fit using the logarithmic scale from Eq. 2.25 to obtain the ground state BOA accuracy in 1D by comparing the ground state BOA vibrational level using the harmonic approximation to the ground state exact electron-ion energy levels for each \( R_m \).

will be given by the energy difference between the initial and final states of the electronic transitions (see Eq. 1.104).

In the frozen-ion approximation we obtain only electronic energy levels. Therefore, we can relate the frozen-ion approximation to the PES’s in the BOA which are obtained from frozen-ion electronic eigenvalues for several values of \( R \). The electronic transition energies between the initial and final states depend on the interionic distances \( R \) at which we freeze the ions (see Fig. 2.3 to visualise the electronic energy differences between the PES’s for different \( R \) values).

We have selected the following interionic distances: \( R = 0.529, R_{eq}, 3.175 \) and 11.642 Å. Note that \( R_{eq} \) is given in Table 2.4 for \( R_m \approx 5.45 \times 10^{-4}, R_m \approx 4.84 \times 10^{-3}, R_m = 0.1 \) and \( R_m = 1 \), respectively.

We plot the dipole moment \( d(t) \) time evolution from Eq. 1.104 for \( R_m \approx 5.45 \times 10^{-4} \) as an example of \( R_m \), using \( R = R_{eq} \) in Fig. 2.12 where we see that we have a constant “almost harmonic” pattern which corresponds to a function such as:

\[
d(t) = -a_0 \sin c_0 t, \tag{2.26}
\]

where \( a_0 \) is the amplitude of the oscillation, \( c_0 \) is the main dipole moment frequency oscillation at \( R = R_{eq} \). The corresponding plots for the other \( R \neq R_{eq} \) and the different types of electron-ion mass ratios \( R_m \) are not shown as we obtain a similar pattern.

In the frozen-ion approximation, the dipole response to an initial “kick” is a periodic oscillation, whose frequency depends on the energy difference between the initial and final states of the electronic transitions (see Eq. 1.104). Since in the frozen-ion approximation there is no energy exchange between the electron and the ions, the oscillations are periodic and undamped.
We can Fourier Transform the $d(t)$ time evolution to obtain a $\sigma_{abs}$ spectrum using Eq. 1.105 for the different values of $R$ and electron-ion mass ratios $R_m$ considered. Here we only show in Fig. 2.13 the $\sigma_{abs}$ spectra for the different values of $R$ for the electron-ion mass ratio $R_m \approx 5.45 \times 10^{-4}$, as for the other $R_m$ they are quite similar. This is because the first four BOA PES for each $R_m$ shown in Fig. 2.3, are similar and therefore the electronic transition energies will only change slightly as a function of $R_m$.

Taking into account the definition of the dipole moment in Eq. 1.104 where $\hat{x}$ is an odd operator, we see that for the even-even or odd-odd electronic transitions the dipole transition is zero by symmetry. Therefore, these transitions will be forbidden and they do not show a peak in the $\sigma_{abs}$ spectra. The even-odd or odd-even electronic transitions are allowed and show a peak in the $\sigma_{abs}$ spectra. The frequency of these allowed electronic transitions will be given by the energy difference between the initial and final states of the electronic transitions.

In Fig. 2.13 we see a few peaks with a large amplitude. These peaks correspond to the allowed electronic transitions between the electronic ground state energy level and higher excited state electronic energy levels. Note that the photoabsorption cross section in the $\sigma_{abs}$ spectrum is given in the logarithmic scale. The black lines in Fig. 2.13 correspond to the photoabsorption frequencies of the electronic allowed and forbidden transitions for a converged calculation below the molecular dissociation energy. For $R = 11.642 \text{Å}$ we need more time to resolve the main electronic transition peak as this electronic transition energy is very small. The oscillations seen in Fig. 2.13 d) are related to the interference of the linear combination of atomic orbitals shown in Fig. 2.14, where the electron can be with one proton or the other for energies above the molecular dissociation threshold. We plot in Fig. 2.15, the $H$ atom spectrum along with the spectrum in Fig. 2.13 d) for $R_m \approx 5.45 \times 10^{-4}$ to see the origin of the interference effect. We see that for the $H$ atom
we do not have this interference effect. On the other hand, we see that the frequency of the electronic transitions depends on the $R$ value we choose (see Fig. 2.13).

For any $R$ that we have selected, the main transition with the largest amplitude corresponds to a transition from the electronic ground state energy level to the electronic first excited energy level in Fig. 2.13. Therefore the linear response spectra is dominated by a single electronic transition. This effect is shown in the $d(t)$ time evolution in Fig. 2.12, which is why we see a constant “almost harmonic” pattern.

As we have a main electronic transition we can simply model the electronic dynamics after a “kick” using a two-level system (2LS) given by the ground state and first excited state energy levels. The other electronic transitions with a smaller amplitude in Fig. 2.13 correspond to a transition from the ground state energy level to the third and fifth excited state energy levels, respectively.

The results for the photoabsorption frequencies of these three electronic transitions from the ground state energy level at $R = R_{eq}$ for each electron-ion mass ratio $R_m$ at the fixed gs PES equilibrium position $R_{eq}$ calculated using the BOA for $H_2^+$. 

Table 2.8. Photoabsorption frequencies given for a transition from the gs PES to the 1Ex PES, a transition from the gs PES to the 3Ex PES and a transition from the gs PES to the 5Ex PES for each electron-ion mass ratio $R_m$ at the fixed gs PES equilibrium position $R_{eq}$ calculated using the BOA for $H_2^+$. 

2.5. Linear response spectra from exact numerical electron-ion propagation 

In this section we have obtained the linear response optical spectra from exact numerical electron-ion propagation of Eqs. 1.32, 1.104 and 1.105 for the four different types of electron-ion mass ratios $R_m$.

In this case the ions are not frozen at given interionic distance $R$ as in the frozen-ion approximation but they are allowed to evolve, according to the electron-ion time-propagation (see Eq.1.101).

When we perform the exact electron-ion propagation for the different electron-ion mass ratios, the corresponding dipole moment $d(t)$ time evolution does not show a constant “almost harmonic” pattern as in the frozen-ion calculations but the behaviour can be fitted, for $R_m \approx 5.45 \times 10^{-4}$ and $R_m \approx 4.84 \times 10^{-3}$ only, to a damped function (see Fig. 2.16) as:

$$d(t) = -ae^{-\frac{t}{2}} \sin ct,$$

(2.27)

where $a$ is the amplitude of the damped dipole moment oscillation, $b$ is the damping coefficient and $c$ is the main damped dipole moment frequency oscillation.
From the Fourier Transformation of the $d(t)$ in Eq. 1.104 we obtain the photoabsorption cross section spectra in Eq. 1.105. Then we plotted the corresponding $\sigma_{abs}$ spectra for the different electron-ion mass ratios in Fig. 2.17.

In order to fit the main peak in Figs. 2.17 when the logarithmic scale for $\sigma_{abs}$ is not used in Figs. 2.18, we use a Gaussian-like function:

$$\tilde{\sigma}(\omega) \propto \sqrt{\frac{\omega}{2\pi b^2}} e^{-\frac{(\omega-c)^2}{2b^2}},$$  \hspace{1cm} (2.28)

For $R_m \approx 5.45 \times 10^{-4}$ and $R_m \approx 4.84 \times 10^{-3}$ in Figs. 2.17 a) and b), the main peak can be fitted using a Gaussian symmetric function as shown in Figs. 2.18 a) and b), respectively. This is possible because a ground state to first excited state single electronic transition dominates over the other transitions giving a reasonably symmetric peak. Even though, for these two cases, the one with $R_m \approx 4.84 \times 10^{-3}$ in Fig. 2.18 b) shows a main peak with a larger asymmetry [8] than with $R_m \approx 5.45 \times 10^{-4}$ in Fig. 2.18 a). This is because in the effective BOA 2LS picture, one implicitly assumes that the electron-ion ground state can be factorised in an electronic times ionic ground state (Gaussian), where the ionic ground state depends on the electronic ground state only. If the BOA breaks down, one can no longer assume this electron-ion decoupling process (Non-Gaussian).
The main exact electron-ion photoabsorption transition frequency obtained by exact numerical propagation can be related to the main frozen-ion electronic transition frequency for $R_m \approx 5.45 \times 10^{-4}$ and $R_m \approx 4.84 \times 10^{-3}$ (see Tables 2.8 and 2.9). The damped behaviour in Fig. 2.16 is due to the fact that the electron transfers part of its energy to the ions.

For $R_m = 0.1$ and $R_m = 1$ in Figs. 2.16, 2.17 and 2.18 c) and d), more than one single dominant electronic transition is necessary to describe the dynamics after a “kick”. In Figs. 2.18 c) and d) we show the main broad photoabsorption peaks with a large asymmetry (which is larger for $R_m = 1$ as expected) that cannot be fitted using a Gaussian symmetric function in 2.17 c) and d). The results for b and c for $R_m \approx 5.45 \times 10^{-4}$ and $R_m \approx 4.84 \times 10^{-3}$ are shown in Tables 2.9 and 2.10. This is also the case when we use a Gaussian function to fit the main peak in Figs. 2.18 a) and b) to get the corresponding results for b and c which are also shown in Tables 2.9 and 2.10.

Table 2.9. 2LS main photoabsorption frequency from the $d(t)$ fitted time evolution using a damped function (Eq. 2.27) and the $\sigma_{abs}$ fitted spectra using a Gaussian function (Eq. 2.28) for $R_m \approx 5.45 \times 10^{-4}$ in Figs. 2.16 a) and 2.18 a) and for $R_m \approx 4.84 \times 10^{-3}$ in Figs. 2.16 b) and 2.18 b) calculated using the exact electron-ion time propagation for $H_2^+$. 

<table>
<thead>
<tr>
<th>$R_m$</th>
<th>$d(t) \rightarrow c$ [fs$^{-1}$]</th>
<th>$d(t) \rightarrow hc$ [eV]</th>
<th>$d(\omega) \rightarrow c$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.45 \times 10^{-4}$</td>
<td>15.539 (1)</td>
<td>10.228 (7)</td>
<td>10.237 (3)</td>
</tr>
<tr>
<td>$4.84 \times 10^{-3}$</td>
<td>14.324 (9)</td>
<td>9.428 (6)</td>
<td>9.44 (1)</td>
</tr>
</tbody>
</table>

**Figure 2.15.** Comparison between the $\sigma_{abs}$ spectrum for $H_2^+, R_m \approx 5.45 \times 10^{-4}$ and $R = 11.642A$ shown in Fig. 2.13 d) and the $H$ spectrum, to explain the origin of the oscillations above the molecular dissociation threshold.
Therefore, we can qualitatively explain the exact electron-ion dynamics using the BOA picture (see Fig. 2.8, to visualize the BOA picture). We assume that the exact electron-ion excitation takes place around the most stable interionic configuration for the gs PES which corresponds to $R = R_{eq}$. This exact excitation is mainly dominated by an electronic excitation. Then, we propagate the exact electron-ion time-dependent Schrödinger Equation, so that the electron moves along the excited PES’s at which it has been kicked to. During this process, the electronic photoabsorption frequency will change, as the electron loses potential energy which is transferred to the ions as kinetic energy. Note that the ions can evolve until they reach the borders of the simulation box and reflect back to combine again which is unphysical.
For the exact electron-ion propagation, the width of the peak has a physical meaning which is related to two effects. We also use the BOA picture to understand this. First, the ions are allowed to evolve so that the main electronic transition occurs around the minimum of the gs PES with a probability distribution that is maximum at \( R = R_{eq} \). Second, as explained before, due to the electron-ion energy transfer process, the electronic photoabsorption frequency will change as the electron moves along the excited PES. Note that the peaks in Fig. 2.17 are mainly dominated by the electronic excitations as we cannot distinguish ionic excitations because they are much lower in energy. However, we must take into account that in the exact electron-ion propagation the ions are allowed to evolve and therefore can also be excited.

For \( R_m \approx 5.45 \times 10^{-4} \) and \( R_m \approx 4.84 \times 10^{-3} \) we want to understand qualitatively why the Gaussian provides a good fit for the exact 2LS electron-ion dynamics after we have applied a “kick”. For the electronic wavefunction we have the same effect as in the BOA. The “kick” excites an electron from the gs PES to the 1Ex PES and the energy difference between the PES’s determines the transition. However, in the exact propagation, now the ions are not fixed. Once we apply the “kick”, the ionic wave-packets in the gs and 1Ex PES’s will independently evolve on the two adiabatic PES’s. The gs PES ionic wavefunction localised initially at \( R = R_{eq}(t = 0) \) will be correlated to the ionic wavefunction which moves with time \( R(t) \) along the 1Ex PES (see Fig. 2.19).
Figure 2.18. a) Non-logarithmic plot of Fig. 2.17 a) that can be fitted as a Gaussian for $R_m \approx 5.45 \times 10^{-4}$ b) As a) but for $R_m \approx 4.84 \times 10^{-3}$ c) Non-logarithmic plot of Fig. 2.17 c) that cannot be fitted as a Gaussian for $R_m = 0.1$ d) As d) but for $R_m = 1$
2.5. $H_2^+$ EXACT ELECTRON-ION PROPAGATION

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.19.png}
\caption{a) $G_s$ and $1\text{Ex}$ adiabatic PES’s for $R_m \approx 5.45 \times 10^{-4}$ where the ionic wavepacket is localised around $R_{eq}$ at the $g_s$ PES before the “kick”. b) As a) but after the “kick”. The ionic wavepacket in the $1\text{Ex}$ PES keeps its original Gaussian shape. c) The ionic wavepackets in the $g_s$ PES and $1\text{Ex}$ PES evolve independently when we propagate. The ionic wavepacket in the $1\text{Ex}$ PES remains Gaussian (localised around its peak position) and is out of phase with respect to the ionic wavepacket in the $g_s$ PES.}
\end{figure}
The accuracy of the BOA in computing the electron-ion spectrum of \( \text{H}_2 \)

In this chapter we perform the same analysis for \( \text{H}_2 \) as we did for the \( \text{H}_2^+ \) molecule in the previous chapter. We use the same value for the Soft Coulomb parameter \( a \), as well as the same \( R_m \) values for the same reasons as for \( \text{H}_2^+ \).

We show the numerical real-space approach results obtained from the different numerical methods (BOA and exact diagonalisation of the electron-ion Hamiltonian) to solve the time-independent Schrödinger Equation for \( \text{H}_2 \) (Eq. 1.45). The time-dependent simulations (Eqs. 1.104 and 1.105) of the “kicked” \( \text{H}_2 \) molecule are subject of ongoing research. Therefore, they are not reported in this thesis.

In the BOA we first diagonalise Eq. 1.65 at fixed ionic positions \( R \) to find the electronic PES’s. We fit the bottom of the PES’s and then numerically diagonalise the fitted potential using Eqs. 1.68 and 2.11 to obtain the BOA electron-ion eigenvalues.

For the exact numerical solution, we diagonalise the electron-ion Hamiltonian in Eq. 1.45.

3.1. Exact numerical diagonalisation of the electron-ion Hamiltonian

In this section, we perform the exact numerical diagonalisation of the electron-ion Hamiltonian of the time-independent internal Schrödinger Equation (Eq. 1.45) using the code Octopus [5].

For the \( \text{H}_2 \) molecule the molecular dissociation reference energy corresponds to the energy of two 1D \( \text{H} \) atoms in their ground state very far apart.

The positive binding energy with respect to the molecular dissociation energy is then defined as:

\[
\epsilon_b(\text{H}_2) = \epsilon_{\text{H}_2^}\text{(groundstate)} - \epsilon_{\text{H}_2}\text{(groundstate)}. \tag{3.1}
\]

The eigenvalues for the ground state obtained by exact numerical electron-ion diagonalisation of the \( \text{H}_2 \) molecule (Eq. 1.45) and two \( \text{H} \) atoms (Eq. 2.3) with the corresponding binding energies are shown in Table 3.1 for \( R_m \approx 5.45 \times 10^{-4}, R_m \approx 4.84 \times 10^{-3} \) and \( R_m = 0.1 \). \( R_m = 1 \) is not shown in the table because there are no bound electron-ion energy levels below the molecular dissociation energy (see Fig. 3.1 d)). Therefore for \( R_m = 1 \), the energy of the bound electron-ion energy levels will depend on the extent of the simulation box.

<table>
<thead>
<tr>
<th>( R_m )</th>
<th>( \epsilon_{\text{H}_2} \text{(gs)} ) [eV]</th>
<th>( \epsilon_{\text{H}_2^}\text{(gs)} ) [eV]</th>
<th>( \epsilon_b(\text{H}_2) ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 5.45 \times 10^{-4} )</td>
<td>-39.3401 (3)</td>
<td>-36.4495 (3)</td>
<td>2.8906 (3)</td>
</tr>
<tr>
<td>( 4.84 \times 10^{-3} )</td>
<td>-38.9760 (3)</td>
<td>-36.4365 (2)</td>
<td>2.5395 (3)</td>
</tr>
<tr>
<td>( 0.1 )</td>
<td>-37.2654 (3)</td>
<td>-36.1540 (2)</td>
<td>1.1114 (3)</td>
</tr>
</tbody>
</table>

Table 3.1: \( H_2 \) and \( H \cdots H \) ground state (gs) eigenvalues with the corresponding binding energies \( \epsilon_b(\text{H}_2) \) for \( R_m \approx 5.45 \times 10^{-4}, R_m \approx 4.84 \times 10^{-3} \) and \( R_m = 0.1 \) obtained by exact numerical diagonalisation of the electron-ion Hamiltonian of Eqs. 1.45 and 2.3.
Since in the $H_2$ molecule there are two electrons and two protons (which are fermions), the antisymmetry of the wavefunction must be enforced both for the protons and the electrons.

From Eq. 1.36 we see that the potential for the $H_2$ molecule is invariant under the interionic and interelectronic distance coordinate transformations $R \rightarrow -R$ and $r \rightarrow -r$. This means that the resulting total molecular eigenfunctions will be even or odd under the same transformation. Physically the even ionic and electronic eigenfunctions correspond to the singlet state while the odd ones to the triplet state, respectively.

In Fig. 3.1, we show the electron-ion energy spectrum below the molecular dissociation energy for the different electron-ion mass ratios. Numerical parameters such as the simulation box ($L_R$, $L_\xi$, $L_r$) and the grid spacing ($\Delta R$, $\Delta \xi$, $\Delta r$) introduced in Sec. 1.6 are varied till convergence by visual inspection. From numerical inspection, the convergence of the eigenvalues is of the order of $1 - 10\text{meV}$.

For $R_m \approx 5.45 \times 10^{-4}$ the convergence of the discrete electron-ion energy levels is good below the molecular dissociation energy for $\Delta \xi = \Delta R = 0.053$ and $L_R = L_\xi = 5.29\text{Å}$. For $R_m \approx 4.84 \times 10^{-3}$ we need $\Delta \xi = \Delta R = 0.053$ and $L_R = L_\xi = 7.94\text{Å}$, while for $R_m = 0.1$ we need $\Delta \xi = \Delta R = 0.106$ and $L_R = L_\xi = 10.58\text{Å}$, to achieve a good convergence of the discrete electron-ion energy levels below the molecular dissociation energy. If we increase the box size and/or decrease the spacing the electron-ion energy spectra are not going to change as shown with the blue and red lines in Fig. 3.1.

We have 22, 8, 2 and no bound electron-ion energy lines below the molecular dissociation energy for $R_m \approx 5.45 \times 10^{-4}$, $R_m \approx 4.84 \times 10^{-3}$, $R_m = 0.1$ and $R_m = 1$, respectively. In Fig. 3.1 the number of electron-ion energy levels we see below the molecular dissociation energy is smaller than the real number of bound electron-ion energy levels (see Fig. 2.1). We have selected.

As the potential minima are farther apart, the left and right eigenfunction components in the ionic potentials (see Fig. 2.1 for $H_2^+$), will not overlap and the singlet-triplet degeneracy will be maintained. However, this does not happen for $R_m = 0.1$ because as the electron-ion mass ratio increases, the potential minima get closer in the $R$ axis.

### 3.2. BOA numerical diagonalisation of the electron-ion Hamiltonian

In this section, we solve the time-independent internal Schrödinger Equation (Eq. 1.45) using the BOA for each $R_m$ we have selected.

In the BOA we first diagonalise Eq. 1.65 at fixed ionic positions $R$ to find the electronic PES’s. We fit the bottom of the PES’s and then numerically diagonalise the fitted potential using Eq. 1.68 to obtain the BOA electron-ion eigenvalues.

In the BOA the molecular dissociation energy corresponds to the gs PES dissociation limit of the molecule for very large interionic distances $R$. We refer all the electronic PES energies to this gs PES dissociation limit which has been set to zero.

The positive binding energy with respect to the molecular dissociation energy limit in the BOA is then defined as:

$$
\varepsilon_{\text{b(BOA)}}(H_2) = \varepsilon_{H-\cdot-H(ground state)} - \varepsilon_{\text{gs(BOA)}},
$$

where $\varepsilon_{\text{gs(BOA)}}$ corresponds to the first vibrational energy level calculated from the BOA.

We have used $\Delta R = \Delta \xi = 0.053$ and $L_\xi = L_r = 26.45\text{Å}$ for our calculations and fixed values of $R$ up to $21.16\text{ Å}$. Note that for $H_2$ we could have used a smaller
3.2. H₂ BOA ELECTRON-ION DIAGONALISATION

![Figure 3.1](image)

**Figure 3.1.** (a) Electron-ion energy spectrum below the molecular dissociation energy of H₂ for \( R_m \approx 5.45 \times 10^{-4} \). The red electron-ion energy lines have been obtained using \( \Delta \xi = \Delta R = \Delta r = 0.053 \) and \( L_R = L_\xi = L_r = 5.29 \text{Å} \), whereas the blue ones using \( \Delta \xi = \Delta R = \Delta r = 0.0265 \) and \( L_R = L_\xi = L_r = 7.94 \text{Å} \) (b) As (a) but for \( R_m \approx 4.84 \times 10^{-3} \). Here the red electron-ion energy lines have been obtained using \( \Delta \xi = \Delta R = \Delta r = 0.053 \) and \( L_R = L_\xi = L_r = 7.94 \text{Å} \), whereas the blue ones using \( \Delta \xi = \Delta R = \Delta r = 0.0265 \) and \( L_R = L_\xi = L_r = 10.58 \text{Å} \) (c) As (a) but for \( R_m = 0.1 \). Here the red electron-ion energy lines have been obtained using \( \Delta \xi = \Delta R = \Delta r = 0.106 \) and \( L_R = L_\xi = L_r = 10.58 \text{Å} \), whereas the blue ones using \( \Delta \xi = \Delta R = \Delta r = 0.053 \) and \( L_R = L_\xi = L_r = 13.23 \text{Å} \) (d) For \( R_m = 1 \), there are no bound electron-ion energy levels below the molecular dissociation energy.

simulation box because the PES’s are narrower for the H₂ molecule (see Fig. 3.8) than the \( \text{H}_2^+ \) molecule (see Fig. 2.8).

To see the qualitative behaviour of the PES’s, we plot the first four adiabatic PES’s for each \( R_m \) in Fig. 3.2. The kinks we see in the third excited state PES are probably a fingerprint of a higher excited PES.

In Table 3.2 we show the BOA electronic excitation energies for the second excited (2Ex) PES and third excited (3Ex) PES given with respect to the molecular dissociation energy limit, and the dissociated \( \text{H}_2 \) excitation energies for each \( R_m \).

We plot (Fig. 3.3) the electronic ground state potential energy surface for the frozen ion calculation as a function of the fixed values of \( R \) for each \( R_m \).

As the gs PES (Fig. 3.4 (a)) is anharmonic we approximate the gs PES around its classical minimum \( R_{eq} \) by a fourth order polynomial (Fig. 3.4 (c)) for \( R_m \approx 5.45 \times 10^{-4} \) as an example of one of the \( R_m \)’s. To calculate the vibrational or ionic structure we diagonalise Eq. 2.11. The BOA electron-ion diagonalised energy levels are shown in Fig. 3.4 (c).

The gs PES (Fig. 3.4 (a)) can also be approximated to a harmonic potential in Fig. 3.4 (b).

The eigenvalues for a harmonic oscillator have also been plotted in Fig. 3.4 (b) for \( R_m \approx 5.45 \times 10^{-4} \). As the harmonic fit is appropriate to fit the PES’s around the minimum \( R_{eq} \) we have obtained their corresponding vibrational frequency \( \lambda \) in wavenumbers using...
Figure 3.2. a) First four adiabatic PES’s for \( R_m \approx 5.45 \times 10^{-4} \) using the BOA with a soft coulomb potential in 1-D where \( \Delta \xi = 0.053 \) and \( L_\xi = 26.45 \) a.u. where we have used fixed values of \( R \) up to 21.16 \( \AA \) for \( H_2^+ \). b) As a) but for \( R_m \approx 4.84 \times 10^{-3} \). c) As a) but for \( R_m = 0.1 \). d) As a) but for \( R_m = 1 \).

The BOA electronic excitation energies in the dissociation limit have been obtained by fitting the PES’s for large values of \( R \) which we will show later how. These BOA electronic excitation energies in the dissociation limit correspond to the excitation energies of the dissociated \( H_2 \) molecule, as for very large interionic distances \( R \) in the gs BOA dissociation limit, we have two 1D \( H \) atoms in their ground state very far apart.

Table 3.2. BOA electronic excitation energies \( \varepsilon_{dl(BOA)} \) for the second excited (2Ex) PES and third excited (3Ex) PES in the dissociation limit and \( H \cdots H \) excitation energies \( \varepsilon_x(H \cdots H) \) for each \( R_m \). The results for each \( R_m \) are shown in Table 3.3.

<table>
<thead>
<tr>
<th>( R_m \approx 5.45 \times 10^{-4} )</th>
<th>2Ex/3Ex PES ( \varepsilon_{dl(BOA)} ) [eV]</th>
<th>( H \cdots H (gs \rightarrow 1Ex)\varepsilon_x(H \cdots H) ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_m = 0.1 )</td>
<td>10.74681 (2)</td>
<td>10.7457 (2)</td>
</tr>
<tr>
<td>( R_m = 1 )</td>
<td>9.446684 (7)</td>
<td>11.0741 (3)</td>
</tr>
</tbody>
</table>

Table 3.3. \( H_2 \) vibrational frequencies in wavenumbers for the gs, 2Ex and 3Ex adiabatic PES’s for each \( R_m \) obtained by a harmonic fit around the PES’s minima

<table>
<thead>
<tr>
<th>( \lambda (\text{cm}^{-1}) )</th>
<th>( R_m \approx 5.45 \times 10^{-4} )</th>
<th>( R_m = 4.84 \times 10^{-3} )</th>
<th>( R_m = 0.1 )</th>
<th>( R_m = 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>gs PES</td>
<td>2917 (11)</td>
<td>8687 (11)</td>
<td>39002 (402)</td>
<td>111905 (876)</td>
</tr>
<tr>
<td>2Ex PES</td>
<td>1848 (12)</td>
<td>5501 (1)</td>
<td>24146 (164)</td>
<td>61462 (97)</td>
</tr>
<tr>
<td>3Ex PES</td>
<td>1643 (173)</td>
<td>4909 (1)</td>
<td>22943 (302)</td>
<td>61752 (6459)</td>
</tr>
</tbody>
</table>
We have also used the Morse potential and the corresponding eigenvalues (Eqs. 2.12 and 2.14) to describe the adiabatic ground state PES Fig. 3.4 d) for $R_m \approx 5.45 \times 10^{-4}$. In Fig. 3.5 we see that the Morse potential is similar to the gs PES.

We only show Fig. 3.4 for $R_m \approx 5.45 \times 10^{-4}$ because we can see the same ideas as for $H_2^+$ in a clearer way. Note that for $H_2^+$ we used $R_m \approx 4.84 \times 10^{-3}$ because we had more bound electron-ion energy levels.

Table 3.4 summarizes the results obtained for the parameters in Figs. 3.4 b and c) as well as for the other $R_m$ for which we do not show a figure. Note that $R_m = 1$ is useless to determine the BOA accuracy because the exact electron-ion energy levels are above the molecular dissociation energy and therefore depend on the extent of the simulation box.

For $R_m = 0.1$, $\varepsilon_{\text{gs BOA}}$ is the energy of the first vibrational state calculated from the minimum of the BOA gs PES using the anharmonic fit, instead of using the harmonic fit as for $H_2^+$. In this case, the electron-ion energy levels are higher in energy than for $H_2^+$ because the gs PES is narrower. For the BOA to be accurate for these energy levels that are higher in energy, we need to use a better approximation than the harmonic one to fit the gs PES (see Fig. 3.6).

As for $H_2^+$ we can calculate the first correction to the harmonic energy relative to a fourth order expansion of the morse potential using time-independent perturbation theory. Using Eq. 2.16 the eigenvalues are more accurate (see Fig. 3.7) with respect to the exact diagonalised levels than in Fig. 3.4 b) using only the harmonic eigenvalues $\varepsilon_n = \hbar \omega (n + \frac{1}{2})$. 

**FIGURE 3.3.** a) Electronic ground state PES for $R_m \approx 5.45 \times 10^{-4}$ using the BOA with a soft coulomb potential in 1-D where $\Delta \xi = 0.053$ and $L_\xi = 26.45 \text{Å}$, where we have used fixed values of $R$ up to $21.16 \text{Å}$ for $H_2$. The 22 bound exact electron-ion energy levels of $H_2$ (horizontal black lines) from Fig. 3.1 a) have been added to the figure. b) As a) but for $R_m \approx 4.84 \times 10^{-3}$ adding the 8 bound exact electron-ion energy levels from Fig. 3.1 b). c) As a) but for $R_m = 0.1$ adding the 2 bound exact electron-ion energy levels from Fig. 3.1 c). d) As a) but for $R_m = 1$. In this case we have no bound exact electron-ion energy levels as shown in Fig. 3.1 d).
3.4. **BOA vs Exact Electron-Ion Diagonalisation**

In Fig. 3.4 we show the first three electronic excited PES’s together with the electronic gs PES. These PES’s are similar for the other \( \mathbf{R}_m \) that we have considered.

The non-covalent long-range minimum is not so appreciable for the \( \mathbf{H}_2 \) molecule (see Fig. 3.8 b) as for the \( \mathbf{H}_2^+ \) molecule (see Fig. 2.8 b)). This is because the charged proton-dipole interaction for the dissociating \( \mathbf{H}_2^+ \) molecule is stronger than the neutral dipole-dipole interaction for the dissociating \( \mathbf{H}_2 \) molecule for large interatomic distances.

The minimum for the second and third excited states can be fitted by using a harmonic potential and an anharmonic potential. The results of the fitting parameters are shown in Table 3.5 for each \( \mathbf{R}_m \).

To obtain the dissociation limit energies of the PES’s we need to determine the decaying order \( b \) from Eq. 2.18.

To determine the power law decaying order \( b \) analytically we have used time-independent perturbation theory (see details in Appendix D) for \( \mathbf{H}_2 \). We want to start from a Hamiltonian of two isolated \( \mathbf{H} \) atoms perturbed by the presence of each other very far apart (see new coordinates in the new reference frame in Fig. 3.9). We obtain \( b=3 \) as for \( \mathbf{H}_2^+ \).

The results for the dissociation energies in Eq. 2.18 using \( b = 3 \) were shown in Table 3.2 for each \( \mathbf{R}_m \) that we have selected.

3.3. **Validity of the BOA numerical diagonalisation of the electron-ion Hamiltonian**

As seen in Fig. 2.2 we have less bound electron-ion energy levels for \( \mathbf{H}_2 \) than for \( \mathbf{H}_2^+ \) in Fig. 3.1.
3.3. $H_2$ BOA ELECTRON-ION DIAGONALISATION VALIDITY

Figure 3.5. (a) Morse potential for $R_m \approx 5.45 \times 10^{-4}$. We see that it is qualitatively similar to the electronic gs PES obtained by the BOA. (b) Zoom of the tail region of the Morse potential in (a) where we see that the Morse potential decays exponentially to zero much slower than the power law tail from the data as opposed to the $H_2^+$ case.

Figure 3.6. Electronic ground state PES for $R_m = 0.1$ using the BOA with a soft coulomb potential in 1-D where $\Delta \xi = 0.053$ and $L_\xi = 26.45\,\text{Å}$, where we have used fixed values of $R$ up to 21.16 Å for $H_2$. A fourth order anharmonic fit of the gs PES with the corresponding BOA ion-electron diagonalised eigenvalues and the 2 exact bound electron-ion energy lines below the molecular dissociation energy are shown.
TABLE 3.4. \( H_2 \) ground state fitted PES parameters for each \( R_m \) using the fourth order anharmonic fit around the minimum where: \( \varepsilon_0 \) is the energy that corresponds to the minimum of the gs PES at the equilibrium interionic distance \( R_{eq} \); \( \varepsilon_{gs(exact)} \) is the energy for the ground state eigenvalue obtained by exact electron-ion diagonalisation of \( H_2 \); \( \varepsilon_{gs(BOA)} \) is the ground state energy of the first vibrational state calculated from the minimum of the BOA gs PES; \( \varepsilon_b(BOA) \) is the binding energy in the BOA picture (Eq. 3.2); \( \varepsilon_b(exact) \) is the binding energy in the exact electron-ion picture (Eq. 3.1); \( \varepsilon_{zp} \) is the zero point energy of the harmonic oscillator \( \frac{1}{2} \hbar \omega \) from the minimum \( \varepsilon_0 \) of the gs PES; \( R_{eq} \) is the equilibrium interionic distance that corresponds to the minimum of the gs PES; \( k_1, k_2 \) and \( k_3 \) are the fitting parameters used in Eq. 2.11.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( R_m \approx 5.45 \times 10^{-4} )</th>
<th>( R_m \approx 4.84 \times 10^{-5} )</th>
<th>( R_m = 0.1 )</th>
<th>( R_m = 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{eq}(\text{Å}) )</td>
<td>0.8468 (7)</td>
<td>0.8474 (7)</td>
<td>0.8595 (7)</td>
<td>0.9561 (8)</td>
</tr>
<tr>
<td>( \varepsilon_0 ) (eV)</td>
<td>-3.069 (2)</td>
<td>-3.069 (2)</td>
<td>-3.066 (2)</td>
<td>-2.999 (2)</td>
</tr>
<tr>
<td>( k_1 ) (eV/Å)</td>
<td>15.77 (6)</td>
<td>15.75 (6)</td>
<td>15.35 (5)</td>
<td>12.64 (5)</td>
</tr>
<tr>
<td>( k_2 ) (eV/Å)</td>
<td>-47.4 (7)</td>
<td>-47.3 (8)</td>
<td>-46.0 (6)</td>
<td>-37.4 (4)</td>
</tr>
<tr>
<td>( k_3 ) (eV/Å)</td>
<td>58 (3)</td>
<td>58 (3)</td>
<td>56 (3)</td>
<td>46 (3)</td>
</tr>
<tr>
<td>( \varepsilon_{gs(BOA)} ) (eV)</td>
<td>-2.8885 (5)</td>
<td>-2.530 (1)</td>
<td>-0.94962 (3)</td>
<td>3.94 (3)</td>
</tr>
<tr>
<td>( \varepsilon_{gs(exact)} ) (eV)</td>
<td>-2.89071 (3)</td>
<td>-2.53937 (3)</td>
<td>-1.11145 (2)</td>
<td></td>
</tr>
<tr>
<td>( \varepsilon_{zp} ) (eV)</td>
<td>0.181 (2)</td>
<td>0.539 (1)</td>
<td>2.420 (3)</td>
<td>6.94 (3)</td>
</tr>
<tr>
<td>( \varepsilon_b(BOA) ) (eV)</td>
<td>2.8885 (5)</td>
<td>2.530 (1)</td>
<td>0.94962 (3)</td>
<td>-3.94 (3)</td>
</tr>
<tr>
<td>( \varepsilon_b(exact) ) (eV)</td>
<td>2.8906 (3)</td>
<td>2.5395 (3)</td>
<td>1.1114 (3)</td>
<td></td>
</tr>
</tbody>
</table>

FIGURE 3.7. As Fig. 3.4 b) using the first correction to the harmonic energy relative to a fourth order expansion of the morse potential. The eigenvalues in this case are then given by Eq. 2.16.
### Table 3.5. $H_2$ last two excited state fitted PES parameters for each $R_m$ obtained by a harmonic fit and an anharmonic fit around the minimum using Eq. 2.11 where for each PES: $R_{eq}$ is the equilibrium separation; $\varepsilon_0$ is the energy minimum; $k_1$, $k_2$ and $k_3$ are the fitting parameters; $\varepsilon_{gs}(BOA)$ is the energy of the first ionic excitation; $\varepsilon_b(BOA)$ is the binding energy in the BOA picture (see Eq. 3.2); $\varepsilon_{dl}(BOA)$ is the BOA energy in the dissociation limit, the values are given in Table 3.2) and $\varepsilon_{zp}$ is the zero-point energy.

<table>
<thead>
<tr>
<th>$R_m \approx 5.45 \times 10^{-3}$</th>
<th>2Ex PES</th>
<th>3Ex PES</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{eq}(A)$</td>
<td>1.3095 (8)</td>
<td>1.299 (1)</td>
</tr>
<tr>
<td>$\varepsilon_0$ (eV)</td>
<td>7.221 (1)</td>
<td>9.396 (2)</td>
</tr>
<tr>
<td>$k_1\frac{\varepsilon_0}{A}$</td>
<td>6.33 (4)</td>
<td>5.00 (4)</td>
</tr>
<tr>
<td>$k_2\frac{\varepsilon_0}{A}$</td>
<td>-17.5 (1)</td>
<td>-18.7 (1)</td>
</tr>
<tr>
<td>$k_3\frac{\varepsilon_0}{A}$</td>
<td>30.8 (7)</td>
<td>36.1 (8)</td>
</tr>
<tr>
<td>$\varepsilon_{gs}(BOA)$ (eV)</td>
<td>7.3361 (4)</td>
<td>9.4976 (4)</td>
</tr>
<tr>
<td>$\varepsilon_{zp}$ (eV)</td>
<td>0.115 (1)</td>
<td>0.102 (2)</td>
</tr>
<tr>
<td>$\varepsilon_b(BOA)$ (eV)</td>
<td>3.4107 (4)</td>
<td>1.2492 (4)</td>
</tr>
<tr>
<td>$R_{eq}(A)$</td>
<td>1.3106 (8)</td>
<td>1.299 (1)</td>
</tr>
<tr>
<td>$\varepsilon_0$ (eV)</td>
<td>7.233 (1)</td>
<td>9.398 (2)</td>
</tr>
<tr>
<td>$k_1\frac{\varepsilon_0}{A}$</td>
<td>6.31 (4)</td>
<td>5.03 (4)</td>
</tr>
<tr>
<td>$k_2\frac{\varepsilon_0}{A}$</td>
<td>-17.4 (1)</td>
<td>-18.7 (1)</td>
</tr>
<tr>
<td>$k_3\frac{\varepsilon_0}{A}$</td>
<td>30.8 (7)</td>
<td>36.0 (8)</td>
</tr>
<tr>
<td>$\varepsilon_{gs}(BOA)$ (eV)</td>
<td>7.574 (1)</td>
<td>9.70 (2)</td>
</tr>
<tr>
<td>$\varepsilon_{zp}$ (eV)</td>
<td>0.341 (1)</td>
<td>0.30 (2)</td>
</tr>
<tr>
<td>$\varepsilon_b(BOA)$ (eV)</td>
<td>3.163 (1)</td>
<td>1.04 (2)</td>
</tr>
<tr>
<td>$R_{eq}(A)$</td>
<td>1.3347 (9)</td>
<td>1.293 (2)</td>
</tr>
<tr>
<td>$\varepsilon_0$ (eV)</td>
<td>7.463 (1)</td>
<td>9.443 (2)</td>
</tr>
<tr>
<td>$k_1\frac{\varepsilon_0}{A}$</td>
<td>5.88 (4)</td>
<td>5.31 (7)</td>
</tr>
<tr>
<td>$k_2\frac{\varepsilon_0}{A}$</td>
<td>-16.5 (1)</td>
<td>-19.0 (4)</td>
</tr>
<tr>
<td>$k_3\frac{\varepsilon_0}{A}$</td>
<td>30.9 (7)</td>
<td>35 (2)</td>
</tr>
<tr>
<td>$\varepsilon_{gs}(BOA)$ (eV)</td>
<td>8.959 (5)</td>
<td>10.866 (9)</td>
</tr>
<tr>
<td>$\varepsilon_{zp}$ (eV)</td>
<td>1.496 (1)</td>
<td>1.423 (7)</td>
</tr>
<tr>
<td>$\varepsilon_b(BOA)$ (eV)</td>
<td>1.615 (5)</td>
<td>-0.292 (9)</td>
</tr>
<tr>
<td>$R_{eq}(A)$</td>
<td>1.4552 (2)</td>
<td>1.587 (6)</td>
</tr>
<tr>
<td>$\varepsilon_0$ (eV)</td>
<td>8.75709 (5)</td>
<td>8.816 (2)</td>
</tr>
<tr>
<td>$k_1\frac{\varepsilon_0}{A}$</td>
<td>3.813 (6)</td>
<td>3.8 (4)</td>
</tr>
<tr>
<td>$k_2\frac{\varepsilon_0}{A}$</td>
<td>-10.9 (2)</td>
<td>25 (7)</td>
</tr>
<tr>
<td>$k_3\frac{\varepsilon_0}{A}$</td>
<td>38 (1)</td>
<td>188 (42)</td>
</tr>
<tr>
<td>$\varepsilon_{gs}(BOA)$ (eV)</td>
<td>12.567 (3)</td>
<td>12.6 (2)</td>
</tr>
<tr>
<td>$\varepsilon_{zp}$ (eV)</td>
<td>3.809 (3)</td>
<td>3.8 (2)</td>
</tr>
<tr>
<td>$\varepsilon_b(BOA)$ (eV)</td>
<td>-3.120 (3)</td>
<td>-3.2 (2)</td>
</tr>
</tbody>
</table>
3. \( H_2 \) BOA VS EXACT ELECTRON-ION DIAGONALISATION

**FIGURE 3.8.** a) First four adiabatic potential energy surfaces for \( R_m \approx 5.45 \times 10^{-4} \) obtained by the BOA with the soft coulomb potential in 1-D using \( \Delta \xi = 0.055 \) and \( L_\xi = 26.45 \AA \) and fixed values of \( R \) up to 21.16 \( \AA \). b) Zoom of the minimum for the first excited electronic state from a) to show we cannot appreciate a non-covalent long-range minimum.

**FIGURE 3.9.** Schematic representation of the \( H_2 \) molecule in 1D: \( V_1 \) and \( V_2 \) are the proton velocities; \( R_1 \) and \( R_2 \) are the proton positions; \( v_1 \) and \( v_2 \) are the electron velocities; \( r_1 \) and \( r_2 \) are the electron positions; \( R = R_2 - R_1 = r_2 - r_1 \) and \( j = r_1 - R_1 = r_2 - R_2 \).

The gs PES is much stiffer for \( H_2 \) than for \( H_2^+ \), because as shown in Tables 2.4 for \( H_2^+ \) and 3.4 for \( H_2 \), the values for \( k_1 \) are larger for \( H_2 \) than for \( H_2^+ \) and therefore \( \omega = \sqrt{k_1} \mu_1 \) is also larger for \( H_2 \). We can also visualise this if we compare the gs PES in Figs. 2.7 for \( H_2^+ \) and 3.5 for \( H_2 \). This is also the case for the vibrational frequencies, where for \( H_2 \) in Table 3.3, the values are larger than for \( H_2^+ \) in Table 2.3.

This leads to less bound states for the \( H_2 \) molecule than for the \( H_2^+ \) molecule because as the potential is more localized the eigenvalues shift to higher energies. At the same time, if we compare the gs PES depth in Fig. 2.5 for \( H_2^+ \) and Fig. 3.4 for \( H_2 \) we also see that the \( H_2^+ \) molecule has a deeper minimum so that we can have more bound exact electron-ion energy levels.

On the other hand, as the gs PES for \( H_2 \) is very stiff the Morse potential decays to zero much slower than the power law tail from the electronic gs PES obtained by the BOA (see Fig. 3.5) whereas for \( H_2^+ \) the opposite occurs (see Fig. 2.7).
3.3. \( \text{H}_2 \) BOA ELECTRON-ION DIAGONALISATION VALIDITY

\[
\begin{array}{l}
\varepsilon_{\text{gs}}(\text{BOA}) \ [\text{eV}] \rightarrow R_m \approx 5.45 \times 10^{-4} \\
\varepsilon_{\text{gs}}(\text{exact}) \ [\text{eV}] \rightarrow R_m \approx 4.84 \times 10^{-4} \\
\varepsilon_{\text{gs}}(\text{BOA}) \ [\text{eV}] \rightarrow R_m = 0.1 \\
\varepsilon_{\text{gs}}(\text{BOA}) \ [\text{eV}] \rightarrow R_m = 1
\end{array}
\]

\[
\begin{array}{cccccc}
\text{gs PES} & 2.8885 (3) & 2.530 (1) & 0.94962 (3) & -3.94 (3) \\
2\text{Ex PES} & 3.4107 (4) & 3.163 (1) & 1.615 (5) & -3.120 (3) \\
3\text{Ex PES} & 1.2492 (4) & 1.04 (2) & -0.292 (9) & -3.2 (2)
\end{array}
\]

**Table 3.6.** Binding energies for the gs, 2Ex and 3Ex adiabatic PES using the BOA for \( \text{H}_2 \) for the three electron ion mass ratios \( R_m \) considered, which have been defined with respect to the ground state vibrational state for the gs, 2Ex and 3Ex PES’s.

\[
\begin{array}{cccc}
R_m \approx 5.45 \times 10^{-4} & -2.89071 (3) & -2.8885 (5) & 0.0022 (3) \\
R_m \approx 4.84 \times 10^{-4} & -2.53937 (2) & -2.530 (1) & 0.009(1) \\
R_m = 0.1 & -1.11145 (2) & -0.94962 (3) & 0.16183 (3)
\end{array}
\]

**Table 3.7.** \( \text{H}_2 \) ground state eigenvalues obtained by exact electron-ion diagonalisation \( \varepsilon_{\text{gs(exact)}} \) and ground state BOA vibration levels obtained from each PES using the harmonic approximation \( \varepsilon_{\text{gs(BOA)}} \) (except for \( R_m = 0.1 \)) for the different electron-ion mass ratios where \( \Delta \varepsilon = \varepsilon_{\text{gs(BOA)}} - \varepsilon_{\text{gs(exact)}} \) has been calculated.

With respect to the binding energies in Table 3.6 for \( \text{H}_2 \) we see that they also increase with respect to the \( \text{H}_2^+ \) molecule in Table 2.6.

To determine the accuracy of the BOA for the gs PES for each electron-ion mass ratio we compare the BOA ground state vibrational energy level \( \varepsilon_{\text{gs(BOA)}} \) obtained using the harmonic approximation (anharmonic for \( R_m = 0.1 \)) with respect to the ground state diagonalised exact electron-ion eigenvalue \( \varepsilon_{\text{gs(exact)}} \) for \( \text{H}_2 \). The values that correspond to these eigenvalues are given for each electron-ion mass ratio in Table 3.7, as well as the difference between them \( \Delta \varepsilon = \varepsilon_{\text{gs(BOA)}} - \varepsilon_{\text{gs(exact)}} \). Note that this analysis has not been performed for \( R_m = 1 \) because we have no bound electron-ion energy levels.

We plot the power law relation given in Eq. 2.25 in Fig. 3.10.

For \( \text{H}_2 \), using Eq. 2.25 we obtain \( b = 0.95 \ (4) \). The fitting is worst than for \( \text{H}_2^+ \) because we have only used three types of \( R_m \). This is due to the fact that for \( R_m = 0.1 \) the exact diagonalised energy levels are close to the dissociation limit of the gs PES. For bound states that are higher in energy, the fitted PES’s (Eqs. 1.68 and 2.11) used to calculate the BOA electron-ion eigenvalues are not as accurate (see Fig. 3.6). This did not happen for the \( \text{H}_2^+ \) molecule because the potential is not as narrow as for the \( \text{H}_2 \) molecule.
Figure 3.10. Power law fit from Eq. 2.25 to obtain the ground state BOA accuracy in 1D by comparing the ground state BOA vibrational level using the harmonic approximation (except for $R_m = 0.1$) to the ground state exact electron-ion diagonalised eigenvalues for each $R_m$. 
Conclusions and Future Work

In this thesis we were interested in a fully quantum-mechanical description of a system of coupled ions and electrons in a molecule. In particular, we have analysed the validity of the Born Oppenheimer Approximation (BOA) (see Sec. 1.2) which is used in the vast majority of electronic structure calculations. The BOA is so widespread because it leads to a significant computational simplification compared to the full electron-ion problem. Physically, in the BOA the electronic and ionic motion are essentially decoupled. Due to their much smaller mass, electrons move much faster than ions and one treats them as moving in the essentially static field due to the ions.

As we want to understand what happens when we go beyond the BOA, i.e., when we do not decouple the electron-ion problem, we have fictitiously varied the electron-ion mass ratio \( \frac{m_e}{m_I} \) \[24\]. For small mass ratios, the electronic transitions will require more energy than ionic transitions and therefore there will be little coupling between electrons and ions. However, as the mass ratio increases, the energy required for electronic and ionic transitions will become comparable, therefore leading to a larger electron-ion coupling.

To investigate the electron-ion coupling we have used small and simple systems such as the \( \text{H}_2^+ \) and \( \text{H}_2 \) molecules in 1D (see Sec. 1.3). This choice has the advantage that one can in fact solve the electron-ion problem exactly. Moreover, for two identical particles the molecular wavefunction can be factorised into a spin and spatial part. Due to the exchange symmetry of the molecular wavefunction for two identical fermions, the spin part of the total wavefunction can be directly determined if we know the spatial part of the wavefunction (see Sec. 1.3.5).

The magnitude of the electron-ion coupling determines the domain of applicability of the BOA. In order to quantitively determine the domain of validity of the static BOA calculations we have used a perturbation theory argument in terms of the small parameter \( \kappa = \left( \frac{m_e}{m_I} \right)^{\frac{1}{4}} \) to show that for the molecular ground state in 1D the BOA is accurate up to corrections of fourth order in \( \kappa \) (see Sec. 1.4.1) \[1\], \[24\].

We have found some quantitative and qualitative differences in 1D with respect to 3D. In 1D, the BOA error is the term of fourth order in \( \kappa \) (see Eq. 1.94) (see Eq. 2.25 and Figs. 2.11 and 3.10 for the \( \text{H}_2^+ \) and \( \text{H}_2 \) molecules, respectively). However in 3D, the BOA error is the term of sixth order in \( \kappa \) \[1\], \[24\]. Even though the qualitative features of the Potential Energy Surfaces (PES)'s, such as the repulsive barrier, the attractive minimum and the molecular dissociation limit for large interatomic distances (see Figs. 2.3 for \( H_2^+ \) and 3.2 for \( H_2 \)) are similar in 1D and 3D for diatomic molecules, we find that small differences exist. In 1D the asymptotic behaviour of the PES's, obtained for large interatomic distances using Eq. 2.18 decays to the third order, whereas in 3D to the fourth order. The decaying order is related to a non-covalent long range interaction between a proton and a hydrogen atom for \( H_2^+ \) and between two hydrogen atoms for \( H_2 \).

These quantitative and qualitative differences in 1D and 3D can be explained by taking rotations in 3D into account which do not contribute in 1D.

We have also found some qualitative differences in the domain of applicability of the BOA between the \( \text{H}_2^+ \) and \( \text{H}_2 \) molecules. The non-covalent long-range minimum in the first excited PES for the \( \text{H}_2^+ \) molecule (see Fig. 2.8 b)) is not so appreciable for the \( \text{H}_2 \) molecule (see Fig. 3.8 b)). This is because the charged proton-dipole interaction for the
dissociating \( H_2^+ \) molecule is stronger than the neutral dipole-dipole interaction for the dissociating \( H_2 \) molecule for large interatomic distances. Moreover, we find that as the \( H_2 \) molecule is more tightly bound than the \( H_2^+ \) molecule, the BOA error obtained from a fourth order anharmonic fit of the ground state PES is worse for \( H_2 \) than for \( H_2^+ \) for larger electron-ion mass ratios \( R_m \) to describe the ground state energy for the full electron-ion problem (see Fig. 2.11 for \( H_2^+ \) and Fig. 3.10 for \( H_2 \)).

The time dependent propagation simulations have only been performed for the \( H_2^+ \) molecule for the moment and they are currently in progress for the \( H_2 \) molecule. We have investigated the linear response absorption spectrum of \( H_2^+ \) from an exact electron-ion and a frozen-ion approximation. This has been done to determine the domain of applicability of the BOA as the frozen-ion approximation can be interpreted as a qualitative picture of the BOA. In the frozen-ion approximation we obtain an electronic transition spectrum at a fixed \( R \) value. However, in the BOA picture the spectrum would contain a superposition of electronic transitions for all the \( R \) values.

In the frozen-ion case, the transitions in the absorption spectrum (see Fig. 2.13) are in agreement with the frozen-ion diagonalisation calculation (see Table 2.8). An interesting feature, which cannot easily be seen by diagonalisation, is the interference of the linear combination of the two possible configurations of the dissociated \( H_2^+ \) molecule shown in Fig. 2.14 in the continuum part of the spectrum in Fig. 2.13 d). This interference is absent for the hydrogen atom (see Fig. 2.15).

In the electron-ion time dependent photoabsorption spectra for \( H_2^+ \) we have found an unexpected line shape, i.e., non-Lorentzian but Gaussian-like (see Fig. 2.17). The Gaussian-like line shape is not fully symmetric, the asymmetry of the peaks increases as the mass ratio increases [8]. This is due to an electronic decoherence due to the electron-ion interaction (see Fig. 2.19). The domain of applicability of the BOA for the time-dependent simulations is only reasonable for small mass ratios \( R_m \) as the electron-ion dipole moment oscillations can be fitted with Eq. 2.27 using a single frequency for \( R_m \approx 5.45 \times 10^{-4} \) and \( R_m \approx 4.84 \times 10^{-3} \) in Figs. 2.16 a) and b) like in the frozen-ion approximation. This is also the case when we use a Gaussian function to fit the main peak in Figs. 2.18 a) and b).

The present work is a first step towards the interpretation of more complex non-adiabatic electron-ion coupled processes, such as the attosecond time-resolved and ultra-short pump-probe pulse experiments described in [18], [9], [4], [12], [8], [7], [13], [14], [6], [11], [3], [15]. In addition, our results can be relevant to determine the domain of applicability of the BOA for more realistic systems in 3D, such as other diatomic molecules with a larger number of electrons and ions (e.g. \( N_2, O_2 \)).
17. J. R. Hiskes, *Dissociation of molecular ions by electric and magnetic fields*, Physical Review 122 (1961), no. 4, 1207–1217. 1.3.2
Centre of mass transformation for the $H_2^+$ and $H_2$ molecules

A.1. Centre of mass transformation for the $H_2^+$ molecule

1st step: Partial centre-of-mass transformation for the protons ($r$ fixed)

We define the following partially transformed coordinates from the two previous coordinates $R_1$ and $R_2$ and their time-derivatives:

\[ R_{CM(1)} = \frac{R_1 + R_2}{2} \Rightarrow V_{CM(1)} = \frac{V_1 + V_2}{2}, \quad (A.1) \]

\[ R = R_2 - R_1 \Rightarrow V = V_2 - V_1, \quad (A.2) \]

\[ r = r \Rightarrow v = v, \quad (A.3) \]

where $R_{CM(1)}$ is the centre of mass coordinate of the protons and $R$ is the distance between the protons.

In matrix form this partial transformation reads:

\[
\begin{pmatrix}
R_{CM(1)} \\
R \\
r
\end{pmatrix}
= A_1
\begin{pmatrix}
R_1 \\
R_2 \\
r
\end{pmatrix}
= \begin{pmatrix}
\frac{1}{2} & \frac{1}{2} & 0 \\
-1 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
R_1 \\
R_2 \\
r
\end{pmatrix}, \quad (A.4)
\]

and the inverse transformation is:

\[
\begin{pmatrix}
R_1 \\
R_2 \\
r
\end{pmatrix}
= A_1^{-1}
\begin{pmatrix}
R_{CM(1)} \\
R \\
r
\end{pmatrix}
= \begin{pmatrix}
1 & -\frac{1}{2} & 0 \\
1 & \frac{-1}{2} & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
R_{CM(1)} \\
R \\
r
\end{pmatrix}. \quad (A.5)
\]

By substituting Eqs. A.5 in Eq. 1.22 we obtain:

\[
E = \frac{1}{2} 2M V_{CM(1)}^2 + \frac{1}{2} \mu_I V^2 + \frac{1}{2} v^2 - \frac{1}{\sqrt{(r - R_{CM(1)} + \frac{R}{2})^2 + a^2}} + \frac{1}{\sqrt{(R_{CM(1)} + \frac{R}{2} - r)^2 + a^2}} \quad + \frac{1}{\sqrt{R^2 + a^2}}, \quad (A.6)
\]

where the reduced mass for the ions is:

\[
\mu_I = \frac{M}{2}. \quad (A.7)
\]

2nd step: Centre-of-mass transformation for the electron ($R$ is fixed)

Now we define the following transformed coordinates from the two previous coordinates $R_{CM(1)}$ and $r$ and their time-derivatives:
A. CENTRE OF MASS TRANSFORMATION FOR THE $H_2^+$ AND $H_2$ MOLECULES

\[ R_{CM(2)} = \frac{2MR_{CM(1)} + r}{2M + 1} \Rightarrow V_{CM(2)} = \frac{2MV_{CM(1)} + v}{2M + 1}, \quad \text{(A.8)} \]

\[ R = R \Rightarrow V = V, \quad \text{(A.9)} \]

\[ \xi = r - R_{CM(1)} \Rightarrow V_\xi = v - V_{CM(1)}, \quad \text{(A.10)} \]

where $R_{CM(2)}$ is the global centre of mass coordinate and $\xi$ is the distance between $R_{CM(1)}$ and $r$. The internal coordinates are $R$ and $\xi$.

In matrix form this transformation reads:

\[
\begin{pmatrix}
R_{CM(2)} \\
R \\
\xi
\end{pmatrix} = A_2
\begin{pmatrix}
R_{CM(1)} \\
R \\
r
\end{pmatrix},
\]

and the inverse transformation is:

\[
\begin{pmatrix}
R_{CM(1)} \\
R \\
r
\end{pmatrix} = A^{-1}_2
\begin{pmatrix}
R_{CM(2)} \\
R \\
\xi
\end{pmatrix}, \quad \text{(A.12)}
\]

By substituting Eqs. A.12 into Eq. A.6 we finally obtain:

\[
E = \frac{1}{2}(2M + 1)V^2_{CM(2)} + \frac{1}{2}\mu_I V^2 + \frac{1}{2}\mu_e V^2 +
- \frac{1}{\sqrt{(\frac{R}{2} + \xi)^2 + a^2}} - \frac{1}{\sqrt{(\frac{R}{2} - \xi)^2 + a^2}} + \frac{1}{\sqrt{R^2 + a^2}}. \quad \text{(A.13)}
\]

where the reduced electron mass is:

\[
\mu_e = \frac{2M}{2M + 1}. \quad \text{(A.14)}
\]

If we rewrite Eq. A.13 in terms of the classical momenta given by:

\[
P_{CM(2)} = (2M + 1)V_{CM(2)}; \quad P_R = \mu_I V; \quad P_\xi = \mu_e V_\xi; \quad \text{(A.15)}
\]

we obtain the following energy:

\[
E = \frac{1}{2}\frac{P^2_{CM(2)}}{2M + 1} + \frac{1}{2}\frac{P^2_R}{\mu_I} + \frac{1}{2}\frac{P^2_\xi}{\mu_e} +
- \frac{1}{\sqrt{(\frac{R}{2} + \xi)^2 + a^2}} - \frac{1}{\sqrt{(\frac{R}{2} - \xi)^2 + a^2}} + \frac{1}{\sqrt{R^2 + a^2}}. \quad \text{(A.16)}
\]

The quantum momentum operators in 1-D are canonically defined as:

\[
\hat{P}_{R_{CM(2)}} = -i\frac{\partial}{\partial R_{CM(2)}}; \quad \hat{P}_R = -i\frac{\partial}{\partial R}; \quad \hat{P}_\xi = -i\frac{\partial}{\partial \xi}. \quad \text{(A.17)}
\]
A.2. Centre of mass transformation for the $H_2$ molecule

1st step: Partial centre-of-mass transformation for the protons and the electrons

We define the following partially transformed coordinates from the four previous coordinates $R_1, r_1, r_2, R_2$ and their time-derivatives:

$$
R_{CM(1)} = \frac{R_1 + R_2}{2} \Rightarrow V_{CM(1)} = \frac{V_1 + V_2}{2},
$$
(A.18)

$$
r_{CM(1)} = \frac{r_1 + r_2}{2} \Rightarrow v_{CM(1)} = \frac{v_1 + v_2}{2},
$$
(A.19)

$$
R = R_2 - R_1 \Rightarrow V = V_2 - V_1,
$$
(A.20)

$$
r = r_2 - r_1 \Rightarrow v = v_2 - v_1,
$$
(A.21)

where $R_{CM(1)}$ is the centre of mass coordinate of the ions, $r_{CM(1)}$ is the centre of mass coordinate of the electrons, $R$ is the distance between the ions and $r$ is the distance between the electrons.

In matrix form this partial transformation reads:

$$
\begin{pmatrix}
R_{CM(1)} \\
R \\
r \\
r_{CM(1)}
\end{pmatrix}
= B_1
\begin{pmatrix}
R_1 \\
R_2 \\
r_1 \\
r_2
\end{pmatrix}
= \begin{pmatrix}
\frac{1}{2} & \frac{1}{2} & 0 & 0 \\
-1 & 1 & 0 & 0 \\
0 & 0 & -\frac{1}{2} & 1 \\
0 & 0 & \frac{1}{2} & 1
\end{pmatrix}
\begin{pmatrix}
R_1 \\
R_2 \\
r_1 \\
r_2
\end{pmatrix},
$$
(A.22)

and the inverse transformation is:

$$
\begin{pmatrix}
R_1 \\
R_2 \\
r_1 \\
r_2
\end{pmatrix}
= B_1^{-1}
\begin{pmatrix}
R_{CM(1)} \\
R \\
r \\
r_{CM(1)}
\end{pmatrix}
= \begin{pmatrix}
1 & -\frac{1}{2} & 0 & 0 \\
1 & \frac{1}{2} & 0 & 0 \\
0 & 0 & -\frac{1}{2} & 1 \\
0 & 0 & \frac{1}{2} & 1
\end{pmatrix}
\begin{pmatrix}
R_{CM(1)} \\
R \\
r \\
r_{CM(1)}
\end{pmatrix}.
$$
(A.23)

By substituting Eqs. A.23 into Eq. 1.34 one obtains:

$$
E = \frac{1}{2} M V_{CM(1)}^2 + \frac{1}{2} \mu_1 V^2 + \frac{1}{2} 2v_{CM(1)}^2 + \frac{1}{2} \tilde{\mu}_e v^2 +
\frac{1}{\sqrt{(r_{CM(1)} - \frac{r_1}{2} - R_{CM(1)} + \frac{R_2}{2})^2 + a^2}} +
\frac{1}{\sqrt{(R_{CM(1)} + \frac{R_2}{2} - r_{CM(1)} - \frac{r_1}{2})^2 + a^2}} +
\frac{1}{\sqrt{(r_{CM(1)} + \frac{r_1}{2} - R_{CM(1)} + \frac{R_2}{2})^2 + a^2}} +
\frac{1}{\sqrt{(R_{CM(1)} + \frac{R_2}{2} - r_{CM(1)} - \frac{r_1}{2})^2 + a^2}} +
\frac{1}{\sqrt{R^2 + a^2}} + \frac{1}{\sqrt{r^2 + a^2}}.
$$
(A.24)

where $\mu_1$ was defined in Eq.A.7 and the reduced mass of the electrons is:

$$
\tilde{\mu}_e = \frac{1}{2}.
$$
(A.25)

2nd step: Global centre-of-mass transformation for the molecule ($R$ and $r$ fixed)

Now we define the following transformed coordinates from the two previous coordinates $R_{CM(1)}, r_{CM(1)}$ and their time-derivatives:
where $R_{CM(2)}$ is the global centre of mass coordinate and $\xi$ is the distance between $R_{CM(1)}$ and $r_{CM(1)}$. The internal coordinates are $R$, $r$ and $\xi$.

In matrix form this transformation reads:

$$
\begin{bmatrix}
R_{CM(2)} \\
R \\
r \\
\xi
\end{bmatrix}
= B_2
\begin{bmatrix}
R_{CM(1)} \\
R \\
r \\
r_{CM(1)}
\end{bmatrix},
$$

(A.30)

and the inverse transformation is:

$$
\begin{bmatrix}
R_{CM(1)} \\
R \\
r \\
r_{CM(1)}
\end{bmatrix}
= B_2^{-1}
\begin{bmatrix}
R_{CM(2)} \\
R \\
r \\
\xi
\end{bmatrix},
$$

(A.31)

By substituting Eqs. A.31 into Eq. A.24 we obtain:

$$
E = \frac{1}{2} (2M + 2) V_{CM(2)}^2 + \frac{1}{2} \mu_I V^2 + \frac{1}{2} \mu_{ei} V^2 + \frac{1}{2} \tilde{\mu}_e v^2 + \\
- \frac{1}{\sqrt{(R^2 + r^2 + \xi^2 + \alpha^2)}} - \frac{1}{\sqrt{(R^2 + r^2 - \xi^2 + \alpha^2)}} + \\
- \frac{1}{\sqrt{(R^2 + r^2 + \xi^2 + \alpha^2)}} - \frac{1}{\sqrt{(R^2 + r^2 - \xi^2 + \alpha^2)}} + \\
+ \frac{1}{\sqrt{R^2 + \alpha^2}} + \frac{1}{\sqrt{r^2 + \alpha^2}}.
$$

(A.32)

where the reduced mass of a combined particle formed by the ions and electrons is:

$$
\mu_{ei} = \frac{2M}{1 + M}.
$$

(A.33)

If we rewrite Eq. A.32 in terms of the classical momenta given by:

$$
P_{CM(2)} = (2M + 2) V_{CM(2)}; P_R = \mu_I V; P_{\xi} = \mu_{ei} V_{\xi}; P_r = \tilde{\mu}_e v;
$$

(A.34)

we obtain the following energy:
A.2. CENTRE OF MASS TRANSFORMATION FOR THE $H_2$ MOLECULE

$$E = \frac{1}{2} \frac{P_{CM(2)}^2}{2M} + 2 + \frac{1}{2} \frac{P_R^2}{\mu_I} + \frac{1}{2} \frac{P_{\epsilon R}^2}{\mu_{\epsilon I}} + \frac{1}{2} \frac{P_{\epsilon \xi}^2}{\mu_{\epsilon I}} +$$

$$- \frac{1}{\sqrt{(\frac{R}{2} - \frac{\epsilon}{2} + \xi)^2 + a^2}} - \frac{1}{\sqrt{(\frac{R}{2} - \frac{\epsilon}{2} - \xi)^2 + a^2}} +$$

$$- \frac{1}{\sqrt{(\frac{R}{2} + \frac{\epsilon}{2} + \xi)^2 + a^2}} - \frac{1}{\sqrt{(\frac{R}{2} + \frac{\epsilon}{2} - \xi)^2 + a^2}} +$$

$$+ \frac{1}{\sqrt{R^2 + a^2}} + \frac{1}{\sqrt{r^2 + a^2}}.$$  \hspace{1cm} (A.35)

The quantum momentum operators in 1-D for the $H_2$ molecule are then:

$$\hat{P}_{R_{CM(2)}} = -i \frac{\partial}{\partial R_{CM(2)}} ; \hat{P}_R = -i \frac{\partial}{\partial R} ; \hat{P}_r = -i \frac{\partial}{\partial r} ; \hat{P}_\xi = -i \frac{\partial}{\partial \xi}.$$  \hspace{1cm} (A.36)
The Hellmann-Feynman Theorem

We use the Hellmann Feynman theorem to calculate the first-order correction to the energy. Consider a Hamiltonian $\hat{H}(R)$ which depends on some parameter $R$ and let $|\psi\rangle$ be an eigenstate of that Hamiltonian:

$$\hat{H}(R)|\psi\rangle = \varepsilon|\psi\rangle$$  \hspace{1cm} (B.1)

The Hellmann Feynman theorem then relates the derivative of an eigenvalue of the Hamiltonian $\hat{H}(R)$ with respect to $R$, to the expectation value of the derivative of the eigenstate of the Hamiltonian $\hat{H}(R)$ with respect to that same parameter. This can be seen as follows:

$$\frac{\partial \varepsilon}{\partial R} = \frac{\partial}{\partial R} \langle \psi | \hat{H}(R) | \psi \rangle =$$

$$\langle \frac{\partial}{\partial R} \psi | \hat{H}(R) | \psi \rangle + \langle \psi | \hat{H}(R) \frac{\partial}{\partial R} \psi \rangle + \langle \psi | \frac{\partial}{\partial R} \hat{H}(R) | \psi \rangle =$$

$$\varepsilon \langle \frac{\partial}{\partial R} \psi | \psi \rangle + \varepsilon \langle \psi | \frac{\partial}{\partial R} \psi \rangle + \langle \psi | \frac{\partial}{\partial R} \hat{H}(R) | \psi \rangle = \varepsilon \langle \frac{\partial}{\partial R} \psi | \psi \rangle + \langle \psi | \frac{\partial}{\partial R} \hat{H}(R) | \psi \rangle =$$

$$\langle \psi | \frac{\partial}{\partial R} \hat{H}(R) | \psi \rangle = \frac{\partial}{\partial R} \varepsilon \langle \psi | \psi \rangle = \frac{\partial}{\partial R} \varepsilon$$ \hspace{1cm} (B.2)

where:

$$\langle \psi | \psi \rangle = 1 \rightarrow \frac{\partial}{\partial R} \langle \psi | \psi \rangle = 0.$$ \hspace{1cm} (B.3)
APPENDIX C

Time-independent Perturbation Theory analysis to obtain the first correction to the harmonic energy from a fourth order expansion of the Morse potential

The expansion of the Morse potential (Eq. 2.12) until fourth order reads:

\[
(\varepsilon_d - \varepsilon_0)\left(a^2(R - R_{eq})^2 - a^3(R - R_{eq})^3 + \frac{7}{12}a^4(R - R_{eq})^4\right) + \varepsilon_0. \tag{C.1}
\]

For a quantum harmonic oscillator we have that:

\[
\hat{H}^{(0)} = \hbar \omega (\hat{n} + \frac{1}{2}), \tag{C.2}
\]

and:

\[
\hat{H}^{(1)} = \hbar \omega \left[-\frac{a}{2} \sqrt{\frac{\hbar}{\mu I \omega}} \left(\frac{1}{\sqrt{2}} (\hat{a} + \hat{a}^\dagger)\right)^3 + \frac{7}{24} a^2 \frac{\hbar}{\mu I \omega} \left(\frac{1}{\sqrt{2}} (\hat{a} + \hat{a}^\dagger)\right)^4\right], \tag{C.3}
\]

where we use the ladder operators:

\[
\hat{a} = \sqrt{\frac{\mu I \omega}{2\hbar}} (\hat{x} + \frac{i}{\mu I \omega} \hat{p}); \tag{C.4}
\]

\[
\hat{a}^\dagger = \sqrt{\frac{\mu I \omega}{2\hbar}} (\hat{x} - \frac{i}{\mu I \omega} \hat{p}), \tag{C.5}
\]

and:

\[
\hat{x} = \sqrt{\frac{\hbar}{2\mu I \omega}} (\hat{a} + \hat{a}^\dagger); \tag{C.6}
\]

\[
\langle \psi^{(o)} | \hat{x}^2 | \psi^{(o)} \rangle = \delta_{o,j}; \tag{C.7}
\]

\[
\delta_{o,j} = \begin{cases} 1 & \text{if } j = o, \\ 0 & \text{otherwise} \end{cases} \tag{C.8}
\]

Note that we have used \( x = R - R_{eq} \)

To calculate the first correction to the harmonic energy from Eq. C.3 we use:

\[
\langle \psi^{(o)} | \hat{x}^4 | \psi^{(o)} \rangle = \sum_{\psi^{(j)}} \langle \psi^{(o)} | \hat{x}^2 | \psi^{(j)} \rangle \langle \psi^{(j)} | \hat{x}^2 | \psi^{(o)} \rangle, \tag{C.9}
\]

which vanishes unless \( j = o - 4; o - 2; o; o + 2; o + 4 \) and:

\[
\langle \psi^{(o)} | \hat{x}^2 | \psi^{(j)} \rangle = \sum_{\psi^{(p)}} \langle \psi^{(o)} | \hat{x} | \psi^{(p)} \rangle \langle \psi^{(p)} | \hat{x} | \psi^{(j)} \rangle, \tag{C.10}
\]

which vanishes unless \( p = o - 2; o; o + 2 \) because:

\[
\langle \psi^{(o)} | \hat{x} | \psi^{(p)} \rangle = \delta_{p,o-1} \sqrt{\frac{p + 1}{2}} + \delta_{p,o+1} \sqrt{\frac{p}{2}}. \tag{C.11}
\]
From first-order perturbation theory we get to:

$$\varepsilon^{(1)} = \frac{7}{16} a^2 \frac{h}{\mu I \omega} [\hat{n}^2 + \hat{n} + \frac{1}{2}].$$  \hspace{1cm} (C.12)

All first-order time-independent perturbation theory components for the $\hat{x}^3$ term vanish as:

$$\langle \psi^{(o)} | \hat{x}^3 | \psi^{(o)} \rangle = \sum_{\psi^{(j)}} \langle \psi^{(j)} | \hat{x} | \psi^{(j)} \rangle \langle \psi^{(j)} | \hat{x} | \psi^{(o)} \rangle,$$  \hspace{1cm} (C.13)

which vanishes unless $j = o - 3; o - 1; o + 1; o + 3$, leading to a fourth order term. Even though, we must consider second order perturbation theory for the $\hat{x}^3$ term, as its order of magnitude is the same as the $\hat{x}^4$ term using first-order perturbation theory taking into account that:

$$\varepsilon^{(0)}_n - \varepsilon^{(0)}_o \approx \hbar \omega \approx \frac{1}{2} k x^2,$$  \hspace{1cm} (C.14)

i.e., the expectation value of a harmonic oscillator.

From second-order perturbation theory we get to:

$$\varepsilon^{(2)} = -\frac{30}{32} a^2 \frac{\hbar}{\mu I \omega} [\hat{n}^2 + \hat{n} + \frac{11}{30}]$$  \hspace{1cm} (C.15)

Therefore, from Eqs. C.12 and C.15, the first correction to the harmonic energy from a fourth order expansion of the Morse potential is given by:

$$\varepsilon_n = \hbar \omega [(\hat{n} + \frac{1}{2}) - \frac{a^2 \hbar}{2 \mu I \omega} (\hat{n} + \frac{1}{2})^2].$$  \hspace{1cm} (C.16)
Time-independent Perturbation Theory analysis to obtain the asymptotic behaviour for large $R$ values in the gs PES dissociation limit for $H_2$

The electronic Hamiltonian in Eq.1.67 in the new reference frame (see Fig.3.9) reads:

$$\hat{H} = -\frac{\partial^2}{\partial j^2} - \frac{2}{\sqrt{j^2 + 1}} - \frac{1}{\sqrt{(R-j)^2 + 1}} + \frac{1}{\sqrt{(R+j)^2 + 1}} + \frac{2}{\sqrt{R^2 + 1}}, \quad (D.1)$$

where $\hat{H}^{(0)}$ is the Hamiltonian of the two isolated $H$ atoms:

$$\hat{H}^{(0)} = -\frac{\partial^2}{\partial j^2} - \frac{2}{\sqrt{j^2 + 1}}, \quad (D.2)$$

and:

$$\hat{H}^{(1)} = -\frac{1}{\sqrt{(R-j)^2 + 1}} - \frac{1}{\sqrt{(R+j)^2 + 1}} + \frac{2}{\sqrt{R^2 + 1}}, \quad (D.3)$$

will be treated as perturbation, i.e., a small correction to $\hat{H}^{(0)}$. For large interatomic separations $R \gg j, 1$, $\hat{H}^{(1)}$ reads:

$$\hat{H}^{(1)} = \frac{2}{R} - \frac{1}{R} \left( \frac{1}{1 - \frac{j}{R}} \right) - \frac{1}{R} \left( \frac{1}{1 + \frac{j}{R}} \right), \quad (D.4)$$

which we can expand:

$$\hat{H}^{(1)} = \frac{2}{R} - \frac{1}{R} \left( 1 - (1 + \frac{j}{R} + \frac{j^2}{R^2} + O(\frac{j^3}{R^3})) \right) + \frac{1}{R} \left( 1 - (1 - \frac{j}{R} + \frac{j^2}{R^2} - O(\frac{j^3}{R^3})) \right) = -\frac{2j^2}{R^3} + O(\frac{1}{R^4}). \quad (D.5)$$

By symmetry the first term in Eq.(D.5) is not zero leading to at least a third order decay with respect to the distance between each proton and electron as in the $H_2^+$ case for the first-order energy correction in 1D.