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OBERLIN COLLEGE
DEPARTMENT OF PHYSICS

SENIOR THESIS

**Model of the One-Dimensional
Molecular Hydrogen Cation**

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Executive Summary

The hydrogen molecule ion is the simplest molecule, consisting of only two protons and an electron. As such, understanding this problem is essential in order to extend quantum mechanical techniques to more complex molecules such as the next simplest hydrogen molecule. The non-ionized hydrogen molecule represents the simplest system with only axial symmetry exhibiting Pauli exclusion principle effects due to the two identical electrons (fermions) in the neutral molecule. Both molecules have been treated in great detail both experimentally and theoretically and the nature of their solutions and energies are well understood.

Dimensional scaling of the problem can provide insight into the nature of the exact solutions to a system. For example, the problem may be solvable in certain dimensions other than three due to the simplicity of the problem or some symmetry that is present in other dimensionalities. In the present work, the former results in the hydrogen molecule ion being exactly solvable in closed form in one dimension.

Solutions for the energies for a scaling of the hydrogen molecule ion Hamiltonian done by Herschbach et. al. and by López et. al. (Ref. [7, 2]) results in the energy for the three-dimensional problem being bounded by the $D \rightarrow 1$ and $D \rightarrow \infty$ limits, both of which can be solved in closed form. [1]

In the present work, a model of the one-dimensional hydrogen molecule ion is developed in which the charge distributions and electric fields are both mathematically fully described in one dimension. The wavefunctions governing the spacial coordinate for this model were found to be combinations of Airy functions of the first type and the wavefunctions for a free particle (sine and cosine functions) and the energies were found to be similarly governed by the Airy function and trigonometric functions.

Various physical interpretations of this model are introduced with example numerical calculations. In one interpretation, the model describes a single electron bound between two plates of positive charge. The results of this problem assume that the plates are fixed in space and have a relatively simple function governing the energies. Another interpretation assumes that the particles in one dimension are uniform in charge and area, making it appropriate for application to the hydrogen molecule and for comparison to the hydrogen atom. Numerical analysis of these results show that the

molecule will have lower energy than un-bonded hydrogen atoms, suggesting that this molecule will bond.

The scaling of units with the dimensional scaling performed is briefly discussed in the process. There are some difficulties associated with the dimensional scaling of units of charge, energy, and mass in a physically reasonable way that solves the problem. Some elegant mathematical relationships that help provide insight into possible solutions for this problem are presented, but the problem is left unresolved, resulting in a barrier for generalization of the model to dimensionalities greater than three.

Suggestions for other potentially illuminating extensions on the work are made. One is some possibilities for extension of the physical interpretation of the problem to the hydrogen molecule based on a change of variables suggested by Goldman (Ref. [13]). Others include techniques for three dimensions and beyond for the hydrogen molecule and hydrogen molecule ion respectively.

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Section 1

Introduction

The hydrogen molecule and its ion are the two simplest molecules and as such there is great interest in understanding these molecules; there exists an extensive literature on both of them. The hydrogen molecule also provides a fundamental experimental test of the Pauli exclusion principle in a system with only axial symmetry. Theoretical results for the hydrogen atom can be compared to experimental spectra as a test of the principles of quantum mechanics.

The Schrödinger Equation for the hydrogen molecule ion (H_2^+) in the clamped nuclei case can be separated using a change in variables to elliptic coordinates into two ordinary differential equations that can be treated analytically. [4, 3]

Our interest in H_2^+ in dimensionalities other than $D=3$ arose while studying existing work on the energies of the ion. In the work of Scott, Aubert-Frécon, and Grotendorst [1], the mathematics that governs the eigenenergies for the three dimensional ion are shown to be similar to the Lambert-W function that governs the eigenenergies of the one dimensional generalization of the ion.

The main body of work on H_2^+ in other dimensionalities generalizes the Hamiltonian for the Coulomb potential by simply substituting

$$\nabla^2 = \sum_{k=1}^D \frac{\partial^2}{\partial x_k^2}$$

for the Laplacian and

$$z_{ij}^2 = \sum_{k=1}^D (x_{ik} - x_{jk})^2$$

for the square of a distance z_{ij} , where x are the Cartesian coordinates for any two points i and j . A suitable dimensional scaling of this substitution in the $D \rightarrow 1$ limit results in the Hamiltonian for (H_2^+) becoming a double delta function potential. [5, 2]

This work models dimensionally generalized H_2^+ as two point charges in $D=1$ rather than generalizing the Hamiltonian in this way.

1.1 Review

Change of Variables in Three Dimensions

This section is a summary of Ref. [3] with some reference to Ref. [1].

Schrödinger's equation for the hydrogen molecule ion in $D=3$ is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi - \left(\frac{e^2}{r_A} + \frac{e^2}{r_B} \right) \psi = E\psi.$$

This can be separated using prolate-spheroidal coordinates where

$$\xi = \frac{r_A + r_B}{R}$$

$$\eta = \frac{r_A - r_B}{R}$$

(elliptic coordinates) and the azimuthal angle ϕ .

Using separation of variables, we write the trial wavefunction

$$\psi(\xi, \eta, \phi) = \Xi(\xi)H(\eta)\Phi(\phi).$$

This allows us to separate the elliptic part of Schrödinger's equation to

$$\frac{d}{d\xi} \left[(\xi^2 - 1) \frac{d\xi}{d\xi} \right] + \left[\frac{mR^2 E}{2\hbar^2} \xi^2 + \frac{mRe^2}{\hbar^2} \xi + A \right] \xi = 0$$

$$\frac{d}{d\eta} \left[(\eta^2 - 1) \frac{dH}{d\eta} \right] + \left[\frac{mR^2 E}{2\hbar^2} \eta^2 + A \right] H = 0$$

where A is the separation constant.

Analytic treatments of this problem, as well as the limitations or difficulties of these solutions in application, are discussed in detail in Ref. [4, 1]

Double Delta Function Model

This section is primarily a paraphrase of the work of Frost (Ref. [6]) with some mathematical information and clarifying notational choices taken from Ref. [1]. More information concerning the delta function potential is available in Ref. [8]. Information on the appropriateness of this model is discussed in detail in Ref. [7, 2].

In this one-dimensional model of the hydrogen molecule ion, delta function potentials are placed at $x = \pm \frac{R}{2}$. Schrödinger's equation in this case becomes

$$-\frac{1}{2} \frac{d^2\psi}{dx^2} - q[\delta(x - R/2) + \delta(x + R/2)]\psi = E\psi$$

in atomic units and the solutions are of the form

$$\psi = Ae^{-c|x - \frac{R}{2}|} + Be^{-c|x + \frac{R}{2}|}$$

The allowed energies are governed by

$$E_{\pm} = -\frac{c_{\pm}^2}{2}$$

where

$$c_{\pm} = q(1 \pm e^{-c_{\pm}R})$$

or

$$c_{\pm} = q + \frac{W(\pm qRe^{-qR})}{R}$$

where W is the Lambert-W Function (the use of the \pm symbol provides clarity in referring to the eigenparameter). Note that c_+ is associated with the symmetric wavefunction and lower energy while c_- is with the anti-symmetric wavefunction and higher energy.

Section 2

The Hydrogen Molecule Ion

2.1 Deriving the Hamiltonian

A point charge in three dimensions at the origin is described by the charge distribution

$$\rho(x, y, z) = q\delta(x, y, z) = q\delta(x)\delta(y)\delta(z).$$

Similarly, a point charge in two dimensions is described by

$$\sigma(x, y) = q\delta(x, y) = q\delta(x)\delta(y)$$

and a point charge in one dimension by

$$\lambda(x) = q\delta(x).$$

The D=2 case is analogous to a uniform line charge distribution in D=3 and the D=1 case is analogous to a uniform plane charge distribution. In these cases $\rho = \lambda\delta(x)\delta(y)$ and $\rho = \sigma\delta(x)$ respectively.

To reinforce the analogy, consider Poisson's equation

$$\nabla^2 V = -\rho/\epsilon_0. \tag{2.1}$$

In 1-D the Laplacian reduces to a simple derivative. In this case,

$$\frac{d^2 V}{dx^2} = -\rho/\epsilon_0 = -\left|\frac{dE}{dx}\right|. \tag{2.2}$$

Now consider an infinite plane of uniform charge density σ . In this case,

$$E = \frac{\sigma}{2\epsilon_0} \hat{x} \quad (2.3)$$

and

$$\frac{dE}{dx} = \frac{\sigma}{\epsilon_0} \delta(x) \hat{x}$$

which satisfies Poisson's equation for a "point charge" in 1-D of magnitude σ . Infinite plates will be used analogously to point charges in 1-D for the remainder of this work.

Now consider a system comprised of an "electron", which is such a plane charge, with a uniform charge density of $-\sigma$ and two "protons" both having uniform charge density $\lambda\sigma$. In three dimensions, the plane charges are all normal to the x axis such that the problem remains one-dimensional. This system is the one-dimensional hydrogen molecule ion that is the subject of this work.

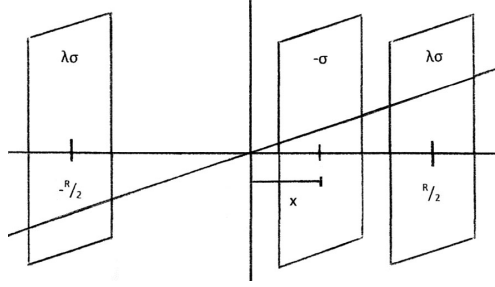


Figure 2.1: Diagram of Infinite Plane Analogue with Clamped Nuclei

If the protons are clamped with a separation of R and the origin is placed at the midpoint between the protons, then the first proton produces an electric field

$$E_1(x) = \begin{cases} \frac{\lambda\sigma}{2\epsilon_0} \hat{x} & \text{if } x > \frac{R}{2} \\ -\frac{\lambda\sigma}{2\epsilon_0} \hat{x} & \text{if } x < \frac{R}{2} \end{cases}$$

and the second

$$E_2(x) = \begin{cases} \frac{\lambda\sigma}{2\epsilon_0} \hat{x} & \text{if } x > -\frac{R}{2} \\ -\frac{\lambda\sigma}{2\epsilon_0} \hat{x} & \text{if } x < -\frac{R}{2} \end{cases}$$

resulting in

$$E(x) = \begin{cases} \frac{\lambda\sigma}{\epsilon_0} \hat{x} & \text{if } x > \frac{R}{2} \\ 0 & \text{if } -\frac{R}{2} < x < \frac{R}{2} \\ -\frac{\lambda\sigma}{\epsilon_0} \hat{x} & \text{if } x < -\frac{R}{2}. \end{cases}$$

As $\frac{F}{A} = -\sigma E$ and $F = -\frac{dV}{dx}$, this gives us

$$\frac{V(x)}{A} = \begin{cases} \frac{\lambda\sigma^2}{\epsilon_0}(x - \frac{R}{2}) & \text{if } x > \frac{R}{2} \\ 0 & \text{if } -\frac{R}{2} < x < \frac{R}{2} \\ -\frac{\lambda\sigma^2}{\epsilon_0}(x + \frac{R}{2}) & \text{if } x < -\frac{R}{2}, \end{cases} \quad (2.4)$$

where V is the potential energy function for a given position of the electron and A is the area of the electron. This is a good approximation as long as the plates are so large that for all electron positions x , x is much less than the smallest dimension of the plane charges. In the present work it is sufficient if $R \ll \sqrt{A}$.

Let

$$\alpha = \frac{\lambda\sigma^2}{\epsilon_0} A$$

so that

$$V(x) = \begin{cases} \alpha(x - \frac{R}{2}) & \text{Region I} \\ 0 & \text{Region II} \\ -\alpha(x + \frac{R}{2}) & \text{Region III.} \end{cases} \quad (2.5)$$

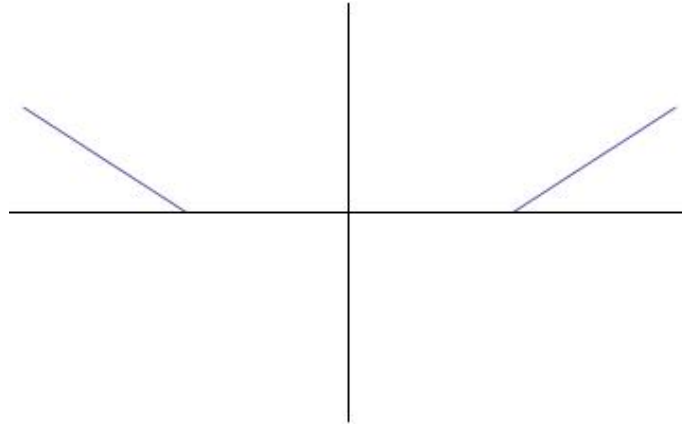


Figure 2.2: The Potential Energy Function $V(x)$

2.2 Solving Schrödinger's equation

2.2.1 Analytical Solutions

In Region I, Schrödinger's equation is

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2} \left[\alpha \left(x - \frac{R}{2} \right) - E \right] \psi. \quad (2.6)$$

Let $y = \left(x - \frac{R}{2} - \frac{E}{\alpha} \right)$, then

$$\frac{d^2\psi}{dx^2} = \frac{2m\alpha}{\hbar^2} (y)\psi.$$

Let $z = \left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} y$, then

$$\frac{d^2\psi}{dz^2} = z\psi,$$

which has the general solution $\psi = a\text{Ai}(z) + b\text{Bi}(z)$ where Ai and Bi are the Airy functions of the first and second types. However, Bi cannot be normalized and therefore

$$\psi_1(z) = a\text{Ai}(z)$$

or

$$\psi_1(x) = a\text{Ai} \left[\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \left(x - \frac{R}{2} - \frac{E}{\alpha} \right) \right]. \quad (2.7)$$

In Region II, the potential is that of a free particle and the solutions are

$$\psi_2(x) = A \sin(kx) + B \cos(kx) \quad (2.8)$$

where $k = \frac{\sqrt{2mE}}{\hbar}$.

By exploiting the symmetry of the configuration and equations (2.7) and (2.8) we get

$$\psi^+(x) = \begin{cases} a\text{Ai} \left[\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \left(x - \frac{R}{2} - \frac{E}{\alpha} \right) \right] & x > \frac{R}{2} \\ B \cos(kx) & -\frac{R}{2} \leq x \leq \frac{R}{2} \\ a\text{Ai} \left[\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \left(-\left(x + \frac{R}{2} \right) - \frac{E}{\alpha} \right) \right] & x < -\frac{R}{2} \end{cases} \quad (2.9)$$

$$\psi^-(x) = \begin{cases} a\text{Ai} \left[\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \left(x - \frac{R}{2} - \frac{E}{\alpha} \right) \right] & x > \frac{R}{2} \\ A \sin(kx) & -\frac{R}{2} \leq x \leq \frac{R}{2} \\ -a\text{Ai} \left[\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \left(-\left(x + \frac{R}{2} \right) - \frac{E}{\alpha} \right) \right] & x < -\frac{R}{2} \end{cases} \quad (2.10)$$

where + and - denote the symmetric and antisymmetric wavefunctions about the origin.

We are left with three physical conditions on ψ :

- 1) $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$
- 2) ψ is continuous
- 3) $\frac{d\psi}{dx}$ is continuous.

Beginning with the continuity conditions (2 and 3) at $x = \frac{R}{2}$, we get

$$a\text{Ai} \left[\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \left(-\frac{E}{\alpha} \right) \right] = B \cos \left(\frac{kR}{2} \right) \quad (2.11)$$

and

$$a \left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \text{Ai}' \left[\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \left(-\frac{E}{\alpha} \right) \right] = -Bk \sin \left(\frac{kR}{2} \right) \quad (2.12)$$

for the symmetric case and

$$a \text{Ai} \left[\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \left(-\frac{E}{\alpha} \right) \right] = A \sin \left(\frac{kR}{2} \right) \quad (2.13)$$

and

$$a \left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \text{Ai}' \left[\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \left(-\frac{E}{\alpha} \right) \right] = Ak \cos \left(\frac{kR}{2} \right) \quad (2.14)$$

for the anti-symmetric case. The normalization constants a , A , and B can be eliminated by dividing (2.11) by (2.12) and (2.13) by (2.14) resulting in

$$\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \frac{\text{Ai}' \left[\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \left(-\frac{E}{\alpha} \right) \right]}{\text{Ai} \left[\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \left(-\frac{E}{\alpha} \right) \right]} = \begin{cases} -k \tan \left(\frac{kR}{2} \right) & \text{Symmetric} \\ k \cot \left(\frac{kR}{2} \right) & \text{Anti-symmetric.} \end{cases} \quad (2.15)$$

To facilitate numerical analysis of these constraints, we define the dimensionless variables

$$u = \left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \left(-\frac{E}{\alpha} \right) \quad (2.16)$$

and

$$\nu = \frac{kR}{2} = \frac{R\sqrt{2mE}}{2\hbar}. \quad (2.17)$$

From (2.16) and (2.17)

$$E = -u\alpha \left(\frac{2m\alpha}{\hbar^2} \right)^{-\frac{1}{3}} = \frac{2\nu^2 \hbar^2}{mR^2} \quad (2.18)$$

and therefore

$$u = -\frac{2\nu^2 \hbar^2}{\alpha m R^2} \left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}}.$$

Making these substitutions results in

$$\left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \frac{\text{Ai}' \left[-\frac{2\hbar^2}{\alpha m R^2} \left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \nu^2 \right]}{\text{Ai} \left[-\frac{2\hbar^2}{\alpha m R^2} \left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \nu^2 \right]} = \begin{cases} -\nu \frac{2}{R} \tan(\nu) & \text{Symmetric} \\ \nu \frac{2}{R} \cot(\nu) & \text{Anti-symmetric.} \end{cases} \quad (2.19)$$

Now define

$$\beta = \left(\frac{2\hbar^2}{\alpha m R^2} \left(\frac{2m\alpha}{\hbar^2} \right)^{\frac{1}{3}} \right)^{\frac{1}{2}} = \frac{1}{R} \left(\frac{4\hbar^2}{m\alpha} \right)^{\frac{1}{3}} :$$

then

$$\frac{1}{\beta} \frac{\text{Ai}'[-\beta^2 \nu^2]}{\text{Ai}[-\beta^2 \nu^2]} = \begin{cases} -\nu \tan(\nu) & \text{Symmetric} \\ \nu \cot(\nu) & \text{Anti-symmetric} \end{cases} \quad (2.20)$$

which is equivalent to

$$0 = \begin{cases} \frac{1}{\beta} \text{Ai}'[-\beta^2 \nu^2] \cos(\nu) + \nu \text{Ai}[-\beta^2 \nu^2] \sin(\nu) & \text{Symmetric} \\ \frac{1}{\beta} \text{Ai}'[-\beta^2 \nu^2] \sin(\nu) - \nu \text{Ai}[-\beta^2 \nu^2] \cos(\nu) & \text{Anti-symmetric.} \end{cases} \quad (2.21)$$

The roots of this equation define the energies as given by equation (2.18)

$$E = \frac{2\nu^2 \hbar^2}{mR^2}$$

However, we can proceed no further without values for the charge density of the nucleus ($\lambda\sigma$) and the separation of the nuclei (R).

2.2.2 Numerical Analysis

In this section some numerical values are explored for the model presented above.

Normalization of the wavefunctions requires the identities

$$\int_0^\infty \text{Ai}^2[t] dt = \frac{1}{3^{2/3} \Gamma[\frac{1}{3}]^2} \quad (2.22)$$

where $\Gamma[\frac{1}{3}] = 2.6789385\dots$ and

$$\int_z^\infty \text{Ai}^2[t] dt = -z \text{Ai}^2[z] + \text{Ai}'^2[z]. \quad (2.23)$$

See Ref. [9, 11] for more information.

Zero Electron Area Limit

Up to this point it has been implicitly assumed that all of the “particles” have the same area and approximate charge distribution. If we are more careful in differentiating the areas of the protons and electron and their

charge densities, then it can be seen that α is independent of the electron area—see equation (2.5). In this case,

$$\alpha = -\frac{\lambda\sigma q_e}{\epsilon_0}, \quad (2.24)$$

where q_e is the total charge of the electron plate.

If we assume that the electron has negligible area, the system takes on a new physical interpretation. It describes two large plates of uniform charge density $\lambda\sigma$ fixed a distance R apart and a single electron. In this situation, as R and $\lambda\sigma$ are fixed and q_e and m can be assumed to be that of an electron, it is possible to find solutions for the energies and wavefunctions.

As an example calculation, if the plates are charged to a density of 10^{-4} C/m² and separated by 1 mm, then $\alpha = 1.81 \times 10^{-12}$ N and $\beta = 3.00 \times 10^{-6}$. Plugging into equations (2.21) and (2.18) gives the first two energies as $E_0 = 0$ J and $E_1 = 6.02 \times 10^{-32}$ J, the former corresponding to an anti-symmetric wavefunction and the latter to a symmetric one.

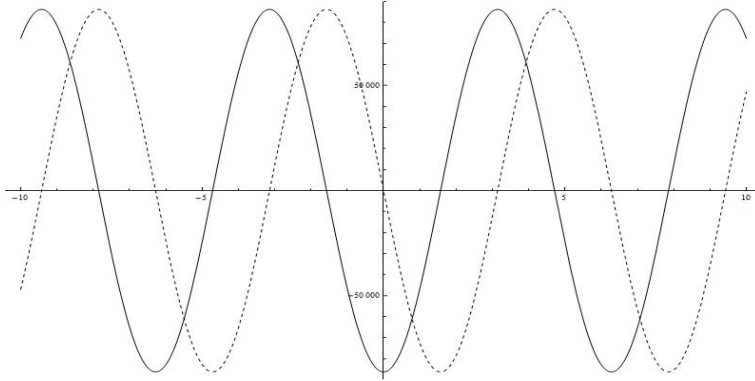


Figure 2.3: Equation (2.21) as a function of ν for $\alpha = 1.81 \times 10^{-12}$ and $R = 1$ mm. The roots of the solid line give allowed energies corresponding to symmetric wavefunctions, those of the the dotted line the energies of anti-symmetric ones. For this problem, ν is assumed to be positive.

The wavefunction for $E = 0$ is trivial and cannot be normalized. The first two non-trivial normalized wavefunction are plotted below.

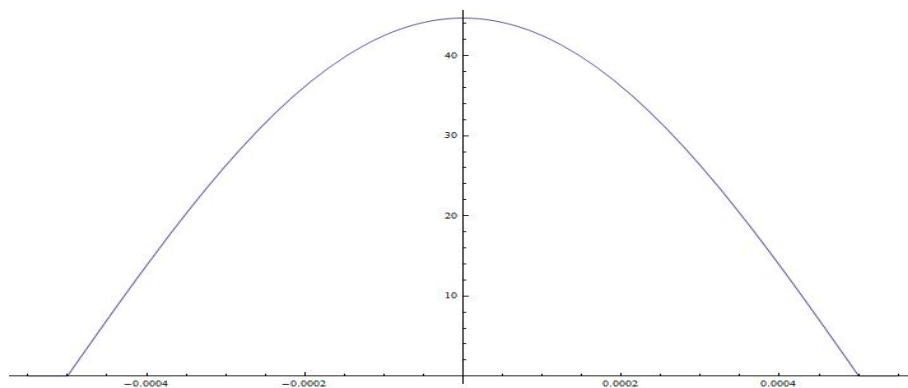


Figure 2.4: Wavefunction for $E = 6.02 \times 10^{-32}$ J

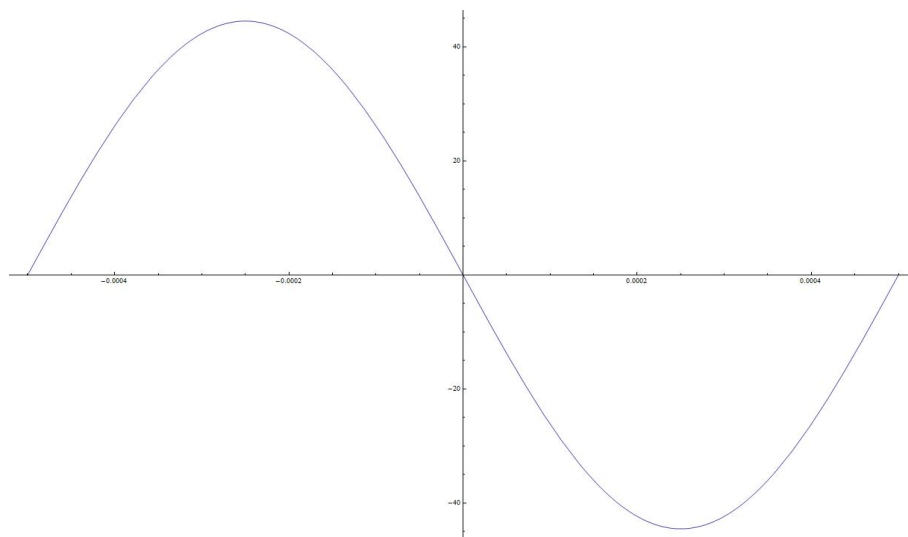


Figure 2.5: Wavefunction for $E = 2.41 \times 10^{-31}$ J

Uniform Particles, Radii, and the Hydrogen Atom Problem

Another simplifying assumption is to assume that all of the plane charges have the same area A and charge density $\pm\sigma$. If the problem is to be one-dimensional this is especially desirable because if the areas are allowed to vary between particles the charges and masses of the particles become functions of variables other than x . Though it has no effect on the solutions to this problem, it is also reasonable to visualize the charge and mass distributions as having axial symmetry.

In order to get an idea of the internuclear distance R , we add the internuclear potential energy to the electronic energy yielding

$$U(R) = E_{\text{electronic}}(R) + V_{\text{nuclear}}(R) = \frac{2\nu^2\hbar^2}{mR^2} - \frac{\lambda^2\sigma^2A_p}{2\epsilon_0}R, \quad (2.25)$$

where ν is governed by equation (2.21) and A_p is the area of the protons, and look for stable nuclear radii by finding energy minima with respect to R .

In addition to finding the internuclear radius for given values of A , m and σ , in this case it is interesting to compare the molecule energy to that of the unbound atoms. In order to determine this, it is necessary to solve the analogous atom problem of one proton and one electron. In this case the potential energy part of the Hamiltonian is

$$V(x) = \frac{\lambda\sigma^2A_e}{2\epsilon_0}|x|. \quad (2.26)$$

It is easy to show using the methods of section 2.2 that the solutions for this problem are of the form

$$\psi = \text{Ai} \left[\left(\frac{2m\gamma}{\hbar^2} \right)^{\frac{1}{3}} \left(x - \frac{E}{\gamma} \right) \right] \quad (2.27)$$

where $\gamma = \frac{\lambda\sigma^2A_e}{2\epsilon_0}$.

Again, the allowed energies are governed by the continuity of the wavefunction and its derivative. For symmetric wavefunctions, these conditions are satisfied when

$$\left(\frac{2m\gamma}{\hbar^2}\right)^{\frac{1}{3}} \text{Ai}' \left[\left(\frac{2m\gamma}{\hbar^2}\right)^{\frac{1}{3}} \left(x - \frac{E}{\gamma}\right) \right] = - \left(\frac{2m\gamma}{\hbar^2}\right)^{\frac{1}{3}} \text{Ai}' \left[\left(\frac{2m\gamma}{\hbar^2}\right)^{\frac{1}{3}} \left(-x - \frac{E}{\gamma}\right) \right]$$

For $x = 0$. Therefore, the energies are determined by

$$\text{Ai}' \left[\left(\frac{2m\gamma}{\hbar^2}\right)^{\frac{1}{3}} \left(-\frac{E}{\gamma}\right) \right] = 0. \quad (2.28)$$

Similarly, for the anti-symmetric case allowed energies correspond to roots of the Airy function.

There is one more point that must be addressed before beginning a numerical analysis. It may seem that there is no physical reason to choose one particular value of A over another. This is because A appears in our calculation of the potential energy function as a relic of how dimensional scaling was performed. In scaling Poisson's equation from $D=3$ to $D=1$ the units of charge were scaled by one unit of length for each change in the dimensionality. As a result of this scaling, the electric field in this model diverges in the correct number of dimensions (1 for $D=1$, 2 for $D=2$, etc.) and the dependence of the electric field due to a point charge on the distance from its source has the desirable characteristic of also scaling with a change in dimensionality. The relationship between units of charge and energy, however, does not scale and as a result it was necessary to use the three-dimensional analogue of "infinite" parallel plates of charge in order to avoid this problem.

It is possible to eliminate the area from the Hamiltonian in Schrödinger's equation by rewriting $m = \rho A$ where ρ is the mass per unit area for an electron plate. In Region I (equation 2.5), Schrödinger's equation becomes

$$\frac{d^2\psi}{dx^2} = \frac{2\rho}{\hbar^2} \left[\frac{q^2}{\epsilon_0} \left(x - \frac{R}{2}\right) - AE \right] \psi$$

and in Region II

$$\frac{d^2\psi}{dx^2} = \frac{2\rho}{\hbar^2} (-AE) \psi$$

where $q = \sigma A$. This results, however, in the eigenparameter having the units of energy \times area and ultimately A works itself back into the solutions either explicitly or hidden in the eigenparameter. It was expected when beginning this work that the areas could be eliminated from the solutions for infinite planes, but for the quantum problem this does not seem to be the case. Truly reducing the problem to one dimension requires a more sophisticated treatment of scaling the units of charge and energy and would also ultimately require abandoning the three-dimensional analogue of parallel plates.

From equations (2.18) and (2.21) or from reworking Schrödinger's equation it can be seen that if ρ and $q = \sigma A$ are the values that are fixed, then the energies have an explicit $\frac{1}{A}$ dependence on the area that not only simplifies calculations but also suggests that scaling units is not unmotivated by physical results. At this point in time, the author has yet to find a physically satisfying way of scaling units for this problem that generalizes to all dimensionalities. (While the solutions are elegant, it seems unphysical that the masses and energies should scale in Schrödinger's equation but the charges should not).

With the understanding of these difficulties, using numerical values will hopefully provide insight as to if this one-dimensional molecule bonds or not and how equation (2.25) depends on R . One reasonable choice for a set of numerical values is $\sigma = e/A$, where e is the elementary charge and $m = m_e$ (λ is now assumed to be 1 as it is in the three-dimensional hydrogen molecule ion problem).

Based on the necessity for A to be much larger than the inter-nuclear distance, this example calculation will be performed using $A_p = A_e = A = (100a_0)^2$ where a_0 is the Bohr radius. In the process of making the numerical calculations it was discovered that the system had the property that smaller energies (both the electronic energy and the sum in equation 2.25) were sometimes associated with greater radii. While this was not expected, it is reasonable given the dependence of the energies on R .

For the given parameters, the energy with the smallest associated inter-nuclear distance R achievable with the numerical methods used gave $R = 1.05 \times 10^{-9}$ m and the electronic energy $E = 1.45 \times 10^{-19}$ J (U, the total energy in the clamped nuclei approximation, was $U = -5.27 \times 10^{-18}$ J).

Note that $R \approx \frac{1}{5}\sqrt{A}$ which indicates that the model is reasonable, but not ideal for the parameters used. For the given choice of the other parameters, the energy appeared during the numerical calculations to scale with changes in the area. More useful parameters for the model may include choosing $\rho = \frac{m}{A}$ in order to adjust A more freely. The normalized wavefunction for this state is plotted below.

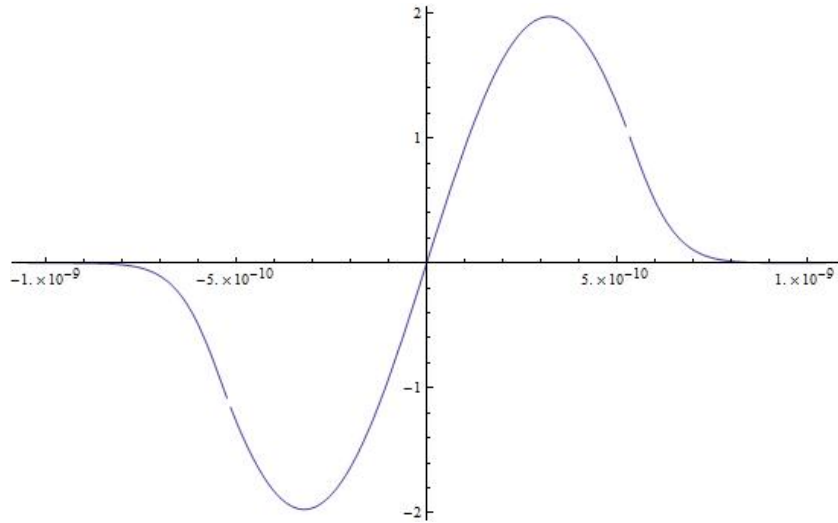


Figure 2.6: Anti-symmetric Wavefunction for $E = 1.45 \times 10^{-19}$ J. This wavefunction minimizes the inter-nuclear distance R and is the first eigenstate for which numerical calculations for R converged for the given parameters.

The solution to the analogous hydrogen atom problem with the same parameters gives the ground state energy $E_1 = 5.56 \times 10^{-19}$ J

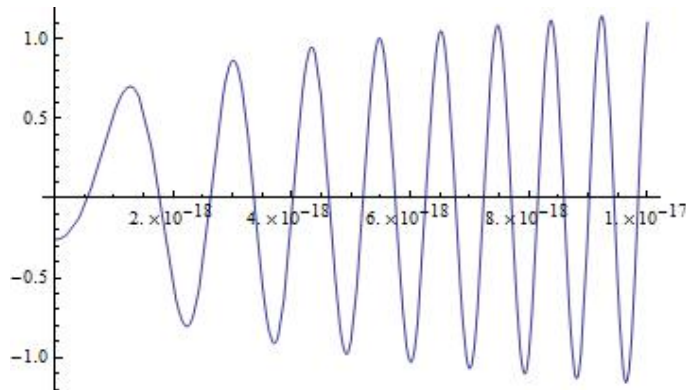


Figure 2.7: The roots of this function give eigenenergies for the symmetric wavefunctions for the analogous atom for the given parameters. The ground state is the first root of this function.

This value is greater than both the electronic energy E and the total energy U for the molecule state given above. It is therefore clear that the molecule does form in $D=1$ for the given parameters. Numerical experiments indicate that due to the negative contribution of the internuclear repulsion term and the energies for the atom being restricted to positive values, this should be the case for any reasonable choice for the variables used as parameters. As there is at this time only numerical evidence, it is unclear what effect using other variables (such as ρ) or drastically different values for the chosen variables could have.

Section 3

Conclusions

A model for the one-dimensional hydrogen molecule ion was developed based on the premise that the electric fields and charge distribution be confined to one dimension. This resulted in each nucleus having the charge distribution

$$\rho = \sigma\delta(x)$$

where σ is the generalized charge. The three-dimensional interpretation of this charge distribution is of an infinite plane charge of uniform charge distribution σ .

The spatial wavefunctions for this molecule were found to be combinations of Airy functions and trigonometric functions and their energies were governed by

$$\frac{1}{\beta} \frac{\text{Ai}'[-\beta^2\nu^2]}{\text{Ai}[-\beta^2\nu^2]} = \begin{cases} -\nu \tan(\nu) & \text{Symmetric} \\ \nu \cot(\nu) & \text{Anti-symmetric,} \end{cases}$$

where $E \propto \nu^2$ and β is a dimensionless variable that depends on physical parameters such as the internuclear separation R and the generalized charges σ .

The equilibrium internuclear separation R and its relationship to the electronic energies was explored using numerical calculations with a set of fixed parameters and one variable parameter. The bond strength of the hydrogen molecule ion was also compared to that of the analogous one-dimensional hydrogen atom using numerical calculations using the same parameters. The ion was found to have lower energy and therefore should form for parameters within certain assumed restrictions.

3.1 Future Work

Mathematical Relationships Between Dimensionalities

One concern is the problem of dimensionally scaling units presented in section 2.2.2. This is an unexpected challenge that arose from giving a quantum treatment to infinite planes of charge. If this problem is solved, perhaps by allowing the units of E to scale, it would be possible to cast this problem in abstract dimensionality. In this case the charge distribution would be

$$\rho^D = q^D \delta(x_1, x_2, x_3, \dots, x_D) = q^D \delta(x_1) \delta(x_2) \delta(x_3) \dots \delta(x_D)$$

where q^D is the dimensionally scaled charge.

This would be interesting not only because it gives insight into what physical properties remain applicable, but also because it would allow comparison of the solutions in different dimensionalities. In the work of Frantz and Hershbach [7] and of López-Cabrera et. al. [2] it is shown that dimensional scaling of the Hamiltonian results in certain energy degeneracies and mathematical relationships between different dimensionalities. While the model presented in this work is, mathematically, a more distant cousin of the three-dimensional problem, it would only be possible to draw conclusions on this subject after working on the problem in more than one dimension.

It can also be hoped that the problem can be solved exactly and in closed form for other dimensionalities. For example, the scaled Hamiltonian [7, 2] reduces to a simple problem in the $D \rightarrow \infty$ limit as well.

The Hydrogen Molecule

Introducing two electrons allows for the exploration of the Pauli exclusion principle and electron correlation in this much simplified one-dimensional model and is a logical extension.

Adding a second electron requires adding the inter-electron repulsion term to the Hamiltonian. This additional term is

$$V_{\text{inter-electron}} = -\frac{\sigma^2 A}{2\epsilon_0} |x_2 - x_1| \quad (3.1)$$

where x_1 and x_2 are the electron coordinates. In this case, Schrödinger's equation becomes

$$\frac{\partial^2 \psi(x_1, x_2)}{\partial x_1^2} + \frac{\partial^2 \psi(x_1, x_2)}{\partial x_2^2} = \frac{2m}{\hbar^2} \left(V_n(x_1) + V_n(x_2) - \frac{\sigma^2 A}{2\epsilon_0} |x_2 - x_1| - E \right) \psi(x_1, x_2).$$

The challenge in finding analytic solutions to this problem is finding a new set of variables that allows the separation of this equation.

One method of rewriting Schrödinger's equation for the hydrogen molecule is to rewrite the positions of the electrons as

$$x_> = \text{Max}[x_1, x_2]$$

$$x_< = \text{Min}[x_1, x_2],$$

as inspired by the work of Goldman [13]. In this case, the Hamiltonian can be simplified significantly; however, care is required to symmetrize or anti-symmetrize the wavefunction when setting up analytic or numerical solutions. Using the one-dimensional problem allows exploration of this change of variables in a relatively simple system.

Correlated Calculations

This project came about as a result of an initial attempt to explore the method of uncoupling correlated variational calculations developed by Goldman [13].

In order to explore the relationship between the mathematics that allowed the uncoupling of integrals in the correlated calculations and the physical problem, an understanding of the existing work on the hydrogen molecule and its ion was necessary. In the course of reading the existing literature on these molecules, this problem presented itself as being of interest.

Having worked this model of the one-dimensional ion, it may be possible to revisit the original problem presented by Ref. [13]. Especially using the information contained in Refs. [4] and [1] there may be sufficient information to make a start on the problem with some restrictions in three-dimensions.

The one-dimensional model can be used to explore analogous mathematical transformations to the three-dimensional ones used by Goldman in order to develop an understanding of the mathematics involved.

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