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Approximating Eigenvalues for Double Well Potentials

A Thesis

Presented to the

Department of Mathematics

and the

Faculty of the Graduate College

University of Nebraska

In Partial Fulfillment

of the Requirements for the Degree

Master of Arts

University of Nebraska at Omaha

by

Chad Fulk

June 2001

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Thesis Acceptance

Acceptance for the faculty of the Graduate College,
University of Nebraska, in partial fulfillment of the
requirements for the degree Master of Arts,
University of Nebraska at Omaha.

Committee

John Herdell

Matadre

Chairperson MeW

Date: 6/6/2001

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APPROXIMATING EIGENVALUES FOR DOUBLE WELL POTENTIALS

Chad Fulk, MA

University of Nebraska, 2001

Advisor: Dr. Wai-Ning Mei

One dimensional double well potentials usually refer to those potentials which have two equivalent or non-equivalent minima. They have been used to model diverse systems ranging from the electronic structure of diatomic molecules to electron-lattice coupling in high temperature superconductors [1][2]. However, one difficulty to the utility of these models is that exact analytical solutions for almost all double well potentials have not been found, in spite of the fact that this type of potential is constantly utilized as an illustrative example in the literature. Despite intensive research into this problem, only a few types of double wells have been exactly solved to date [3]. The most common way to estimate the eigenvalues of the double well potential is through numerical methods. The usefulness of the system would be greatly enhanced if the true eigenfunctions could be determined for every case. The goal of this thesis is to find a good analytical scheme to obtain the eigenfunctions for the schödinger equation with polynomial double well potential ($V(x) = x^4 - \beta x^2$ where β is a positive integer). To achieve this goal, a combination of two methods are used: the linear combination of atomic orbitals to form molecular orbitals (LCAO-MO) method, and the Rayleigh-Ritz method using variational parameters. Specifically, the trial wavefunctions are expressed in terms of two linear combinations, namely: $\Psi(x, \alpha, \beta, \delta_1, \dots, \delta_n)_{left}$ and $\Psi(x, \alpha, \beta, \delta_1, \dots, \delta_n)_{right}$. It is found that coupling oc-

curs in Gerard functions and anticoupling in un-Gerard. In each method, Ψ contains a complete set of wave functions known to be the exact solutions of the harmonic oscillator. Then the variational parameters are optimized to get the approximate eigenfunction and eigenvalues. The results show that the calculated energy agrees with the numerical results over the entire range of the coupling parameters. The greater the number of terms used to represent ψ the more accurate the eigenvalues, position and expectation values. . We also use the resultant wave functions to verify the Heisenburg uncertainty relation by calculating the expectation values of $\langle x^2 \rangle$ and $\langle p^2 \rangle$, i.e. the position and momentum operators. Thus we determine an approximation method that is useful for revealing the properties of the physical systems that can be modeled with these potentials.

Acknowledgments

The author would like to acknowledge the financial supports from the Department of Physics of the University of Nebraska at Omaha, NSF grant "Complex System Simulation Collaboration Laboratory", and Department of Army grant "Theoretical Study of Microwave-Activated Materials", and Nebraska-EPSCOR grant "Complex Design and Synthesis of Novel Ferroelectrics". Furthermore I would like to express my appreciation to Dr. Wai-Ning Mei for his encouragement and enthusiasm on the project, Dr. Valentin Matache and Dr. Jack Heidel for their excellent tutorage and suggestions.

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Introduction

Single atoms have well established wave functions but for even the simplest diatomic models such as H_2^+ , since there are two equivalent force centers, the analytic solutions are difficult to obtain. In the late 19th century first Rayleigh then Ritz wrote papers in elastomechanics [12] in which they outlined the use of the variational method to obtain approximated wave eigenfunctions to flexible multibody systems. This idea and other methods including LCAO:MO method from chemistry were utilized throughout the 20th century. Most of the research emphasis is on finding specific potentials and trial wave functions in order to find exact solutions but a perhaps more useful is a versatile method that would give a good approximation to any potential . The utilization of computers together with sophisticated numerical methods give very accurate energy eigenvalues of H_2^+ and many other complex systems however these methods say little about the physical nature of the system. Specifically, they could not elucidate bonding and antibonding behaviors. We are left with a choice, to numerically find a realistic solution and sacrifice physical insight that may be gained through an analytical solution or have a elegant mathematical solution that may not map as well to the real system. Of course it would be ideal to find an analytical solution which matches perfectly to the physical system. Some of the few exact analytical solutions known to exist are ,for example, the Razavy potential [3] and the multiple finite square well [4].

We shall adopt the LCAO:MO and Rayleigh-Ritz methods as reasonable methods to acquire an analytical approximation. Analytical solutions of, first, the square well are

used as a simple example, then the polynomial double well will be examined. If suitably accurate the model will exhibit properties of real physical systems. Emphasis is placed on the ground and first excited state eigenvalues, and their associated position and momentum expectation values. Finally the tunneling probability is calculated and examined.

We start with the time independent Schrödinger equation: $\hat{H}\Psi = E\Psi$ where E is the energy eigenvalue, Ψ is the exact eigenfunction and \hat{H} is the Hamiltonian given by: $\frac{d^2}{dx^2} + V(x)$ (if restricted to one-dimension). Natural units are used for simplicity (i.e. $\hbar = 1, 2m = 1$). Since \hat{H} , the Hamiltonian, is a Hermitian operator, its solutions form a complete set. That means they can be used to span any vector in Hilbert space. Therefore it is not difficult to prove the following theorem which is the basis of the variational method. That is, for any given trial wavefunction, $|\Psi_{trial}\rangle$, we can show that $E_{trial} \geq E_{exact}$ where $E_{trial} = \langle \Psi_{trial} | \hat{H} | \Psi_{trial} \rangle$ and $E_{exact} = \langle \Psi_{exact} | \hat{H} | \Psi_{exact} \rangle$. Usually the exact energy E is not easy to find, so we rely on a numerical approach such as the Runge-Kutta method. Thus the goal here is to, first choose a trial wave function based on intuition and understanding of the system, then minimize its expectation value. If possible we will find a systematic way to improve the trial wavefunction, step by step.

Using the Rayleigh-Ritz method we select a trial eigenfunction. Based on the symmetry of the double well potential, it is not difficult to guess that eigenfunctions can be split into two categories:

$$\Psi_{trial}^{even} = \Psi_{left} + \Psi_{right}$$

$$\Psi_{trial}^{odd} = -\Psi_{left} + \Psi_{right}$$

where in the simplest case: $\Psi_{left} = Ne^{-\alpha^2(x+a)^2}$ and $\Psi_{right} = Ne^{-\alpha^2(x-a)^2}$ where N is the normalization constant. This type of function will be referred to as class 1 equations. We then add orthonormal terms to Ψ with variational parameters. The equation's parameters are optimized giving the analytical wave function then placed back in to the Schrödinger equation. Integrating the complete function over all space and solving for the energy eigenvalues:

$$\langle \Psi^\dagger | \hat{H} | \Psi \rangle = E \langle \Psi^\dagger | \Psi \rangle. \quad (1)$$

α and a are the variables varied to minimize the equation and normalize N . Further improvements can be made on the trial functions by adding higher order even Gerard harmonic oscillator functions. Each excited state, n , is weighted with additional variational parameters δ_n where n can go to any positive integer. As n gets larger the function becomes increasingly more complex. We find that the computation becomes tedious when n is greater than 10. An alternative to class 1 functions is to allow each higher order harmonic oscillator function have different parameters α_n and a_n . This type of equation will be referred to as class 2 equations. It turns out that, the rate of convergence is faster than the previous scheme and position expectation values are vastly improved for wells depths where the δ_n parameter is dominant. Once the optimized solution trial eigenfunctions are found the expectation values operators:

- Position expectation: $\sqrt{\langle x^2 \rangle} = \sqrt{\langle \Psi^\dagger x^2 \Psi \rangle} \quad (2)$

- Momentum expectation: $\sqrt{\langle p^2 \rangle} = \sqrt{\langle \Psi^\dagger (-\frac{d^2}{dx^2}) \Psi \rangle} \quad (3)$

- Tunneling probability: $T \langle \Psi_{ground}^\dagger | \Psi_{1^{st}excited} \rangle = \langle \Psi_{ground}^\dagger | \hat{H} | \Psi_{1^{st}excited} \rangle \quad (4)$

can be calculated. These expectation values can be used to verify the Heisenberg uncertainty relation, i.e. $\Delta x \Delta p \geq \frac{1}{2}$, where $\Delta x = \sqrt{\langle x^2 \rangle}$ or the root mean square position, and $\Delta p = \sqrt{\langle p^2 \rangle}$ or root mean square momentum..

Further more, to demonstrate the efficacy of the described techniques, the infinite square well will be solved exactly first and then the polynomial double well will be approximated. With the resulting analytic solution we quantitatively compare the eigenvalues to established numerical results and qualitatively compare the results with natural phenomena. Namely we explore the rate of convergence of the trial functions eigenvalues to numerical values and the position and expectation values to look for particle behavior. It is found that the energy eigenvalues and uncertainty relation are most accurate the more terms are added to the wave function and at shallow potentials. The convergence is found to be adequate with many terms using same parameters α, a (class 1) and superior using only a few harmonics with different α, a (class 2). While there is little change in the final accuracy of the eigenvalues there is a greater difference in the expectation values for deep wells indicating the properties for class 2 equations more closely reflects particle interactions.

Chapter 1

Establishment of Method

In this chapter we develop the methods to approximate the solutions of the Schrödinger equation. The Ritz-Rayleigh method is perhaps the most straight-forward and has resulted in genuine insight into the nature of quantal effects in solids. Put simply, in the variational method we guess a form of the wavefunction based on physical insight into the problem. The wavefunction is given several parameters which we use to vary its detailed form. It is then used to calculate the expectation value of the Hamiltonian. The parameters are then minimized which gives an approximate result for the n^{th} state energy eigenvalues. The optimized wavefunction is an approximate n^{th} state eigenfunction. Thus the overall problem we wish to solve is one of eigenvalues or specifically a set of linear algebraic equations that are solutions to the Schrödinger equation. Specifically, we use the variational approach to get a solution that is obtained as an element of a Hilbert space of admissible functions. This solution minimizes the norm of the energy of the system. This energy norm can be replaced by position, momentum and tunneling norms respectively to find expectation eigenvalues where appropriate.

Recall the Schrödinger wave equation:

$$\hat{H}\Psi = E\Psi \quad (5)$$

where \hat{H} is the Hamiltonian operator, Ψ is an arbitrary wave function that must satisfy all boundary conditions, and E represents the energy eigenvalue. It is necessary for \hat{H} to be self-adjoint to obtain a solution [10].

Definition1 An operator $\hat{H} \in \mathcal{L}(V)$, where V is a finite dimensional, nonzero, inner-product space over \mathbf{C} , is called self-adjoint if $\hat{H}=(\hat{H}^\dagger)^T$, i.e $V=C^n$ for some n . (\dagger denotes complex conjugate) [9].

We must guess the trial function Ψ . We choose a function φ based on our knowledge of the physical system we are modeling and intuition. As long as the function meets all boundary conditions and is well-behaved (i.e. integrable) it will give us an approximate eigenvalue E greater than the actual energy eigenvalue.

Proposition 1 The first energy eigenvalue E'_1 of any trial function (φ) will be greater than the eigenvalue E_1 of actual function (ψ) i.e $E'_1 \geq E_1$

Proof We wish to minimize $E'(\varphi)$ so that $\min\{E'(\alpha, \beta, \gamma, \dots)\} \geq E_1$ Assume that φ is continuous and belongs to $\mathcal{L}^2(\mathbf{R})$.

Let $\{\psi_k : k = 1, 2, \dots\}$ be an orthonormal basis of the latter space,

therefore $\varphi = \sum_{k=1}^{\infty} a_k \psi_k$, converges being in the norm of $\mathcal{L}^2(\mathbf{R})$

Substituting φ into $E'(\varphi) \equiv \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} = \frac{\sum_{k=1}^{\infty} |a_k|^2 E_k}{\sum_{k=1}^{\infty} |a_k|^2}$

Since $E_1 \rightarrow E_{\infty}$ are in increasing order then the exact E_1 is the smallest eigenvalue, so $E_k \geq E_1$ for every k .

Therefore

$$E' \geq \frac{\sum_{k=1}^{\infty} |a_k|^2 E_1}{\sum_{k=1}^{\infty} |a_k|^2} = E_1 \blacksquare$$

Depending on what eigenfunction we want we can use the appropriate operator.

Those operators are given as:

- Energy operator: $\hat{H}_E = \left(\frac{d^2}{dx^2} + V(x) \right)$ (6)
- Momentum Expectation Operator: $\hat{H}_p = \frac{d^2}{dx^2}$ (7)
- Position Expectation Operator: $\hat{H}_x = x$ (8)

We consider now the Fourier expansion of Ψ with respect to an orthonormal basis of eigenfunctions of \hat{H} .

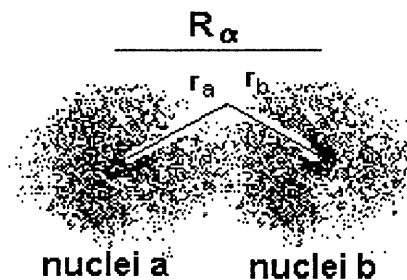
Proposition 2 *Given a continuous and piecewise differential function $\psi(r)$ in $0 \leq r \leq \infty$ and an orthonormal sequence of eigenfunctions φ_i of \hat{H} , then the Fourier series of φ is $\sum_{i=1}^{\infty} c_i \varphi_i(r) = \psi(r)$ where $c_n = \int_0^{\infty} \sigma \varphi_n \psi dr$, $\sigma = \frac{1}{\|\varphi_n\|} = \frac{1}{\sqrt{\int_{-\infty}^{\infty} |\varphi_n|^2 dr}}$ [4].*

Now we need to optimize the trial wavefunction by minimizing (5) with respect to the coefficients c_i . That is: $\frac{d\Psi}{dc_i} = 0$, then solving all equations simultaneously in $\sum_{i=1}^{\infty} c_i \varphi_i(r)$ gives us our trial wavefunction [11]. Substituting the optimized wave function back into the Schrödinger wave equation we can get the associated eigenvalues from the appropriate operator.

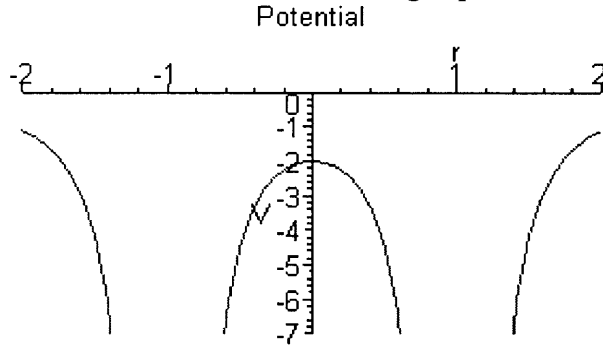
Chapter 2

LCAO-MO Method

The goal is to get an analytical solution to the one dimensional double well potential. To do this we need to simplify the problem by making some approximations. First we will restrict our observations to the x-axis, we will also assume that the particle acting in the potential well has no effect on the potential itself (Born-Oppenheimer Approximation), and we assume that either there is only one particle in the potential well or at least, if there are many particles they do not interact with each other and can all occupy the same space. Finally we assume the particle is nonrelativistic. We will be solving for the particles probability density as a function of displacement from the origin. To formulate the argument the spherically symmetric case of a diatomic molecule, H_2^+ , is used. The Schrödinger equation is a second order partial differential equation which gives us the probability density of the particle as a function of the displacement from the potential sources r_a, r_b : $H^e \psi_\epsilon^e(r_{a,b}, R_\alpha) = E_\epsilon^e(r) \psi_\epsilon^e(r_{a,b}, R_\alpha)$ where \hat{H}_ϵ^e is the electronic Hamiltonian operator and $\psi_\epsilon^e(r_{a,b}, R_\alpha)$ is the spherically symmetric electronic wave function with minimum potential a distance R_α apart.



In other words we are looking at a charged particle being acted upon by two much more massive oppositely charged particles. The two large particles have a coulombic interaction with the small particle: $V_{en} = -\frac{Z_a e^2}{r_a} - \frac{Z_b e^2}{r_b}$ where r_a, r_b represent the small particles distance from the center of the two larger particles.



coulmbic potential of H_2^+

This gives the Hamiltonian: $\hat{H}^e = -\nabla^2 + V_{en}$ which reduces to $\hat{H}^e = -\frac{d^2}{dr^2} + V_{en}$

in one-dimension. For simplicity we set all use natural units for all constants, (i.e. all constants are equal to 1). Now we need a solution, a second order PDE's solution can be represented by a complete set of basis functions.

We can now rewrite the wave equation as a Cauchy sum of square summable orthonormal functions: $\psi_\epsilon^e = \sum_{i=1}^{\infty} c_i \varphi_i$. The coefficients can be solved by differentiating the terms with respect to each c_i , finding the minima by solving the subsequent linear algebraic equations. To get a feasible solution the sum must be truncated to N functions. To get a good approximation we must take a N large enough such that the $(N + 1)^{st}$ term is negligible. To find the easiest set of basis functions we can expand ψ_ϵ^e into a linear combination of two wavefunctions each representing all the possible wavefunctions for each well, $\psi_\epsilon^e = \sum_{i=1}^N c_i \psi_i^a + \sum_{j=1}^N c_j \psi_j^b$. It should be noted that the combination of different wavefunctions on different wells are not necessarily orthogonal therefore we must normal-

ize the entire function. We need only to recognize the $i,j=1$ wavefunctions to demonstrate the method as the phenomena we are studying becomes redundant at higher energies [14]. Thus we are left with $\psi_1^e(r) \simeq N(A_1\psi_1^a(r) + B_1\psi_1^b(r))$. This limits our observations to the 1st even (Gerard) and odd (un-Gerard) solutions. This basis now gives us an approximate eigenfunction to a double well. .

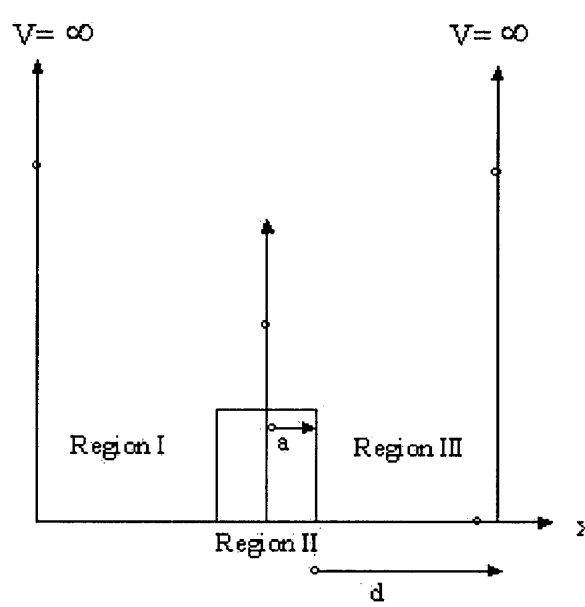
2.0.1 Double Square-Well Potential

Using the LCAO:MO method we look at simple example whose solution is known exactly [3], the infinite double square well. The well is constructed with a symmetric width, a , and depth, V_0 and separated by a barrier of width d whose walls outside a have infinite potential. This is an approximation to the H_2^+ well in one-dimension. Thus the wavefunction will take the form: $\psi_E(x) = \sum_{k=1}^{\infty} a_k \psi_k^{left}(x) + \sum_{l=1}^{\infty} b_l \psi_l^{right}(x)$, where $a_k = b_k$ for all Gerard functions ψ_E and $-a_k = b_k$ for all un-Gerard eigenfunctions. Here we focus on the ground (the first Gerard eigenfunction) and the first excited (the first un-Gerard eigenfunction) states. With normalization this gives:

- Ground State: $\psi_g(x) = \frac{1}{\sqrt{N_g}}(\psi_1^{left} + \psi_1^{right})$ (9)

- 1st Excited State: $\psi_1(x) = \frac{1}{\sqrt{N_1}}(-\psi_1^{left} + \psi_1^{right})$ (10)

Since our potential has discontinuous points it will be split into three regions. In regions I and III the potential is 0, in region II, V_0 , and ∞ everywhere else.



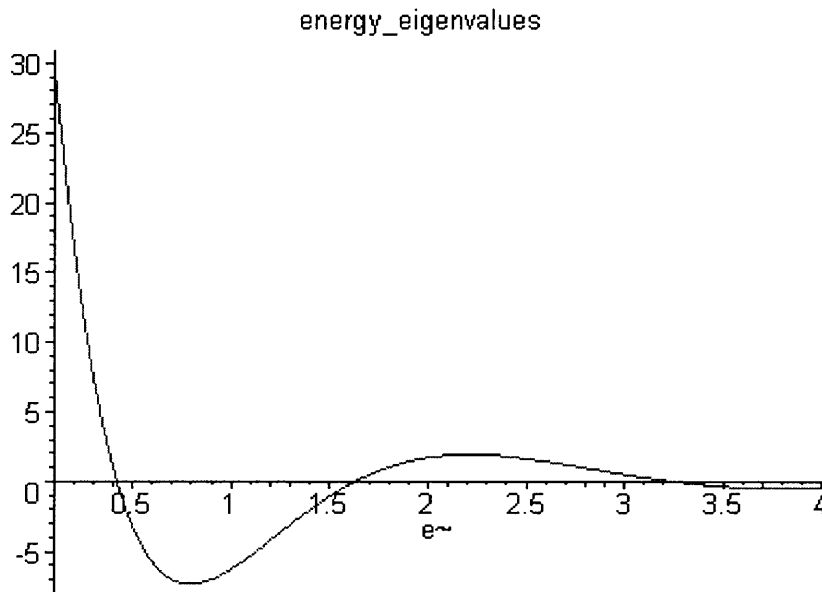
In nite square well potential

Understanding the well-known solutions of a single well square potential and making well chosen modifications we can obtain appropriate solutions for each region, treating each well as an infinite square well where boundary conditions must be matched.

- Regions I and III: $\psi_{I,III} = \begin{cases} A \cos(\alpha_o(x-x_o)) & \text{if even} \\ A \sin(\alpha_o(x-x_o)) & \text{if odd} \end{cases}$ where $\alpha_o \equiv \sqrt{E_o} = \text{constant}$ (11)
- Region II: $\psi_{II} = B e^{(\pm\beta_o(x-x_o))}$ where $\beta_o \equiv \sqrt{V_o - E_o} = \text{constant}$ (12)

Now since the well potential goes to infinity outside boundaries of regions I and III the function must go to 0. The function must be differentiable and uniformly continuous so the functions derivatives and logarithmic derivatives must be equal to each other at each regional boundary. This gives six sets (one for each regional boundary) of algebraic equations. Since the well is symmetric about $x=0$ we need only to solve three of the equations

since the other three are degenerate. Placing these in matrix form the resulting eigenfunction is obtained by taking the determinant. Setting the function equal to 0 and solving for E_o solves for all eigenvalues since we are looking only at the ground state the first (and smallest) eigenvalue, E_0 , is used. This technique is repeated with odd eigenfunctions to get the 1st odd eigenvalue E_1 , (i.e. first excited state). Often the eigenfunctions are transcendental and the equations are not easily solved [14]. This can be remedied by plotting the equation on an eigenfunction vs E plot and observing the crossings of the E-axis.



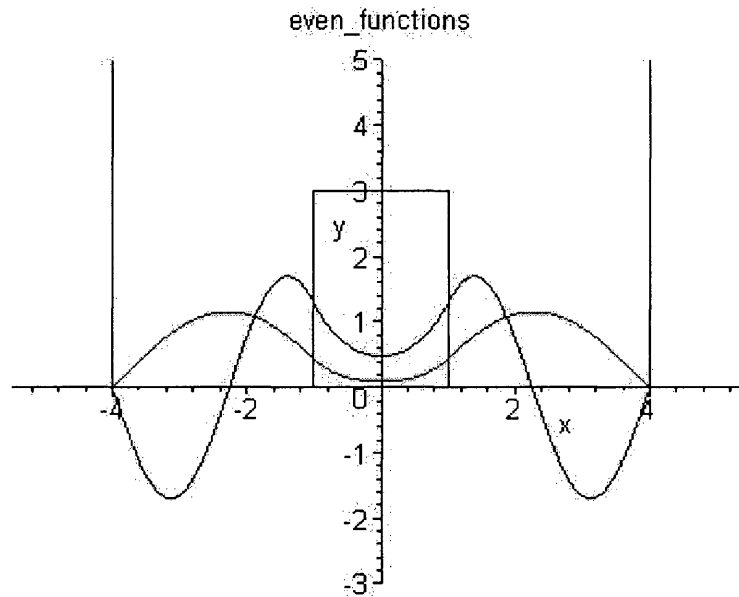
First three gerard energy eigenvalues (E_0, E_1, E_2)

Results may also be gained through numerical approximations.

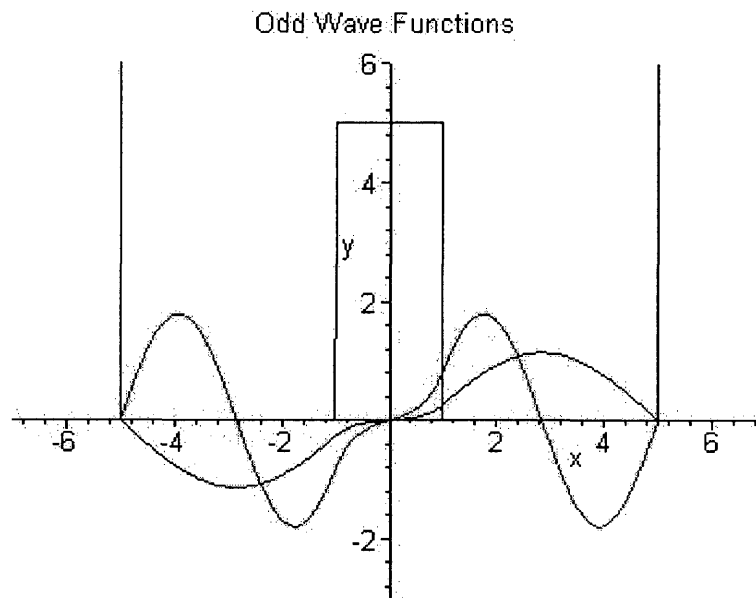
Results

Thus using the technique above we begin to model the properties of molecular interactions. Here the separation d corresponds to the molecular separation between two atoms and the particle in the well is an electron acting in the electric potential of two positive, noninteracting, and immobile nuclei. We can see in the plots if the Gerard eigenfunctions

have a greater probability density across the boundary and its peaks are closer to the region $\pm d$ than the un-Gerard eigenfunction. This is classically impossible since the boundary potential is greater than the kinetic energy of the particle. That is, there is insufficient energy for the particle to be anywhere in this boundary region (Region II).



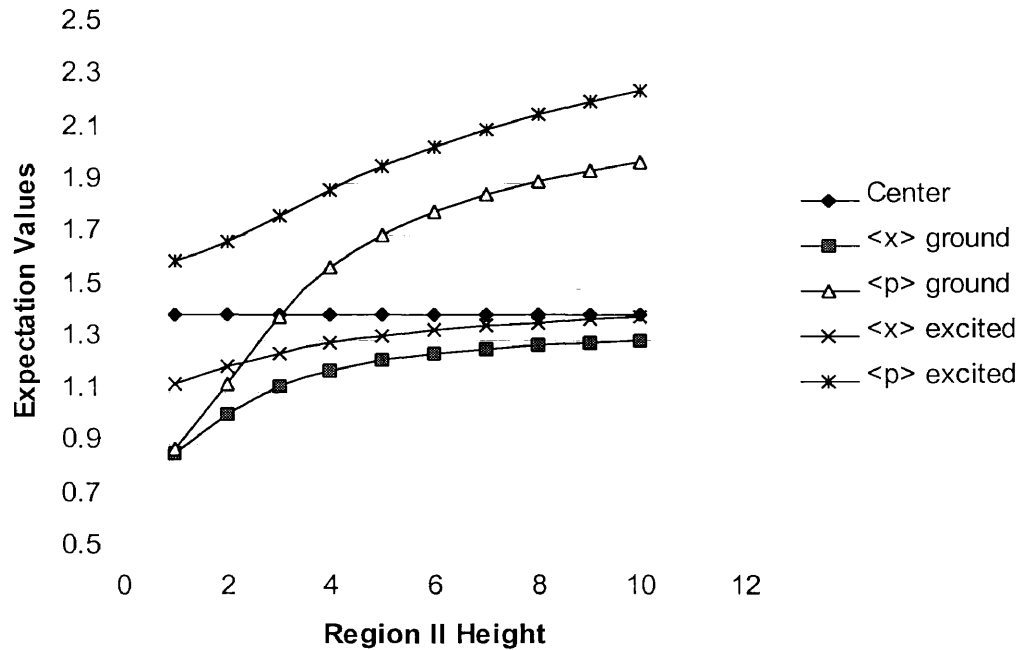
Looking at the E_1 eigenfunction we see that the function has a node at $x = 0$ indicating a zero probability at this point and, in fact, all un-Gerard functions have at a node at $x = 0$.



Near zero probability density in region II

In these plots we can see that the un-Gerard functions always have a node at $x = 0$. When looking at the expectation values it can be seen that in the first excited state, since the particle has zero probability to be at $x = 0$, the particle stays near the nuclei. In the ground state the particle has greater movement since it can exist in the classically forbidden boundary region.

Comparison of well center to expectation values



This freedom of position results in a restriction in momentum allowing a lower energy. All first excited state momentum expectation values are higher than ground values. This is consistent with the ground state having a lower energy than the first excited state.

The square well gives an exact solution to a double well system [3] so we expect to see similar results for the polynomial potential. In these plots we vary the region II potential height. The polynomial potential will not only deepen its wells but increase the interatomic distance. This will modify the results but we should still be able to observe similar particle behavior.

Chapter 3

Variational Method

The LCAO:MO method gives us a linear combination of orthonormal wavefunctions to get the eigenfunctions for the double well model. This method works well in the square well case since an exact solution can be obtained but for more complex potentials we need to expand on this idea. We must find a set of trial wave functions ψ_n^{trial} that are reasonably close to the true eigenfunctions ψ_n , that is, trial wavefunctions that are correctly bounded on all coordinates. In actuality any function that is correctly bounded, orthonormal, is square integrable and can be expanded into an infinite sequence will work but it will converge to the true solution very slowly, so the idea is to make an educated guess based on intuition and known physical properties. Any number of parameters can be included in ψ that may be adjusted to optimize ones guess. Using this guess in a truncated sum one can get close to the true eigenfunctions that solve the Schrödinger equation (or perhaps exactly if the guess is the eigenfunction).

Starting with the time independent Schrödinger equation:

$$-\frac{d^2\psi_n}{dx^2} + V(x)\psi_n = E_n\psi_n \quad (13)$$

we must find an eigenfunction ψ_n that gives the eigenvalues E_n such that ψ_n and E_n are unique for every n . Thus we can write the true eigenfunction ψ_n as an infinite sum of orthonormal functions that converges uniformly to ψ_n . [4] No matter what function we choose for φ_n in the sum, when minimized, we will always get an approximate n^{th} eigenvalue ($E'(\psi_n)$) that is equal to or larger than the actual n^{th} eigenvalue (E_n).

Thus now the idea is to adjust the coefficients c_n in the sum $\psi = \sum_{n=1}^s c_n \varphi_n$ to get the approximate eigenvalue as close to the actual eigenvalue as possible. In the truncated sum there are s basis functions and s unknown linear coefficients. Trial basis functions are chosen to be linearly independent and their inner products form the elements of a s by s matrix given by:

$$M_{n,m} = \langle \varphi_n | \hat{H} | \varphi_m \rangle. \quad (14)$$

Note that since the functions φ are also orthogonal, $\langle \varphi_n | \varphi_m \rangle = \begin{cases} 0 & \text{if } n \neq m \\ \delta_{n,m} & \text{if } n = m \end{cases}$. We are left with a square, positive definite matrix of dimension s . Now substituting our expansions and noting that they are uniformly convergent we get

$$M_{n,m} = \sum_{n=1}^s c_n H_{n,m} c_m. \quad (15)$$

where c_n and c_m are variational constants. The minimum trial energy is found by differentiating with respect to each c_n, c_m (treating c_n independent of c_m) and setting equal to zero.

Since the resulting equation is linear it has exactly one c_n root corresponding to the n^{th} eigenfunction giving a total of s roots. Each value c_n represents the weight that the φ_n function contributes to the complete function. The lowest eigenvalue is an approximation to the ground state system energy and the corresponding eigenfunction provides an approximation to the ground state wave function when substituted into the expansion ψ .

The variational method is not limited to the ground state. It can be shown similarly that the M roots of the determinant are sequentially upper bounds for excited states. [9]

We are not bound by linear coefficients as the only method of optimizing the trial function. It is also possible to scale and translate the function by the use of variational parameters. In the case of scaling our matrix becomes:

$$M(\alpha)_{m,n} = \frac{\langle \varphi_n(\alpha) | H | \varphi_m(\alpha) \rangle}{\langle \varphi_n(\alpha) | \varphi_m(\alpha) \rangle} \quad (16)$$

where the minimum can be found by differentiating with respect to α its roots solved. The value α then determines the scaling of the φ_n function. Note however the same α is used in all expansion terms of ψ instead of a separate term for each φ_n as in the c_n parameters. (The case for a different α for each φ_n will be explored later). Finally the function can also be translated by some value a . The method is the same: create a matrix

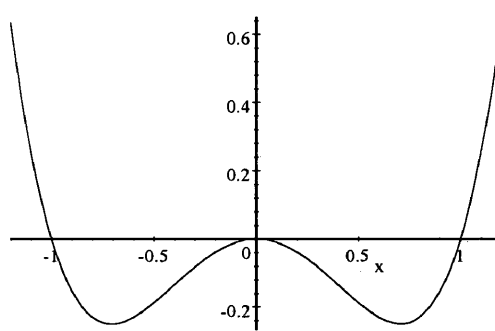
$$M(x + a)_{m,n} = \frac{\langle \varphi_n(x+a) | H | \varphi_m(x+a) \rangle}{\langle \varphi_n(x+a) | \varphi_m(x+a) \rangle} \quad (17)$$

and differentiate with respect to a and solve for the roots. Again since x and a are independent we get only one root per eigenfunction. These parameters will be useful since we can take advantage of the symmetry properties of the potential to simplify our calculations.

3.0.2 Polynomial Double Well Potential

Using the LCAO:MO method (demonstrated for the infinite double square well) in combination with the variational method we will give an approximate solution to a more realistic potential, the polynomial well:

$$V(x) = x^2 - \beta x^4. \quad (18)$$

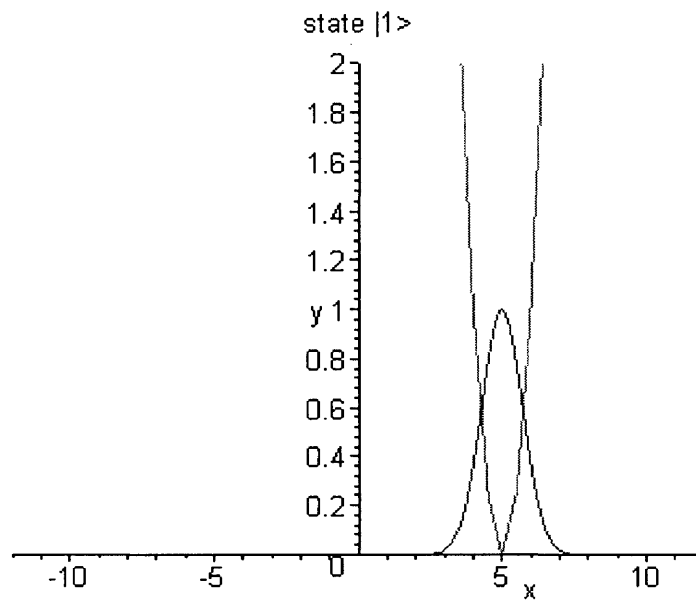


Polynomial double well potential

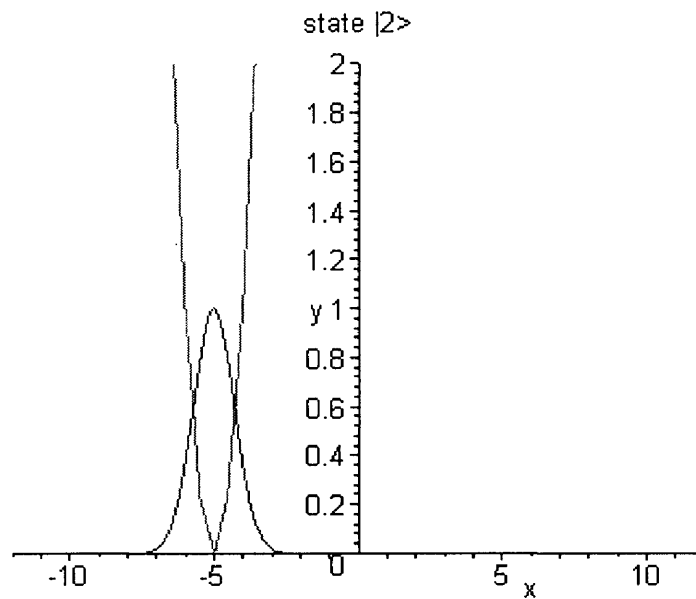
This potential more closely models molecular interactions as it is continuous and smooth over all x .

We can develop our method using the simplest diatomic molecule H_2^+ in a time independent two state system. This system can be described as a linear combination of its base states. To describe these states we can examine the two hydrogen molecules at some great distance from each other such that there is no interaction between them. Now we must find a wavefunction for $\psi_1^{a,b}$ that is reasonably close to the actual solution, has an orthonormal basis and meets all boundary conditions, ($\psi \rightarrow 0$ as $x \rightarrow \infty$). Since the square well is a simple analogue to the polynomial well a similar shape is prudent. The gaussian function with a Hermitian expansion meets this criteria and can be easily scaled and translated. Since the one electron can only be on one molecule or the other, thus our two states, when normalized, can be given as:

- $|1\rangle = N e^{-\alpha^2(x-a)^2} \quad (19)$



- $|2\rangle = Ne^{-\alpha^2(x+a)^2}$ (20)



If we allow the states to interact using the variational method we have a linear combination of terms giving us two new states for the system:

- $|I\rangle = N[|1\rangle - |2\rangle]$ (21) (un-Gerard state)
- $|II\rangle = N[|1\rangle + |2\rangle]$ (22) (Gerard state)

Thus we have constructed a basis set that will take the form of the LCAO:MO approximation, that is a linear combination of the 1st eigenfunctions (atomic orbitals):

$$\psi_1^e(x) \simeq A_1\psi_1^a(x) \pm B_1\psi_1^b(x) \quad (23)$$

Since the well is symmetric about $x=0$ we will displace a gaussian $x+a$ and $x-a$ away from the origin. Giving us:

$$\psi_1 \simeq \sum_{n=1}^N \delta_{n-1} \hat{H}_n(\psi_1^a)\psi_1^a + \delta_{n-1} \hat{H}_n(\psi_1^b)\psi_1^b \quad (24)$$

where $\hat{H}_n(\psi_1^{a,b}) = (-1)^n e^{x^2} \frac{d^n}{dx^n} (e^{-x^2})$ [5], $\psi_1^{a,b} = N e^{(-\alpha(x\pm a)^2)}$, α , a and δ_{n-1} are variational parameters and N is a normalization constant. More specifically α determines the scaling or "steepness" of the gaussian curve, a is the translation of the function, and δ_n determines the weight of the n^{th} function. Then using the variational method we will optimize the variational parameters to get the energy eigenvalue. Each term, n , represents a specific harmonic for each particle. The approximate solution for the eigenvalue E should get more accurate as $N \rightarrow \infty$ and we will analyze the values of the variational parameters. The approximate solution is compared against numerical values found by the Runge-Kutta method. Once the eigenfunctions are found we can find their momentum, position and tunneling expectation values by using the appropriate operator functions (2),(3),(4) on the wavefunctions.

We tested 10 incremental depths of the potential ($\beta = 1..10$) for each wave equation. The eigenfunctions were solved using an algorithm written in MAPLE which outputted,

in Fortran 90 code, the Ψ_{trial} function to a text file. Then its parameters were optimized using an algorithm written in Fortran 90 using three IMSL subroutines U4INF, UMINF and EVAR. These optimized parameters were then put back in another MAPLE algorithm to plot the solutions. Finally using these, the eigenvalues and wavefunctions were analyzed. For a qualitative indicator of the accuracy the effective potential was also calculated and plotted. Then this process was repeated for class 2 equations.

Chapter 4

Results and Discussion

An efficient method has been developed in this paper which outlines the Rayleigh-Ritz and LCAO-MO methods of approximation for finding a solution to the Schrödinger equation, specifically solutions to a polynomial double well potential. A summary of these results is as follows:

For the accuracy of results:

- The more excited oscillator state harmonic wave functions used, the more accurate the results
- The deeper the well the less accurate the results
- Class 2 equations have less error for each higher order oscillator excited states than class 1 equations.

The analysis led to the following observations:

- Gerard functions exhibit the least particle restriction and thus have lower energy eigenvalues.
- un-Gerard functions exhibit more particle restriction properties and thus have higher energy eigenvalues.

For a deeper well (i.e a large β in the potential (18))

- The higher order harmonic states become the dominant factor in the above properties
- Transition probability is increased and the difference in energy is decreased.

4.0.3 Convergence of Eigenvalues

As described by the theory, the greater the number of terms used to approximate the actual wave function the more accurate the approximate function. Yet the optimization of the parameters is more difficult for high order sums as many values of each parameters turn out to be relative minima within a small range for each parameter. Thus we must find a balance between accuracy and computational magnitude. To find the parameters using IMSL an initial guess has to be made. We suspected that the initial terms would have the largest values as they would be the dominant orbitals in the lower energy states. After some initial testing this was found to be false. For small values β , the δ_n parameters increased slowly with higher n, but it was found that the higher order δ_n parameters became dominant at higher β values. This would suggest that the greater the potential the more dominant role the higher order harmonics play in the particle/nuclei interactions.

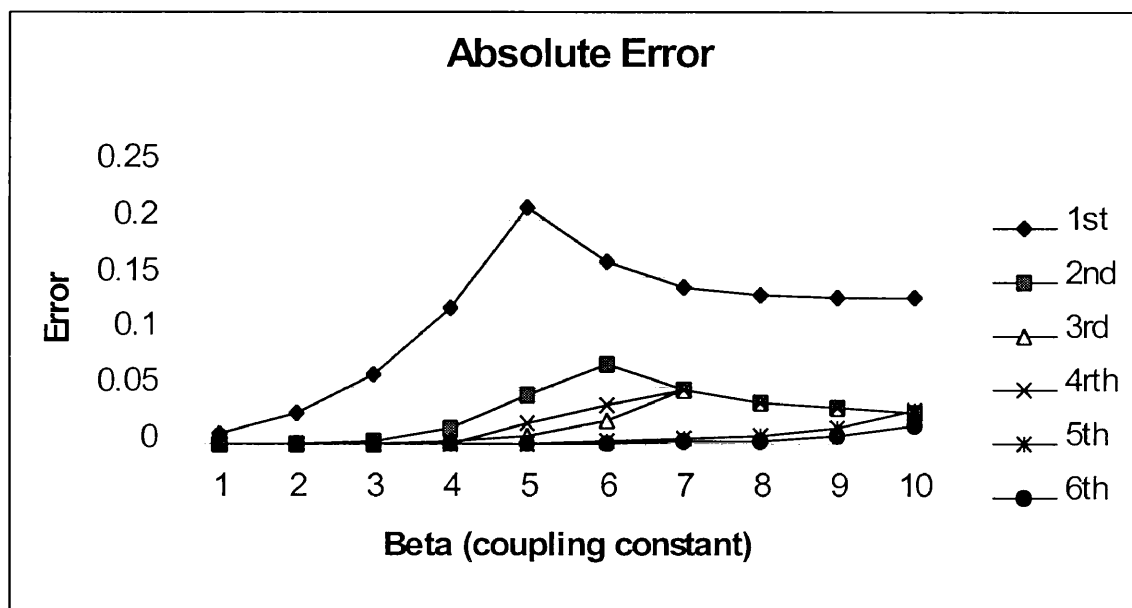
At higher β values the difference in energy eigenvalues between the ground and first excited state becomes very small, as seen in the table below:

β	E_0	E_1	Δ
1	0.65765366	2.8345412	2.176887571
2	0.13778639	1.7130308	1.575244381
3	-0.59349246	0.37766436	0.9711570935
4	-1.7103488	-1.2479197	0.4624291367
5	-3.4101398	-3.2506718	$0.8378871668x10^{-1}$
6	-5.7481861	-5.7067879	$0.4139817808x10^{-1}$
7	-8.6710993	-8.6624463	$0.8653021287x10^{-2}$
8	-12.136323	-12.134807	$0.1516380937x10^{-2}$
9	-16.126178	-16.125950	$0.2279068494x10^{-3}$
10	-20.633566	-20.633536	$0.29850363x10^{-4}$

Thus we need an accuracy of $2x10^{-5}$ to resolve the energy states. Again, the greater number of higher order harmonic terms in the wavefunction the more accurate the approximation. We wish then to find the minimum number of harmonic terms in the function to achieve this approximation. Here is sample data for moderate well depth. The convergence is rapid for the first 4 sums but slows for higher order terms,

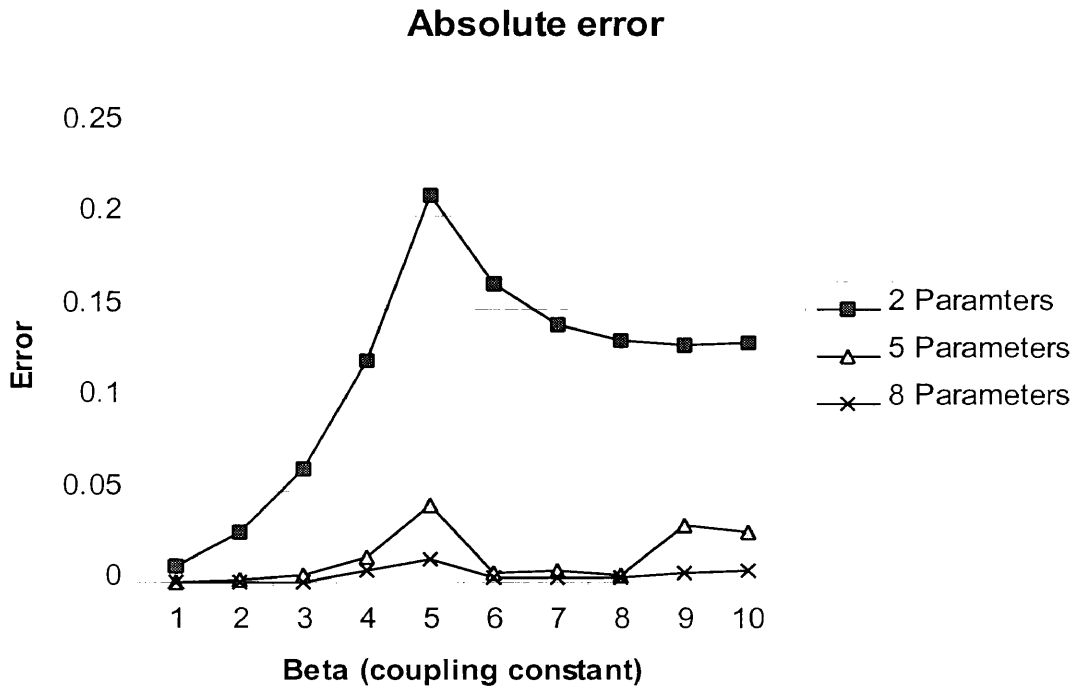
n	Approximated value	Difference from numerical value	
1	-1.588592382	.121756418	
2	-1.697049414	.013299386	
3	-1.708520425	.001828375	$\beta = 4$, groundstate
4	-1.710018555	.000330245	
5	-1.710348800	.000127600	
6	-1.710284900	.000063900	

This falls well within the resolution range but when higher β values are examined, there is a significant rise in error. Maximum error occurs when the wavefunction is missing a dominant higher order harmonic wavefunction. This can be seen in the movement of the peak error as more terms are added in the plot below:



Class 1 equations begin to fail at β values greater than 8 for a 6th order function as the error peaks at $\beta \geq 10$ are not eliminated. To find a sum that may converge faster to the true Ψ class 2 equations are used. These equations are extremely cumbersome and we are only able to calculate them to the 3rd order (8 variational parameters and 144000 terms in the energy equation). The class 2 equation allows each harmonic term in the trial function

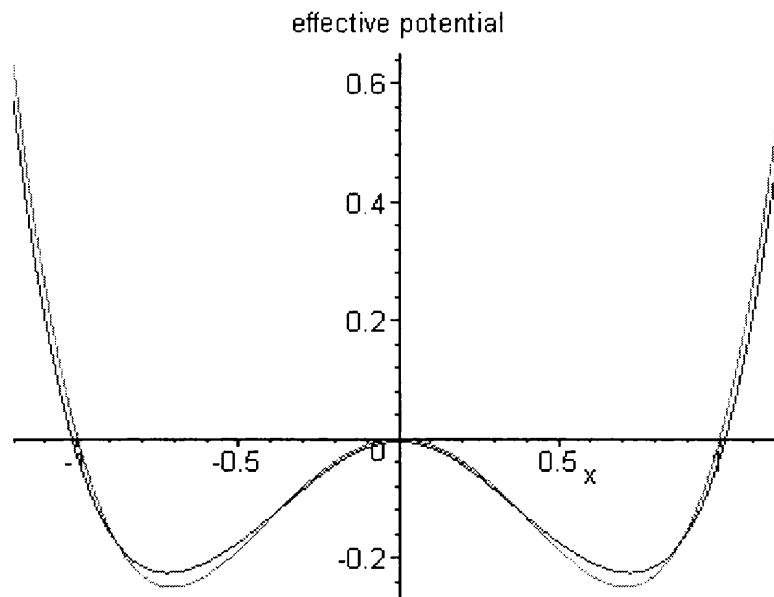
to be shifted and scaled independently of all other harmonics.



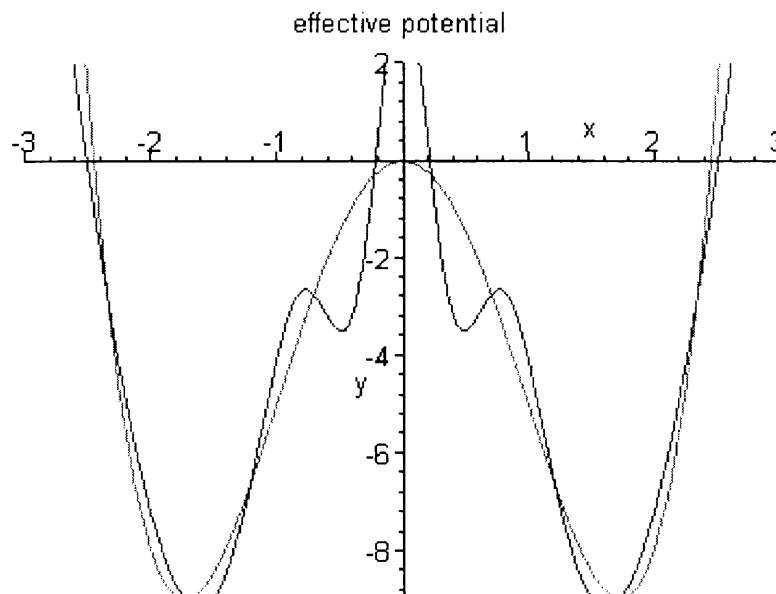
This method allows a much more rapid convergence and gives accurate results for coupling values up to 9. The first term is unaffected by this method as it only consists of one term and therefore does not contain any extra scaling or translating parameters. The 2nd term converges on par with the 4th term without different parameters. The 8 parameter performs slightly better than the highest order class 1 equation examined. This rapid convergence suggests class 1 equations do not allow the difference in shifting towards the origin of the lower and higher order functions.

Finally as a qualitative indicator of the functions validity, the functions effective potential is observed. Plugging the optimized values back in to the original function and solving the Schrödinger equation for its potential we are able to see the exact potential to

the approximate function and how close it compares to the actual potential. In general it was found that the function is accurate at low potentials:



At higher potentials the function became poor near the origin:



The effective potential near zero explodes at large β because the function's value across the boundary approach zero. Thus the potential may become unbounded as the functions become more complex.

In general, it is found that the dominant order harmonic term has a large shifting towards the origin for Gerard functions indicating a strong coupling. The opposite is found for un-Gerard functions: there was a larger separation of the dominant order harmonic term indicating an anticoupling. The implications of this shifting can be explored by looking at the expectation values of the functions.

4.0.4 Expectation Values

We can see why the ground state is a lower energy than the first excited state and what role the coupling properties of the higher order harmonics play through the uncertainties of the function. The Heisenburg uncertainty relation states that the more confined the position of a particle the greater the allowed range in momentum assuming a similar uncertainty or

$$\Delta x \Delta p \geq \frac{1}{2}. \quad (25)$$

Since the particles are moving in random directions at an even distribution of speeds the average momentum is 0, thus we explore the root mean square of the momentum.

Note the following expectation values:

β	Ground		1st excited		
	$\sqrt{\langle x^2 \rangle}$	$\sqrt{\langle p^2 \rangle}$	$\sqrt{\langle x^2 \rangle}$	$\sqrt{\langle p^2 \rangle}$	
1	0.671373881	0.767255287	1.017516356	1.494863803	
2	0.777154698	0.703196647	1.10325483	1.397649325	
3	0.94027211	0.701566767	1.210794229	1.310778074	
4	1.175873432	0.838719394	1.340781276	1.251374668	for n=5
5	1.422366689	1.048317558	1.487447756	1.234624492	
6	1.623826875	1.201513929	1.642694514	1.262791168	
7	1.787097294	1.293673364	1.79091472	1.310210182	
8	1.929581278	1.357194934	1.930327946	1.363205599	
9	2.058828868	1.405778816	2.062728168	1.42548685	
10	2.178566846	1.443789318	2.183506898	1.468119389	

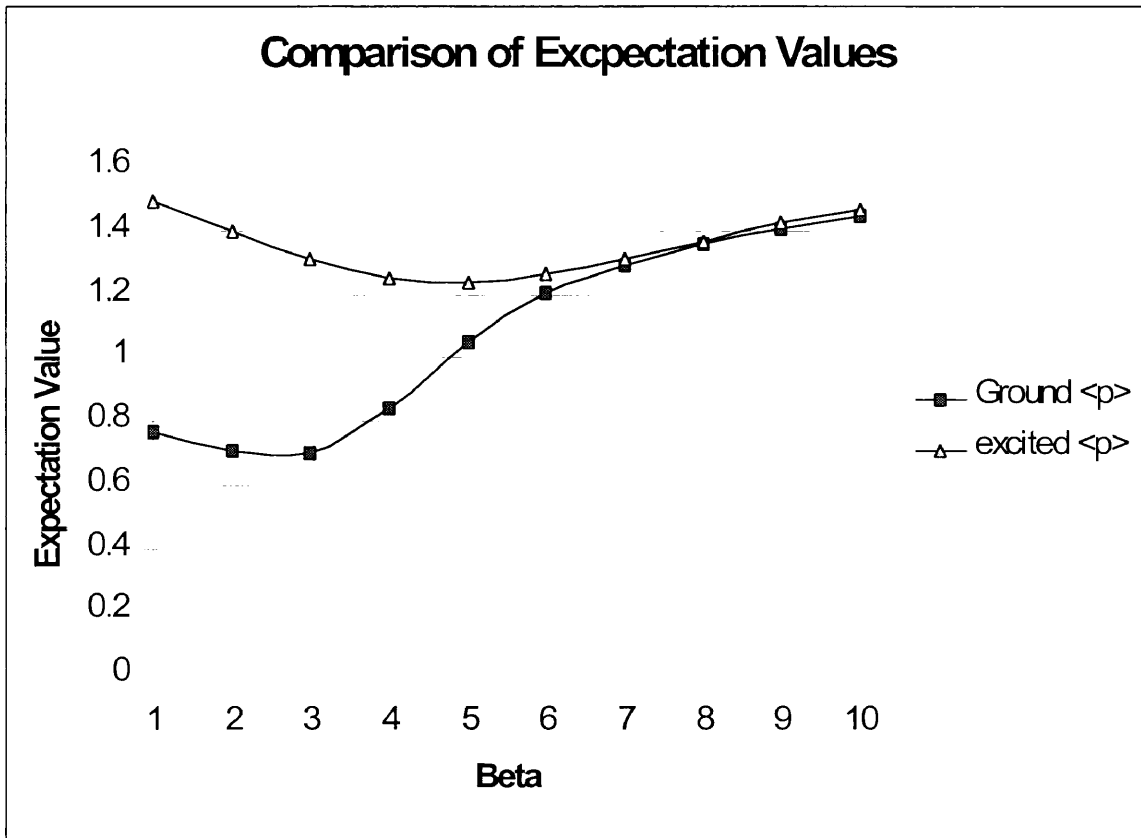
for $\beta = 6$	Ground State		1st excited	
	Δx	Δp	Δx	Δp
<i>Class1</i> ($n = 5$)	1.623826875	1.048317558	1.642694514	1.262791168
<i>Class2</i> ($n = 3$)	1.52431671	1.04357550	1.531332952	1.332564332

Note that the momentum expectation values for the ground state are always smaller

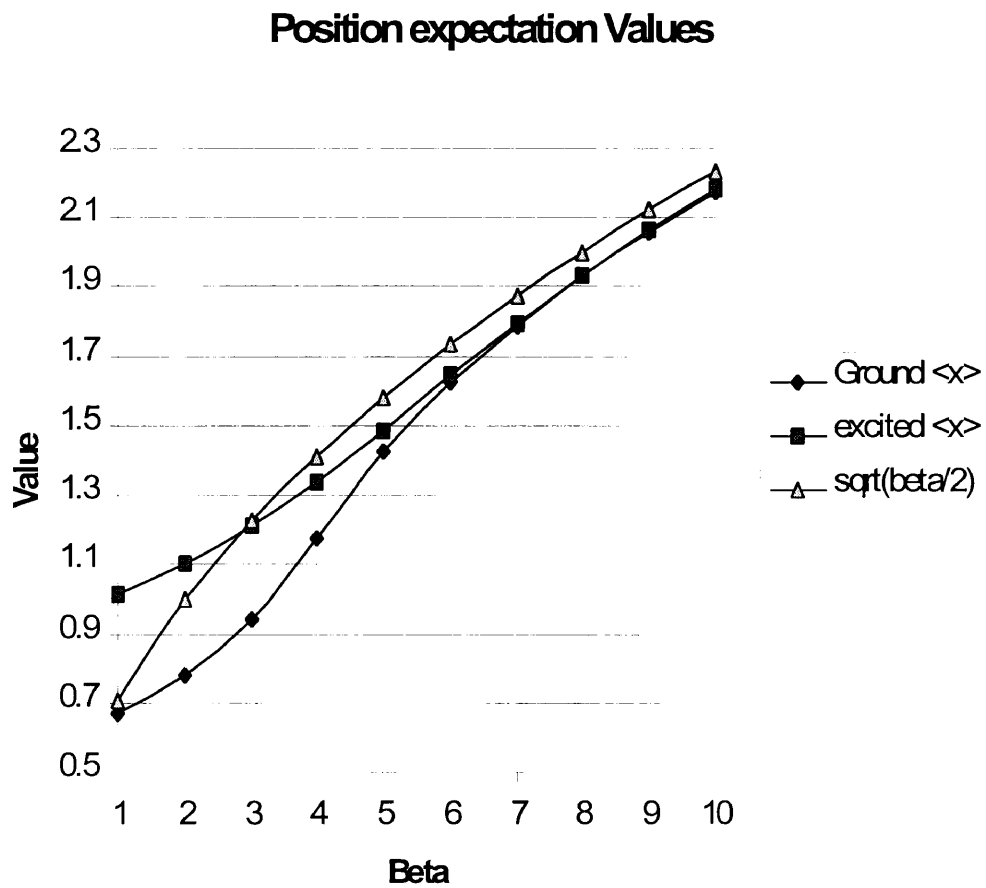
than the 1st excited state. Since

$$KE \propto p^2 \quad (26)$$

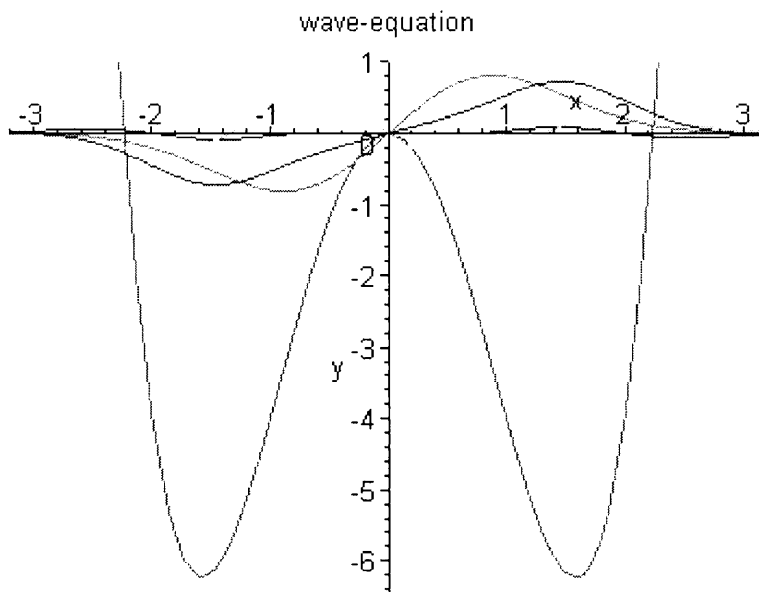
the ground state has a lower energy than the first excited state.



The greater number of nodes in the Schrödinger wave the more restricted the particle. A ground state wave contains no nodes while the first excited wave contains one node. In general all solutions for energy E_n have $n - 1$ nodes. This observation is backed up by the position expectation values. For the ground state, as β increased the position expectation was compared to the minimas of each well. The ground state values were larger than the 1st excited state for all values.

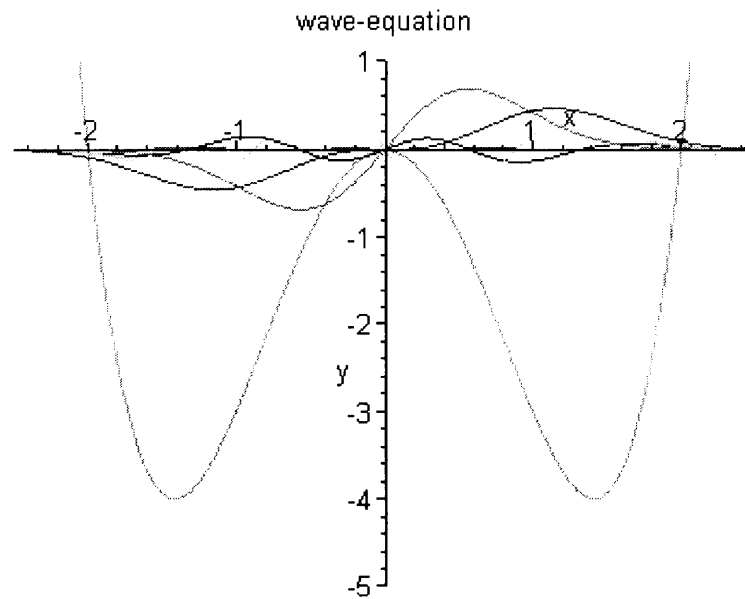


Looking at the first excited state (un-Gerard wavefunction) plots we notice the node at $x = 0$. This results in a zero probability density for this position.

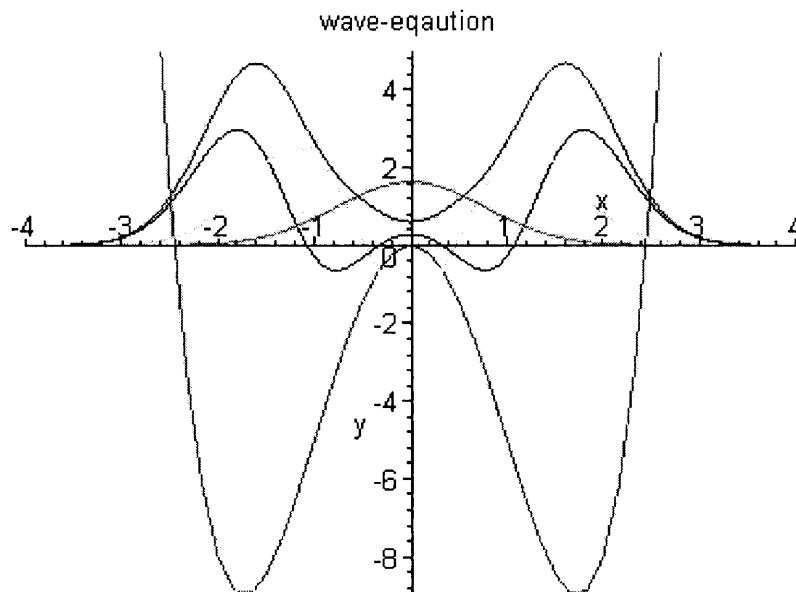


$\beta = 5$ 1st excited state

This node restricts the position uncertainty of the particle. The lowest energy then is attained when the particle is near one of the nuclei, although there is equal probability for the particle to be at either nucleus. The wave function maxima's exhibit this by being farther from the origin than the ground state. The position expectation values also is larger than the ground position expectation values indicating that the particle is closer to the nuclei. Since the particle is restricted to being near one nuclei its momentum uncertainty can be larger, again demonstrating that all un-ground states can not be the lowest energy state. When higher term un-ground functions are examined it can be seen that all orders of functions have a zero node at $x = 0$, indicating none of the harmonics have any coupling across the boundary.

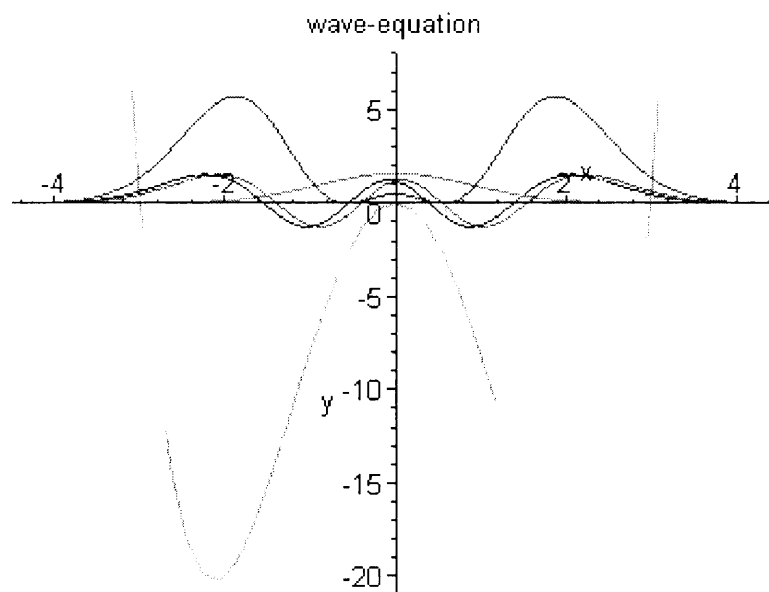


For the ground state it can be seen in the plot the wavefunction is not zero near $x=0$ indicating a probability that the particle is in the boundary region:



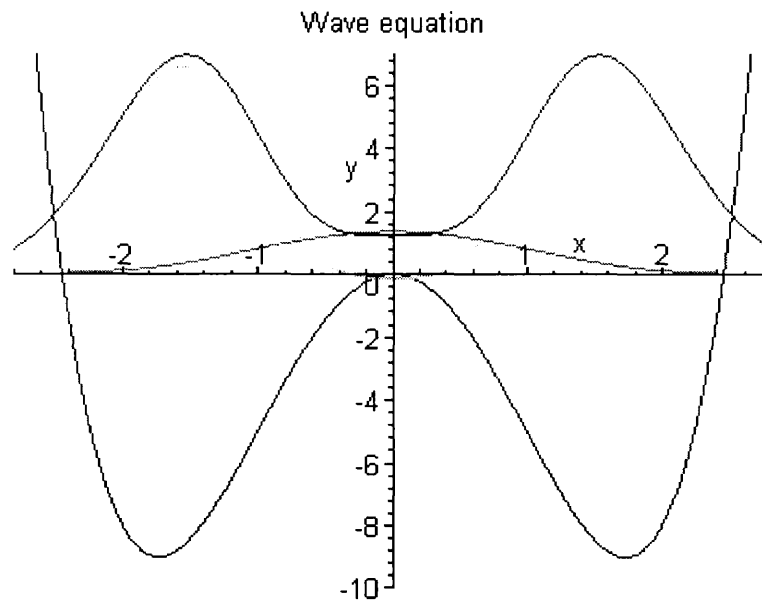
Since the particle is allowed to be in the boundary region the particle has a much larger position uncertainty in relation to the potential minimas. It can also be seen that the

particle peaks are closer to the origin. This means the particle has a higher probability that it will be found closer to the origin, and farther from the nuclei. Since the particle now has the freedom of movement across the molecule it is allowed less freedom of momentum allowing a lower energy. Thus Gerard functions, specifically the first Gerard function, has the lowest energy state. The magnitude of the probability density across the boundary is largely due the dominant harmonic orbital. Looking again at the plot we note the higher order harmonic orbital. It's maxima are found very close to the origin such that it's two components (left and right waves) overlap indicating at strong coupling.

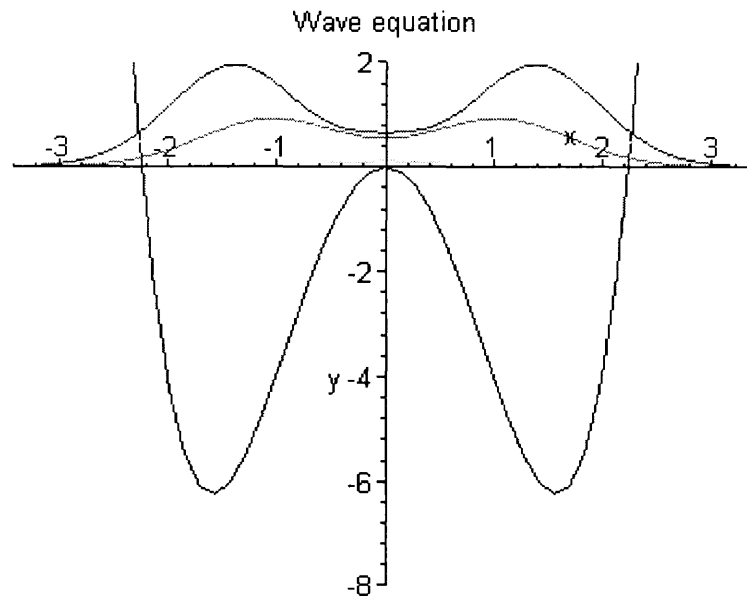


Note highest order harmonic here shown as two functions: Ψ_{left} and Ψ_{right} . They very nearly overlap each other in phase indicating a strong coupling.

The class 1 equations did not reflect as strongly the coupling behavior of the dominant oscillator harmonic term as did the class 2 equations. Observe the following plots



Class 2: 2 harmonic terms.



class 2: 3 term harmonic

In this case the higher order terms, when optimized, translate closer to the origin than the lower order terms. Class 2 equations give a lower energy eigenvalue for equivalent order sums and thus is more indicative of the physical system.

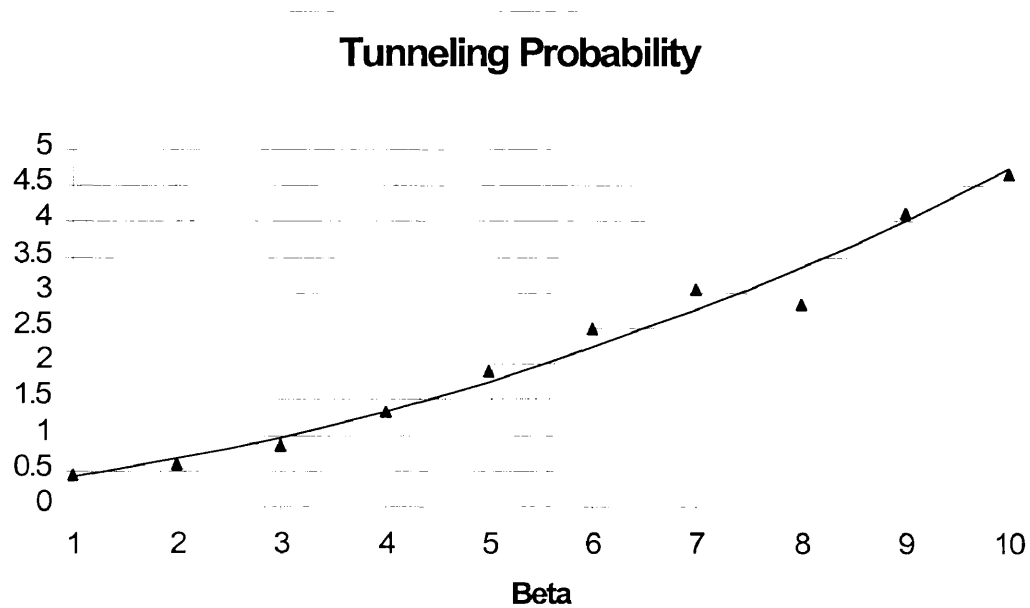
In conclusion, for a very stable solid (i.e a large potential) it is the higher frequency vibrations in the lattice that play the dominant roll in the systems properties.

4.0.5 Tunneling Probability

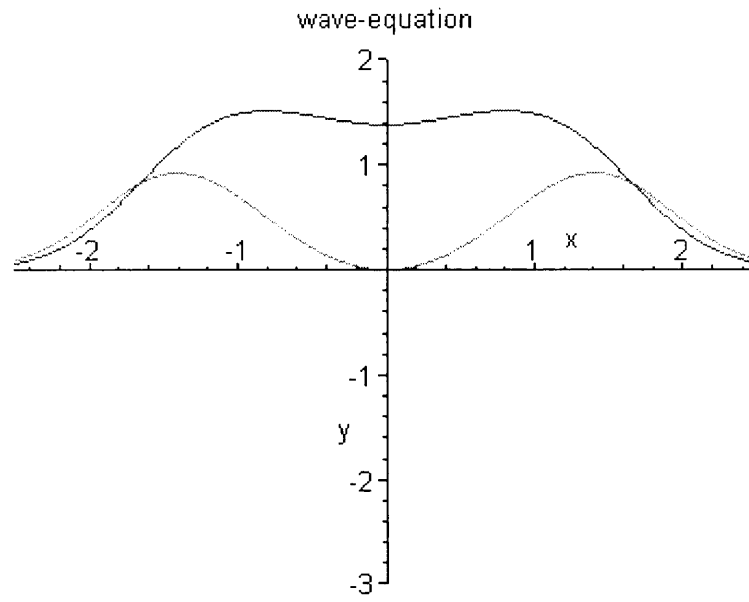
It is of interest to calculate how stable the system is by measuring the tunneling probability, or the probability that the system will change states from Ψ_{ground} to $\Psi_{excited}$ independently of time. The wave will change states from ground to first excited if the electric field potential, V , is satisfied. Each nuclei can be represented as a positive point charge with a static electric field. Each electric field always has a curl of 0 (i.e. $\nabla \times E = 0$) thus at sufficent distance the electric field consists of concentric rings around each nuclei. The potential then is given as:

$$V = xE \quad (27)$$

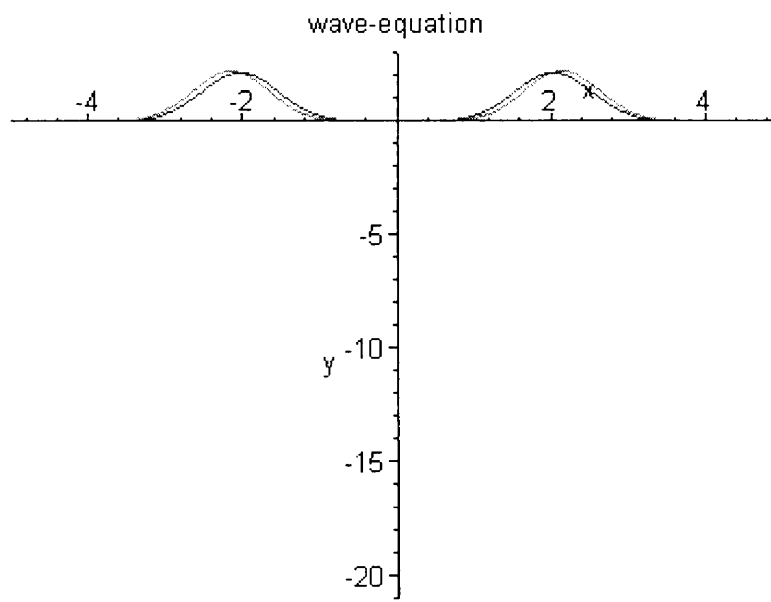
as long as x is perpendicular the electric field lines. [13] In each state our E is discrete thus our potential V is satisfied for some value x . We use this as our Hamiltonian. We then calculate the tunneling probability as given in equation (4).



Tunneling probability increases with increasing depth of wells. This finding is consistent with the very small difference in ground state to 1st excited state energies at large β . This would indicate that a material with strong force centers oscillates very easily between the ground and first excited state. This is easily seen when Ψ_{ground} is compared to $x\Psi_{excited}$. As β increases the functions become almost identical.



$$\beta = 3$$



$$\beta = 9$$

4.0.6 Further Study

It should be noted that we cannot be sure if the optimized parameters we found give us the absolute minima. Further study of an improved method of finding the optimized parameters may solve this problem. Limiting this even further it was found that for very complex terms the truncating error in IMSL increases to a significant level for any $\beta > 10$ and for any further harmonic order terms taken in class 2 equations. For very deep wells it is very high harmonic terms which are needed for accuracy. Also the effective potential seems to indicate larger error near the origin. This effects the observations as we were drawing a correlation of a greater probability distribution at the origin to stronger coupling.

Di mi se mai fu fatta alcuna cosa

Leonardo Da Vinci

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