

SCHRÖDINGER EQUATIONS FOR HYDROGEN
MOLECULAR IONS

by

Louis Michel Ritchie

June 22, 2020

*Report presented for the degree of ICFP Master 2 in Physics
Internship Supervisor: Jean-Philippe Karr
Laboratoire Kastler Brossel, Sorbonne University*

Contents

1	Introduction	2
2	Variational solution of the three-body Schrödinger equation	3
3	Results	6
3.1	Non Born-Oppenheimer curves	6
3.1.1	Convergence	6
3.1.2	Vibrational Wavefunctions	7
3.1.3	Comparison to the Adiabatic curve	7
3.2	Analytical Electronic Potential	8
4	Conclusion	14
I	Appendix	16

Chapter 1

Introduction

The Born-Oppenheimer (BO) approximation is a widely used approximation in molecular physics [1]. It assumes that the nuclear and electronic motions can be separated, due to the nuclear mass being much larger than the electronic mass. This allows the Schrödinger equation for the electron to be solved in the static field of two fixed nuclei. This approximation greatly simplifies calculations but the accuracy is limited to $\sim \left(\frac{m}{M}\right)$, or roughly 10^{-3} (where m is the electron mass and M is the reduced nuclear mass,) since we ignore the nuclear kinetic energies when solving the Schrödinger equation. The precision can be improved by including corrections to the BO picture (also called “non-adiabatic corrections”) in a perturbative expansion in powers of $\frac{m}{M}$. However, this becomes quite tedious when going to high perturbative orders. Alternatively, one can use a non-BO approach [2] where the coupled motion of every particle in the molecule is included. This can give extremely accurate solutions but is more computationally difficult.

The Hydrogen molecular ion (HMI), H_2^+ is the simplest molecule found in nature, composed of two protons and a single electron. It often serves as a benchmark system in quantum chemistry and has been studied theoretically since the beginnings of quantum mechanics in the late 1920’s [3]. In this study, we calculate the potential energy curves (PEC) of H_2^+ from a full three-body approach i.e. that includes effects beyond the BO approximation in an attempt to improve on the commonly used Born-Oppenheimer approximation and compare them to a BO curve that includes ‘adiabatic’ corrections, i.e. that includes the averaged nuclear kinetic energy. As an exploratory idea we also attempt to obtain a non-adiabatic correction potential for the electron from the non-BO potential curves.

Chapter 2

Variational solution of the three-body Schrödinger equation

The Schrödinger equation for a three-body diatomic system with nuclear charges Z_1 and Z_2 and one electron with charge Z_3 , such as H_2^+ is,

$$\left(-\frac{1}{2m_{13}}\nabla_R^2 - \frac{1}{2m_{23}}\nabla_{r_1}^2 - \frac{1}{m_3}\nabla_R\nabla_{r_1} + \frac{Z_1Z_3}{R} + \frac{Z_2Z_3}{r_1} + \frac{Z_1Z_2}{r_2} \right) \Psi = E\Psi \quad (2.1)$$

where for the hydrogen molecular ion $m_{13} = \frac{m_e m_p}{m_e + m_p}$ is the proton-electron reduced mass and the distances r_1, r_2 and R are defined in Figure 2.1.

Most of the high precision calculations performed on three-body systems such as H_2^+ have been based on a variational approach [4]. The variational principle states that for a normalisable wavefunction Ψ , the quantity,

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (2.2)$$

provides an upper bound to the true ground state E_0 , i.e. $E \geq E_0$.

In the approach used here, the wavefunction (for angular momentum $L = 0$ so we only have the radial component) can be expanded in a basis set of exponential functions,

$$\Psi(r_1, r_2, R) = \sum_{n=1}^N \{ C_n \text{Re} (e^{-\alpha_n r_1 - \beta_n r_2 - \gamma_n R}) + D_n \text{Im} (e^{-\alpha_n r_1 - \beta_n r_2 - \gamma_n R}) \} \quad (2.3)$$

The exponents $\alpha_n, \beta_n, \gamma_n$ are complex numbers, however in practice only γ_n must be complex to reproduce the oscillating behaviour of the vibrational wavefunction. These exponents are pseudo-randomly generated in several intervals, the bounds

of which act as variational parameters to be optimised. Finding the extrema of E in (2.2) with respect to the linear parameters C_n, D_n , i.e. solving the set of equations $\frac{\partial E}{\partial C_n} = 0$ is equivalent to solving a generalised eigenvalue problem,

$$\mathbf{H}c = \lambda \mathbf{O}c \quad (2.4)$$

where c is a vector of coefficients ($\Psi = \sum_{i=1}^N c_i \Psi_i$), \mathbf{H} is the Hamiltonian matrix with elements $H_{ij} = \langle \Psi_i | H | \Psi_j \rangle$ and \mathbf{O} is the overlap matrix $O_{ij} = \langle \Psi_i | \Psi_j \rangle$. The lowest of the eigenvalues λ_0 is an upper bound to E_0 . In addition to this the remaining eigenvalues $\lambda_1, \lambda_2 \dots$ are also upper bounds to the exact energies $E_1, E_2 \dots$ [4].

Having obtained the non-BO wavefunction the nuclear density function is given by,

$$f(R) = \int d\tau_R \cdot \Psi^*(r_1, r_2, R) \Psi(r_1, r_2, R) \quad (2.5)$$

where $d\tau_R$ corresponds to integration over the electronic coordinates [5]. $f(R)$ corresponds to the density of the vibrational motion and contains the anharmonicity and non-BO effects. The Schrödinger equation for the nuclear motion is then given by,

$$\left(-\frac{1}{2\mu} \frac{d^2}{dR^2} + V(R) \right) \Psi(R) = E \Psi(R) \quad (2.6)$$

where μ is the effective mass of two nuclei, $V(R)$ is the non-BO potential energy function to be determined, E is the energy eigenvalue and $\Psi(R)$ is defined by taking the square root of the density function $\Psi(R) = \sqrt{f(R)}$. Hence, from (2.6) the unknown non-BO potential energy function is given by,

$$V(R) = \frac{1}{2\mu} \frac{d^2 \Psi(R)}{dR^2} \frac{1}{\Psi(R)} + E \quad (2.7)$$

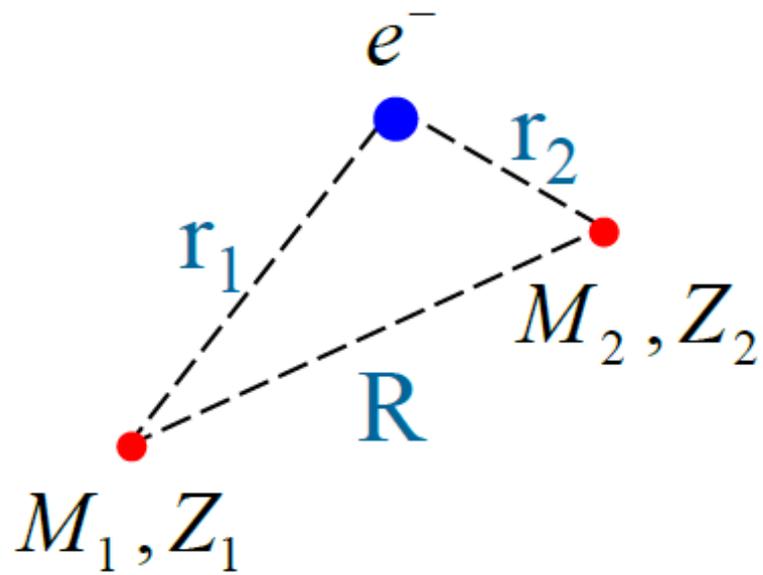


Figure 2.1: The three body diagram for a diatomic molecule with one electron. R is the internuclear distance, and r_1, r_2 are the the distances from nucleus 1 and 2 to the electron respectively.

Chapter 3

Results

3.1 Non Born-Oppenheimer curves

In this section we describe the non-BO results obtained using the variational method with exponential basis sets explained above in §2. We first discuss the convergence of the potentials, then the vibrational wavefunctions, and finally we compare our results to the BO approximation with adiabatic corrections.

3.1.1 Convergence

In the non-BO calculations we choose a basis size N . Table 3.1 shows the energy level as a function of increasing basis size for two different vibrational levels. Figure 3.1 shows the successive differences in the non-BO potential as the basis size is increased for several values of the internuclear distance R and for two different values of ν . As the basis size increased the difference in the calculated potential decreased for a given R , that is the potentials converged. From these figures we can estimate the precision to be on the order of a few 10^{-11} . For some values of R the convergence is significantly worse, for example in Figure 3.1a, for $R = 4$ the precision is quite low. This is because the vibrational wavefunction for $\nu = 0$ is very close 0 at $R = 4$ (shown in Figure 3.2), hence the potential is imprecise. Likewise for $R = 2$ for $\nu = 5$ in Figure 3.1b. We also see that convergence becomes much slower as the vibrational level is increased (See Table 3.1), hence for higher ν -states we chose a maximum basis size of $N = 6000$.

Table 3.1: Convergence of the Energy level with increasing Basis size N , for two different vibrational states. The convergence of the energy level is slower for larger ν states.

Vibrational state ν	Basis size N	Energy (a.u)
$\nu = 0$	1000	-0.5971390629555438
	2000	-0.5971390630813752
	3000	-0.5971390630813767
	4000	-0.5971390630813767
$\nu = 5$	1000	-0.5528407417054417
	3000	-0.5528407499111175
	5000	-0.5528407499111184
	7000	-0.5528407499111184

3.1.2 Vibrational Wavefunctions

Figure 3.2 shows the non-BO wavefunctions at vibrational levels $\nu = 0$ to 11 for the ground electronic state. In general for a state ν the wavefunctions have ν nodes and $\nu + 1$ peaks. The vibrational motion is anharmonic, so as ν increases the centre of the vibrational wavefunctions shifts to the right and the furthest peak on the right (large R) becomes larger, so as the vibrational level increases it becomes more likely for the nuclei to be further apart.

3.1.3 Comparison to the Adiabatic curve

Figure 3.3 shows the difference between the non-BO curves we have calculated for the different vibrational levels and the potential energy curve calculated with adiabatic corrections, i.e. that includes the average nuclear kinetic energy. Note that by solving the Schrödinger equation in one of these potentials e.g. $\nu = 0$, we will obtain the exact vibrational wavefunction for the $\nu = 0$ state, but not for the other ν states. As the vibrational level increases more and more holes start appearing in the potential curves. This is because as ν increases the number of nodes (places where the wavefunction goes to zero) in the vibrational wavefunction increases, and since the potential (recall (2.7)) is undefined when $\Psi \rightarrow 0$ we experience numerical precision problems, so the points in the vicinity of nodes are discarded. We also see that the differences between the non-BO curves and the adiabatic curve are on the order on $10^{-6} a.u$ which reflects the fact that the adiabatic curve is accurate to $\sim \left(\frac{m}{M}\right)^2$, whereas the non-BO curves are exact.

The non-BO curves for different ν also differ from each other on the order of 10^{-6} , corresponding to the non-adiabatic corrections at orders $\left(\frac{m}{M}\right)^2$ and above which depend on ν . On the other hand the first order correction included in the adiabatic curve is the same for all ν and can simply be added to the electronic curve. This ν dependence means that we cannot possibly find a curve that gives precise results for all vibrational states, hence we must compromise and average the curves. As the curves are roughly parallel, i.e. the difference between the curves is roughly constant versus R , averaging the curves will result in a curve that will be more precise for ν in the mid-range, and will be less precise for high and low vibrational levels. The adiabatic curve is quite precise for $\nu = 0$ but gets progressively worse for increasing ν , hence we can expect the non-BO to give a slight improvement over the adiabatic curve in the sense that the error is more balanced over the range of vibrational levels. In Figure 3.4a we show the non-BO curve averaged over the different vibrational levels $\nu = 0, \dots, 11$ and the adiabatic curve. The averaged curve is quite bumpy since for different ν , the curves differ from each other by a few 10^{-6} , so when they are averaged the noise is of the same order. Also the averaged curve in this case is not very meaningful because depending on the value of R , the averaging is performed using different sets of ν , e.g. the averaging at $R = 2$ uses a smaller set of vibrational states than $R = 4$ (Figure 3.3). To do this averaging correctly, one would have to repeat the calculations using a smaller R step and interpolate the curves.

3.2 Analytical Electronic Potential

Here we attempt to obtain a more precise expression for the electronic wavefunction and potential without having to perform the full three-body calculation. From (2.3) we deduce the electronic wavefunction for each value of R ,

$$\Phi_{el}(R; r_1, r_2) = \sum_{n=1}^N \{C_n \Re(e^{-\gamma_n R}) + D_n \Im(e^{-\gamma_n R})\} e^{-\alpha_n r_1 - \beta_n r_2} \quad (3.1)$$

where we have used the fact that α_n and β_n are real numbers. We now construct an effective ‘‘corrective’’ potential $V_{el}(R, r_1, r_2)$ for the electron which should be added to the Hamiltonian so that the exact electronic wavefunction would be a solution to an electronic Schrödinger equation,

$$\left(-\frac{1}{2m_r} \Delta_r - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} + \frac{Z_1 Z_2}{R} + V_{el}(R, r_1, r_2) \right) \Phi_{el} = V(R) \Phi_{el} \quad (3.2)$$

where $V(R)$ is the non-BO potential for a chosen value of R calculated in §3.1. The form of the operator Δ_r can be found in the appendices. From this we deduce

the form of the electronic potential, in a similar way to Nakashima et al. [5],

$$V_{el}(R; r_1, r_2) = \frac{1}{2m_r} \frac{\Delta_r \Phi_{el}}{\Phi_{el}} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{Z_1 Z_2}{R} \quad (3.3)$$

Shown in Figure 3.5 is the ground state electronic wavefunction along the internuclear axis z and the corresponding potential, calculated at the equilibrium internuclear distance $R = 2$. We see singularities in the wavefunction at $z = \pm 1$, corresponding to the positions of the protons. This wavefunction is symmetric with respect to z and is the wavefunction of the $1s\sigma$ bonding orbital of the H_2^+ molecule. The electronic “correction” potential shown in Figure 3.5b has the expected order of magnitude of $\sim \frac{m}{M}$. It reflects the singularities in the wavefunction by exhibiting discontinuities at the positions of the nuclei. Our hope was to find a simple analytical approximation for the potential $V_{el}(R; r_1, r_2)$ which could be used to improve BO calculations of the electronic wavefunctions. However the discontinuities observed likely mean that this idea of constructing a corrective electronic potential is not worth pursuing.

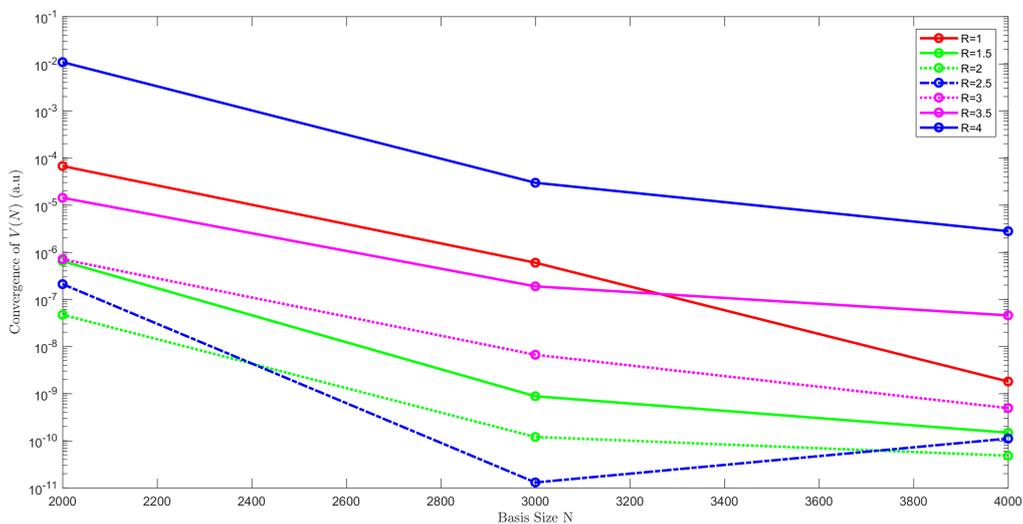
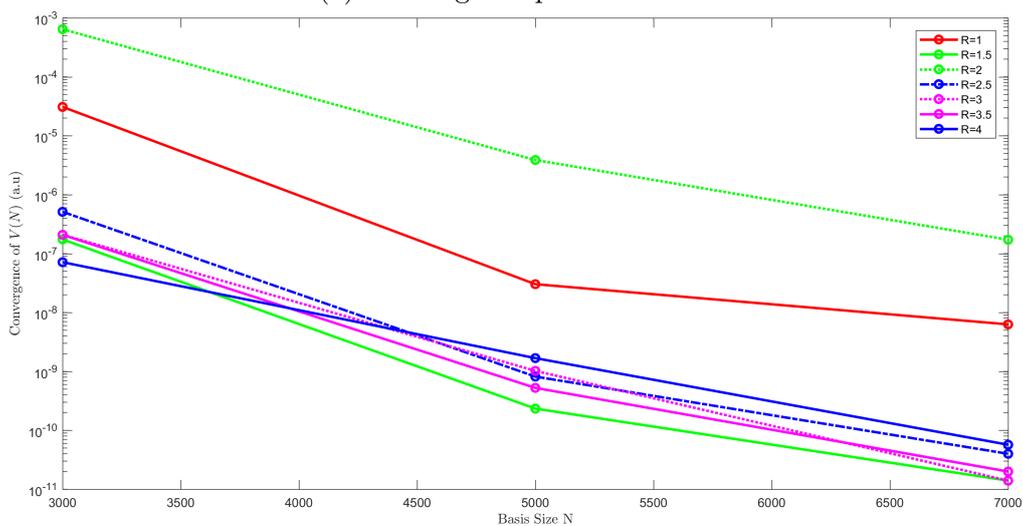
(a) Convergence plot for $\nu = 0$ (b) Convergence plot for $\nu = 5$

Figure 3.1: Estimated precision of potential with increasing basis size for two different vibrational levels.

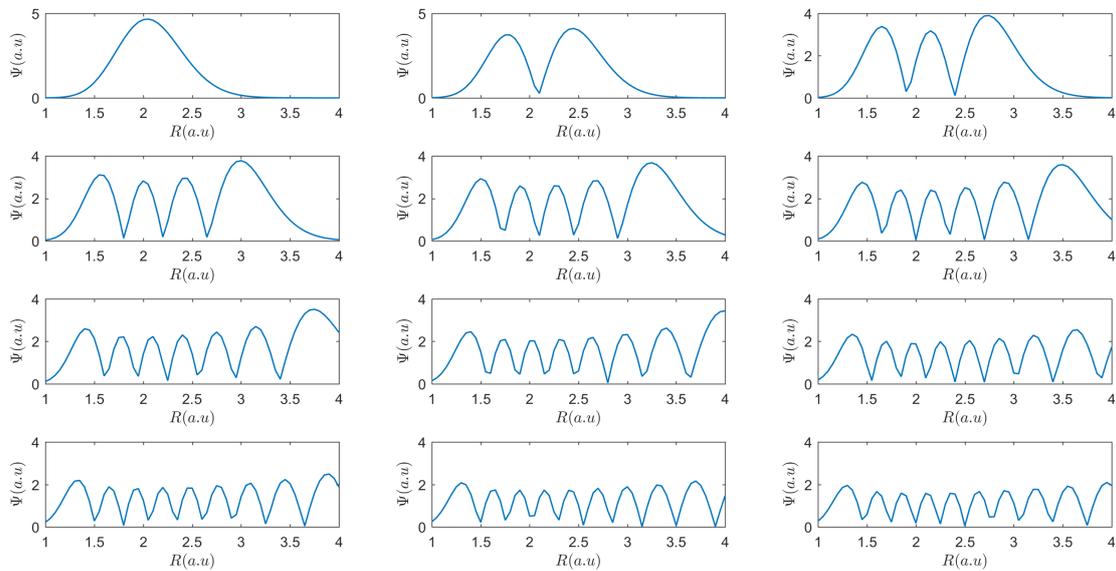


Figure 3.2: absolute value of the vibrational wavefunctions for $v = 0, \dots, 11$ states. For a state ν there are ν nodes and $\nu+1$ maxima. As the level increases the nuclear density shifts to higher R .

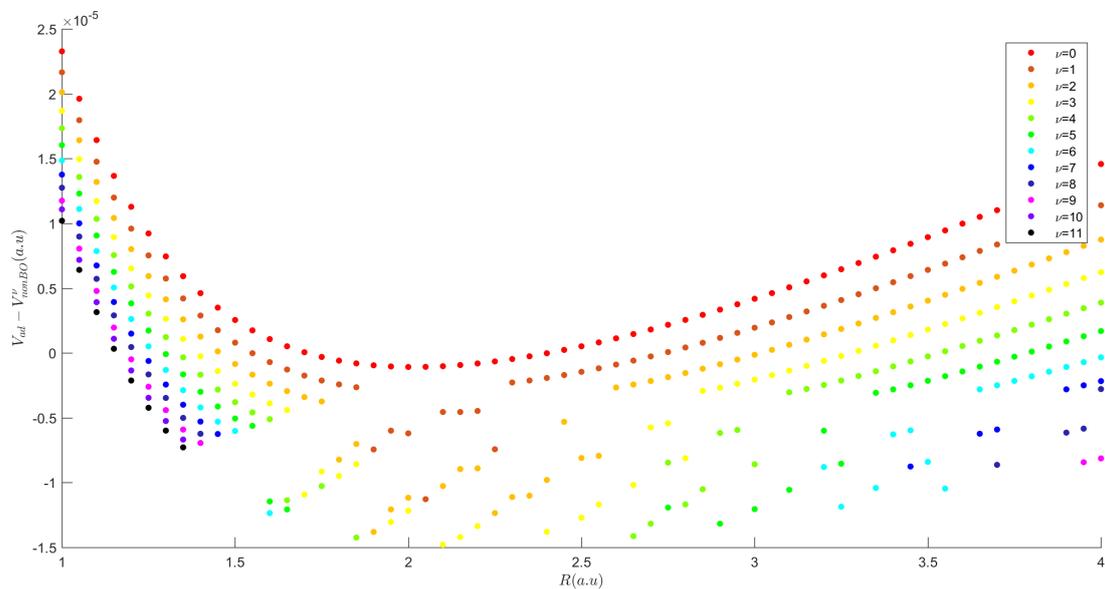
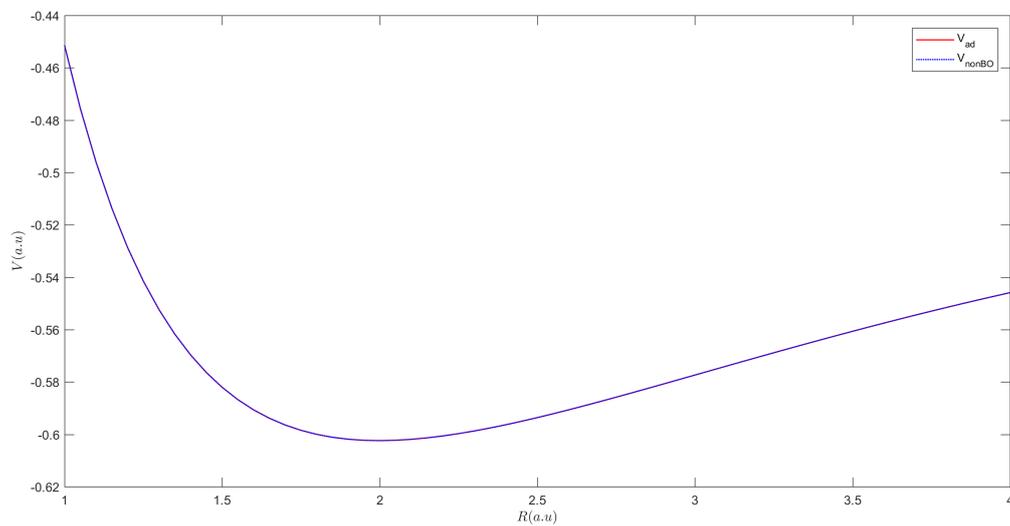
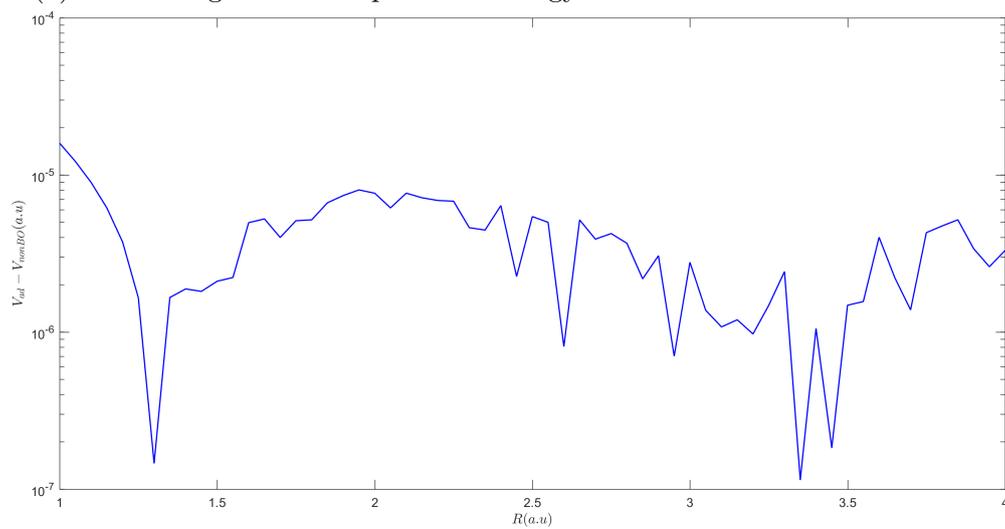


Figure 3.3: Difference between the adiabatic curve and the non-BO curves for $v = 0, \dots, 11$.

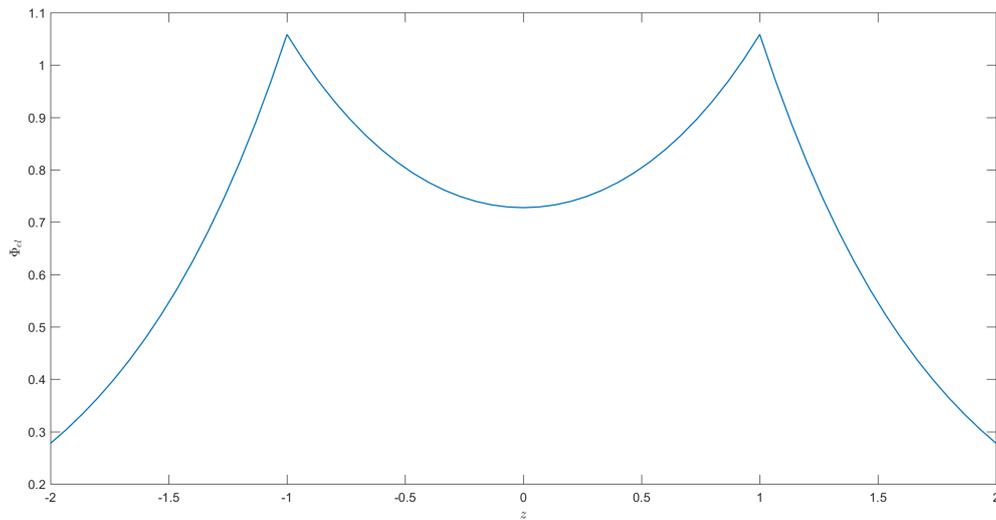


(a) The averaged non-BO potential energy curves and the adiabatic curve.

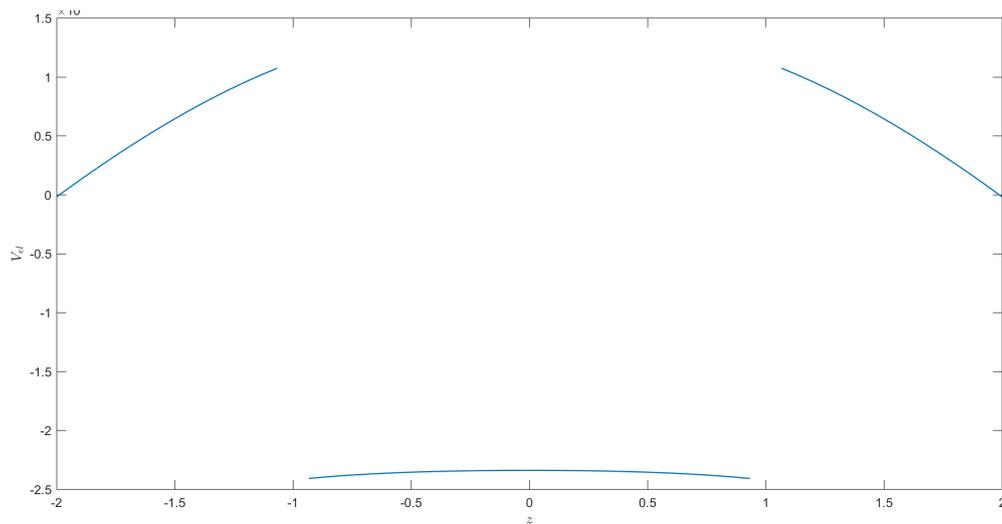


(b) The difference between the adiabatic and averaged non-BO curve

Figure 3.4: The averaged non-BO curve and its difference from the adiabatic curve.



(a) Electronic wavefunction for $v = 0$, at $(r, R) = (0, 2)$ for the H_2^+ molecule, where r is the distance from the internuclear axis. The largest electron density occurs at the two nuclei at $z = \pm 1$.



(b) Electronic potential for $v = 0$, at $(r, R) = (0, 2)$. The singularities in the potential are not completely unexpected since the wavefunction has singularities at the positions of the two nuclei.

Figure 3.5: Analytical Electronic potential and Wavefunction for the ground state of the H_2^+ molecule.

Chapter 4

Conclusion

In this study, we calculated the potential energy curves for the Hydrogen molecular ion from a variational method using pure exponential basis sets, which included the fully coupled motion of the protons and electron in the Schrödinger equation. The non-BO potential energy curves were compared to the adiabatic curve and from this comparison, we expect that an average of potential energy curves calculated for different vibrational states should yield slightly more precise vibrational wavefunctions. Finally, we constructed an analytical electronic corrective potential, with the hope improving the electronic part of the wavefunction. However, due to it having discontinuities the idea is not likely to be worth further pursuit.

Bibliography

- [1] M. Born and R.Oppenheimer, Ann. Phys. **389**, 457 (1927).
- [2] D.M. Bishop and L.M.Cheung, Phys. Rev. A **16**, 640 (1977)
- [3] C.A. Leach and R.E. Moss. Annu. Rev. Phys. Chem. **46**, 5542 (1995).
- [4] Drake G. (2006) High Precision Calculations for Helium. In: Drake G. (eds) Springer Handbook of Atomic, Molecular, and Optical Physics. Springer Handbooks. Springer, New York, NY.
- [5] H. Nakashima and H. Nakatsuji, J. Chem. Phys. **139**,074105(2013).

Appendix I

The Δ_r operator used in (2.1) is given by,

$$\Delta_r = \left(\partial_{r_1}^2 + \frac{2}{r_1} \partial_{r_1} \right) + \left(\partial_{r_2}^2 + \frac{2}{r_2} \partial_{r_2} \right) + \frac{r_1^2 + r_2^2 - R^2}{r_1 r_2} \partial_{r_1} \partial_{r_2} \quad (1)$$

The coordinates r_1 and r_2 shown in Figure 2.1 can be expressed in terms of r, Z using the following relations,

$$r_1 = \sqrt{r^2 + (z + R/2)^2} \quad (2)$$

$$r_2 = \sqrt{r^2 + (z - R/2)^2} \quad (3)$$