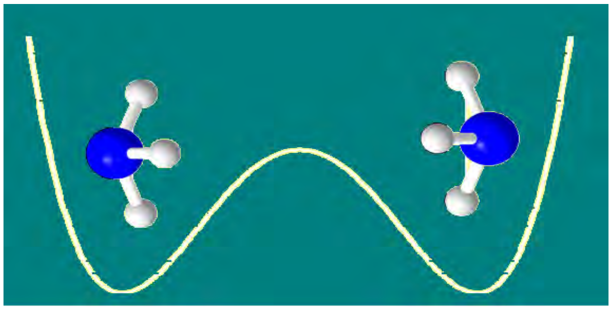
TIME DEPENDENT QUANTUM MECHANICAL APPROACH : CASE STUDIES OF AMMONIA MOLECULE



By

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Dedicated to My family, Wosene and her family

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Abstract

The aim of this thesis work is to implement time dependent Quantum mechanical approaches to study inversion phenomena of ammonia Molecule. This approaches will enable us visualize the time evolution of the orientation of the molecule inside the symmetric double well potentials. To study this approach diffusion Quantum Monte Carlo(DQMC) method, which propagates the time dependent Schrödinger equation in imaginary time, had been used.

Since solving the schrödinger equation exactly with double well potential is not possible, numerical approach had been used. In order to get each energy eigenstates, the time independent Schrödinger equation with symmetric double well potential had been descritised and changed in to eigenvalue problem. The QL and QR algorithm had been used to solve the eigenvalue problem giving us energy eigenstates. The wave functions corresponding to the eigen energy states had also been obtained. In addition to this, the quantum mechanical energy splitting effect had been studied for different symmetrical double well potentials.

The diffusion function will be obtained as a linear combination of the product of wave function of the time independent eigenfunctions which decay exponentially in real time. The probability density, which shows where the Nitrogen atom is most probably to be found, being the square of the diffusion function. The full cycle of the ammonia‘s orientation inside the symmetric double well had been done for different time steps.

Finally comparison between theoretical and computational results had been done for different time steps. The simulations shows that similar results had been found in both theoretical and computational approaches.

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HIRUY TADDESE MENGISTU
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Introduction

The ammonia molecule is pyramidal shaped with the three Hydrogen atoms forming the base and the Nitrogen atom at the top. The Hydrogen atoms form a rigid triangular plane whose axis passes through the Nitrogen atom. The potential energy of the system is thus a function of only one parameter, the distance between the Nitrogen atom and the plane defined by the three Hydrogen atoms. This potential energy is modelled by double well potential which is symmetrical about the plane of Hydrogen atoms which reflects the repulsion between the Nitrogen and Hydrogen atoms [1]. The double minima represents the possible positions of Nitrogen atom with respect to the plane defined by the three Hydrogen atoms. We take this direction to define an x-axis of coordinates, with x=0 being at the plane of the Hydrogen atoms.

The classical description of the encounter between moving Nitrogen and the double well potential barrier is quite straightforward. If the Nitrogen atom is located in one of the wells and does not have sufficient energy to overcome the potential barrier, it will be confined forever inside that well. If, on the other hand, its energy is larger than the height of the potential barrier its motion will not be significantly affected by the barrier when it continues to move across.

The quantum mechanical description of the same encounter between a Nitrogen and the potential barrier leads to predictions that exhibit essential differences from the

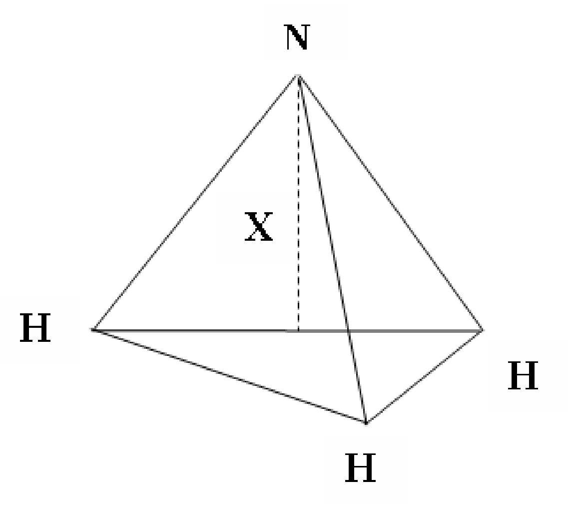

Figure 1: Geometry of Ammonia molecule

classical model. According to quantum mechanics, a quantum particle may pass through a potential barrier even if its energy is smaller than the height of the barrier. This quantum mechanical effect is popularly known as tunnelling. Ammonia molecule, which has symmetric double well potential, will have two possible orientations due to the tunnelling effect. This effect on ammonia is called ammonia inversion. Classically, the ammonia molecule in its ground state does not have enough energy to go over the barrier. Therefore, a classical ammonia molecule will not experience inversion.

The tunnelling phenomenon also results in a splitting of the ground state vibrational level of the Nitrogen atom into two levels with different energy values. These states would have been degenerate with out the tunnelling effect [2]. The energy level splitting resulting from barrier penetration is an important quantum mechanical effect.

The energy of ammonia is determined by the translational, rotational, and vibrational components. However in this thesis work, we will only be interested in the motion of the Nitrogen atom along a direction normal to the plane of the Hydrogen atoms by taking the molecule to be in a fixed state as regards of other degrees of freedom.

To study the inversion phenomenon of ammonia, time dependent quantum mechanical approach had been used for the first time. The work employs essentially a diffusion Quantum Monte Carlo (DQMC) method, based on propagating the time dependent Schrödinger equation (TDSE) in imaginary time. Since solving analytically the time independent schrödinger equation with double well potentials is not possible, descretization with the symmetric double well potential had been done to give eigenvalue problem. The coefficient matrix of the eigenvalue problem is tridiagonal matrix. The QL and QR algorithm had been used to solve the eigenvalue problem to get the energy eigenvalues with no need of changing the coefficient matrix of the eigenvalue problem into tridiagonal matrix since we had it from the very beginning. Going back to time independent Schrödinger equation, using the energy eigenvalues found, we will get the wave functions for each corresponding eigen energy states.

Finally the diffusion function has been obtained as a linear combination of the wave functions of time independent schrödinger equation (TISE) which decays exponentially in real time. The probability density, which will show the position of the Nitrogen atom, is taken by squaring the diffusion function.

The outline of the thesis is as follows. Chapter one discusses about double well potentials. In chapter two tunnelling effect and ammonia inversion is discussed. The new time dependent approach used, Diffusion Quantum Monte Carlo, is discussed in chapter three. Mathematical formulations used for the work is formulated in chapter three. Mathematical formulation are discussed in chapter four. Finally, result and discussion are discussed in chapter five while the final chapter is devoted to conclusion and future directions.

Chapter 1

Double well potentials

Double well potentials arise when motion around two stable positions is possible. The general form of double well potentials is given as [3].

$$V(x) = -\lambda X^2 + KX^4, (\lambda, K > 0) \tag{1.0.1}$$

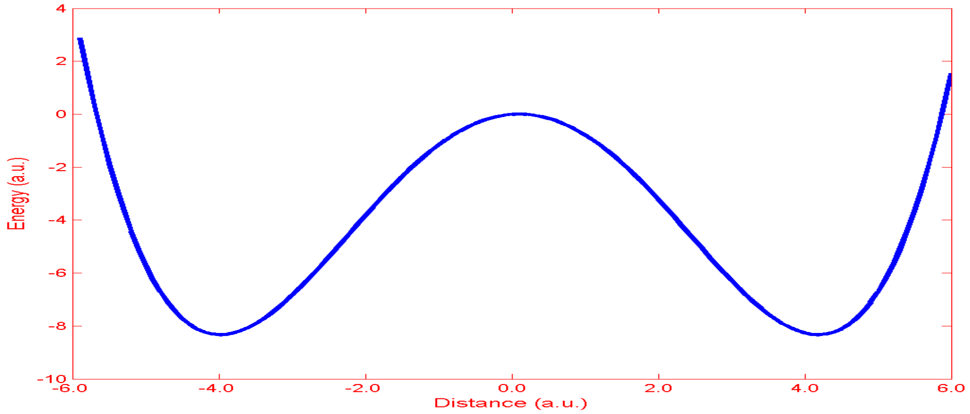

Figure 1.1: General form of Symmetric Double well potentials

In Fig.1.1 we have two minima of the symmetric double well potential which correspond to two symmetrical configurations of the molecule in the case of quantum mechanics. In the case of symmetric potentials, $V(x) = V(-x)$, the wave functions are either symmetric or asymmetric. That is to say, the wave functions must have either even or odd parity, $\Psi(x) = \pm\Psi(-x)$, with respect to change of sign of position x [4, 5]. This is because of the fact that they are functions of symmetric potential with the same eigenvalue energy.

If two similar potential wells are separated by a barrier then their energy eigenvalues will be degenerate. But if the two similar wells are combined to form a single symmetric double well potential then the energy eigenvalues will no more become degenerate. Energy splitting will occur because of the tunnelling effect happening inside the double well.

The time independent Schrödinger equation has no analytical solution with double-well potentials. The only methods to solve is to use approximate methods or numerical methods [6]. In the next chapter we will see the quantum mechanical tunnelling effect and the behavior of ammonia molecule due to this effect inside the symmetric double well potential.

Chapter 2

Quantum mechanical tunnelling and Ammonia inversion

2.1 Quantum mechanical tunnelling

Quantum mechanical tunnelling is one of the most intriguing properties of matter and fundamental in numerous phenomena in physics and chemistry. It is one of the most striking illustrations of the qualitative difference between quantum mechanics and classical mechanics. In quantum mechanics a quantum particle can tunnel a region in which the potential energy function exceeds the total energy of the particle. To surmount a barrier of height V, a particle with energy E must ”borrow” an amount of energy $V - E$, where $V > E$. According to the quantum mechanical tunnelling, this energy must be ”repaid” after the particle tunnelled through the barrier.

We now turn to a more detailed discussion of effects associated with the penetration of the wave function into the classically forbidden region. Consider first a potential well bounded by barriers of finite height and width as in Fig. 2.1. The wave function decays exponentially in the classically forbidden region and is still non-zero at the points $x = b$. In the regions where $x > b$, however, the total energy is again greater than the potential energy and the wave function is again oscillatory. It follows that there is a probability of finding the particle both inside and outside the potential well and also at all points within the barrier. Quantum mechanics therefore implies that a particle is able to pass through a potential energy barrier which would have been impenetrable according to classical mechanics.

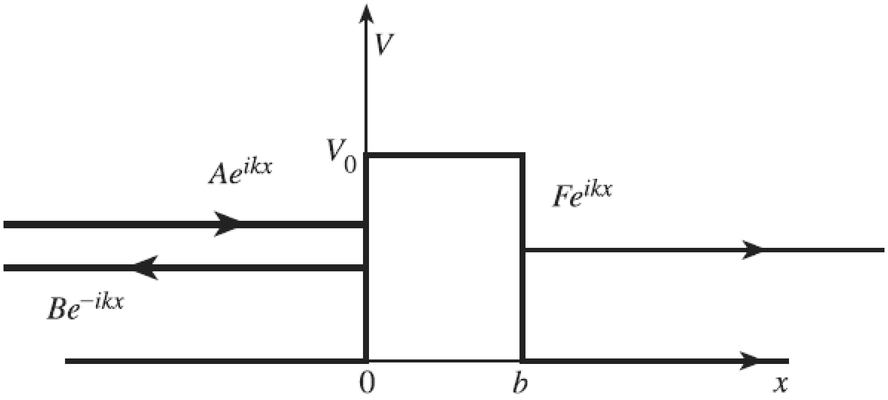

Figure 2.1: A beam of particles incident on a potential barrier.

To study the tunnelling effect in more detail we consider the case of a beam of particles of momentum $\hbar k$ and energy $E = \hbar^2 k^2/2m$ approaching a barrier of height V_0 (where $V_0 > E$) and width b (Fig. 2.1). A fraction of the particles will be reflected at the barrier with momentum $-\hbar k$, but some will tunnel through to emerge with momentum $\hbar k$ at the far side of the barrier. The incident, transmitted and reflected beams are all represented by plane waves, so the wave function on the incident side, which we take to be $x < 0$, is

$$\Psi_1(x) = Ae^{i\mu x} + Be^{-i\mu x} \tag{2.1.1}$$

where

$$\mu = \sqrt{\frac{2mE}{\hbar^2}}$$

Inside the barrier the wave function has the same form:

$$\Psi_2(x) = Ce^{\lambda x} + De^{-\lambda x} \tag{2.1.2}$$

where

$$\lambda = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

and beyond the barrier, which is the region $x > b$, particles may emerge moving in the positive x direction, so the wave function will have the form

$$\Psi_3(x) = FAe^{i\mu x} \tag{2.1.3}$$

We note that because the barrier does not reach all the way to infinity, we cannot drop the first term in Eqn.(2.1.2) as we did in the square-well case.

The boundary conditions requiring both Ψ and $d\Psi/dx$ be continuous at $x = 0$ and $x = b$ can be applied in much the same way as before. These conditions lead to

$$A + B = C + D \tag{2.1.4}$$

$$A - B = \frac{\lambda}{i\mu}(C - D) \tag{2.1.5}$$

$$Ce^{\lambda b} + De^{-\lambda b} = Fe^{i\mu b} \tag{2.1.6}$$

and

$$Ce^{\lambda b} - De^{-\lambda b} = \frac{i\mu}{\lambda} Fe^{i\mu b} \tag{2.1.7}$$

Adding Eqns.(2.1.4) and (2.1.5), we obtain

$$2A = (1 + \frac{\lambda}{i\mu})C + (1 - \frac{\lambda}{i\mu})D \tag{2.1.8}$$

and adding Eqns. (2.1.6) and (2.1.7), we get

$$2Ce^{\lambda b} = (1 + \frac{i\mu}{\lambda})Fe^{i\mu b} \tag{2.1.9}$$

and

$$2De^{-\lambda b} = (1 - \frac{i\mu}{\lambda})Fe^{i\mu b} \tag{2.1.10}$$

We can combine Eqns.(2.1.9) and (2.1.10) to express F in terms of A as

$$\frac{F}{A} = \frac{4i\mu\lambda e^{-i\mu b}}{(2i\mu\lambda + \lambda^2 - \mu^2)(e^{-i\lambda b} + 2i\mu\lambda - \lambda^2 + \mu^2)e^{\lambda b}} \tag{2.1.11}$$

The fraction of particles transmitted is just the ratio of the probabilities of the particles being in the transmitted and incident beams, which is just $|F|^2/|A|^2$ and can be evaluated directly from Eqn.(2.1.11). In nearly all practical cases, the tunnelling probability is quite small, so we can ignore the term in $e^{(-\mu b)}$ in Eqn.(2.1.11). In this case the tunnelling probability becomes

$$\frac{|F|^2}{|A|^2} = \frac{16\lambda^2\mu^2 e^{-2\lambda b}}{(K^2 + k^2)^2} = \frac{16(V_0 - E)}{(V_o)^2} e^{(-2\lambda b)} \tag{2.1.12}$$

The tunnelling probability, which is greater than zero, proves that there is a probability for a particle to appear in other side of the potential barrier V_0, even in cases where the energy of the incoming particle is less than the potential barrier. So far we had seen the tunnelling effect happening for a given potential barrier, in the next section we will be focusing on the tunnelling phenomena of ammonia molecule inside symmetric double well potential, which is the target of this work.

2.2 Ammonia inversion

As we saw in the previous section, quantum mechanics predicts that a quantum particle can pass a potential barrier even if the particle has an energy less than the barrier's height. It has a finite probability to cross and tunnel the barrier to the other side of the barrier. Chemical systems characterized by a two minima potential, like ammonia are good examples of quantum tunnelling. In the case of ammonia this phenomena of tunnelling is characterized by energy difference between the first two energy levels.

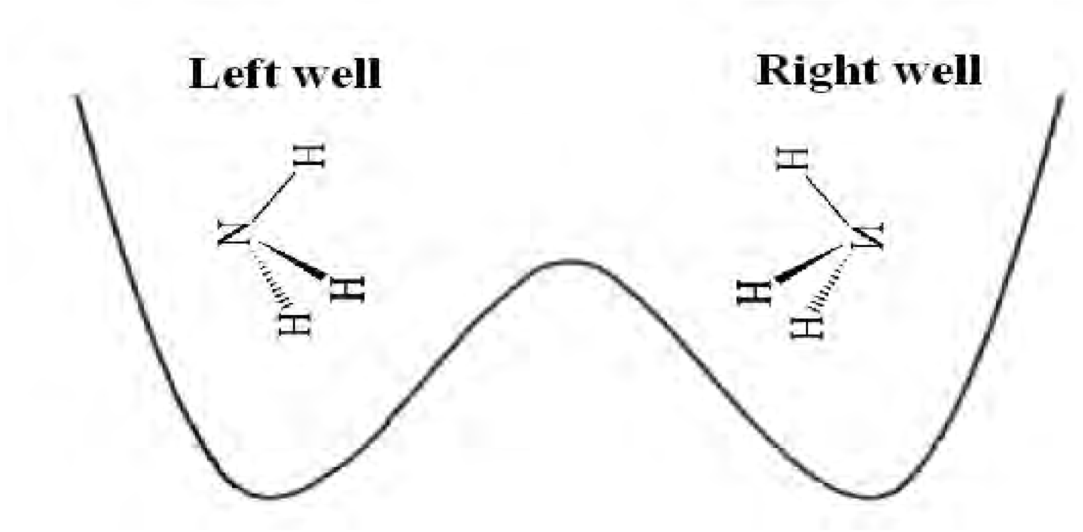

Figure 2.2: Ammonia molecule inside the two possible positions

Now we will consider the case for ammonia molecule and proceed to see its features inside the double well potentials. Obviously Nitrogen atom is at one of the two symmetric equilibrium positions of the double well potentials (Fig.2.2). Since both regions are equilibrium positions, the potential energy for the motion of the Nitrogen atom along the axis of the tetrahedron must have two minima and have the symmetry with the potential barrier between the two regions. If Nitrogen atom is initially inside left well then it may eventually leak through the potential barrier and appear inside the right well.

Based on the quantum mechanical tunnelling, the ammonia molecule will have two possible orientations, turning in and out like umbrella (Fig. 2.2). This phenomenon is called ammonia inversion. An important real life application of the inversion doubling of ammonia is the ammonia maser. This motion is hindered by the double well potentials barrier. Tunnelling give rise to an energy splitting of states. These states would have been degenerate with out tunnelling and would be localized on either side of the potential barrier.

The hindered inversion motion in NH_3 can be analyzed on the basis of symmetry arguments. This analysis leads to a better understanding of quantum tunnelling happening inside the double well potential. Now take two wave functions, Ψ_s and Ψ_a, which represent wave functions where the Nitrogen atom is predominantly localized left and right of the plane, X = 0, respectively. Where Ψ_s and Ψ_a are eigen function of energy eigenvalue E_s and E_a , the first symmetric and asymmetric energy eigenvalues. Such wave functions, predominantly localized in one well but spilling over into the other well, are solutions to the Schrödinger equation. However, they do not satisfy the requirement that energy eigen states of this equation have definite parity when the potential is symmetric. One can form a linear combination of $\Psi_L(x)$ and $\Psi_R(x)$ which does satisfy this requirement as [1, 5, 9]:

$$\Psi_R(x) = \frac{1}{\sqrt{2}}(\Psi_s(x) + \Psi_a(x)) \tag{2.2.1}$$

and

$$\Psi_L(x) = \frac{1}{\sqrt{2}}(\Psi_s(x) - \Psi_a(x)) \tag{2.2.2}$$

Ψ_L can represent ammonia molecule with the Nitrogen atom on the left of the triangular plane of the three Hydrogen atoms while Ψ_R can show the opposite orientation of the Nitrogen atom , right of the triangular plane. In addition to these the two wave functions satisfy the parity requirement with Ψ_R having even parity and Ψ_L having odd parity.

The motion of a wave packet which represents the particle in symmetric double-well, under certain condition, is taken from the superposition of the eigenfunctions of the two lowest states of the system. When this happens then the wave packet oscillates between the two wells with a well defined frequency, periodic inversion, and it also preserves its shape after successive back and forth tunnelling.

Table -1 gives the first eight energy levels of NH_3 . The symbol s and a refer to symmetric and asymmetric character of the corresponding wave functions respectively.

Energy level	Energy in ev
0a	0.00
0s	9.84×10^{-5}
1a	0.1178
1s	0.1222
2a	0.1980
2s	0.2367
3a	0.2950
3s	0.3547

Table-1 Energy eigenvalues of Ammonia molecule[7]

Emission or absorption of radiation in a region of spectrum corresponds to a transition between the two energy levels. When an atom becomes excited it can then spontaneously return to the lower level by spontaneous emission. If there is a radiation of the same frequency incoming at the moment the molecule is at excited state, then it's impossible for the incoming radiation to be absorbed since the molecule is already in excited state. The incoming radiation can stimulate the molecule to emit its energy in the form of radiation. This will be emitted before the corresponding spontaneous emission. Thus it follows that such process of amplification can take place if there is a large number of atoms or molecules in the excited state [8].

The two first stationary inversion states have different energies, and the transition frequency between them is around 24 GHz [8]. It turns out that the energy difference corresponds to a frequency in the microwave region. This was the break through to the invention of MASER (Microwave Amplification by Stimulated Emission of Radiation). Townes, Basov and Prokhov had shared the 1964 Nobel prize in physics, for fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the Maser-Laser principle [8].

Ammonia molecules spontaneously emits microwaves at a frequency of 24 GHz, and that spontaneous emission could stimulate other excited ammonia molecules to emit at the same frequency, building up a signal that oscillated on its own. Alternatively, an external 24-GHz signal could stimulate the ammonia molecules to emit at 24 GHz, amplifying the signal.

On the classical theory we picture the Nitrogen atom flipping back and forth at a characteristic frequency of about 24,000 million vibrations per second. At any given instant the Nitrogen atom is on one side of the Hydrogens or on the other. From the quantum point of view the Nitrogen atom at a given time has a certain probability of being on either side of the double well, in a sense it is partly on both sides.

One real application of ammonia maser was in construction of the first atomic clock, a device that uses an internal frequency of atoms (or molecules) to measure the passage of time. An atomic clock relies on counting periodic events determined by the difference of two different energy states of an atom. A transition between two energy states with energies E_1 and E_2 may be accompanied by the absorption or emission of a photon (particle of electromagnetic radiation). These clocks are the most accurate time standards known. A basic advantage of atomic clocks is that the frequency-determining elements, atoms of a particular molecule are the same everywhere. Thus, atomic clocks constructed and operated independently will measure the same time interval. So far we have seen the tunnelling phenomena happening inside ammonia‘s double well potential and the application of ammonia maser. In the next chapter we will be focusing on the diffusion quantum Monte Carlo method, the time dependent approach used to study ammonia's inversion.

Chapter 3

Diffusion Quantum Monte Carlo (DQMC)

The one dimensional time dependent Schrodinger equation is

$$H\Psi(x,t) = i\frac{\partial\Psi(x,t)}{\partial t} \tag{3.0.1}$$

where $\Psi(x,t)$ is the time dependent wave function and H is the Hamiltonian given as

$$H = -\frac{\hbar^2 d^2}{2mdx^2} + V(x) \tag{3.0.2}$$

Diffusion-type equation similar to the random-walk Quantum Monte Carlo equation can be taken by first assuming the validity of Eqn.(3.0.1) in imaginary time τ and then replacing τ by it, where t is real time. Replacing the wave function $\Psi(x,t)$ in Eqn.(3.0.1) by a diffusion function $R(x,\tau)$ transforms the time dependent schrödinger equation(TDSE) into diffusion-type equation as

$$HR(x,\tau) = -\frac{\partial R(x,\tau)}{\partial t} \tag{3.0.3}$$

We can write $R(x,\tau)$ as [9]

$$R(x,\tau) = C_0\phi_0(x) + \sum_{i=1}^{\infty} C_i\phi_i(x)e^{-(E_i-E_0)\tau} \tag{3.0.4}$$

where ϕ_i is solution to the time independent Schrödinger equation(TISE) with energy eigenvalue E_i. C_i are linear time independent coefficients. E_o and ϕ_o refer to the ground state. Eqn.(3.0.4) indicates that at any non zero finite time, $R(x,\tau)$ is linear combination of TISE eigen functions, ϕ_i, with time dependent coefficients which decay exponentially in real time. The probability density of Nitrogen atom will be R^2. In the next chapter we will see briefly all the mathematical formulations used.

Chapter 4

Mathematical formulations

4.1 Eigenvalue problem

In this section we will be dealing with forming an eigenvalue problem of the time independent Schrödinger equation with symmetric double well potential which will enable us get the energy eigenvalues associated with a symmetric double well potential. Once the energy eigenvalues are found then the corresponding eigen functions can be found. The TISE has a general form as

$$H\Psi(x) = E\Psi(x) \tag{4.1.1}$$

where

$$H = -\frac{\hbar^2 d^2}{2mdx^2} + V(x)$$

Descretizing from X_{min} to X_{max} with step size h given by

$$h = \frac{X_{max} - X_{min}}{N}$$

we obtain

$$\frac{-\hbar^2(\Psi(x_k+h)) - 2\Psi(x_k) + \Psi(x_k-h))}{2mh^2} + V(x)\Psi(x) = E_n\Psi(x_k) \tag{4.1.2}$$

where N is the number of descritisations done between X_{min} and X_{max}. Eqn.(4.1.2) can be rewritten in short form as

$$d_k\Psi_k + e_{k-1}\Psi_{k-1} + e_{k+1}\Psi_{k+1} \tag{4.1.3}$$

where

$$d_k = \frac{2}{h^2} + V_k$$
$$e_k = \frac{-1}{h^2}$$

Finally we will get a matrix form of this equation:

$$\begin{pmatrix} d_1 & e_1 & & & & & \\ e_1 & d_2 & e_2 & & & & \\ & e_2 & d_3 & e_3 & & & \\ & & \ddots & \ddots & \ddots & & \\ & & & \ddots & \ddots & \ddots & \\ & & & & & d_{N-2} & e_{N-2} \\ & & & & & e_{N-2} & d_{N-1} \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \vdots \\ \vdots \\ \Psi_{N-2} \\ \Psi_{N-1} \end{pmatrix} = E \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \vdots \\ \vdots \\ \Psi_{N-2} \\ \Psi_{N-1} \end{pmatrix} \tag{4.1.4}$$

This is a matrix with tridiagonal matrix of dimension of $N-1 \times N-1$ and will thus yield $N-1$ eigenvalues. It is important to notice that we do not set up a matrix of dimension $N \times N$ since we can fix the value of the wave function at $K = N$. Similarly we know that wave function at the other end point, that is the initial X_0. In short the matrix form in Eqn.(4.1.4) can be rewritten as a matrix eigen value problem:

$$AX = \lambda X \tag{4.1.5}$$

where A is the coefficient matrix , λ is the eigenvalue and X is the eigenvector. Evidently Eqn.(4.1.5) can hold only if

$$det|A - \lambda X| = 0 \tag{4.1.6}$$

where A is the coefficient matrix, λ is the eigen value and X is the eigenvector. This proves that there are always N (not necessarily distinct) eigenvalues. Root-searching in the characteristic Eqn.(4.1.6) is usually a very poor computational method for finding eigenvalues. In the next section we will see a better method to solve the eigenvalue problem, the **QL**/**QR** method.

4.2 The QR and QL algorithm

Now we will use the **QR** and **QL** algorithm to obtain the required eigenvalues from the triadiagonal matrix obtained. The basic idea behind the **QR** algorithm is that any real matrix $\mathbf{A}_1$ can be decomposed into the form [10]:

$$A_1 = Q_1.R_1 \tag{4.2.1}$$

where $\mathbf{Q}_1$ is orthogonal and $\mathbf{R}_1$ is upper triangular matrix. From Eqn.(4.2.1) it follows that

$$Q_1^{-1} A_1 Q_1 = R_1 Q_1 = A_2 \tag{4.2.2}$$

We now factorize A_2 to obtain

$$A_2 = Q_2.R_2 \tag{4.2.3}$$

where, as before $\mathbf{Q}_2$ is orthogonal and $\mathbf{R}_2$ is upper triangular matrix. From Eqn.(4.2.3) we can obtain A_3 and so on. The process will continue to construct a sequence of $A_1, A_2, A_3, ..., A_k$ where

$$A_k = Q_k.R_k \tag{4.2.4}$$

There is nothing special about choosing decomposition of $\mathbf{A}_1$ into upper triangular matrix **R**. We can make it lower triangular matrix . This is called the **QL** algorithm. Since

$$A_1 = Q_1.L_1 \tag{4.2.5}$$

where $\mathbf{L}_1$is lower triangular matrix and $\mathbf{Q}_2$ is orthogonal matrix. The **QL** algorithm consists of similar sequence as the **QR** case.

The factorization into upper triangular matrix and orthogonal matrix can be carried out by performing premultiplication upon the the given matrix A_1 by orthogonal matrix P of the form $I - 2VV^T$ so as to successively reduce the column of A_1. Where V is a vector of the form

$$V = [0, v_1, v_2, v_3, ...v_n]^T \tag{4.2.6}$$

and with the property

$$V^TV = 1 \tag{4.2.7}$$

Thus P_1A_1 contains zeros in its first column, $P_2P_1A_1$ will have zeros in its second column below the diagonal, and so on. By carrying out this procedure with each column of A_1, we obtain an upper triangular matrix, so that we have

$$R = P_{n-1}P_{n-2}....P_2P_1A_1 \tag{4.2.8}$$

to complete the construction, we define the orthogonal matrix as

$$Q^T = P_{n-1}P_{n-2}....P_2P_1 \tag{4.2.9}$$

so that

$$A_1 = QR \tag{4.2.10}$$

the sequence will converge to a matrix where the eigenvalues appear on the diagonal with increasing order of absolute magnitude [9]. In the next chapter we will be discussing computationally obtained results and also comparison with the theoretical results.

Chapter 5

Results and discussions

5.1 Wave functions and time evolution of Ammonia molecule

We have remarked that the energy eigenstates of NH_3 have symmetry about x=0 and do not give a definite left-right preference to the location of the Nitrogen. On the other hand, they give states of the molecule that correspond to a classical motion of equilibrium. The symmetric and asymmetric wave functions obtained are obtained as shown in Fig. 5.1 and Fig. 5.2 respectively.

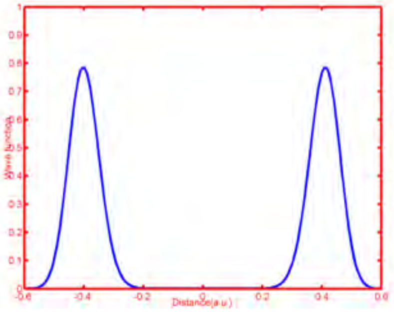

Figure 5.1: Ground state (symmetric) wave function

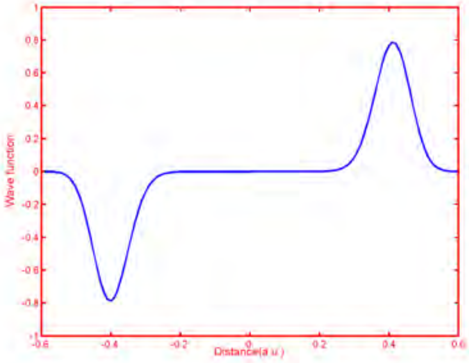

Figure 5.2: First excited state (asymmetric) wave function

In Fig.5.3 the probability density assuming the Nitrogen atom is initially inside the right. Fig.5.4 shows that the Ammonia molecule had shifted its position from right to left in half a period time. After a full period of inversion the the ammonia molecule is back to its original position, left well, Fig.5.5.

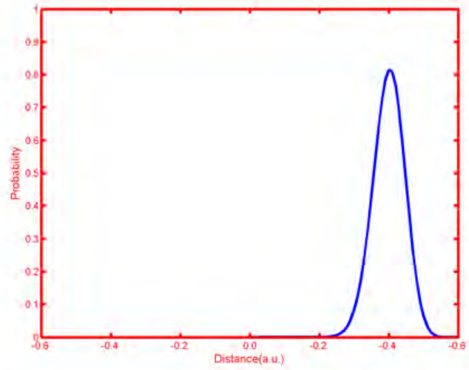

Figure 5.3: Probability density for Orientation of Nitrogen atom after time, t=0

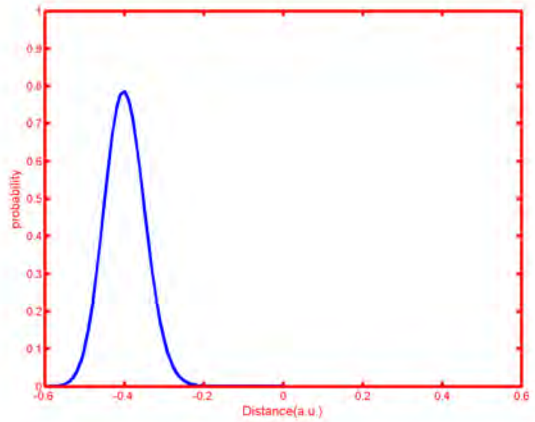

Figure 5.4: Probability density for Orientation of Nitrogen atom after time, t=T/2

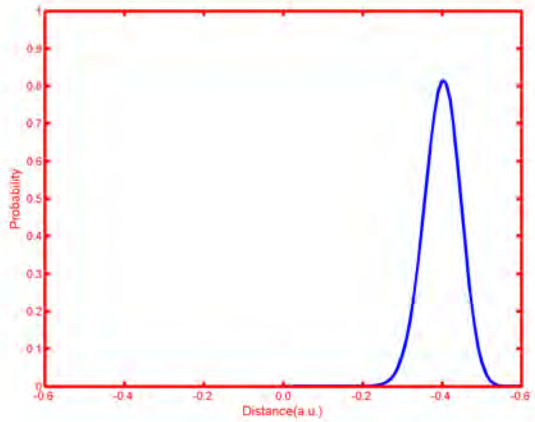

Figure 5.5: Probability density for Orientation of Nitrogen atom after time, t=T

These results can be compared with the theoretical solution of time dependent Schrödinger equation, Eqn.(3.0.1), whose solution is given as

$$\Psi(x,t) = \Sigma_{i=1}^{\infty} C_i \Psi_i(x) e^{(-iE_i t/\hbar)} \tag{5.1.1}$$

where C_i is constants and Ψ_i is solutions of the time independent Schrödinger equation corresponding to E_i, where E_i is the i^{th} energy state. Taking the first two wave functions, symmetric and asymmetric, the time dependent wave function of two-level energy system will be

$$\Psi(x,t) = C_1\Psi_1 e^{-iE_1t/\hbar} + C_2\Psi_2 e^{-iE_2t/\hbar} \tag{5.1.2}$$

Taking the same initial assumption, the Nitrogen atom being inside the right well, for the orientation of Nitrogen atom as done for the computational case: the initial wave function will be given by Ψ_R as

$$\Psi(x,t=0) = \Psi_R = C_1\Psi_1 + C_2\Psi_2 \tag{5.1.3}$$

To satisfy the condition that the Nitrogen atom is on the right well the coefficients C_1 and C_2 must be taken as

$$C_1 = C_2 = \frac{1}{\sqrt{2}} \tag{5.1.4}$$

Substituting the values of C_1 and C_2 into Eqn.(5.1.3) we will have the wave function

$$\Psi(x,t) = \frac{1}{\sqrt{2}}(\Psi_1 e^{-iE_1t/\hbar} + \Psi_2 e^{-iE_2t/\hbar}) \tag{5.1.5}$$

$$\Psi(x,t) = \frac{1}{\sqrt{2}}(\Psi_1(x,t) + \Psi_2(x,t)e^{-2i\pi\nu t})e^{-iE_1t/\hbar} \tag{5.1.6}$$

We have $\triangle E = h\nu$. At time $t = 1/(2\nu)$, half a period, the wave function in Eqn.(5.1.6) will be given by Ψ_L

$$\Psi(x,t=1/(2\nu)) = \Psi_L = \frac{1}{\sqrt{2}}(\Psi_1(x) - \Psi_2(x))e^{-iE_1t/\hbar} \tag{5.1.7}$$

The probability density will be

$$|\Psi(x, t = 1/(2\nu))|^2 = |\Psi_L|^2. \tag{5.1.8}$$

At time $t = 1/(\nu)$, full period, the wave function is given by

$$\Psi(x, t = 1/(\nu)) = \Psi_R = \frac{1}{\sqrt{2}}(\Psi_1(x) + \Psi_2(x))e^{iE_1 t/\hbar} \tag{5.1.9}$$

The probability density will be

$$|\Psi(x, t = 1/(\nu))|^2 = |\Psi_R|^2. \tag{5.1.10}$$

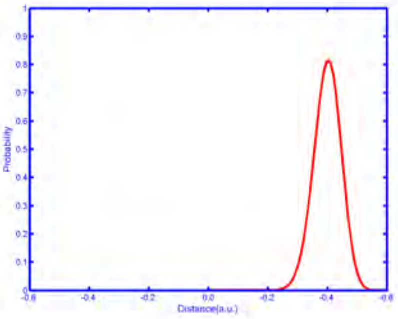

Figure 5.6: Probability for Orientation of Nitrogen atom after time, t=0(Theoretical)

From the theoretical results taken, Fig.5.5, 5.7, and 5.8 by assuming that the Nitrogen atom is initially inside the right well, it can be seen that the Nitrogen atom is most probably to be found inside the left well at time $t = T/2$. This shows that the Nitrogen atom had undergone tunnelling process to pass the potential barrier. Where as Fig.(5.8) shows that the Nitrogen atom is back to its initial position, right well, after time t=T. From the comparison done between the diffusion quantum Monte Carlo approach and the theoretical approach, similar orientations of Nitrogen atom through time inside the symmetric double well potential is obtained.

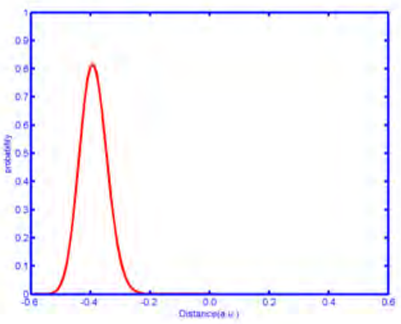

Figure 5.7: Probability for Orientation of Nitrogen atom after time, t=T/2(Theoretical)

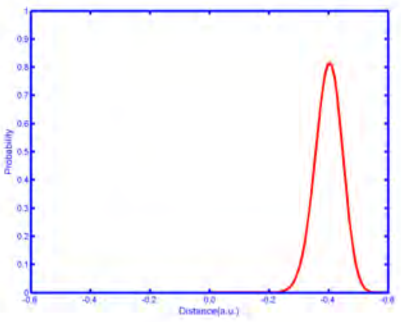

Figure 5.8: Probability for Orientation of Nitrogen atom after time, t=T(Theoretical)

The full cycle of the Nitrogen atom from left to right region can be viewed from Fig. 5.9. We start by assuming the Nitrogen atom is inside the right well at time t=0.0, having high probability density in the right side of the double well. As time progresses the probability density of the Nitrogen atom to be found in the right of the double well decrease. In contrast the probability of Nitrogen to be found on the left well increases and it perks in the left region at time t=T/2. After the half a period the probability of Nitrogen to be found inside the left will start to decrease while the probability to the right well becomes increasing.

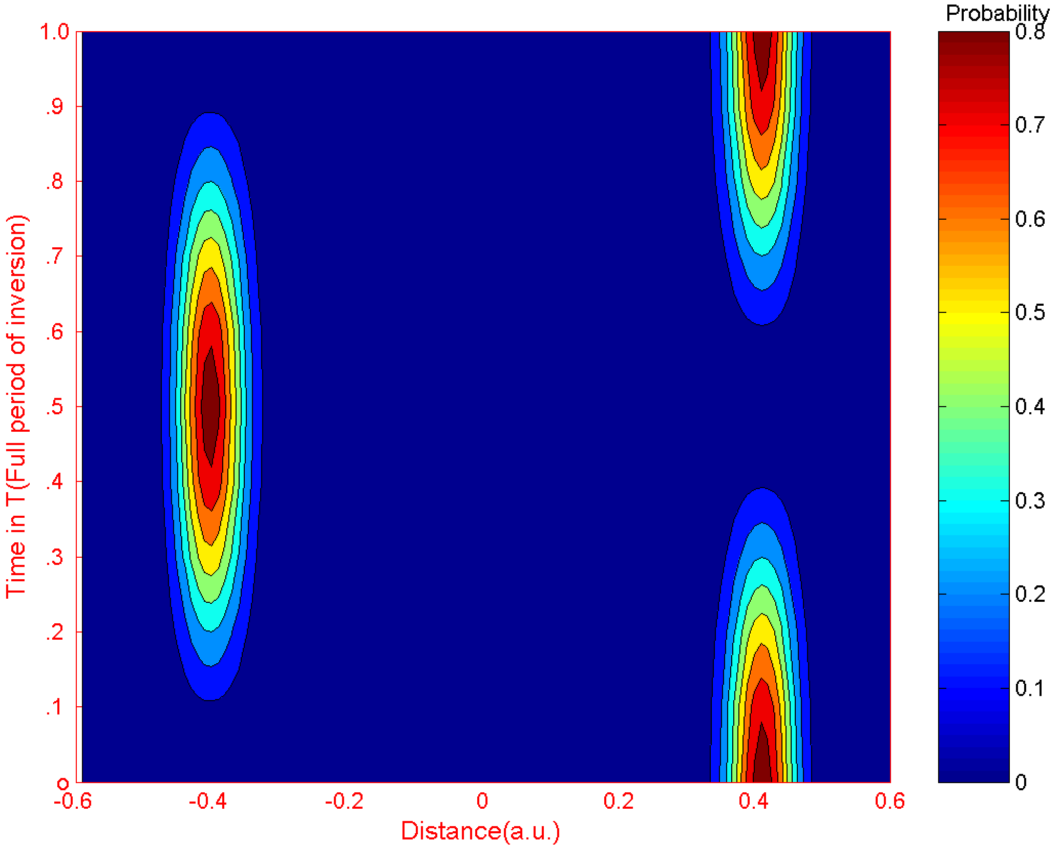

Figure 5.9: Inversion of Ammonia molecule for one full period of inversion

5.2 Energy eigenvalue and energy splinting of selected double well potentials

In this section energy eigenvalues of selected symmetric double well potentials are obtained numerically. In addition to this the energy splitting is studied when the potential well is deep and shallow.

The first potential taken has a form :

$$V(X) = -\lambda X^2 + K X^4 \tag{5.2.1}$$

where k=2 and $\lambda = \omega^2$

The results obtained are summarized in Table-2.

Value of λ	n	Energy(a.u.)	$E_1 - E_0$
1	0	0.5926044	1.8152392
	1	2.4078436	
	2	5.0789313	
	3	8.162036	
	4	11.576575	
	5	15.255767	
3	0	0. -0.08701962	1.0597467
	1	0.97272706	
	2	3.341396	
	3	6.0197506	
	4	9.0919485	
	5	12.456016	
5	0	-1.326539	0.37534422
	1	- .9511948	
	2	1.5596318	
	3	3.6671898	
	4	6.410784	
	5	9.451503	

Table -2 gives eigenvalue and energy splinting for the potential in equation (5.2.1)

Value of λ	n	Energy(a.u.)	$E_1 - E_0$
7	0	-3.6851745	0.061463118
	1	-3.6237113	
	2	-0.08546664	
	3	1.060407	
	4	3.6166477	
	5	6.2605762	
9	0	-7.259849	0.0054769516
	1	-7.254372	
	2	-2.3043284	
	3	-2.023389	
	4	1.0645814	
	5	2.9131956	
11	0	-11.918601	0.00038909912
	1	-11.918212	
	2	-5.9918256	
	3	-5.9635706	
	4	-1.3386927	
	5	-0.7057324	

The second potential taken has a form :

$$V(X) = -\lambda X^2 + KX^4 \tag{5.2.2}$$

where k=3 and $\lambda = \omega^2$

The results obtained are summarized as below in table form.

Value of λ	n	Energy(a.u.)	$E_1 - E_0$
1	0	0.7506027	2.1737635
	1	2.9243662	
	2	6.0318146	
	3	9.606143	
	4	13.549093	
	5	17.785818	
4	0	-0.1260935	1.1894339
	1	1.0633404	
	2	3.767524	
	3	6.81426	
	4	10.311033	
	5	14.137667	
7	0	-1.8762014	0.3328632
	1	-1.5433382	
	2	1.4538763	
	3	3.7053106	
	4	6.7808237	
	5	10.182805	

Table-3 gives eigenvalue and energy splinting for the potential in equation (5.2.2)

Value of λ	n	Energy	$E_1 - E_0$
10	0	-5.370616	0.034593582
	1	-5.3360224	
	2	-0.7603474	
	3	0.17260505	
	4	3.1482892	
	5	5.955593	
13	0	-10.618178	0.0017843246
	1	-10.616394	
	2	-4.3771243	
	3	-4.2558484	
	4	0.015289508	
	5	1.4697373	

From energy eigenvalues obtained at Table 2 and 3, it can be seen that there is no degeneracy in the energy eigenvalues. In addition to this energy splitting will be lower when the potential well is deeper, λ is large, and the amount will increase when the potential well is shallow.

Chapter 6

Conclusions and Future Directions

6.1 Conclusions

In this thesis work double well potential and Inversion phenomena of ammonia molecule using time dependent quantum mechanical approach had been studied. All the numerical calculations had been programmed using FORTRAN95.

For the case of double well potentials, two parameter functions automatically leads to the energy splitting of the lowest pairs of energy levels. Increase of barrier height will make pairs of eigenvalues of double well potential converge to a single degenerate eigenvalue. Conversely, when the barrier height shrinks, each eigenvalue of the pair of double well potentials wells splits into a pair of eigenvalues.

In the case of Ammonia Molecule, the wave functions which are not possible to get theoretically had been successfully obtained using numerical approach. Based on quantum mechanics it will have two possible orientations in which the Nitrogen atom will be oscillating back and forth between the two wells of double well with frequency 24 GHz. The time dependent approach used, Diffusion quantum monte carlo, had given exactly the same result as the theoretical results in obtaining the time evolutions of the orientation of ammonia inside the symmetric double well potential.

6.2 Future directions

So far what is done is simulation of the time evolution of ammonia molecule having symmetric double well potential and evaluation of eigenvalues of different double well potentials. In future, based on the result obtained here, any one who is interested in this area can do for other molecules which have more than two wells , multiple well potentials.

Appendix A

Subroutine for solving tridiagonal matrix to get energy eigenvalues(QL/QR algorithm) the FTN95 subroutine will solve eigenvalues for the double well/any multiple well potential.

```
SUBROUTINE eigenVtridaiagonalmat(NM,N,D,E,Z,IER)
REAL,dimension(100,100)::z
REAL,dimension(10000)::d,e,POT
real::B,C,F,G,H,P,R,S,EPS,EPS1,xd1,xd2,lamda,betta
INTEGER I,J,K,L,M,N,NM,JM
DATA EPS /0.D0/,JM /30/
real::rho,lm,beta
! n is the number of total discritisation to be done ( on both wells)
print*,”eneter the gap of the potential”
read*,xd1 print*,”enter the number of discritisations to be done in total”
read*,n
!n=120
!xd1 is the distance to the left from the center of the symmetric double well potential
! xd1=-6.0!.0
```

```
IER = 0
print*,” the step size ,delta x”
read*,xd2
print*,”enter coefficients of the double well potential,lamda”
read*,lamda
print*,”enter coefficients of the double well potential,betta”
read*,betta

    !xd2=.1
!xd2 is the step size in position (delta x )
do i=1,n!120
!xd1 is position od the double well
xd1=xd2 +xd1
pot(i)=-lamda*xd1**2 + betta*xd1**4
    !pot(i) potential function of the double well !pot(i)=-16*xd1**2 + 3*xd1**4
end do
do i=1,n-1 !119
! e(i) elements of the symmetric tridiagonal matrix above /below the diagonal !
!d(i) Diagonal elements of the symmetric tridiagonal matrix
e(i)=(-1.0/(2.0*xd2**2.0)
d(i)=(pot(i)+1.0/(1.0*xd2**2.0) ) end do d(120)=pot(120)+ 2/(xd2**2)
IF (N.EQ.1) GO TO 38
! MACHINE EPSILON
IF (EPS.NE.0.D0) GO TO 12
```

```
EPS = 1.D0
10 EPS = EPS/2.D0
EPS1 = 1.D0+EPS
IF (EPS1.GT.1.D0) GO TO 10
12 DO 14 I = 2,N
14 E(I-1) = E(I)
E(N) = 0.D0
F = 0.D0
B = 0.D0
DO 28 L = 1,N
J = 0
H = EPS*(ABS(D(L))+ABS(E(L)))
IF (B.LT.H) B = H
! SEEK SMALLEST ELEMENT OF SUBDIAGONAL
DO 16 M = L,N
IF (ABS(E(M))¡B) GO TO 18
16 CONTINUE
18 IF (M==L) GO TO 26
! START ITERATION
20 IF (J.EQ.JM) GO TO 36
J = J+1
! SHIFT
G = D(L)
P = (D(L+1)-G)/(2.D0*E(L))
```

```
R = SQRT(P*P+1.D0)
D(L) = E(L)/(P+SIGN(R,P))
H = G-D(L)
DO 22 I = L+1,N
22 D(I) = D(I)-H
F = F+H
! QL TRANSFORMATION
P = D(M)
C = 1.D0
S = 0.D0
DO 24 I = M-1,L,-1
G = C*E(I)
H = C*P
IF (ABS(P).GE.ABS(E(I))) THEN
C = E(I)/P
R = SQRT(C*C+1.D0)
E(I+1) = S*P*R
S = C/R
C = 1.D0/R
ELSE
C = P/E(I)
R = SQRT(C*C+1.D0)
E(I+1) = S*E(I)*R
S = 1.D0/R
```

```
C = C*S
ENDIF
P = C*D(I)-S*G
D(I+1) = H+S*(C*G+S*D(I))
! ELEMENTS OF EIGENVECTORS
DO 24 K = 1,N
H = Z(K,I+1)
Z(K,I+1) = S*Z(K,I)+C*H
Z(K,I) = Z(K,I)*C-S*H
24 CONTINUE
E(L) = S*P
D(L) = C*P
IF (ABS(E(L)).GT.B) GO TO 20
! CONVERGENCE
26 D(L) = D(L)+F
28 CONTINUE
! SORT EIGENVALUES AND EIGENVECTORS
! IN ASENDING ORDER
DO 34 L = 2,N
I = L-1
K = I
P = D(I)
DO 30 J = L,N
IF (D(J).GE.P) GO TO 30
```

```
K = J
P = D(J)
30 CONTINUE
IF (K.EQ.I) GO TO 34
D(K) = D(I)
D(I) = P
DO 32 J = 1,N
P = Z(J,I)
Z(J,I) = Z(J,K)
32 Z(J,K) = P
34 CONTINUE
GO TO 38
! NO CONVERGENCE
36 IER = L
38 RETURN
end
```

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