Vibrational Energies of the Hydrogen Bonds of $H_3O_2^-$ and $H_5O_2^+$

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(ABSTRACT)

We approximate the vibrational energies of the symmetric and asymmetric stretches of the hydrogen bonds of the molecules $H_3O_2^-$ and $H_5O_2^+$ by applying an improvement to the standard time-independent Born-Oppenheimer approximation. These two molecules are symmetric around a central hydrogen which participates in hydrogen bonding. Unlike the standard Born-Oppenheimer approximation, this approximation appropriately scales the hydrogen nuclei differently than the heavier oxygen nuclei. This results in significantly more accurate approximations for the stretching vibrational energies, which we compare to experimental measurements.

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Dedication

I dedicate this thesis to Mom, Dad, Kelly, and Nick.
Thank you.

Contents

List of Figures

List of Tables

Chapter 1

Introduction

We study the two molecular ions $H_3O_2^-$ and $H_5O_2^+$. We wish to approximate the vibrational energies of the symmetric and asymmetric stretches of the hydrogen bonds in these two symmetric molecules. These molecules are the two main structures involved in charge transport in water. $H_5O_2^+$ is the primary structure for proton transfer in water, and $H_3O_2^-$ is the main structure for the transport of OH^- through water. This makes them interesting in the field of contemporary aqueous chemistry for understanding aqueous charge transport. Both of these molecules have been studied with electronic structure theory, but here we wish to investigate using a numerical approximation focused on simplicity.

To approximate the vibrational energies, we would normally proceed with the standard time-independent Born-Oppenheimer approximation. However, the standard approach assumes that all of the nuclei in the molecule have a mass proportional to ϵ^{-4}, where

$$\epsilon \;=\; \left(\frac{m}{M}\right)^{1/4}$$

where m is mass of an electron and M is the mean nuclear mass in the molecule. We define the true value of ϵ as $\epsilon_0 \;=\; 0.0821$. This value is defined by letting the mass of an electron to be 1, and setting the mass of a C^{12} nucleus to be ϵ^{-4}. Then, unlike the standard Born-Oppenheimer approximation, we will use an approximation which scales the mass of a hydrogen nucleus to ϵ^{-3} rather than ϵ^{-4}.

Since we wish to use a model that focuses more on simplicity, we do not want to consider all vibrational energies of the molecules. We can separate the two vibrational modes of interest and reduce the 15-dimensional problem for $H_3O_2^-$ and 21-dimensional problem for $H_5O_2^+$ to only two dimensions each. Then we are able to find eigenvalues of the Hamiltonians numerically for the desired energies in each problem. We can then discuss the accuracy of the approximations by comparing to experimental results.

Chapter 2

Mathematical Background

2.1 Postulates and Basics

2.1.1 Postulates

Let us start by stating the first 5 postulates of quantum mechanics:

Postulate 1
The state of a quantum mechanical system is completely specified by the wave function $\psi(r,t)$*.*

Postulate 2
To every observable in classical mechanics, there corresponds a linear, Hermitian operator in quantum mechanics.

Operators are denoted with a hat. Hermitian operators have real spectrum.

Postulate 3
In any precise measurement of the observable associated with $\hat{A}$*, the value that will be observed is an eigenvalue* a *of* $\hat{A}$*, which satisfies* $\hat{A}\,\psi_a \;=\; a\,\psi_a$*.*

The set of all values a, such that $(\hat{A} - aI)$ is not invertible is called the spectrum of $\hat{A}$.

Postulate 4
The average value of the observable a *corresponding to* $\hat{A}$ *is* $\langle a\rangle \;=\; \int_{-\infty}^{\infty} \overline{\psi}\hat{A}\psi d\tau$*.*

We use $\overline{\psi}$ to denote the complex conjugate of ψ.

Postulate 5
The wave function of a system evolves in time according to the time-dependent Schrödinger equation $\hat{H}\Psi(x,t) \; = \; i\hbar\frac{d\Psi}{dt}$.

The operator $\hat{H}$ is the energy operator.

2.1.2 Operators and Wave Functions

If $\hat{A}\hat{B}f(x) \; = \; \hat{B}\hat{A}f(x)$ for all $f \in \mathcal{H}$, where $\mathcal{H} \; = \; L^2([a,b],dx)$, then operators $\hat{A}$ and $\hat{B}$ commute, but in general, operators do not commute. The commutator is defined by $[\hat{A},\hat{B}] \; = \; \hat{A}\hat{B} - \hat{B}\hat{A}$.

We will primarily use Dirac notation. Using this, we denote the wavefunction $\psi_n(x) \; = \; |n\rangle$ and the adjoint $\overline{\psi_n}(x) \; = \; \overline{|n}\rangle \; = \; \langle n|$
Wave functions will be normalized.

$$\int_{-\infty}^{\infty} \overline{\psi_n}(x)\psi_n(x)dx \; = \; \langle n|n\rangle \; = \; 1$$

$$\int_{-\infty}^{\infty} \overline{\psi_m}\hat{A}\psi_n dx \; = \; \langle m|\hat{A}|n\rangle.$$

Hermitian operators defined on a Hilbert space, which correspond to observables, are self-adjoint. $\hat{A}^* \; = \; \hat{A}$. Suppose $\hat{A}$ has eigenvalues a_n with corresponding eigenvectors $|n\rangle$. Also suppose the eigenvalues are distict, $a_n \; \neq \; a_m$. Since $\hat{A}$ is such a Hermitian operator,

$$\langle m|\hat{A}|n\rangle \; = \; \overline{\langle n|\hat{A}|m\rangle}.$$

$$\langle m|\hat{A}|n\rangle \; = \; a_n\langle m|n\rangle$$

$$\langle n|\hat{A}|\overline{m}\rangle \; = \; \overline{a_m}\langle m|n\rangle$$

$$\langle m|\hat{A}|n\rangle - \langle n|\hat{A}|\overline{m}\rangle \;=\; (a_n - \overline{a_m})\langle m|n\rangle \;=\; 0$$

Recall $\overline{a_m} \;=\; a_m$ since $\hat{A}$ is Hermitian.

Then $\langle m|n\rangle \;=\; 0$ if $m \;\neq\; n$, so eigenfunctions corresponding to distinct eigenvalues are orthogonal.

The function $\delta_{nm} \;=\; \langle n|m\rangle \;=\; \begin{cases} 1 & if\ n \;=\; m \\ 0 & if\ n \;\neq\; m \end{cases}$ is called the Kronecker delta function.

2.2 The Ground State of the Hydrogen Atom

2.2.1 Solving the Schrödinger Equation

For many simple problems, such as a particle in a box or the bound states of the hydrogen atom, the Schrödinger equation can be solved exactly. These simple problems can be solved just by using $\hat{H} \;=\; \hat{T}+\hat{V}$, where $\hat{T} \;=\; -\dfrac{\hbar^2}{2m}\nabla^2$ is the kinetic energy operator, and $\hat{V}$ is the potential energy operator specific to the problem. However, our problem of interest is much too complicated for one to be able to solve analytically, hence we must consider methods of approximation.

First let's work through the problem for the hydrogen atom for the bound states, not considering the scattering states. The potential energy for this problem depends only on the distance, r, from the proton to the electron, and the potential $V(r)$ is given by the coulombic potential $V(r) \;=\; -\dfrac{e^2}{4\pi\epsilon_0 r}$, where $e \;=\; 1.60217733\times 10^{-19}$ C is the charge on the proton and here $\epsilon_0 \;=\; 8.854187816\times 10^{-12}$ $\mathrm{C^2J^{-1}m^{-1}}$ is the permittivity of the vacuum. We also take the nuclear mass to be infinity since the nuclear mass $M \gg m_e$.

Then our Hamiltonian operator is $\hat{H} \;=\; -\dfrac{\hbar^2}{2m_e}\nabla^2 - \dfrac{e^2}{4\pi\epsilon_0 r}$, where $m_e \;=\; 9.1093897\times 10^{-31}$ kg is the mass of an electron.

The Schrödinger equation for this problem is now

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(r,\theta,\phi) - \frac{e^2}{4\pi\epsilon_0 r}\psi(r,\theta,\phi) \;=\; E\psi(r,\theta,\phi).$$

Here ∇^2 in spherical coordinates is

$$\nabla^2 \;=\; \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}.$$

Now we return to the Schrödinger equation,

$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\psi(r,\theta,\phi) \;=\; E\psi(r,\theta,\phi).$$

This can be simplified some by multiplying both sides by $2m_e r^2$.

$$-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - 2m_e r^2\left[\frac{e^2}{4\pi\epsilon_0 r} + E\right]\psi(r,\theta,\phi) \;=\; 0$$

$$-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \hat{L}^2\psi - 2m_e r^2\left[\frac{e^2}{4\pi\epsilon_0 r} + E\right]\psi(r,\theta,\phi) \;=\; 0$$

where

$$\hat{L}^2 \;=\; \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

We notice that a good choice for the angular portion of ψ is that it be an eigenfunction of the angular momentum operator $\hat{L}$. We could choose something that is not, but, for convenience, here we will choose ψ to be such a function. Any square integrable function of θ and ϕ (with respect to the correct measure) can be expanded in angular momentum eigenfunctions.

The usual eigenfunctions of the angular momentum operator, $\hat{L}^2$, are called Spherical Harmonics, which can be seen in Table 2.1. The operator $\hat{L}^2$ has lots of degeneracy, so there are other eigenfunctions, but these are the most useful for us in these problems.

$$\hat{L}^2 Y_l^{m_l}(\theta,\phi) \;=\; \hbar^2 l(l+1) Y_l^{m_l}(\theta,\phi); \quad l \;=\; 0,1,2...; \quad -l \;\leq\; m_l \;\leq\; +l$$

Then we can conveniently write the eigenfunction as $\psi(r,\theta,\psi) \;=\; R(r)Y_l^{m_l}(\theta,\phi)$.

Our Schrödinger equation becomes

$$-\frac{\hbar^2}{2m_e r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{\hbar^2 l(l+1)}{2m_e r^2} + V(r) - E\right]R(r) \;=\; 0.$$

This leaves just a second order ordinary differential equation for $R(r)$. Solutions to this equation are called radial wave functions, given by

$$R_{nl}(r) \;=\; -\left[\frac{(n-l-1)!}{2n[(n+1)!]^3}\right]^{1/2}\left(\frac{2}{na_0}\right)^{l+3/2} r^l e^{-r/na_0} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right);$$

$$0 \;\leq\; l \;\leq\; n-1; \quad n \;=\; 1,2...$$

where $a_0 \;=\; 4\pi\epsilon_0\hbar^2/m_e e^2 \;=\; 5.29177249\times 10^{-11}$ m is the Bohr radius, and L_α^β denotes the generalized Laguerre polynomial. The first few solutions of R_{nl} can be seen in Table 2.2.

This allows us now to solve the Schrödinger equation for the hydrogen atom.

For the wave functions $\psi_{nlm_l}(r,\theta,\phi) \;=\; R_{nl}(r)Y_l^{m_l}(\theta,\phi)$, we obtain an equation for the quantized energies E_n.

$$E_n \;=\; -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2} \;=\; -\frac{m_e e^4}{32\pi^2\epsilon_0^2\hbar^2 n^2}; \qquad n = 1,2,3...$$

Table 2.1: The First Few Spherical Harmonics [12]

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^1 = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi}$$

$$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$Y_2^1 = -\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{i\phi}$$

$$Y_2^{-1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{-i\phi}$$

$$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{2i\phi}$$

$$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{-2i\phi}$$

Table 2.2: The First Few Radial Wave Functions [12]

$$
\begin{aligned}
R_{10}(r) &= 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho} \\
R_{20}(r) &= \left(\frac{Z}{2a_0}\right)^{3/2} (2-\rho)e^{-\rho/2} \\
R_{21}(r) &= \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \rho e^{-\rho/2} \\
R_{30}(r) &= \frac{2}{27}\left(\frac{Z}{3a_0}\right)^{3/2} (27-18\rho+2\rho^2)e^{-\rho/3} \\
R_{31}(r) &= \frac{1}{27}\left(\frac{2Z}{3a_0}\right)^{3/2} \rho(6-\rho)e^{-\rho/3} \\
R_{32}(r) &= \frac{4}{27\sqrt{10}}\left(\frac{Z}{3a_0}\right)^{3/2} \rho^2 e^{-\rho/3}
\end{aligned}
$$

Z is the nuclear charge, $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2 = 5.29177249 \times 10^{-11}$ m is the Bohr radius, and $\rho = Zr/a_0$.

The ground state wave function for hydrogen is $\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho}$, corresponding to the lowest energy E_1.

$$E_1 = -\frac{m_e e^4}{8\epsilon_0^2 h^2}$$

Note however, in general we will write the ground state as ψ_0 and ground state energy as E_0.

2.2.2 Quantum Numbers

The hydrogen atomic wave functions depend on three values: n, l, and m_l. These are called good quantum numbers, which are associated with conserved quantities. The value n is called the principle quantum number which takes values $\{1, 2, 3...\}$. As we have seen, energy is dependent only on the principle quantum number. The value l is called the angular-momentum quantum number which can take values $\{0, 1, 2..., n-1\}$. The magnitude of the angular momentum of the electron about the proton of the hydrogen atom is dependent on only l. The value m_l is called the magnetic quantum number, which can take $2l+1$ distinct values $\{-l, -l+1, ..., 0, 1, ..., l-1, l\}$. The z component of angular momentum is determined by m_l. Also the energy of the hydrogen atom in a magnetic field is determined by m_l, which is why it is called the magnetic quantum number.

2.2.3 Spin

Electrons also have a property called spin. An electron can exist in one of two district states described by the fourth quantum number m_s, called the spin quantum number, which takes the value of either $\frac{1}{2}$ or $-\frac{1}{2}$. The spin angluar momentum operator $\hat{S}$ is given by

$$\hat{S} = \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix}.$$

The eigenfunctions of $\hat{S}_z$ are denoted as α and β. And written in the basis of α and β, the Pauli spin matricies when $s = \frac{1}{2}$ are

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Let $s = \frac{1}{2}$.

$$\hat{S}^2\alpha = \hbar^2 s(s+1)\alpha$$

$$\hat{S}^2\beta = \hbar^2 s(s+1)\beta$$

$$\hat{S}_z\alpha = \frac{1}{2}\hbar\alpha$$

$$\hat{S}_z\beta = -\frac{1}{2}\hbar\beta$$

The eigenfunctions α and β are assumed to be orthonormal. Spin is not a classical concept, so when we integrate formally, we write

$$\langle\alpha|\alpha\rangle = \int \overline{\alpha}\alpha \; d\sigma = 1$$

$$\langle\beta|\beta\rangle = \int \overline{\beta}\beta \; d\sigma = 1$$

$$\langle\alpha|\beta\rangle \;=\; \int \overline{\alpha}\beta \; d\sigma \;=\; 0$$

$$\langle\beta|\alpha\rangle \;=\; \int \overline{\beta}\alpha \; d\sigma \;=\; 0$$

where σ is called the spin variable, which does not correlate to a classical variable.

The eigenfunctions α and β are denoted in the form of $|s \; m_s\rangle$.

$$\alpha \;=\; \left|\frac{1}{2}\;\frac{1}{2}\right\rangle, \qquad \beta \;=\; \left|\frac{1}{2}\;-\frac{1}{2}\right\rangle$$

We now want to include these spin functions in our wave function along with the spatial functions. We also assume that the spatial and spin parts of the wave functions are independent of one another.

$$|n\; l\; m_l\; m_s\rangle \;=\; \Psi_{n,l,m_l,m_s}(r,\theta,\phi,\sigma) \;=\; \begin{cases} \psi_{n,l,m_l}(r,\theta,\phi)\alpha(\sigma) \\ \qquad\quad \text{or} \\ \psi_{n,l,m_l}(r,\theta,\phi)\beta(\sigma) \end{cases}$$

2.3 Perturbation Theory

For more complicated problems, we are unable to solve the Schrödinger equation exactly and must consider methods of approximating solutions. One method is called perturbation theory. When trying to solve the Schrödinger equation for a particular problem which we are unable to solve exactly, we can write it in terms of a simpler problem which we are able to solve exactly. For example, we could solve the Schrödinger equation for a helium atom by applying perturbation theory to the solution of the hydrogen atom.

Suppose we want to solve a particular problem, $\hat{H}\psi_n \;=\; E_n\psi_n$. We can write

$$\hat{H} \;=\; \hat{H}(\lambda) \;=\; \hat{H}^{(0)} + \lambda\hat{H}^{(1)}$$

where $\hat{H}^{(0)}\psi_n^{(0)} \;=\; E_n^{(0)}\psi_n^{(0)}$ is a problem previously solved for exactly. Thus $\psi_n^{(0)}$ and $E_n^{(0)}$ are both already known. For now, λ will simply be used as a place holder variable for the problem. We are assuming these operators $H^{(0)}$ and $H^{(1)}$ have discrete spectra for which perturbation theory will converge.

Suppose we can express ψ_n and E_n each as a power series in λ.

$$\psi_n \;=\; \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + ...$$

$$E_n \;=\; E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...$$

Substituting all of these into the Schrödinger equation, we obtain

$$(\hat{H}^{(0)}+\lambda\hat{H}^{(1)})(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+...) \;=\; (E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2 E_n^{(2)}+...)(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+...).$$

Now writing this equation by grouping terms by powers of λ,

$$(\hat{H}^{(0)}\psi_n^{(0)} - E_n^{(0)}\psi_n^{(0)}) + (\hat{H}^{(0)}\psi_n^{(1)} + \hat{H}^{(1)}\psi_n^{(0)} - E_n^{(0)}\psi_n^{(1)} - E_n^{(1)}\psi_n^{(0)})\lambda$$

$$+(\hat{H}^{(0)}\psi_n^{(2)} + \hat{H}^{(1)}\psi_n^{(1)} - E_n^{(0)}\psi_n^{(2)} - E_n^{(1)}\psi_n^{(1)} - E_n^{(2)}\psi_n^{(0)})\lambda^2 + O(\lambda^3) \;=\; 0.$$

We denote the terms of order λ^3 and higher as $O(\lambda^3)$.

The parameter λ is an arbitrary number, so each coefficient must be equal to 0 for this equation to hold. The λ^0 term we already know to be 0 from the problem previously solved. Now for the λ^1 term we have

$$\hat{H}^{(0)}\psi_n^{(1)} + \hat{H}^{(1)}\psi_n^{(0)} \;=\; E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}.$$

We left multiply by $\overline{\psi_n^{(0)}}$ (and switch to Dirac notation).

$$\langle\psi_n^{(0)}|\hat{H}^{(0)} - E_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|\hat{H}^{(1)}|\psi_n^{(0)}\rangle \;=\; E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle$$

$$(E_n^{(0)} - E_n^{(0)})\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|\hat{H}^{(1)}|\psi_n^{(0)}\rangle \;=\; E_n^{(1)}$$

The first order energy correction is $E_n^{(1)} \;=\; \langle\psi_n^{(0)}|\hat{H}^{(1)}|\psi_n^{(0)}\rangle$.

Then the energy up to first order correction is $E_n \;=\; E_n^{(0)} + E_n^{(1)}$.

To solve for the second order energy correction, we must first solve for the first order correction to the wave function ψ_n. To do this, we return to the original coefficient for the λ^1 term and left multiply this time by $\psi_i^{(0)}$, from the solution of the previously solved problem.

$$\langle\psi_0^{(0)}|\hat{H}^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_0^{(0)}|\hat{H}^{(1)}|\psi_n^{(0)}\rangle \;=\; E_n^{(0)}\langle\psi_0^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}\langle\psi_0^{(0)}|\psi_n^{(0)}\rangle \;=\; E_n^{(0)}\langle\psi_0^{(0)}|\psi_n^{(1)}\rangle$$

$$E_0^{(0)}\langle\psi_0^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_0^{(0)}|\hat{H}^{(1)}|\psi_n^{(0)}\rangle \;=\; E_n^{(0)}\langle\psi_0^{(0)}|\psi_n^{(1)}\rangle$$

$$\langle\psi_0^{(0)}|\psi_n^{(1)}\rangle \;=\; -\frac{\langle\psi_0^{(0)}|\hat{H}^{(1)}|\psi_n^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}; \qquad n \;\neq\; 0$$

We can write $\psi_n^{(1)}$ as a linear combination of wave functions from the previous problem.

$$\psi_n^{(1)} \;=\; \sum_{i\;=\;0}^{\infty} c_i\psi_i^{(0)}$$

$$\sum_{i\,=\,0}^{\infty} c_i \langle \psi_0^{(0)} | \psi_i^{(0)} \rangle \;=\; \sum_{i\,=\,0}^{\infty} c_i \delta_{0i} \;=\; -\frac{\langle \psi_0^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}$$

$$c_0 \;=\; -\frac{\langle \psi_0^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}$$

Similarly, left multiplying by $\psi_i^{(0)}$, we would obtain $c_i \;=\; -\frac{\langle \psi_i^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle}{E_i^{(0)} - E_n^{(0)}};\; i \neq n.$

Now we have solved $\psi_n^{(1)} \;=\; \sum_{i\,\neq\,n}^{\infty} -\frac{\langle \psi_i^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle}{E_i^{(0)} - E_n^{(0)}} \psi_i^{(0)}.$

Continuing this method with the λ^2 term, we would obtain the second order corrections $E_n^{(2)}$ and $\psi_n^{(2)}$, and then any higher order corrections by continuing further.

There is another convenient method of deriving perturbation theory for molecules that was developed by Kato using a complex analysis approach [6]. Under appropriate hypotheses, the following techniques can be made rigorous. There are counterexamples which do not satisfy the hypotheses. For example we must avoid infinite multiplicity eigenvalues. Also the anharmonic oscillator shows that it may not be convergent [14].

First let's look at the case where $\mathcal{H} \;=\; L^2([0,1], dx)$, $H_0 \;=\; 0$, and H_1 is multiplication by x.

$\sigma(H_0 + \lambda H_1) \;=\; [0, \lambda]$

$\sigma_{\text{disc}}(H) \;=\;$ the set of isolated eigenvalues of finite multiplicity

$z_0 \in \sigma(H_0)$

$$P(\lambda) \;=\; \frac{1}{2\pi i} \int_C (z - H_0 - \lambda H_1)^{-1}\, dz$$

$$E(\lambda) \;=\; \frac{\langle \psi_0 | H(\lambda) P(\lambda) | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle}$$

$$\psi(\lambda) \;=\; \frac{P(\lambda)\psi_0}{\langle\psi_0|P(\lambda)|\psi_0\rangle}$$

The reduced resolvent operator is $(z - H)_r^{-1} \;=\; P_{\mathbb{R}\setminus\{z\}}(z - H)^{-1}$.

Again we would minimize to find the optimal energy approximation. In general we would find $\psi_n^{(1)} \;=\; (H^{(0)} - E_n^{(0)})_r^{-1}\, H^{(1)}\, \psi_n^{(0)}$. The reduced resolvent operator $(H_{(0)} - E_n^{(0)})_r^{-1}$ is convenient to use here. Note that we are only considering operators with pure point spectra.

For the example of the anharmonic oscillator, we would let $H_0 \;=\; -\frac{1}{2}\frac{\partial^2}{\partial x^2} + \frac{1}{2}x^2$, and $H_1 \;=\; x^4$.

$$D(H_1) \subseteq D(H_0)$$

$$||H_1\psi|| \;\le\; a||H_0\psi|| + b||\psi|| \text{ for all } \psi \in D(H_0)$$

This example fails however, because this inequality does not hold for any a in this problem.

2.4 Many-Electron Atoms

2.4.1 Notation and Antisymmetry

The problem of solving the Schrödinger equation becomes increasingly more complicated when dealing with many-electron atoms. The helium atom for example would have the general wave function $\psi(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2)$, where $\mathbf{R}$ denotes the position coordinates of the nucleus of the helium atom and $\mathbf{r}_1$ and $\mathbf{r}_2$ denote the positions of each electron, labeled electron 1 and electron 2. However, since the mass of the nucleus $M \gg m_e$, we can approximate the system as having a fixed nucleus relative to the electrons. Thus we will fix the nucleus at the origin of the spherical coordinate system. The wave function would now be written as $\psi(\mathbf{r}_1, \mathbf{r}_2)$, or even more simply as $\psi(1, 2)$. In general, for larger atoms, the wave function is

$\psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n)$, or $\psi(1, 2..., n)$.

In writing $\psi(1, 2)$, we have chosen a labeling of each electron as 1 and 2, but electrons are indistinguishable from each other. Then $\psi(2, 1)$ would also be acceptable. Therefore, our wave function must be a linear combination of all possible labelings of the electron. For helium again, $\Psi_1(1, 2) \ = \ \psi(1, 2) + \psi(2, 1)$ and $\Psi_2(1, 2) \ = \ \psi(1, 2) - \psi(2, 1)$.

Postulate 6
All electronic wave functions must be antisymmetric under the interchange of any two electrons.

Both $\Psi_1(1, 2)$ and $\Psi_2(1, 2)$ seem to be viable wave functions for the ground state of the helium atom. However, $\Psi_2(1, 2)$ is the function that must be the wave function. This is due to Postulate 6, requiring that the wave function is antisymmetric. It is equivalent to say that electrons are fermions, which also is known experimentally. (Actually, it is a very important fact, physically, that electrons are fermions. If they were not, bulk matter would collapse!)

$$\Psi_2(2, 1) \ = \ \psi(2, 1) - \psi(1, 2) \ = \ -\Psi_2(1, 2)$$

Ψ_2 is said to be antisymmetric under the interchange of the two electrons. Since

$$\Psi_1(2, 1) \ = \ \psi(2, 1) + \psi(1, 2) \ = \ \Psi_1(1, 2),$$

Ψ_1 is not antisymmetric.

The more familiar statement, the Pauli Exclusion Principle, that no two electrons can have the same set of quantum numbers, $\{n, l, m_l, m_s\}$, follows from this postulate.

2.4.2 Slater Determinants

For helium, let's assume both electrons are in the same orbital, the 1s orbital. According to the Pauli Exclusion Principle, one electron will be in spin state α and the other will be in state β. Then we will write $\psi(1, 2)$ as a product of two orbitals.

$$\psi(1,2) \;=\; \psi(1)\psi(2) \;=\; 1s\alpha(1)1s\beta(2)$$

$$\Psi(1,2) \;=\; \psi(1,2) - \psi(2,1) \;=\; 1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1)$$

Note that we have dropped the subscript 2 on Ψ. We can now see this is in the form of a determinant of a matrix,

$$\Psi(1,2) \;=\; \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}.$$

This is called a determinantal wave function, or a Slater determinant. Of course, wave functions must be normalized though, so we must include a normalization factor. This is the normalized determinantal wave function for the helium atom, which is an approximation for the ground state of the helium atom.

$$\Psi(1,2) \;=\; \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$$

Generalized to an N-electron system, we use an $N \times N$ determinant, and the normalization constant is $\frac{1}{\sqrt{N!}}$.

$$\Psi(1,2,...,N) \;=\; \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & u_2(1) & \cdots & u_N(1) \\ u_1(2) & u_2(2) & \cdots & u_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ u_1(N) & u_2(N) & \cdots & u_N(N) \end{vmatrix}$$

The functions u_i are the spin orbitals for the system.

For example, the ground-state electron configuration for the beryllium atom is $1s^2 2s^2$, thus the Slater determinant approximation for the wave function of ground-state beryllium would be

$$\Psi(1,2,3,4) \;=\; \frac{1}{\sqrt{4!}}\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) & 2s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) & 2s\beta(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) & 2s\beta(3) \\ 1s\alpha(4) & 1s\beta(4) & 2s\alpha(4) & 2s\beta(4) \end{vmatrix}.$$

2.5 The Hartree-Fock Method

We will begin by assuming we are solving a problem of a closed-shell system. This means the valence shell is full and thus much more stable. Suppose it has $2N$ electrons, or N fully occupied spatial orbitals. The Slater determinant to approximate the wave function for this atom would be

$$\Psi(1,2,...,\,2N) \;=\; \frac{1}{\sqrt{(2N)!}}\begin{vmatrix} u_1(1) & u_2(1) & \cdots & u_{2N}(1) \\ u_1(2) & u_2(2) & \cdots & u_{2N}(2) \\ \vdots & \vdots & \ddots & \vdots \\ u_1(2N) & u_2(2N) & \cdots & u_{2N}(2N) \end{vmatrix}.$$

The normalized Hamiltonian operator for this problem of a $2N$ electron atom is given by

$$\hat{H} \;=\; -\frac{1}{2}\sum_{j\,=\,1}^{2N}\nabla_j^2 - \sum_{j\,=\,1}^{2N}\frac{Z_j}{r_j} + \sum_{j\,=\,1}^{2N}\sum_{j\,>\,i}\frac{1}{r_{ij}}$$

$$=\; \sum_{j\,=\,1}^{2N}\hat{h}_j + \sum_{j\,=\,1}^{2N}\sum_{j\,>\,i}\frac{1}{r_{ij}}$$

where $\hat{h}_j \;=\; -\frac{1}{2}\nabla_j^2 - \frac{Z_j}{r_j}$. We choose the position of the nucleus to be at the origin.

The nuclear charge on the jth nucleus is Z_j. Let r_j be the distance between electron j and the nucleus and $r_{ij} \;=\; |\mathbf{r}_i - \mathbf{r}_j|$ be the distance between electron i and electron j.

To find the energy, E, it is convenient to write it in integral form.

$$E \ = \ \langle \Psi(1,2,...,\, 2N)|\hat{H}|\Psi(1,2,...,\, 2N)\rangle$$

$$= \ \int ... \int \overline{\Psi}(1,2,...,\, 2N)\hat{H}\Psi(1,2,...,\, 2N) \ d\mathbf{r}_1 d\sigma_1 ... d\mathbf{r}_{2N} d\sigma_{2N}$$

$$= \ 2\sum_{j\,=\,1}^{N} I_j + \sum_{i\,=\,1}^{N}\sum_{j\,=\,1}^{N}(2J_{ij} - K_{ij})$$

where

$$I_j \ = \ \int \overline{\psi}_j(\mathbf{r}_1)\hat{h}_j(\mathbf{r}_1)\psi_j(\mathbf{r}_1) \ d\mathbf{r}_1$$

$$J_{ij} \ = \ \int\int \overline{\psi}_i(\mathbf{r}_1)\overline{\psi}_j(\mathbf{r}_2)\frac{1}{r_{12}}\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2) \ d\mathbf{r}_1 d\mathbf{r}_2$$

$$K_{ij} \ = \ \int\int \overline{\psi}_i(\mathbf{r}_1)\overline{\psi}_j(\mathbf{r}_2)\frac{1}{r_{12}}\psi_i(\mathbf{r}_2)\psi_j(\mathbf{r}_1) \ d\mathbf{r}_1 d\mathbf{r}_2$$

Now we can introduce the Fock operator, given by

$$\hat{F}(\mathbf{r}_1) \ = \ \hat{h}(\mathbf{r}_1) + \sum_{j}^{N}[2\hat{J}_j(\mathbf{r}_1) - \hat{K}_j(\mathbf{r}_1)]$$

where $\hat{h}(\mathbf{r}_1) \ = \ -\frac{1}{2}\nabla_1^2 - \frac{Z_1}{\mathbf{r}_1}$.

The operator $\hat{J}_j(\mathbf{r}_1)$ is called the Coulomb operator.

$$\hat{J}_j(\mathbf{r}_1)\psi_i(\mathbf{r}_1) \ = \ \psi_i(\mathbf{r}_1)\int \overline{\psi}_j(\mathbf{r}_2)\frac{1}{r_{12}}\psi_j(\mathbf{r}_2) \ d\mathbf{r}_2$$

The operator $\hat{K}_j(\mathbf{r}_1)$ is called the exchange operator.

$$\hat{K}_j(\mathbf{r}_1)\psi_i(\mathbf{r}_1) \ = \ \psi_i(\mathbf{r}_1)\int \overline{\psi}_j(\mathbf{r}_2)\frac{1}{r_{12}}\psi_i(\mathbf{r}_2)\ d\mathbf{r}_2$$

Then we can consider the eigenvalue problem

$$\hat{F}(\mathbf{r}_1)\psi_i(\mathbf{r}_1) \ = \ \varepsilon_i\psi_i(\mathbf{r}_1); \qquad i \ = \ 1, 2, ..., \ N.$$

Together these equations are called the Hartree-Fock equations.

The eigenvalue ε_i is called the Hartree-Fock orbital energy.

$$\begin{aligned} \varepsilon_i \ &= \ \int \overline{\psi}_i(\mathbf{r}_1)\hat{F}(\mathbf{r}_1)\psi_i(\mathbf{r}_1)\ d\mathbf{r}_1 \\ &= \ I_i + \sum_{j \ = \ 1}^{N}(2J_{ij} - K_{ij}) \end{aligned}$$

We obtain $E \ = \ \sum_{i \ = \ 1}^{N}(I_i + \varepsilon_i)$.

This is actually an iterative method where we choose an initial guess for the orbitals $\psi_i(\mathbf{r})$ to calculate $\hat{F}(\mathbf{r})$ then use that $\hat{F}(\mathbf{r})$, to obtain a new set of $\psi_i(\mathbf{r})$. We would then continue this iterative method until there is a self-consistent set of orbitals as a result.

The initial guess will usually be chosen as a linear combination of functions, $\phi_\nu(\mathbf{r})$, $\nu \ = \ 1, 2, ..., \ K$, which are typically, but not necessarily, Slater orbitals. These functions are called basis functions. Of course, a larger basis set will result in more accurate atomic orbitals.

Another version of the Hartree-Fock Method uses ε_i's as Lagrange multipliers.

$$\langle\psi_i|\hat{F}|\psi_i\rangle \ = \ \varepsilon_i\langle\psi_i|\psi_i\rangle$$

Using the Lagrange method, we would minimize the right hand side, which would minimize the Hartree-Fock Energy, $E = \sum_{i\,=\,1}^{N}(I_i + \varepsilon_i)$, with respect to the constraint that $\psi_i(\mathbf{r}_i)$ is normalized. Because the Hartree-Fock energy is always an overestimate, minimizing this energy will give the best approximation.

2.6 Molecules

2.6.1 Jacobi Coordinates

We need to choose a convenient coordinate system for the nuclei in a molecule. One option is to use Jacobi coordinates. A system with N nuclei will reduce to a problem with $N - 1$ vectors, $\{x_1, x_2, ..., x_{N-1}\}$, after the removal of the motion of the center of mass, where

$$x_1 = r_2 - r_1$$

$$x_j = r_{j+1} - \left(\frac{\sum_{k\,=\,1}^{j} m_k r_k}{\sum_{k\,=\,1}^{j} m_k} \right) ; \quad j = 2, 3, ..., N - 1$$

$$CM = \frac{\sum_{k\,=\,1}^{N} m_k r_k}{\sum_{k\,=\,1}^{N} m_k}$$

The vector x_1 is from the nucleus of the first atom to the nucleus of the second atom; x_2 is the vector from the center of mass of the nuclei of the first and second atoms to the nucleus of the third atom; x_3 is the vector from the center of mass of the first three nuclei to the fourth; and so on. Then CM is the center of mass of all N nuclei.

$$\mu_1 = \frac{1}{\dfrac{1}{m_1} + \dfrac{1}{m_2}} = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu_j = \frac{\left(\displaystyle\sum_{k\,=\,1}^{j} m_k\right) m_{j+1}}{\displaystyle\sum_{k\,=\,1}^{j+1} m_k}; \quad j = 2, 3, ..., N-1$$

Now the expression for kinetic energy becomes much more manageable, with the motion of the center of mass removed.

$$T = -\sum_{j\,=\,1}^{N-1} \frac{1}{2\mu_j} \Delta_{x_j}$$

2.6.2 Clustered Jacobi Coordinates

Another option for the coordinates is to use Clustered Jacobi coordinates. This again reduces the system to $N-1$ vectors after the removal of the center of mass motion. We must first choose a clustering of the r_i coordinates. Suppose we sort them into n different clusters, $\{A_1, ..., A_n\}$, and each cluster has p_j coordinates in it for $j = 1, 2, ..., n$, respectively. Label the coordinates for each as $r_{j,k}$ with masses $m_{j,k}$, where $j = 1, 2, ...n$ denotes which cluster it is in, and $k = 1, 2, ..., p_j$ orders the particles in each cluster.

$$\sum_{j\,=\,1}^{n} p_j = N$$

Then we apply the regular Jacobi method to each cluster.

$$y_{j,1} = r_{j,2} - r_{j,1}; \qquad j = 1, 2, 3, ..., n$$

$$y_{j,k} = r_{j,k+1} - \left(\frac{\sum_{t=1}^{k} m_{j,t} r_{j,t}}{\sum_{t=1}^{k} m_{j,t}} \right); \qquad j = 2, 3, ..., n; \; k = 1, 2, 3, ..., p_j - 1$$

Once this has been done for each of the clusters of particles, we will have the first $N - n$ y coordinates. The last $n - 1$ y coordinates are the Jacobi coordinates for centers of mass of the clusters.

$$CM_j = \frac{\sum_{k=1}^{p_j} m_{j,k} r_{j,k}}{\sum_{k=1}^{p_j} m_{j,k}} \qquad j = 1, 2, 3..., n$$

$$\mu_j = \frac{1}{\sum_{k=1}^{p_j} \frac{1}{m_{j,k}}}; \qquad j = 1, 2, 3..., n$$

Let CM_j be the center of mass of all the particles in cluster A_j, and μ_j be the masses of all the nuclei in cluster A_j.

We will label the last of the $y_{s,t}$ coordinates by letting $s = n + 1$ and $t = 1, 2, 3, ..., n - 1$.

$$y_{n+1,1} = CM_2 - CM_1$$

$$y_{n+1,j} \;=\; CM_{j+1} - \left(\frac{\sum\limits_{t\,=\,1}^{j} \mu_t CM_t}{\sum\limits_{t\,=\,1}^{j} \mu_t} \right); \qquad j \;=\; 2, 3, ..., n-1$$

This gives us the desired $N-1$ vectors.

$$\rho_{j,1} \;=\; \frac{1}{\dfrac{1}{m_{j,1}} + \dfrac{1}{m_{j,2}}} \;=\; \frac{m_{j,1} m_{j,2}}{m_{j,1} + m_{j,2}}; \qquad j \;=\; 1, 2, 3, ..., n$$

$$\rho_{j,k} \;=\; \frac{\left(\sum\limits_{t\,=\,1}^{k} m_{j,t} \right) m_{j,k+1}}{\sum\limits_{t\,=\,1}^{k+1} m_{j,t}}; \quad j \;=\; 1, 2, 3, ..., n; \;\; k \;=\; 2, 3, ..., p_j - 1$$

Let $s_j \;=\; \sum\limits_{k\,=\,1}^{p_j} m_{j,k}$ be the sum all of the masses in cluster A_j for $j \;=\; 1, 2, ..., n$.

$$\rho_{n+1,j} \;=\; \frac{\left(\sum\limits_{t\,=\,1}^{j} s_t \right) s_{j+1}}{\sum\limits_{t\,=\,1}^{j+1} s_t}; \quad j \;=\; 2, 3, ..., n-1$$

Let $p_{n+1} \;=\; n$.

With this coordinate system, the expression for kinetic energy becomes

$$T \;=\; -\sum_{j\,=\,1}^{n+1} \sum_{k\,=\,1}^{p_j - 1} \frac{1}{2\rho_{j,k}} \Delta_{y_{j,k}}$$

2.6.3 The Born-Oppenheimer Approximation

Now we have a good understanding of how to solve problems with atoms, but we want to understand molecules. The simplest molecule we can consider is H_2^+. The Schrödinger equation for this molecule is given by

$$\hat{H}_{mol}\psi_{mol}(\mathbf{r}, \mathbf{R}_A, \mathbf{R}_B) \;=\; E_{mol}\psi_{mol}(\mathbf{r}, \mathbf{R}_A, \mathbf{R}_B).$$

where $\mathbf{r}$ is the coordinate set for the one electron, and $\mathbf{R}_A$ and $\mathbf{R}_B$ are the coordinates for the hydrogen nuclei, labeled A and B.

As when working with just an atom, the nuclei in a molecule move much more slowly than the electrons, so we treat them as stationary compared to the motion of an electron. This allows us to approximate the wave function by separating the wave function into electronic and nuclear functions. This is called the Born-Oppenheimer approximation.

$$\psi_{mol}(\mathbf{r}, \mathbf{R}_A, \mathbf{R}_B) \;\approx\; \psi_{el}(\mathbf{r}, R)\psi_{nucl}(\mathbf{R}_A, \mathbf{R}_B)$$

where $R \;=\; |\mathbf{R}_A - \mathbf{R}_B|$ is the distance between the nuclei.

We can either take $M \to \infty$, or use a change of variables to remove the motion of the center of mass. First let's look at the case where we let $M \to \infty$. Then using the separated wave function approximation in the Schrödinger equation and neglecting terms of order m_e/M, as we take $M \to \infty$, we obtain the electronic Schrödinger equation.

$$\hat{H}_{el}\psi_{el}(\mathbf{r}, R) \;=\; E_{el}(R)\psi_{el}(\mathbf{r}, R)$$

Here $\hat{H}_{el}$ is the Hamiltonian operator with the Born-Oppenheimer approximation.

$$\hat{H}_{el} \;=\; -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

This is written in atomic units, and r_A is the distance between nucleus A and the electron, and r_B is the distance between nucleus B and the electron. We henceforth drop the electronic subscripts.

The wave function now will be referred to as a molecular orbital as opposed to an atomic orbital. It is convenient to change the coordinate system to elliptical coordinates: λ, μ, and ϕ. Let ϕ be the angle the plane of the three particles makes about the axis between the two nuclei.

$$\lambda = \frac{r_A + r_B}{R}, \qquad \mu = \frac{r_A - r_B}{R}$$

This is convenient because now the wave function solution to the Schrödinger equation can be written as a product of separable equations.

$$\psi(r_A, r_B, R) = F(\lambda)S(\mu)\Phi(\phi)$$

However, the change of variables causes the equation for the kinetic energy to become more complicated. Due to this, these functions cannot be solved analytically, even for this simple example. They must be solved numerically in each variable.

Now instead of taking $M \to \infty$, we can use a change of variables to reduce the degrees of freedom by eliminating the center of mass motion from the Hamiltonian. We can do this when finding bound states due to translation invariance. Suppose we have a molecule with N nuclei, with masses labeled m_i for $i = 1, 2, 3, ..., N$, and coordinates r_i for $i = 1, 2, 3, .., N$. There is also a choice in the way we define our coordinates. A convenient choice would be either Jacobi coordinates or clustered Jacobi coordinates that were discussed before.

In their paper, [1], Born and Oppenheimer note the importance of the parameter ϵ. (They call it κ.) Let m be the mass of an electron and let M be any average value of the masses of all of nuclei in the molecule. Here ϵ is defined by

$$\epsilon = \left(\frac{m}{M}\right)^{1/4}.$$

The total energy is represented by the Hamiltonian operator.

$$H(\epsilon) \;=\; H_0 + \epsilon^4 H_1$$

where

$$H_0\left(x, \frac{\partial}{\partial x}; r\right) \;=\; T_E + U$$

$$\epsilon^4 H_1\left(\frac{\partial}{\partial r}\right) \;=\; T_K$$

where x_i are the coordinates of the electrons and r_i are the coordinates for the nuclei. Here T_E is the kinetic energy of the electrons, T_K is the kinetic energy of the nuclei, and U is the potential energy of the system.

For the nuclei, we convert the coordinates into either Jacobi coordinates or clustered Jacobi coordinates. We let $3N-6$ of the coordinates be donoted by the functions $\zeta_i \;=\; \zeta_i(X)$ which denote the relative positions of the nuclei with respect to one another, and the other 6 coordinates are denoted $\theta_i \;=\; \theta_i(X)$ which denote the position and orentnation of the configuration in space.

We can separate H_1 into three parts.

$$H_1 \;=\; H_{\xi\xi} + H_{\xi\theta} + H_{\theta\theta}$$

$H_{\xi\xi}$ contains the $\dfrac{\partial^2}{\partial\xi_i\partial\xi_j}$ terms, $H_{\xi\theta}$ contains the $\dfrac{\partial}{\partial\xi_i}$ terms, and $H_{\theta\theta}$ is independent of all derivatives with respect to ξ_i.

Now we wish to solve the eigenvalue problem for this system.

$$(H_0 + \epsilon^4 H_1)\psi \;=\; E\psi$$

We can develop the problem with respect to small changes of ξ_i, which we denote $\epsilon\zeta_i$. We assume the oscillations are such that ϵ is close to 0. Then we can expand H_0 and H_1.

$$H_0\left(x, \frac{\partial}{\partial x}; \xi + \epsilon\zeta, \theta\right) = H_0^{(0)} + \epsilon H_0^{(1)} + \epsilon^2 H_0^{(2)} + ...$$

where

$$H_0^{(0)} = H_0\left(x, \frac{\partial}{\partial x}; \xi\right)$$

$$H_0^{(1)} = \sum_i \zeta_i \frac{\partial H_0}{\partial \xi_i}$$

$$H_0^{(2)} = \frac{1}{2}\sum_{i,j} \zeta_i\zeta_j \frac{\partial^2 H_0}{\partial \xi_i \partial \xi_j}$$

$$...$$

since $\frac{\partial}{\partial \xi} = \frac{1}{\epsilon}\frac{\partial}{\partial \zeta}$.

$$\epsilon^4 H_1\left(r, \frac{\partial}{\partial r}\right) = \epsilon^4\left(\frac{1}{\epsilon^2}H_{\zeta\zeta} + \frac{1}{\epsilon}H_{\zeta\theta} + H_{\theta\theta}\right)$$

$$= \epsilon^2 H_{\zeta\zeta}^{(0)} + \epsilon^3\left(H_{\zeta\theta}^{(0)} + H_{\zeta\zeta}^{(1)}\right) + \epsilon^4\left(H_{\theta\theta}^{(0)} + H_{\zeta\theta}^{(1)} + H_{\zeta\zeta}^{(2)}\right) + ...$$

where

$$H_{\zeta\zeta}^{(0)} = H_{\zeta\zeta}^{(0)}\left(\xi, \frac{\partial^2}{\partial \zeta_i \partial \zeta_j}\right)$$

$$H_{\zeta\zeta}^{(1)} = \sum_i \zeta_i \frac{\partial H_{\zeta\zeta}^{(0)}}{\partial \xi_i}$$

...

$$H_{\zeta\theta}^{(0)} = H_{\zeta\theta}^{(0)}\left(\xi, \theta, \frac{\partial}{\partial\zeta}, \frac{\partial}{\partial\theta}\right)$$

$$H_{\zeta\theta}^{(1)} = \sum_i \zeta_i \frac{\partial H_{\zeta\theta}^{(0)}}{\partial\xi_i}$$

...

$$H_{\theta\theta}^{(0)} = H_{\theta\theta}^{(0)}\left(\xi, \theta, \frac{\partial^2}{\partial\theta_i\partial\theta_j}\right)$$

$$H_{\theta\theta}^{(1)} = \sum_i \zeta_i \frac{\partial H_{\theta\theta}^{(0)}}{\partial\xi_i}$$

...

From here, the arguments ξ_i are constant. Then the total energy operator is

$$H(\epsilon) = H_0 + \epsilon H_0^{(1)} + \epsilon^2\left(H_0^{(2)} + H_{\zeta\zeta}^{(0)}\right)$$

$$+\epsilon^3\left(H_0^{(3)} + H_{\zeta\theta}^{(0)} + H_{\theta\theta}^{(1)}\right)$$

$$+\epsilon^4\left(H_0^{(4)} + H_{\theta\theta}^{(0)} + H_{\zeta\theta}^{(1)} + H_{\zeta\zeta}^{(2)}\right) + ...$$

We will also expand the approximate solutions of the eigenvectors and eigenvalues in powers of ϵ.

$$\psi \;=\; \psi^{(0)} + \epsilon\psi^{(1)} + \epsilon^2\psi^{(2)} + ...$$

$$E \;=\; E^{(0)} + \epsilon E^{(1)} + \epsilon^2 E^{(2)} + ...$$

Then, by grouping terms by order of ϵ, we obtain the following equations which allow us to solve for the orders of corrections of ψ and E in a similar manner to what is described previously for the perturbation theory.

$$\left(H_0^{(0)} - E^{(0)}\right)\psi^{(0)} \;=\; 0$$

$$\left(H_0^{(0)} - E^{(0)}\right)\psi^{(1)} \;=\; \left(E^{(1)} - H_0^{(1)}\right)\psi^{(0)}$$

$$\left(H_0^{(0)} - E^{(0)}\right)\psi^{(2)} \;=\; \left(E^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^{(0)}\right)\psi^{(0)} + \left(E^{(1)} - H_0^{(1)}\right)\psi^{(1)}$$

$$\left(H_0^{(0)} - E^{(0)}\right)\psi^{(3)} \;=\; \left(E^{(3)} - H_0^{(3)} - H_{\zeta\theta}^{(0)} - H_{\zeta\zeta}^{(1)}\right)\psi^{(0)}$$

$$+\left(E^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^{(0)}\right)\psi^{(1)} + \left(E^{(1)} - H_0^{(1)}\right)\psi^{(2)}$$

$$\left(H_0^{(0)} - E^{(0)}\right)\psi^{(4)} \;=\; \left(E^{(4)} - H_0^{(3)} - H_{\theta\theta}^{(0)} - H_{\zeta\theta}^{(1)} - H_{\zeta\zeta}^{(2)}\right)\psi^{(0)}$$

$$+\left(E^{(3)} - H_0^{(3)} - H_{\zeta\theta}^{(0)} - H_{\zeta\zeta}^{(1)}\right)\psi^{(1)}$$

$$+\left(E^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^{(0)}\right) + \left(E^{(1)} - H_0^{(1)}\right)\psi^{(3)}$$

$$\cdots$$

2.6.4 Molecular Orbitals

Like with atomic wave functions, we will express molecular wave functions as a determinant involving single electron orbitals. Using H_2^+ as an example again, let us start with a trial function for the electronic wave function.

$$\psi = c_A 1s_A + c_B 1s_B$$

The functions $1s_A$ and $1s_B$ are the atomic orbitals of hydrogen centered at the nuclei A and B. This is a linear combination of atomic orbitals. The atomic orbitals which construct a molecular orbital are called basis functions, and the set of these functions is called a basis set. We are using a minimal basis set since two is the minimum number of orbitals that can be used for two nuclei.

Recall the Born-Oppenheimer approximation gives the Hamiltonian for H_2^+ to be

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}.$$

Then with a little rearranging of the equation $\hat{H}\psi = E\psi$, we can obtain the secular equation

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{AB} - ES & H_{BB} - E \end{vmatrix} = 0$$

where

$$H_{AA} \;=\; \int 1s_A \hat{H} 1s_A \; d\mathbf{r} \;=\; \langle 1s_A|\hat{H}|1s_A\rangle \;=\; \langle 1s_B|\hat{H}|1s_B\rangle \;=\; H_{BB}$$

$$H_{AB} \;=\; \int 1s_A \hat{H} 1s_B \; d\mathbf{r} \;=\; \langle 1s_A|\hat{H}|1s_B\rangle \;=\; H_{BA}$$

$$S \;=\; \int 1s_A 1s_B \; d\mathbf{r} \;=\; \langle 1s_A|1s_B\rangle.$$

We use the fact that the orbitals are normalized, $\langle 1s_A|1s_A\rangle = \langle 1s_B|1s_B\rangle = 1$, and $H_{AA} = H_{BB}$ by symmetry. Here S is called an overlap integral because this product is only significant for regions where the two atomic orbitals have a large overlap. This integral then depends on the distance between the two nuclei, R. If the separation is large, imagine $R \to \infty$, then there should be no overlap and $S \to 0$. Or, if we take $R \to 0$, where the two orbitals would overlap completely, $S \to 1$. We can see then that $0 \le S(R) \le 1$. Explicitly, we can find the equation for S in terms of R.

To find S in terms of R, we need to evaluate the overlap integral.

$$S(R) \;=\; \frac{1}{\pi}\int e^{-r_A}e^{-r_B} \; d\mathbf{r}_A$$

$$=\; \frac{1}{\pi}\int_0^{\infty} e^{-r_A}r_A^2 \int_0^{2\pi}\int_0^{\pi} \sin\theta e^{-r_B} \; d\theta \; d\phi \; dr_A$$

where θ is the angle the vector $\mathbf{r}_A$, from nucleus A to the electron, forms with the internuclear axis, and ϕ is the angle of rotation about the internuclear axis.

The first integral we will solve is $I = \int_0^{\pi} \sin\theta e^{-r_B} \; d\theta$. To solve this we need to express r_B in terms of r_A, θ, and ϕ.

$$r_B \;=\; (r_A^2 + R^2 - 2r_A R\cos\theta)^{1/2}$$

$$I \;=\; \int_0^{\pi} e^{-(r_A^2+R^2-2r_AR\cos\theta)^{1/2}} \sin\theta \; d\theta$$

Let $x \;=\; \cos\theta$.

$$I \;=\; \int_{-1}^{1} e^{-(r_A^2+R^2-2r_ARx)^{1/2}} \; dx$$

Let $u(x) \;=\; (r_A^2+R^2-2r_ARx)^{1/2}$.

$du \;=\; \dfrac{1}{2(r_A^2+R^2-2r_ARx)^{1/2}}\,(-2r_AR)\,dx$

$dx \;=\; -\dfrac{udu}{r_AR}$

Then, $u|_1 \;=\; (r_A^2+R^2-2r_AR)^{1/2} \;=\; |R-r_A|$,

and $u|_{-1} \;=\; (r_A^2+R^2+2r_AR)^{1/2} \;=\; r_A+R$.

$$I \;=\; \frac{1}{r_AR}\int_{r_A+R}^{|R-r_A|} -e^{-u}u \; du$$

$$=\; \frac{1}{r_AR}e^{-u}(u+1)\Big|_{r_A+R}^{|R-r_A|}$$

$$I \;=\; \begin{cases} \dfrac{1}{r_AR}\left[e^{-(r_A-R)}(r_A-R+1)-e^{-(R+r_A)}(R+1+r_A)\right] & \text{if } r_A \;>\; R \\[2ex] \dfrac{1}{r_AR}\left[e^{-(R-r_A)}(R+1-r_A)-e^{-(R+r_A)}(R+1+r_A)\right] & \text{if } r_A \;<\; R \end{cases}$$

Now we can return to $S(R)$.

$$S(R) \;=\; \frac{1}{\pi}\int_0^\infty e^{-r_A} r_A^2 \int_0^{2\pi} I \; d\phi \; dr_A$$

$$=\; 2\int_0^\infty e^{-r_A} r_A^2 I \; dr_A$$

$$=\; \frac{2}{R}\int_R^\infty e^{-r_A} r_A [e^{-(r_A - R)}(r_A - R + 1) - e^{-(R+r_A)}(R + r_A + 1)] dr_A$$

$$+\frac{2}{R}\int_0^R e^{-r_A} r_A [e^{-(R - r_A)}(R - r_A + 1) - e^{-(R+r_A)}(R + r_A + 1)] dr_A$$

$$=\; \frac{1}{2R} \times \lim_{b\to\infty} e^{-(R+2r_A)}(-2e^{2R} r_A^2 - 4e^{2R} R r_A + 2R r_A - 2e^{2R}$$

$$+e^{2R} R + R + 2r_A^2 + 4r_A + 2)\Big|_R^b$$

$$+\frac{1}{6R} \times e^{-(R+2r_A)}(6Re^{2r_A} r_A^2 + 6Rr_A + 3R - 4e^{2r_A} r_A^3$$

$$+6e^{2r_A} r_A^2 + 6r_A^2 + 12r_A + 6)\Big|_0^R$$

$$=\; \frac{1}{2R}[0 - e^{-3R}(-2e^{2R}R^2 - 4e^{2R}R + 2e^{2R}R^2 + 2R^2 - 2e^{2R}$$

$$+e^{2R}R + R + 2R^2 + 4R + 2)]$$

$$+\frac{1}{6R}[e^{-3R}(6R^3e^{2R}+6R^2+3R-4e^{2R}R^3+6R^2e^{2R}$$

$$+6R^2+12R+6)-e^{-R}(3R+6)]$$

$$= \left[e^{-R}\left(\frac{3}{2}+\frac{1}{R}\right)+e^{-3R}\left(-2R-\frac{5}{2}-\frac{1}{R}\right)\right]$$

$$+\left[e^{-3R}\left(2R+\frac{5}{2}+\frac{1}{R}\right)+e^{-R}\left(\frac{R^2}{3}+R-\frac{1}{2}-\frac{1}{R}\right)\right]$$

$$S(R) = e^{-R}\left(1+R+\frac{R^2}{3}\right)$$

Then we can return to the determinant, and evaluate it to solve for the energy.

$$(H_{AA}-E)^2-(H_{AB}-ES)^2 = 0$$

$$E = \frac{H_{AA}\pm H_{AB}}{1\pm S}$$

Now we need to take a closer look at the the integrals H_{AA} and H_{AB}. To further evaluate these, we will use the results from Table 2.3.

Let's first look at H_{AA}.

$$H_{AA} = \left\langle 1s_A\right| -\frac{1}{2}\nabla^2-\frac{1}{r_A}-\frac{1}{r_B}+\frac{1}{R}\left|1s_A\right\rangle$$

Table 2.3: Integrals Needed To Evaluate E for H_2^+ with $\psi = c_1\phi_A + c_2\psi_B$ [12]

$$\langle\phi_A|\phi_B\rangle = S(\omega) = e^{-\omega}\left(1+\omega+\frac{\omega^2}{3}\right)$$

$$\langle\phi_A|-\frac{1}{2}\nabla^2|\phi_A\rangle = \langle\phi_B|-\frac{1}{2}\nabla^2|\phi_B\rangle = \frac{\zeta^2}{2}$$

$$\langle\phi_A|-\frac{1}{2}\nabla^2|\phi_B\rangle = \langle\phi_B|-\frac{1}{2}\nabla^2|\phi_A\rangle = \frac{1}{2}\zeta^2 e^{-\omega}\left(1+\omega+\frac{\omega^2}{3}\right) = -\zeta^2\left[\frac{S(\omega)}{2}+K(w)\right]$$

$$\langle\phi_A|-\frac{1}{r_A}|\phi_A\rangle = \langle\phi_B|-\frac{1}{r_B}|\phi_B\rangle = -\zeta$$

$$\langle\phi_A|-\frac{1}{r_B}|\phi_A\rangle = \langle\phi_B|-\frac{1}{r_A}|\phi_B\rangle = \zeta e^{-2\omega}\left(1+\frac{1}{\omega}\right)-\frac{\zeta}{\omega} = \zeta J(\omega)$$

$$\langle\phi_A|-\frac{1}{r_A}|\phi_B\rangle = \langle\phi_B|-\frac{1}{r_B}|\phi_A\rangle = -\zeta e^{-\omega}(1+\omega) = \zeta K(\omega)$$

$\phi(r) = (\zeta/\pi)^{1/2}d^{-\zeta r}$ is a normalized Slater 1s orbital. $\omega = \zeta R$.
For the hydrogen 1s orbital, $\zeta = 1$.

$$= \left\langle 1s_A \right| -\frac{1}{2}\nabla^2 \left| 1s_A \right\rangle + \left\langle 1s_A \right| -\frac{1}{r_A} \left| 1s_A \right\rangle + \left\langle 1s_A \right| -\frac{1}{r_B} \left| 1s_A \right\rangle + \left\langle 1s_A \right| -\frac{1}{R} \left| 1s_A \right\rangle$$

$$= -\frac{1}{2} + J(R) + \frac{1}{R}$$

where, from Table 2.3,

$$J(R) = \left\langle 1s_A \right| -\frac{1}{r_B} \left| 1s_A \right\rangle = e^{-2R}\left(1 - \frac{1}{R}\right) - \frac{1}{R}$$

Then we will look at H_{AB} similarly.

$$H_{AB} = \left\langle 1s_A \right| -\frac{1}{2}\nabla^2 \left| 1s_B \right\rangle + \left\langle 1s_A \right| -\frac{1}{r_A} \left| 1s_B \right\rangle + \left\langle 1s_A \right| -\frac{1}{r_B} \left| 1s_B \right\rangle + \left\langle 1s_A \right| -\frac{1}{R} \left| 1s_B \right\rangle$$

$$= -\frac{S(R)}{2} - K(R) + 2K(R) + \frac{S(R)}{R}$$

$$= -\frac{S(R)}{2} + K(R) + \frac{S(R)}{R}$$

where, from Table 2.3, $K(R) = -e^{-R}(1+R)$.

Returning to the equation found for the energy,

$$E_{\pm} = \frac{H_{AA} \pm H_{AB}}{1 \pm S}$$

$$E_{\pm}(R) = -\frac{1}{2} + \frac{J(R) + \frac{1}{R}}{1 \pm S(R)} \pm \frac{K(R) + \frac{S(R)}{R}}{1 \pm S(R)}$$

$E_+(R)$ is actually less than $E_-(R)$ for all $R > 0$, hence $E_+(R)$ denotes the ground state.

First noting that $-1/2$ is the ground state energy of a hydrogen atom and lone proton separated, $\Delta E_+(R)$ is the energy of H_2^+ compared to the separated hydrogen and proton. The minimum energy which describes the stable molecule is $-0.06483\ E_h$ which is at $R_{eq} = 2.493a_0 = 132$ pm. We call $E_h = \hbar^2/m_e a_0^2 = 4.3597482 \times 10^{-18}$ J the Hartree energy. The exact values are $\Delta E(R) = -0.10264\ E_h$ at bond length $R_{eq} = 2.00a_0 = 106$ pm.

Next we will need to specify the molecular orbitals that correspond to E_+ and E_- by solving for the coefficients c_A and c_B in $\psi = c_A 1s_A + c_B 1s_B$. The algebraic equations that obtained the secular determinant,

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{AB} - ES & H_{BB} - E \end{vmatrix} = 0,$$

are

$$c_A(H_{AA} - E) + c_B(H_{AB} - ES) = 0$$

and

$$c_A(H_{AB} - ES) + c_B(H_{BB} - E) = 0.$$

Substituting $E_+ = \dfrac{H_{AA} + H_{AB}}{1 + S}$ into the first equation, although either will suffice,

$$c_A\left(H_{AA} - \frac{H_{AA} + H_{AB}}{1 + S}\right) + c_B\left(H_A B - \frac{H_{AA} + H_{AB}}{1 + S} S\right) = 0$$

$$c_A\left(\frac{H_{AA}S - H_{AB}}{1 + S}\right) + c_B\left(\frac{H_{AB} - H_{AA}S}{1 + S}\right) = 0.$$

Then, $c_A = c_B$. The molecular orbital corresponding to the electronic ground state energy E_+ is now

$$\psi_+ = c_A(1s_A + 1s_B).$$

To normalize the function,

$$\langle \psi_+ | \psi_+ \rangle = c_A^2(1 + 2S + 1) = 1.$$

$$c_A = \frac{1}{\sqrt{2(1+S)}}$$

This gives us our first approximation to the ground state molecular orbital.

$$\psi_+ = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B)$$

By similarly substituting $E_- = \dfrac{H_{AA} - H_{AB}}{1 - S}$,

$$c_A(H_{AA} - E) + c_B(H_{AB} - ES) = 0$$

$$c_A\left(\frac{-H_{AA}S + H_{AB}}{1 - S}\right) + c_B\left(\frac{H_{AB} - H_{AA}S}{1 - S}\right) = 0.$$

Then, $c_A = -c_B$. ψ_-, the molecular orbital corresponding to E_-, must also be normalized.

$$\langle \psi_- | \psi_- \rangle = c_A^2(1 - 2S + 1) = 1$$

$$c_A = \frac{1}{\sqrt{2(1-S)}}$$

Now we have the approximation for the molecular orbital.

$$\psi_- \;=\; \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B)$$

Note that $c_A^2 \;=\; c_B^2$, which is a result of the symmetry of H_2^+. A solution where $c_A^2 \;\neq\; c_B^2$ indicates that one nucleus is favored by the electron.

ψ_+ describes what is called a bonding orbital, where the state exhibits a stable chemical bond. ψ_- is called an antibonding orbital where the nuclei repel each other for any internuclear distance.

2.6.5 Improving the Approximate Molecular Orbital

Virial Theorem: *Given a system with wave function ψ, the average values of the kinetic and potential operators satify* $\left\langle x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} + z\frac{\partial V}{\partial z}\right\rangle \;=\; 2\langle\hat{T}\rangle$.

Let's try to show that the Virial Theorem is satisfied for ψ_+. Doing so will provide insight into the accuracy of this approximation. First, let's show that actually we only need to check that $\frac{\langle V\rangle}{\langle T\rangle} \;=\; -2$.

We will start with the left hand side of the virial equation. In molecules, we have a coulombic potential.

$$V(x,y,z) \;=\; \frac{Ze^2}{4\pi\epsilon_0(x^2+y^2+z^2)^{1/2}}$$

Let $A \;=\; \frac{Ze^2}{4\pi\epsilon_0}$.

$$\frac{\partial V}{\partial x} \;=\; \frac{-Ax}{(x^2+y^2+z^2)^{3/2}}$$

$$\frac{\partial V}{\partial y} = \frac{-Ay}{(x^2+y^2+z^2)^{3/2}}$$

$$\frac{\partial V}{\partial z} = \frac{-Az}{(x^2+y^2+z^2)^{3/2}}$$

$$\left\langle x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} + z\frac{\partial V}{\partial z}\right\rangle = \left\langle \frac{-Ax^2}{(x^2+y^2+z^2)^{3/2}} + \frac{-Ay^2}{(x^2+y^2+z^2)^{3/2}} + \frac{-Az^2}{(x^2+y^2+z^2)^{3/2}}\right\rangle$$

$$= \left\langle \frac{-A(x^2+y^2+z^2)}{(x^2+y^2+z^2)^{3/2}}\right\rangle$$

$$= \left\langle \frac{-A}{(x^2+y^2+z^2)^{1/2}}\right\rangle = \langle V\rangle$$

So now to attempt to verify the virial theorem for this problem, we simply need to check that $\frac{\langle V\rangle}{\langle T\rangle} = -2$.

$$\langle \hat{T}\rangle = \left\langle \psi_+ \middle| -\frac{1}{2}\nabla^2 \middle| \psi_+ \right\rangle = \frac{\frac{1}{2} - \frac{S(R)}{2} - K(R)}{1+S(R)}$$

$$\langle \hat{V}\rangle = \left\langle \psi_+ \middle| -\frac{1}{r_A} \middle| \psi_+ \right\rangle + \left\langle \psi_+ \middle| -\frac{1}{r_B} \middle| \psi_+ \right\rangle + \frac{1}{R} = \frac{-1+J(R)+2K(R)}{1+S(R)} + \frac{1}{R}$$

Using the results from Table 2.3 and $R = 2.493$, the equilibrium internuclear distance for ψ_+, we find

$$\langle \hat{T}\rangle = 0.3827\ E_h \quad \text{and} \quad \langle \hat{V}\rangle = -0.9475\ E_h.$$

$$\frac{\langle \hat{V} \rangle}{\langle \hat{T} \rangle} \;=\; -1.6156 \;\neq\; -2$$

Hence, ψ_+ does not satisfy the Virial Theorem. In many ways, using ψ_+ as an approximate wave function for the ground state of the molecule does not adequately describe the bonding process for the molecule.

One way to improve the approximation is to use a linear combination of Slater 1s orbitals, rather than atomic 1s orbitals.

$$\phi(\zeta, r) \;=\; \left(\frac{\zeta^3}{\pi}\right)^{1/2} e^{-\zeta r}$$

The function ϕ is one such Slater orbitals, where r is a variational parameter. Then the molecular orbital for H_2^+ can be written as a linear combination of these. Again we need at least two, one for each nuclei.

$$\psi_+ \;=\; c_A \left(\frac{\zeta^3}{\pi}\right)^{1/2} e^{-\zeta r_A} + c_B \left(\frac{\zeta^3}{\pi}\right)^{1/2} e^{-\zeta r_B}$$

As before, by symmetry, we must have $c_A^2 \;=\; c_B^2$. Using Table 2.3, we would find the normalized molecular orbital to be

$$\psi_\pm(\zeta, r_A, r_B, R) \;=\; \frac{1}{\sqrt{2(1 \pm S(\zeta, R))}}(\phi(\zeta, r_A) \pm \phi(\zeta, r_B))$$

where

$$S(\zeta, R) \;=\; e^{-\zeta R}\left(1 + \zeta R + \frac{1}{3}\zeta^2 R^2\right)$$

$$=\; S(\zeta R) \;=\; S(\omega)$$

We let $\zeta R = \omega$.

Let's again attempt to verify the Virial Theorem using ψ_+.

$$\langle \hat{T} \rangle = \frac{\frac{\zeta^2}{2} - \zeta^2 \left[\frac{S(\omega)}{2} + K(\omega) \right]}{1 + S(\omega)} = \zeta^2 T_+(\omega)$$

$$\langle \hat{V} \rangle = \frac{-\zeta + \zeta J(\omega) + 2\zeta K(\omega)}{1 + S(\omega)} + \frac{\zeta}{\omega} = \zeta V_+(\omega)$$

Using $\zeta = 1.238$, $\omega = \zeta R = 1.238 \cdot 2.003 a_0 = 2.480 a_0$, which are found by numerically minimizing the energy $E_+(\zeta, \omega) = \zeta^2 T_+(\omega) + \zeta V_+(\omega)$ with respect to ζ and R, we find

$$\frac{\langle \hat{V} \rangle}{\langle \hat{T} \rangle} = -2.000.$$

Hence, using the Slater orbital for ψ_+ as the approximate wave function does satisfy the Virial Theorem, and gives better insight into bonding behavior.

We have used the minimal basis set of atomic orbitals, only $1s_A$ and $1s_B$, so of course using a larger basis set of atomic orbitals will improve the approximation as well. Suppose we also include the next two normalized Slater-type orbitals, $2s_A$ and $2s_B$.

$$\psi = c_1 1s_A + c_2 1s_B + c_3 2s_A + c_4 2s_B$$

where $1s = \left(\frac{\zeta^3}{\pi} \right)^{1/2} e^{-\zeta r}$, and $2s = \left(\frac{\zeta^5}{3\pi} \right)^{1/2} r e^{-\zeta r}$.

To improve further, rather than including $2s$ orbitals we could include $2p_z$ orbitals. This approximation would include a property called polarization. As a proton gets closer to a hydrogen atom, the positive charge on the proton attracts the electron closer to it thus

Table 2.4: H_2^+ Energy Approximations

Basis Set	ΔE_+	R_{eq}
$1s$ (atomic)	$-.06483E_h$	$2.493a_0$
$1s$ (Slater)	$-.08651E_h$	$2.003a_0$
$1s$, $2s$	$-.08651E_h$	$2.00a_0$
$1s$, $2p_z$	$-.09907E_h$	$2.00a_0$
Exact	$-.10264E_h$	$2.00a_0$

changing the charge distribution on the hydrogen nucleus. This distorts the molecule, or polarizes it. This is an important property that results in a significant improvement to the ground state energy approximation.

$$\psi \;=\; c_1 1s_A + c_2 1s_B + c_3 2p_{zA} + c_4 2p_{zB}$$

For this we would use $1s \;=\; \left(\frac{\zeta_1^3}{\pi}\right)^{1/2} e^{-\zeta_1 r}$, and $2p_z \;=\; \left(\frac{\zeta_2^5}{\pi}\right)^{1/2} r\cos\theta e^{-\zeta_2 r}$.

Minimizing the total energy with respect to ζ_1, ζ_2, and R will determine the values to use for these.

Table 2.4 shows the energy approximation for each of the described approximations. Using a linear combination of $1s$ atomic orbitals was not very accurate. However, the last approximation, using $1s$ and $2p_z$ Slater orbitals resulted in an energy and bond length that were much closer to the exact measurements.

2.7 Molecules with Hydrogen Bonds

To improve the standard Born-Oppenheimer approximation, Hagedorn and Joye formulated an alternate approximation for molecules with symmetric Hydrogen bonds [9]. Previously we defined ϵ by

$$\epsilon \;=\; \left(\frac{m}{M}\right)^{1/4}$$

where m is the mass of an electron and M is the average nuclear mass of the molecule. Instead we will define a true value of ϵ, ϵ_0, by setting the mass of the nucleus of a C^{12} equal to ϵ^{-4}.

$$\epsilon_0^{-4} \approx 1836 \cdot 12 = 22,032$$

$$\epsilon_0 \approx 0.0821$$

Thus, the mass of a H^1 nucleus is $1.015\epsilon^{-3}$. We will scale the masses of the hydrogen nucleus to be ϵ^{-3} instead of ϵ^{-4}. Also we will allow the electron energy to depend on ϵ in a form particularly chosen based on information from the lowest electron potential energy surface for the molecule. The following example reflects changes made based on examination of the FHF^- potential energy surface.

This will lead to a different expansion from the standard Born-Oppenheimer approximation. This model can describe problems with a single or double well in the coordinates for a hydrogen nucleus involved in a hydrogen bond.

We look at the simplest example for this model, a symmetric molecule with three nuclei, which we constrain to move along a fixed line. Thus we do not allow the molecule to rotate or bend. The system has two identical heavy nuclei A and B, and one light nucleus C. One example would be FHF^-. The system should be described by Jacobi coordinates. Suppose x_A and x_B are the positions of the heavy nuclei and x_C is the position of the light nucleus. They have masses m_A, m_B, and m_C, respectively. Let $R = \dfrac{m_A x_A + m_B x_B + m_C x_C}{m_A + m_B + m_C}$ be the center of mass of all three nuclei. Let $x_{AB} = \dfrac{x_A + x_B}{2}$ be the center of mass of the two heavy nuclei since $m_A = m_B$. Let $W = x_B - x_A$ be the vector from nucleus A to nucleus B, and let $Z = x_C - x_{AB}$ be the vector from the center of mass of nuclei A and B to the light nucleus C. Here we assume that the electronic Hamiltonian h_e only depends on the vectors between the nuclei. Let $m_{AB} = m_A + m_B$ and $M = m_A + m_B + m_C$. Then the Hamiltonian

$$\hat{H} = -\frac{1}{2m_A}\Delta_{x_A} - \frac{1}{2m_B}\Delta_{x_B} - \frac{1}{2m_C}\Delta_{x_C} + h_e(x_B - x_A,\ x_C - x_A,\ x_C - x_B)$$

can be written in Jacobi coordinates as

$$\hat{H} \;=\; -\frac{1}{2M}\Delta_R - \frac{m_{AB}}{2m_Am_B}\Delta_W - \frac{M}{2m_{AB}m_C}\Delta_Z + h_e(W,\; Z+\frac{W}{2},\; Z-\frac{W}{2}).$$

We are only interested in the bound states, so we can discard the energy of the center of mass motion. Then we let the mass of an electron to be 1, $m_A \;=\; m_B \;=\; \epsilon^{-4}\mu$ for some fixed μ, and $m_C \;=\; \epsilon^{-3}\nu$ for some fixed ν. Also we let $h_e(W,\; Z+\frac{W}{2},\; Z-\frac{W}{2}) \;=\; h(W,Z)$. Then the Hamiltonian becomes

$$\hat{H} \;=\; -\frac{\epsilon^4}{\mu}\Delta_W - \frac{\epsilon^3}{2\nu}\left(1+\frac{\epsilon\nu}{2\mu}\right)\Delta_Z + h(W,Z).$$

This is an exact computation. To simplify some, we can eliminate the $\frac{\epsilon\nu}{2\mu}$ term, and assume that $\mu \;=\; 2$ and $\nu \;=\; 1$. Now we result in a Hamiltonian which depends on ϵ.

$$H_1(\epsilon) \;=\; -\frac{\epsilon^4}{2}\frac{\partial^2}{\partial W^2} - \frac{\epsilon^3}{2}\frac{\partial^2}{\partial Z^2} + h(\epsilon,W,Z)$$

We will now treat ϵ as a parameter, and allow only the ground state eigenvalue to depend on ϵ. Substituting the physical value $\epsilon \;=\; \epsilon_0 \;\approx\; 0.0821$, defined by setting ϵ_0^{-4} equal to the nuclear mass of C^{12}, would result in the true Hamiltonian.

Notice that we have also introduced the ϵ dependence of the electronic Hamiltonian $h(\epsilon,W,Z)$. We do so by allowing only the ground state eigenvalue of h to depend on ϵ. We expand the energy $E(W,Z)$ around its minimum at $(W_0,0)$ as a Taylor series in Z^2 because of the symmetry. To force the dependence on ϵ, we multiply the Z^2 term by ϵ/ϵ_0, so that when $\epsilon=\epsilon_0$ we would obtain the true eigenvalue of h. The ground state electron level is then assumed to have the form

$$E_1(\epsilon,W,Z) \;=\; E_0 + a_1(W-W_0)^2 + \left(a_2\epsilon - a_3(W-W_0)\right)Z^2 + a_4Z^4 + ...$$

where $a_j \;=\; O(1)$, and $a_1,\; a_3$, and a_4 are assumed to be positive.

When a_2 is negative, $E_1(\epsilon, W, Z)$ has a closely spaced double well near $(W_0, 0)$ instead of a single local minimum. We need to require that the leading terms of $E_1(\epsilon, W, Z)$, $\tilde{E}_1(\epsilon, W, Z)$, are bounded below.

$$\tilde{E}_1(\epsilon, W, Z) \;=\; E_0 + a_1(W - W_0)^2 + \left(a_2\epsilon - a_3(W - W_0)\right) Z^2 + a_4 Z^4$$

To ensure this, we require either

$$a_3^2 \;<\; 4a_1a_4$$

or

$$a_3^2 \;=\; 4a_1a_4 \quad \text{and} \quad a_2 \;\geq\; 0.$$

This is ensures the leading terms are bounded.

$$\tilde{E}_1(\epsilon, W, Z) \;=\; E_0 + a_1(W - W_0)^2 + \left(a_2\epsilon - a_3(W - W_0)\right) Z^2 + a_4 Z^4 \;\geq\; -C$$

for some C. When we rescale the parameters as $w \;=\; \dfrac{(W - W_0)}{\epsilon}$ and $z \;=\; \dfrac{Z}{\epsilon^{1/2}}$, we have that the Hamiltonian

$$-\frac{\epsilon^4}{2}\frac{\partial^2}{\partial W^2} - \frac{\epsilon^3}{2}\frac{\partial^2}{\partial Z^2} + \tilde{E}_1(\epsilon, W, Z)$$

becomes unitarily equivalent to $\epsilon^2 H_{NF}$. We call H_{NF} the Normal Form Hamiltonian, which is ϵ-independent.

$$H_{NF} \;=\; -\frac{1}{2}\frac{\partial^2}{\partial w^2} - \frac{1}{2}\frac{\partial^2}{\partial z^2} + E_{NF}(w, z)$$

where

$$E_{NF}(w,z) \;=\; a_1 w^2 + (a_2 - a_3 w) z^2 + a_4 z^4.$$

Under either of the stated conditions, H_{NF} is essentially self-adjoint on $C_0^\infty(\mathbb{R}^2)$ and has a purely discrete spectrum.

To solve for the solution to the Schrödinger equation, instead of finding $\Psi(\epsilon, W, Z)$, we will first find $\psi\,(\epsilon, W, Z, w, z)$. Note that from here we replace W by $W - W_0$ so that for convenience, now $W_0 \;=\; 0$. Once ψ is found, we determine Ψ by

$$\Psi(\epsilon, W, Z) \;=\; \psi\left(\epsilon, W, Z, \frac{W}{\epsilon}, \frac{Z}{\epsilon^{1/2}}\right).$$

Our Schrödinger equation for ψ is

$$H_2(\epsilon)\psi(\epsilon, W, Z, w, z) \;=\; \mathcal{E}(\epsilon)\psi(\epsilon, W, Z, w, z)$$

where

$$H_2(\epsilon) \;=\; -\frac{\epsilon^4}{2}\frac{\partial^2}{\partial W^2} - \epsilon^3\frac{\partial^2}{\partial W \partial w} - \frac{\epsilon^2}{2}\frac{\epsilon^2}{2}\frac{\partial^2}{\partial w^2} - \frac{\epsilon^3}{2}\frac{\partial^2}{\partial Z^2} - \epsilon^{5/2}\frac{\partial^2}{\partial Z \partial z} - \frac{\epsilon^2}{2}\frac{\partial^2}{\partial z^2}$$

$$+[h(\epsilon, W, Z) - E(\epsilon, W, Z)] + E(\epsilon, \epsilon w, \epsilon^{1/2} z)$$

$$+\sum_{m\,=\,6}^{\infty} \epsilon^{m/2}(T_{m/2}(W,Z) - T_{m/2}(\epsilon w, \epsilon^{1/2} z)).$$

The form of $T_{m/2}$ will be chosen later. If we expand $E(\epsilon, \epsilon w, \epsilon^{1/2} z)$ and $T_{m/2}(\epsilon w, \epsilon^{1/2} z)$ as Taylor series in powers of $\epsilon^{1/2}$, we can let the solutions have the form

$$\psi(\epsilon, W, Z, w, z) \;=\; \psi_0(W, Z, w, z) + \epsilon^{1/2}\psi_{1/2}(W, Z, w, z) + \epsilon^1\psi_1(W, Z, w, z) + \ldots$$

with

$$\mathcal{E}(\epsilon) \;=\; \mathcal{E}_0 + \epsilon^{1/2}\mathcal{E}_{1/2} + \epsilon^1\mathcal{E}_1 + ...$$

Now substituting these into the Schrödinger equation for ψ, we can solve the equation for each order of powers of $\epsilon^{1/2}$.

For the 0 order terms, we obtain

$$[h(\epsilon, W, Z) - E(\epsilon, W, Z)]\psi_0 + E_0\psi_0 \;=\; \mathcal{E}_0\psi_0.$$

We choose $\mathcal{E}_0 \;=\; E_0$, and

$$\psi_0(W, Z, w, z) \;=\; f_0(W, Z, w, z)\Phi(W, Z)$$

where $\Phi(W, Z, \cdot)$ is a normalized ground state eigenvector of $h(\epsilon, W, Z)$. With the assumptions we have made, we can choose $\Phi(W, Z, \cdot)$ to be real and smooth in (W, Z). Also note that $\Phi(W, Z, \cdot)$ is independent of ϵ. Then our choice of Φ satisfies

$$\langle \Phi(W, Z, \cdot), \nabla_{W,Z}\Phi(W, Z, \cdot)\rangle_{\mathcal{H}_{el}} \;=\; 0.$$

This is the inner product in the electronic Hilbert space. We also assume that $f_0(W, Z, w, z)$ is not identically zero.

For the terms of order 1/2, we obtain

$$[h(\epsilon, W, Z) - E(\epsilon, W, Z)]\psi_{1/2} + E_0\psi_{1/2} - \mathcal{E}_0\psi_{1/2} + \mathcal{E}_{1/2}\psi_0.$$

The components in the $\Phi(W, Z)$ direction in the electronic Hilbert space require $\mathcal{E}_{1/2} = 0$.

The components orthogonal to $\Phi(W, Z)$ in the electronic Hilbert space require

$$[h(\epsilon, W, Z) - E(\epsilon, W, Z)]\psi_{1/2} = 0$$

$$\psi_{1/2}(W, Z, w, z) = f_{1/2}(W, Z, w, z)\Phi(W, Z).$$

For the terms of order 1 and 3/2, we follow the same pattern of calculations to find the following.

$$\mathcal{E}_1 = \mathcal{E}_{3/2} = 0$$

$$\psi_1(W, Z, w, z) = f_1(W, Z, w, z)\Phi(W, Z)$$

$$\psi_{3/2}(W, Z, w, z) = f_{3/2}(W, Z, w, z)\Phi(W, Z)$$

For order 2, the terms that are multiples of $\Phi(W, Z)$ require that

$$-\frac{1}{2}\frac{\partial^2 f_0}{\partial w^2}(W, Z, w, z) - \frac{1}{2}\frac{\partial^2 f_0}{\partial z^2}(W, Z, w, z) + E_{NF}(w, z)f_0(W, Z, w, z)$$

$$= \mathcal{E}_2 f_0(W, Z, w, z)$$

where E_{NF} is the Normal Form energy as defined before.

We cannot solve for $\mathcal{E}_2$ or f_0 exactly, but they can easily be approximated numerically with accurate results. These describe the coupled anharmonic vibrational motion of the three nuclei in the molecule.

The terms that are orthogonal to $\Phi(W,Z)$ direction in the electronic Hilbert space require

$$[h(\epsilon,W,Z)-E(\epsilon,W,Z)]\psi_2 \;=\; 0.$$

Then

$$\psi_2 \;=\; f_2(W,Z,w,z)\Phi(W,Z).$$

The scalar functions $f_\alpha(W,Z,w,z)$, for $\alpha \;>\; 0$, can be separated into two parts,

$$f_\alpha(W,Z,w,z) \;=\; f_\alpha^{\|}(W,Z,w,z)+f_\alpha^{\perp}(W,Z,w,z)$$

where for each fixed W and Z, $f_\alpha^{\|}(W,Z,\cdot,\cdot)$ is a multiple of $f_0(\cdot,\cdot)$, and $f_\alpha^{\perp}(W,Z,\cdot,\cdot)$ is perpendicular to $f_0(\cdot,\cdot)$ in $L^2(\mathbb{R}^2,dw\ dz)$. We will choose the operators $T_{3+m/2}$ such that $f_\alpha^{\|}(W,Z,\cdot,\cdot)$ is not dependent on (W,Z). Since we will not be precisely normalizing the approximate eigenfunctions, we let

$$f_\alpha^{\|}(W,Z,w,z) \;=\; 0 \;\text{ for all } \alpha \;>\; 0.$$

For higher order terms, order $m/2$ with $m \;>\; 4$, we separately examine the terms perpendicular and parallel to $\Phi(W,Z)$ in the electronic Hilbert space, as before. We obtain a value for $\mathcal{E}_{m/2}$ and an expression for $f_{(m-4)/2}((W,Z,w,z) \;=\; f_{(m-4)/2}^{\perp}(W,Z,w,z)$.

When $m \;=\; 6$, we can choose T_3 such that f_0 is independent of (W,Z) as desired above. When $m \;>\; 6$, we choose $T_{m/2}$ such that we can let $f_{(m-6)/2}^{\|}(W,Z,w,z) \;=\; 0$.

The terms orthogonal to $\Phi(W,Z)$ in the electronic Hilbert space lead to the equation

$$\psi_{m/2}(W,Z,w,z) \;=\; \left(f_{m/2}^{\|}(W,Z,w,z)+f_{m/2}^{\perp}(W,Z,w,z)\right)\Phi(W,Z)+\psi_{m/2}^{\perp}(W,Z,w,z)$$

where $\psi_{m/2}^{\perp}$ is found by applying the reduced resolvent operator $[h(\epsilon, W, Z) - E(\epsilon, W, Z)]_r^{-1}$ to $\psi_{m/2}(W, Z, w, z)$.

This procedure results in a quasimode whose approximate eigenvalue and eigenvector solutions have asymptotic expansions in orders of $\epsilon^{1/2}$.

Chapter 3

$H_3O_2^-$

3.1 Numerical Approximation

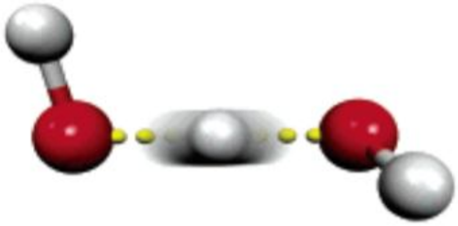

Figure 3.1: Depiction of the $H_3O_2^-$ molecule [11]

To approximate the vibrational bound states for the molecular ion $H_3O_2^-$, we will apply the approximation developed by Hagedorn and Joye, [9], described in the previous chapter. This method was used on a symmetric molecule with three nuclei; their specific example was FHF^-. Our molecule is also symmetric, but on either side of the central hydrogen nucleus, is an OH^-, for a total of 5 nuclei. Let us first label the coordinates of the nuclei. Set x_1 to be the coordinates for the first terminal hydrogen nucleus, x_2 for the first oxygen nucleus, x_3 for the central hydrogen nucleus, x_4 for the second oxygen nucleus, and x_5 for the second terminal hydrogen nucleus. Thus this problem currently has 15 degrees of freedom. We want to convert our coordinates to clustered Jacobi coordinates. There will be three clusters: the two outer OH pairs will each be a cluster and the central hydrogen will be its own third cluster.

$$X_1 = x_1 - x_2$$

$$X_2 = x_5 - x_4$$

The first vector X_1 is the vector from the first oxygen nucleus to the first terminal hydrogen nucleus, and X_2 is the vector from the second oxygen nucleus to the second terminal hydrogen nucleus.

$$Y_1 = \frac{m_O x_4 + m_H x_5}{m_O + m_H} - \frac{m_O x_2 + m_H x_1}{m_O + m_H}$$

$$Y_2 = x_3 - \frac{m_O x_4 + m_H x_5 + m_O x_2 + m_H x_1}{2(m_O + m_H)}$$

We let m_O be the mass of an oxygen nucleus, and m_H be the mass of a hydrogen nucleus. The vector Y_1 is from the center of mass of the first cluster to the center of mass of the second cluster. The vector Y_2 is from the center of mass of all four of those nuclei to the central hydrogen nucleus.

Setting the mass of an electron $m_e = 1$, we define our value of ϵ as before by setting the mass of a C^{12} carbon nucleus equal to ϵ^{-4}, thus $\epsilon = 0.0821$. The mass of the hydrogen nucleus is $m_H \approx 1.015\epsilon^{-3}$. We will scale this so that $m_H = \epsilon^{-3}$. The mass of an oxygen nucleus is $m_O \approx 1.335\epsilon^{-4}$, which we will also scale to $m_O = \frac{4}{3}\epsilon^{-4}$.

Then the kinetic energy of the system can be represented by

$$-\frac{1}{2\mu_1}\Delta_{X_1} - \frac{1}{2\mu_1}\Delta_{X_2} - \frac{1}{2\mu_2}\Delta_{Y_1} - \frac{1}{2\mu_3}\Delta_{Y_2}$$

where

$$\mu_1 = \frac{\frac{4}{3}\epsilon^{-4}\epsilon^{-3}}{\frac{4}{3}\epsilon^{-4} + \epsilon^{-3}} \approx \epsilon^{-3}$$

$$\mu_2 = \frac{\left(\frac{4}{3}\epsilon^{-4} + \epsilon^{-3}\right)^2}{2\left(\frac{4}{3}\epsilon^{-4} + \epsilon^{-3}\right)} \approx \frac{2}{3}\epsilon^{-4}$$

$$\mu_3 = \frac{\epsilon^{-3}\left(\frac{8}{3}\epsilon^{-4} + 2\epsilon^{-3}\right)}{\frac{8}{3}\epsilon^{-4} + 2\epsilon^{-3} + \epsilon^{-3}} \approx \epsilon^{-3}$$

The Hamiltonian for the nuclei when the electrons are in their ground state is

$$-\frac{1}{2\mu_1}\Delta_{X_1} - \frac{1}{2\mu_1}\Delta_{X_2} - \frac{1}{2\mu_2}\Delta_{Y_1} - \frac{1}{2\mu_3}\Delta_{Y_2} + V(X_1, X_2, Y_1, Y_2)$$

where $V(X_1, X_2, Y_1, Y_2)$ is the eigenvalue of $h_{el}(X_1, X_2, Y_1, Y_2)$, the ground state electronic Hamiltonian. V describes the lowest potential energy surface. We can compute this numerically.

Replacing the μ_i's with the approximations found above, we obtain the Hamiltonian

$$-\frac{\epsilon^3}{2}\Delta_{X_1} - \frac{\epsilon^3}{2}\Delta_{X_2} - \frac{3\epsilon^4}{4}\Delta_{Y_1} - \frac{\epsilon^3}{2}\Delta_{Y_2} + V(X_1, X_2, Y_1, Y_2).$$

Currently there are 12 degrees of freedom. Originally the system had 15, 3 for each of the 5 nuclei, but the motion of the center of mass was removed when we converted the coordinates to the clustered Jacobi coordinates. We still have not removed the rotational degrees of freedom. When the whole molecule is rotated, the value of V does not change, thus V is independent of the three Euler angles (θ, ϕ, γ), and V is actually only dependent on 9 variables.

When we rotate the molecule, we rotate Y_1, so this must also be invariant under rotation. Thus, V only depends on the magnitude of Y_1. We will define $y_1 = ||Y_1||$. Let's say this removes dependence on the angles θ and ϕ. We are only interested in vibrational energies, so to remove the last rotational degree of freedom, we look at Y_2. At the point we are expanding the energy around, Y_2 is perpendicular to Y_1. If we assume that the molecule is rotated by θ and ϕ so that Y_1 lies along the z-axis, then we can rotate by γ so that Y_2 lies in the yz-plane. This removes the dependence on γ. Now, based on where we have rotated the molecule, we can write the coordinates for Y_1 and Y_2 in Cartesian coordinates.

$$y_1 \in \mathbb{R}^1, \; y_2 \in \mathbb{R}^2$$

$$Y_1 = (0, 0, \pm y_1)$$

$$Y_2 = (0, y_{2,1}, y_{2,2})$$

The Laplacians with the rotational degrees of freedom removed become

$$\Delta_{y_1} = \frac{\partial^2}{\partial y_1^2} + \frac{2}{y_1}\frac{\partial}{\partial y_1}$$

and

$$\Delta_{y_2} = \frac{\partial^2}{\partial y_{2,1}^2} + \frac{\partial^2}{\partial y_{2,2}^2}.$$

Hence we have a Hamiltonian which depends on only 9 vibrational degrees of freedom.

$$-\frac{\epsilon^3}{2}\Delta_{X_1} - \frac{\epsilon^3}{2}\Delta_{X_2} - \frac{3\epsilon^4}{4}\Delta_{y_1} - \frac{\epsilon^3}{2}\Delta_{y_2} + V(X_1, X_2, y_1, y_2)$$

From theory, there are two vibrational modes proportional to ϵ^2 and the other seven have frequencies proportional to $\epsilon^{3/2}$. The rest have frequencies proportional to $\epsilon^{3/2}$ because for those vibrations, the hydrogens are the particles which are moving, which each have mass ϵ^3. Thus, they result in energies proportional to $\epsilon^{3/2}$, while the vibrations involving the oxygen nuclei, with masses proportional to ϵ^4, have energies proportional to ϵ^2. The two modes proportional to ϵ^2 are the modes we are interested, and we are able to separate them from the rest because they are at different orders of ϵ. We can use Gaussian to approximate the normal modes and easily differentiate the ones we are interested in.

Using the standard time-independent Born-Oppenheimer approximation, the frequencies approximated by Gaussian, in cm^{-1}, were found to be:

198.8727, 323.8248, 465.7150, 589.8409, 1343.4872, 1698.7308, 1869.2271, 3836.9373, and 3891.8648.

These values were obtained by expanding around one of the two minimum points of the potential energy surface, where $\nabla V = 0$, rather than the saddle point, so we do not obtain an imaginary value for one of the modes of interest. The modes of interest are 323.8248, which is the symmetric $O-O$ stretch, and 1869.2271, the asymmetric H stretch.

The vibrational frequencies of interest to us are only dependent on the vector y_1, from the center of mass of the first terminal OH cluster to the second OH cluster, and the vector y_2, from the center of mass of both of the terminal clusters to the central hydrogen nucleus. Then our Hamiltonian of interest is

$$-\frac{3\epsilon^4}{4}\Delta_{y_1} - \frac{\epsilon^3}{2}\Delta_{y_2} + V(y_1, y_2).$$

We can reduce this problem to depend on just two variables. Let w be the distance between the center of mass of the first terminal OH to the center of mass of the second terminal OH. Then we can let z be the distance between the center of mass of both terminal OH groups and the central hydrogen nucleus. This removes one more degree of freedom, describing a bending vibration of the hydrogen bond, which we are not interested in. This gives us the Hamiltonian of interest.

$$H(\epsilon) \;=\; -\frac{3\epsilon^4}{4}\Delta_w - \frac{\epsilon^3}{2}\Delta_z + V(\epsilon, w, z)$$

Here we introduce the ϵ-dependence of V. Again, we allow the dependence of V on ϵ only by allowing the ground state eigenvalue to be dependent on ϵ.

Now we assume we can write the energy $E(\epsilon, w, z)$, as a Taylor series in z^2, which would be expanded around a point where $\nabla V = 0$. From numerical computations, we found $E(w, z)$ has a saddle point, which we label as $(w_0, 0)$, and for this particular problem we will expand around this point instead of a point of minimum value. To force the ϵ dependence of V, we replace the term $a_2\, z^2$ with $\epsilon/\epsilon_0\, a_2\, z^2$ in the Taylor series expansion. Using the true value of ϵ defined before, $\epsilon_0 = 0.0821$, we obtain the true eigenvalue, $V(\epsilon_0, w, z)$, of the electronic Hamiltonian, $h_{el}(\epsilon_0, w, z)$. The potential energy surface was calculated using the Gaussian 09 at 15 points using CCSD(T) with the aug-cc-pvtz basis set.

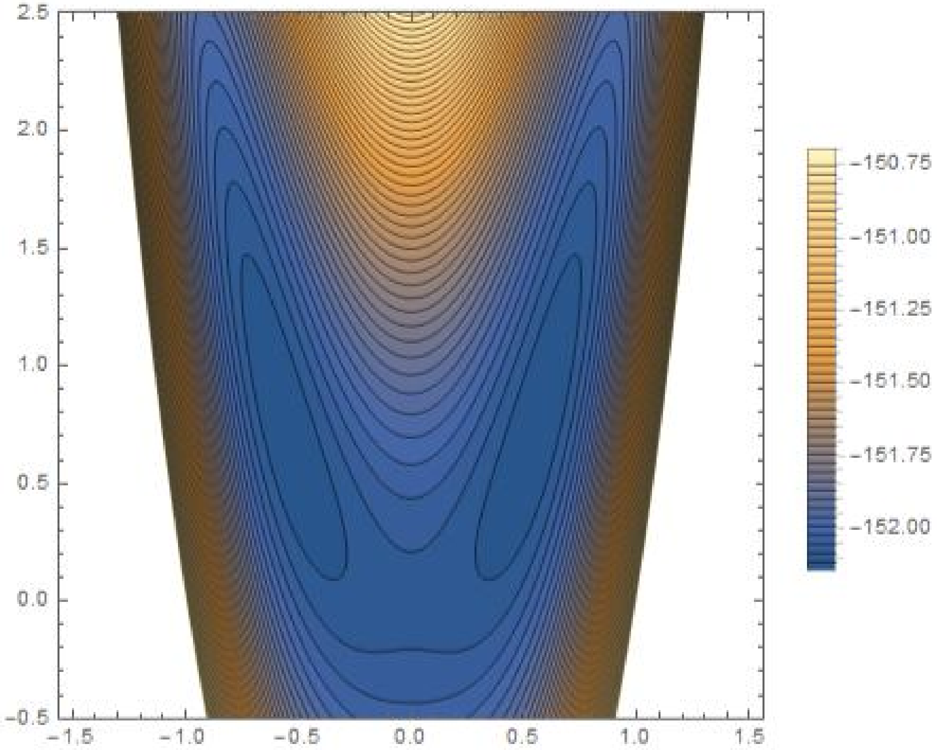

Figure 3.2: The Potential Energy Surface for the ground state of $H_3O_2^-$

Then the ground state electron level has the form

$$E_1(\epsilon, w, z) \;=\; E_0 + a_1(w - w_0)^2 + (a_2\epsilon - a_3(w - w_0))z^2 + a_4 z^4 + \ldots$$

where $a_j \;=\; O(1)$. Terms not showed here are of order $(w - w_0)^\alpha z^{2\beta}$ where α and β are integers satisfying $\alpha + \beta \;\geq\; 3$. These terms only contribute higher order corrections to the energy. The resulting leading order potential energy surface is

$$\tilde{E}_1(\epsilon_0, x, y) \;=\; E_0 + a_1(w - w_0)^2 + a_2\epsilon_0 z^2 - a_3(w - w_0)z^2 + a_4 z^4.$$

If we rescale the variables so that $x \;=\; (w - w_0)/\epsilon$ and $y \;=\; z/\epsilon^{1/2}$, then the Hamiltonian is unitarily equivalent to ϵ^2 times the normal form Hamiltonian, H_{NF}.

$$H_{NF} = -\frac{3}{4}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + E_{NF}(x,y)$$

where the normal form energy is

$$E_{NF} = a_1x^2 + a_2y^2 - a_3xy^2 + a_4y^4$$

This gives us a total energy, to the leading order.

$$\tilde{E}(\epsilon, x, y) = E_0 + a_1x^2 + a_2y^2 - a_3xy^2 + a_4y^4$$

where, with energies measured in Hartrees and distances measured in Angstroms,

$$\begin{aligned} E_0 &= -152.095 \\ a_1 &= 0.211525 \\ a_2 &= -0.319957 \\ a_3 &= 1.01986 \\ a_4 &= 1.71091 \end{aligned}$$

These values were solved for using Gaussian 09, computed using CCSD(T) at 15 points with the aug-cc-pvtz basis set.

From this we find the energies of order ϵ^2 in which we are interested.

Note that we found $a_2 < 0$; this indicates that instead of a unique minimum at $(w_0, 0)$, there is a closely spaced double well. This can be seen in the potential energy surface in Figure 3.2. To guarantee that the leading terms of $E(\epsilon, x, y)$, $\tilde{E}(\epsilon, x, y)$, are bounded below, we need that

$$a_3^2 < 4a_1a_4.$$

The values found from Gaussian do satisfy this condition.

$$a_3^2 \;=\; (1.01986)^2 \;=\; 1.040114 \;<\; 1.447601 \;=\; 4(0.211525)(1.71091) \;=\; 4a_1a_4$$

Thus this approximation is valid for this problem. We can now solve the normal form Hamiltonian to find the energies for the two stretches of interest.

For the symmetric stretch, the excitation energy is approximated to be 533 cm^{-1}.

For the asymmetric stretch, the excitation energy is approximated to be 836 cm^{-1}.

3.2 Accuracy

To determine the accuracy of this method on the $H_3O_2^-$ molecule, we can compare to experimental results. In 2005, a paper was published by McCoy (et al.) on the experimental measurements of the excitations of the hydrogen bond of $H_3O_2^-$ [11]. To be exact, the Ar predissociation yield was measured for $H_3O_2^- \cdot Ar$. There is no experimental data for the symmetric stretch, but for the asymmetric stretch, the excitation energy was measured to be 697 cm^{-1}. With our approximation, we found 836 cm^{-1} for this value, giving us an error of about 139 cm^{-1}. While this might seem like a large error, in terms of our problem, this is actually a reasonably good approximation. The standard Born-Oppenheimer approximations for these excitation energies are much less accurate. If we expanded around the saddle point $(w_0, 0)$, the Born-Oppenheimer approximation would yield an imaginary result, $644i$ cm^{-1}, for the asymmetric stretch. If we expand around one of the points of the minimum values of V, the result would be 1869 cm^{-1}. Clearly applying our approximation yields much better results.

3.3 Improvement

An idea to improve the accuracy of the approximations would be to consider the bends in the terminal hydrogens parallel to the hydrogen bond axis. We will not include any other

Table 3.1: Approximate Vibrational Energies of $H_3O_2^-$

	Symmetric Stretch	Asymmetric Stretch
Simple Approximation	533 cm^{-1}	836 cm^{-1}
Including Terminal H Bends	530.5 cm^{-1}	825.5 cm^{-1}
Experimental Values		697 cm^{-1}

bends or torsions of the molecule though. We again used Gaussian 09, using CCSD(T) at 15 points with the aug-cc-pvtz basis set, to compute the frequencies for the symmetric and asymmetric stretches of the hydrogen bonds of the central hydrogen nucleus.

Including the bends of the terminal hydrogens, the excitation energy for the symmetric stretch is approximated to be 530.5 cm^{-1}.

For the asymmetric stretch, the excitation energy is approximated to be 825.5 cm^{-1}.

The error for the asymmetric stretch using this approximation is 128.5 cm^{-1} when compared to the experimental results. This is not a significant improvement from the original approximation where we approximated the asymmetric stretch to be 836 cm^{-1}. Similarly for the symmetric stretch, although we do not have any experimental results to compare to, there was not a significant difference from the previous approximation of 533 cm^{-1}.

Table 3.1 summarizes the results from the approximations for the energies of this molecular ion.

Chapter 4

$H_5O_2^+$

4.1 Numerical Approximation

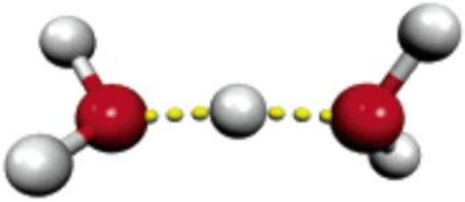

Figure 4.1: Depiction of the $H_5O_2^+$ molecule [11]

We also want to approximate the vibrational bound states for the molecular ion $H_5O_2^+$. As with $H_3O_2^-$ in Chapter 3, we will apply the same method developed by Hagedorn and Joye, [9]. The molecular ion $H_5O_2^+$ is also a symmetric; there is a central hydrogen and on either side is an H_2O. This has a total of 7 nuclei. We will label the nuclear coordinates as x_i for $i = 1, 2, ..., 7$. Suppose x_1 is the three-dimensional coordinate for the first outer hydrogen nucleus; x_2 is the coordinate for the second outer hydrogen nucleus; x_3 is the coordinate for the first outer oxygen nucleus, which is bonded to the first two hydrogen nuclei; x_4 is the coordinate for the central hydrogen nucleus; x_5 is the coordinate for the second oxygen nucleus; x_6 and x_7 are the coordinates for the last two terminal hydrogen nuclei bonded to the second oxygen. Thus, our problem starts with 21 degrees of freedom. We now want to convert the coordinates to clustered Jacobi coordinates. There will be three clusters: the two outer H_2O groups will each be a cluster, and the central hydrogen nucleus will be its own third cluster. m_O denotes the mass of an oxygen nucleus, and m_H denotes the mass of a hydrogen nucleus.

$$X_1 = x_2 - x_1$$

$$X_2 = x_3 - \frac{m_H x_1 + m_H x_2}{2m_H} = x_3 - \frac{x_1 + x_2}{2}$$

$$X_3 = x_7 - x_6$$

$$X_4 = x_5 - \frac{m_H x_7 + m_H x_6}{2m_H} = x_5 - \frac{x_7 + x_6}{2}$$

$$Y_1 = \frac{m_O x_5 + m_H x_7 + m_H x_6}{m_O + 2m_H} - \frac{m_O x_3 + m_H x_1 + m_H x_2}{m_O + 2m_H}$$

$$Y_2 = x_4 - \frac{m_O x_3 + m_O x_5 + m_H x_1 + m_H x_2 + m_H x_7 + m_H x_6}{2m_O + 4m_H}$$

We set the mass of an electron $m_e = 1$ and define the true value of ϵ as before. Thus again we can scale the masses so that $m_H = \epsilon^{-3}$ and $m_O = \frac{4}{3}\epsilon^{-4}$.

We can now write the kinetic energy for the system with the motion of the center of mass removed.

$$-\frac{1}{2\mu_1}\Delta_{X_1} - \frac{1}{2\mu_2}\Delta_{X_2} - \frac{1}{2\mu_1}\Delta_{X_3} - \frac{1}{2\mu_2}\Delta_{X_4} - \frac{1}{2\mu_3}\Delta_{Y_1} - \frac{1}{2\mu_4}\Delta_{Y_2}$$

where

$$\mu_1 = \frac{\epsilon^{-3}\epsilon^{-3}}{\epsilon^{-3} + \epsilon^{-3}} = \frac{1}{2}\epsilon^{-3}$$

$$\mu_2 = \frac{2\epsilon^{-3}\frac{4}{3}\epsilon^{-4}}{2\epsilon^{-3}+\frac{4}{3}\epsilon^{-4}} \approx 2\epsilon^{-3}$$

$$\mu_3 = \frac{(2\epsilon^{-3}+\frac{4}{3}\epsilon^{-4})^2}{2(2\epsilon^{-3}+\frac{4}{3}\epsilon^{-4})} \approx \frac{2}{3}\epsilon^{-4}$$

$$\mu_4 = \frac{(4\epsilon^{-3}+\frac{8}{3}\epsilon^{-4})\epsilon^{-3}}{5\epsilon^{-3}+\frac{4}{3}\epsilon^{-4}} \approx 2\epsilon^{-3}$$

Then the Hamiltonian for the nuclei of this molecule when the electrons are in their ground state is

$$-\frac{1}{2\mu_1}\Delta_{X_1} - \frac{1}{2\mu_2}\Delta_{X_2} - \frac{1}{2\mu_1}\Delta_{X_3} - \frac{1}{2\mu_2}\Delta_{X_4} - \frac{1}{2\mu_3}\Delta_{Y_1} - \frac{1}{2\mu_4}\Delta_{Y_2}$$

$$+V(X_1, X_2, X_3, X_4, Y_1, Y_2)$$

where $V(X_1, X_2, X_3, X_4, Y_1, Y_2)$ is the eigenvalue of $h_{el}(X_1, X_2, X_3, X_4, Y_1, Y_2)$, the ground state electronic Hamiltonian. V describes the potential energy surface for this molecule. This is computed numerically.

We can replace the μ_i's and obtain the Hamiltonian.

$$-2\epsilon^3\Delta_{X_1} - \frac{\epsilon^3}{4}\Delta_{X_2} - 2\epsilon^3\Delta_{X_3} - \frac{\epsilon^3}{4}\Delta_{X_4} - \frac{3\epsilon^4}{4}\Delta_{Y_1} - \frac{\epsilon^3}{4}\Delta_{Y_2}$$

$$+V(X_1, X_2, X_3, X_4, Y_1, Y_2)$$

Now there are 18 degrees of freedom, with 3 of the original 21 removed to eliminate the motion of the center of mass. We can remove three more degrees of freedom from the Euler angles (θ, ϕ, γ). When we rotate the molecule, we rotate Y_1, so it must be invariant under rotation. Then V depends on only the magnitude of Y_1, and we can define $y_1 = ||Y_1||$.

This would remove the dependence on θ and ϕ. At the point we are expanding around, Y_2 is perpendicular to Y_1. Then we can remove the dependence on γ by rotating the molecule so that Y_1 lies along the z-axis and Y_2 lies in the yz-plane.

$$y_1 \in \mathbb{R}^1, \quad y_2 \in \mathbb{R}^2$$

$$Y_1 = (0, 0, \pm y_1)$$

$$Y_2 = (0, y_{2,1}, y_{2,2})$$

The Laplacians with the rotational degrees of freedom removed are

$$\Delta_{y_1} = \frac{\partial^2}{\partial y_1^2} + \frac{2}{y_1}\frac{\partial}{\partial y_1}$$

and

$$\Delta_{y_2} = \frac{\partial^2}{\partial y_{2,1}^2} + \frac{\partial^2}{\partial y_{2,2}^2}.$$

This gives us a Hamiltonian that now depends on 15 vibrational degrees of freedom.

$$-2\epsilon^3\Delta_{X_1} - \frac{\epsilon^3}{4}\Delta_{X_2} - 2\epsilon^3\Delta_{X_3} - \frac{\epsilon^3}{4}\Delta_{X_4} - \frac{3\epsilon^4}{4}\Delta_{y_1} - \frac{\epsilon^3}{4}\Delta_{y_2}$$

$$+V(X_1, X_2, X_3, X_4, Y_1, Y_2)$$

The two vibrational modes of interest to us are proportional to ϵ^2. The other 13 modes all have frequencies proportional to $\epsilon^{3/2}$. We can separate them by orders of ϵ to only study the two modes proportional to ϵ^2.

With the standard time-independent Born-Oppenheimer approximation expanded around the minimum point of the potential energy surface, the frequencies, in cm^{-1}, for the molecule were found using Gaussian to be:
158, 273, 449, 503, 536, 621, 852, 1520, 1522, 1709, 1773, 3743, 3751, 3840, and 3840.

The two frequencies we are interested in are 621, the symmetric stretch, and 852, the asymmetric stretch.

These vibrational frequencies are only dependent on the vectors y_1 and y_2, where y_1 is the vector from the center of mass of first terminal H_2O cluster to the center of mass of the second terminal H_2O cluster, and y_2 is the vector from the center of mass of both terminal H_2O clusters to the central hydrogen nucleus. Then the Hamiltonian for these vibrational frequencies is

$$-\frac{3\epsilon^4}{4}\Delta_{y_1} - \frac{\epsilon^3}{4}\Delta_{y_2} + V(y_1, y_2).$$

This Hamiltonian has three degrees of freedom. This can be reduced to depend on only two variables, w and z, where w is the distance from the center of mass of first terminal H_2O cluster to the center of mass of the second terminal H_2O cluster, and z is the distance from the center of mass of both terminal H_2O clusters to the central hydrogen nucleus. This removes one degree of freedom from the problem, which describes a bending vibration of the hydrogen bond, which we are not currently interested in. Now we have the final Hamiltonian of interest.

$$H(\epsilon) \;=\; -\frac{3\epsilon^4}{4}\Delta_w - \frac{\epsilon^3}{4}\Delta_z + V(\epsilon, w, z)$$

Here we introduce the ϵ-dependence of V. Again, we allow the dependence of V on ϵ only by allowing the ground state eigenvalue to be dependent on ϵ.

Now we can assume that we can expand the energy $E(\epsilon, w, z)$ as a Taylor series in z^2 around a point where $\nabla V \;=\; 0$. For this problem, the approximation for V has a unique minimum at a point $(w_0, 0)$, which we will expand around. Although there is a unique minimum, it is very flat near that point, $(w_0, 0)$. It is not clear whether the true potential energy surface for this molecular ion has a unique minimum or a slight double well. The best approximation we can make is with CCSD(T), which results in the unique minimum. To force th3 ϵ dependence of V, we replace $a_2\, z^2$ with $\epsilon/\epsilon_0\, a_2\, z^2$. Using the true value of ϵ defined before, $\epsilon_0 \;=\; 0.0821$, we obtain the true eigenvalue, $V(\epsilon_0, w, z)$, of the electronic Hamiltonian, $h_{el}(\epsilon_0, w, z)$. The potential energy surface was calculated using Gaussian 09 at 15 points using CCSD(T) with the aug-cc-pvtz basis set. The graph of the potential energy surface can be seen in Figure 4.2. Then the ground state electron level has the form

$$E_1(\epsilon, w, z) \;=\; E_0 + a_1(w-w_0)^2 + (a_2\epsilon - a_3(w-w_0))z^2 + a_4 z^4 + ...$$

where $a_j \;=\; O(1)$. Terms not showed here are of order $(w-w_0)^{\alpha} z^{2\beta}$ where α and β are integers satisfying $\alpha + \beta \;\geq\; 3$. These terms only contribute higher order corrections to the energy.

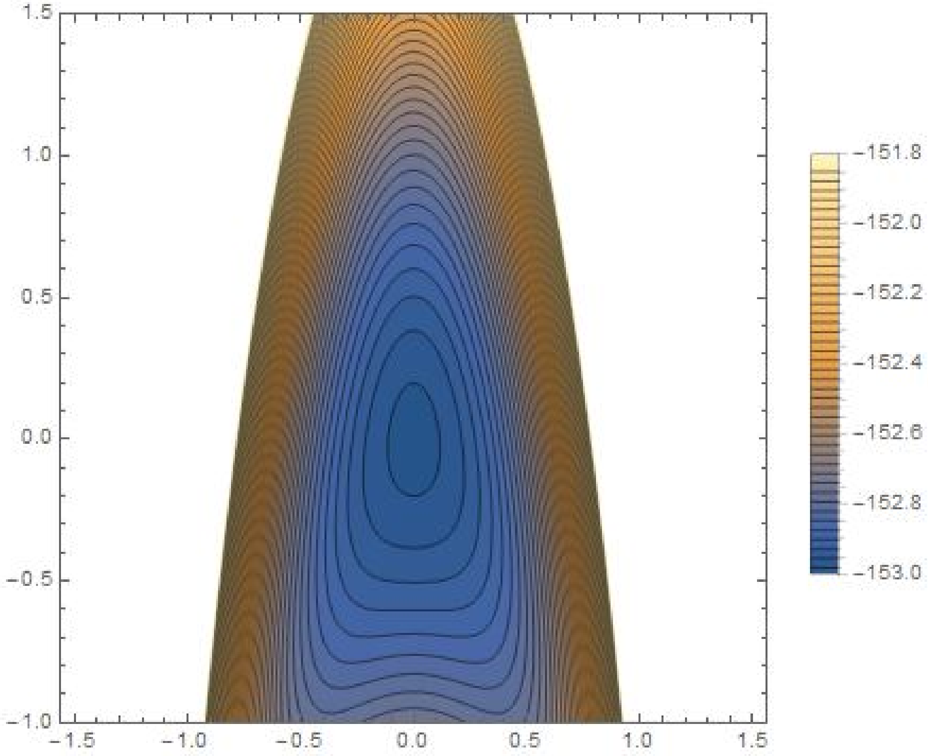

Figure 4.2: The Potential Energy Surface for the ground state of $H_5O_2^+$

Then the leading order potential energy surface is

$$\tilde{E}_1(\epsilon_0, x, y) \;=\; E_0 + a_1(w-w_0)^2 + a_2\epsilon_0 z^2 - a_3(w-w_0)^2 + a_4 z^4.$$

If we rescale the variables so that $x = (w - w_0)/\epsilon$ and $y = z/\epsilon^{1/2}$, then the Hamiltonian is unitarily equivalent to ϵ^2 times the normal form Hamiltonian.

$$H_{NF} = -\frac{3}{4}\frac{\partial^2}{\partial x^2} - \frac{1}{4}\frac{\partial^2}{\partial y^2} + E_{NF}(x, y)$$

where the normal form energy is

$$E_{NF} = a_1 x^2 + a_2 y^2 - a_3 x y^2 + a_4 y^4.$$

This gives us a total leading order energy.

$$\tilde{E}(x, y) = E_0 + a_1 x^2 + a_2 y^2 - a_3 x y^2 + a_4 y^4$$

where, with energies measured in Hartrees and distances measured in Angstroms,

$$\begin{aligned} E_0 &= -152.992 \\ a_1 &= 0.250131 \\ a_2 &= 0.726249 \\ a_3 &= -1.28943 \\ a_4 &= 1.92595 \end{aligned}$$

These values were solved for using Gaussian 09, computed using CCSD(T) at 15 points with the aug-cc-pvtz basis set.

From this we find the energies of order ϵ^2 in which we are interested.

Note that we found $a_2 > 0$; this indicates that the potential energy surface has a unique minimum at $(w_0, 0)$, although it is very flat. This can be seen in the potential energy surface in Figure 4.2.

To guarantee that the leading terms of the energy expansion are bounded below, we need to show that

$$a_3^2 \;\le\; 4a_1a_4.$$

The values found from Gaussian do satisfy this condition.

$$a_3^2 \;=\; (1.28943)^2 \;=\; 1.66263 \;<\; 1.92696 \;=\; 4(0.250131)(1.92595) \;=\; 4a_1a_4$$

Thus this is approximation is valid for this problem.

We can now solve the normal form Hamiltonian to find the energies for the two stretches of interest.

For the symmetric stretch, the excitation energy is approximated to be 597 cm^{-1}.

For the asymmetric stretch, the excitation energy is approximated to be 1279 cm^{-1}.

4.2 Accuracy

To determine the accuracy of the approximations for $H_5O_2^+$, we can compare to experimental results found again by McCoy (et al.) in [11]. However, like with $H_3O_2^-$, the value actually measured was the predissociation yield for $H_5O_2^+ \cdot Ar$ rather than $H_5O_2^+$ itself. The spectrum for this molecule is more affected by the argon than the previous one. There was no data for the symmetric stretch, but for the asymmetric stretch, the excitation energy was found to be 1085 cm^{-1}. Using our approximation, we found the value to be 1279 cm^{-1}. This gives us an error of 194 cm^{-1}. This seems like a large error, but for a problem this complicated and using our simple approximation, this is a reasonably good approximation. It is more accurate than the value found using the standard Born-Oppenheimer approximation, 825 cm^{-1}, found when expanded around the point of the unique minimum of V, $(w_0, 0)$.

Chapter 5

Conclusion

Applying the method of approximation developed by Hagedorn and Joye [9], we approximated the vibrational energies of the symmetric and asymmetric stretches of the hydrogen bonds in the $H_3O_2^-$ and $H_5O_2^+$ molecular ions. This resulted in the approximate energies which are summarized in Table 5.1.

There are several possible causes of error in our approximation for both molecules. When doing the approximations with the Gaussian 09 program, we used the aug-cc-pvtz basis set. With this basis set, we would expect errors to be at least 20 cm^{-1}. The error from the experimental results for $H_3O_2^-$ was 139 cm^{-1}, which could be partially explained by our choice of the basis set. Similarly for the error of $H_5O_2^+$ of 194 cm^{-1}. A portion of the errors may be attributed to using this basis set. Using a larger basis set would result in better accuracy, but would cost much more in computing.

This approximation fixed the terminal OH^- and H_2O groups of their respective molecules, and we did not take into account any other bending or torsion of the molecule. Although we did investigate into including the bends of the terminal hydrogens of $H_3O_2^-$, it did not result in a significant improvement of the accuracy.

To find the potential energy surfaces for $H_3O_2^-$ and $H_5O_2^+$, we used Gaussian to compute this at 15 different points for each molecule. Some error may be attributed to this; using

Table 5.1: Approximate Vibrational Energies

	Symmetric Stretch	Asymmetric Stretch
$H_3O_2^-$	533 cm^{-1}	836 cm^{-1}
$H_5O_2^+$	597 cm^{-1}	1279 cm^{-1}

more points could improve the accuracy.

Another error could be from using the wrong two-dimensional space, (w, z), for these vibrations. Also error in using the wrong reduced masses could have resulted.

It is also possible, but not very likely, there is error in the experimental measurements [11]. Instead of measuring the vibrational energies of $H_3O_2^-$ directly, they measured the energies for $H_3O_2^- \cdot Ar$. It is assumed though that the bonding with Argon does not have an effect on the bonds in which the central hydrogen participates. For the $H_5O_2^+$ molecule, they find a region of low intensity energy bands right below the peak they identify the asymmetric stretch vibration which they specifically attribute to interaction with argon. In general they conclude that the spectrum for $H_5O_2^+$ is very complex due to mixing of the vibrational and rotational energies.

Overall, we conclude that using this method of approximation was successful. While there was some error in the energies that were approximated, the values were more accurate than the results of the standard Born-Oppenheimer approximation that would usually be applied.

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