

Study to Solve the Time Independent Schrodinger Equation using Hamiltonian

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Abstract: In this paper, to describe the quantum mechanical world we must pick a set of base states i and write the physical laws by giving the matrix of co-efficient H_{ij} . For this we have to find out the correct Hamiltonian of the situation but this is a tough work as no one knows the complete H_{ij} for the whole world. We do have excellent approximation for non-relativistic phenomena and for some other special cases - especially we have the forms that are needed for the motions of electron in atoms to describe chemistry. But we don't know the full true H for the whole universe.

Keywords: Hamiltonian, Matrix, Quantum Mechanical World, Ammonia Molecule

1. Introduction

The coefficients H_{ij} are called the Hamiltonian matrix or only Hamiltonian. It is related with energy of the system so we may call it the energy matrix. Since it is related with energy of the system, it has the following property -

$$H_{ij}^* = H_{ji}$$

Let us discuss the case for knowing Hamiltonian for two state system. To illustrate it explicitly we take the case of a Ammonia Molecule.

2. Materials and Methods

2.1 The Ammonia Molecule

We have picked an interesting but simple example in which, by making some reasonable guesses about the Hamiltonian, we can work out some important and even practical results. We are going to take a situation describable by two states; the ammonia molecule.

The ammonia molecule has one nitrogen atom and three hydrogen atoms located in a plane below the nitrogen atom and three hydrogen atoms located in a plane below the nitrogen so that the molecule has the form of a pyramid, as drawn in Fig 1(a). Now this molecule, like any other, has an infinite number of states. It can spin around any possible axis; it can be moving in any direction; it can be vibrating inside, and so on, and so on. It is, therefore, not a two-state system at all. But we want to make an approximation that all other sates remain fixed, because they don't enter into what we are concerned. We will consider only that the molecule is spinning around its axis of symmetry that has zero translational momentum, and is vibrating as little as possible. That specifies all conditions except one: there are still the two possible positions for the nitrogen atoms - the nitrogen may be on one side of the plane of hydrogen atoms or on the other, as shown in fig 1(a) and (b). So we will discuss the molecule as though it were a two state system.

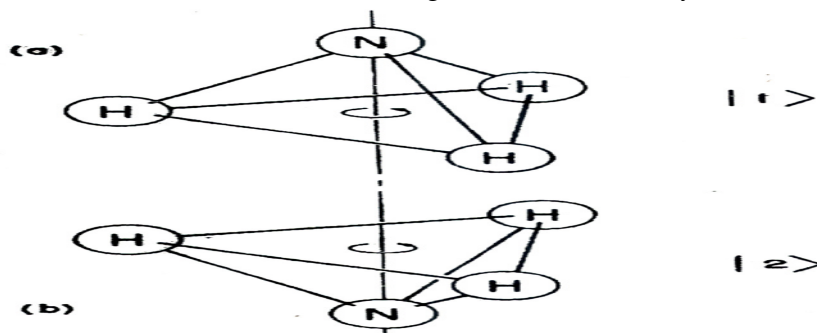


Fig 1: Two equivalent geometric arrangements of the ammonia molecule.

We mean that there are only two states we are going to really worry about, all other things being fixed. Even if we know that it is spinning with a certain angular momentum around the axis and that it is moving with a certain momentum and vibrating in a definite way, there are still two possible states. We will say that the molecule is in the state $|i\rangle$ when the nitrogen is "up", as in Fig 1(a), and is in the state $|2\rangle$ when the nitrogen is "down" as in Fig 1(b). The states $|1\rangle$ and $|2\rangle$ will be taken as the set of base states for our analysis of the behaviour of the ammonia molecule. At any moment, the actual state $|\psi\rangle$ of the molecule can be represented by giving $C_1 = \langle 1|\psi\rangle$, the amplitude to be in state $|1\rangle$, and $C_2 = \langle 2|\psi\rangle$, the amplitude to be in state $|2\rangle$. Then, using Equation $|\phi\rangle = \sum_i |i\rangle \langle i|\phi\rangle$

we can write the state vector $|\psi\rangle$ is

$$\begin{aligned} |\psi\rangle &= |1\rangle \langle 1|\psi\rangle + |2\rangle \langle 2|\psi\rangle \\ |\psi\rangle &= |1\rangle C_1 + |2\rangle C_2 \end{aligned} \quad (1)$$

Now the interesting thing is that if the molecule is known to be in some state at some instant, it will not be in the same state a little while later. The two C-coefficients will be changing with time according to the equations

$$\begin{aligned} i\hbar \frac{dC_1}{dt} &= H_{11}C_1 + H_{12}C_2 \\ i\hbar \frac{dC_2}{dt} &= H_{21}C_1 + H_{22}C_2 \end{aligned}$$

which hold for any two state system. Suppose, for example, that we had made some observation or had made some selection of the molecules so that we know that the molecule is initially in the state $|1\rangle$. At some later time, there is some chance that it will be found in state $|2\rangle$. To find out what this chance is, we have to solve the differential equations which tell us how the amplitudes change with time.

The only trouble is that we don't know what to use for the coefficient H_{ij} in the differential equations just mentioned. There are some things we can say, however. Suppose that once the molecule was in the state $|1\rangle$ there was no chance that it could ever get into $|2\rangle$, and vice versa. Then H_{12} and H_{21} would both be zero, and the equations would read,

$$\begin{aligned} i\hbar \frac{dC_1}{dt} &= H_{11}C_1 \\ i\hbar \frac{dC_2}{dt} &= H_{22}C_2 \end{aligned}$$

We can easily solve these two equations; we get

$$\begin{aligned} C_1 &= (\text{const}) e^{-\frac{i}{\hbar} H_{11}t}, \\ C_2 &= (\text{const}) e^{-\frac{i}{\hbar} H_{22}t}. \end{aligned} \quad (2)$$

These are just the amplitudes for stationary states with the energies $E_1=H_{11}$ and $E_2=H_{22}$. We note, however, that for the ammonia molecule the two states $|1\rangle$ and $|2\rangle$ have a definite symmetry. If nature is at all reasonable, the matrix elements H_{11} and H_{22} must be equal. We will call them both E_0 , because they correspond to the energy the states would have if H_{12} and H_{21} were zero. But Equation (2) does not tell us what ammonia really does. It turns out that it is possible for the nitrogen to push its way through the three hydrogens and flip to other side. It is quite difficult; to get half-way through it requires a lot of energy. How can it get through if it hasn't got enough energy? There is some amplitude that will penetrate the energy barrier. It is possible in quantum mechanics to sneak quickly across a region which is illegal energetically. There is, therefore, some small amplitude that a molecule which starts in $|1\rangle$ will get to the state $|2\rangle$. The coefficients H_{12} and H_{21} are not really zero. Again, by symmetry, they should both be the same at least in magnitude. In fact, we already know that,

in general H_{ij} must be equal to the complex conjugate of H_{ji} , so they can differ only by a phase. It turns out, as we will see, that there is no loss of generality if we take them equal to each other. For later convenience we set them equal to a negative number; we take $H_{12} = H_{21} = -A$. We then have the following pair of equations:

$$i\hbar \frac{dC_1}{dt} = E_0 C_1 - A C_2 \quad (3)$$

$$i\hbar \frac{dC_2}{dt} = E_0 C_2 - A C_1 \quad (4)$$

These equations are simple enough and can be solved in any number of ways. One convenient way is the following. Taking the sum of the two, we get

$$i\hbar \frac{d(C_1 + C_2)}{dt} = (E_0 - A)(C_1 + C_2)$$

Whose solution is

$$(C_1 + C_2) = a e^{-\left(\frac{1}{\hbar}\right)(E_0 - A)t} \quad (5)$$

Then, taking the difference of (3) and (4) we find that which gives

$$C_1 - C_2 = b e^{-\left(\frac{1}{\hbar}\right)(E_0 + A)t} \quad (6)$$

We have called the two integration constants a and b ; they are, of course, to be chosen to give the appropriate starting condition for any particular physical problem. Now, by adding and subtracting (5) and (6), we get C_1 and C_2

$$C_1(t) = \frac{a}{2} e^{-\left(\frac{1}{\hbar}\right)(E_0 - A)t} + \frac{b}{2} e^{-\left(\frac{1}{\hbar}\right)(E_0 + A)t} \quad (7)$$

$$C_2(t) = \frac{a}{2} e^{-\left(\frac{1}{\hbar}\right)(E_0 - A)t} - \frac{b}{2} e^{-\left(\frac{1}{\hbar}\right)(E_0 + A)t} \quad (8)$$

They are the same except for the sign of the second term

Let's now ask the following question about an ammonia molecule. Suppose that at $t = 0$, we know that a molecule is in the state $|1\rangle$ or, in other words, that $C_1(0) = 1$ and $C_2(0) = 0$. What is the probability that the molecule will be found in the state $|2\rangle$ at the time t , or will still be found in state $|1\rangle$ at the time? Our starting condition tells us what a and b are in Eqs. (7) and (8). Letting $t = 0$, we have that

$$C_1(0) = \frac{a + b}{2} = 1 \quad C_2(0) = \frac{a - b}{2} = 0$$

Clearly, $a = b = 1$. Putting these values into the formulas for $C_1(t)$ and $C_2(t)$ and rearranging some terms, we have

$$C_1(t) = e^{-\left(\frac{i}{\hbar}\right)E_0 t} \left(\frac{e^{\left(\frac{i}{\hbar}\right)A t} + e^{-\left(\frac{i}{\hbar}\right)A t}}{2} \right)$$

$$C_2(t) = e^{-\left(\frac{i}{\hbar}\right)E_0 t} \left(\frac{e^{\left(\frac{i}{\hbar}\right)A t} - e^{-\left(\frac{i}{\hbar}\right)A t}}{2} \right)$$

We can rewrite these as

$$C_1(t) = e^{-\left(\frac{i}{\hbar}\right)E_0 t} \cos \frac{A t}{\hbar} \quad (9)$$

$$C_2(t) = e^{-\left(\frac{i}{\hbar}\right)E_0 t} \cos \frac{A t}{\hbar} \quad (10)$$

The two amplitudes have a magnitude that varies harmonically with time.

The probability that the molecule is found in state $|2\rangle$ at the time t is the absolute square of $C_2(t)$

$$|C_2(t)|^2 = \sin^2 \frac{A t}{\hbar} \quad (11)$$

The probability starts at zero, rises to one, and then oscillates back and forth between zero and one, as shown in the curve marked P_2 of Fig 2. The probability of being in the $|1\rangle$ state does not, ofcourse, stay at one. It "dumps" into the second state until the probability of finding the molecule in the first state is zero, as who shown by the curve P_1 of Fig. 2. The probability sloshes back and forth between the two.

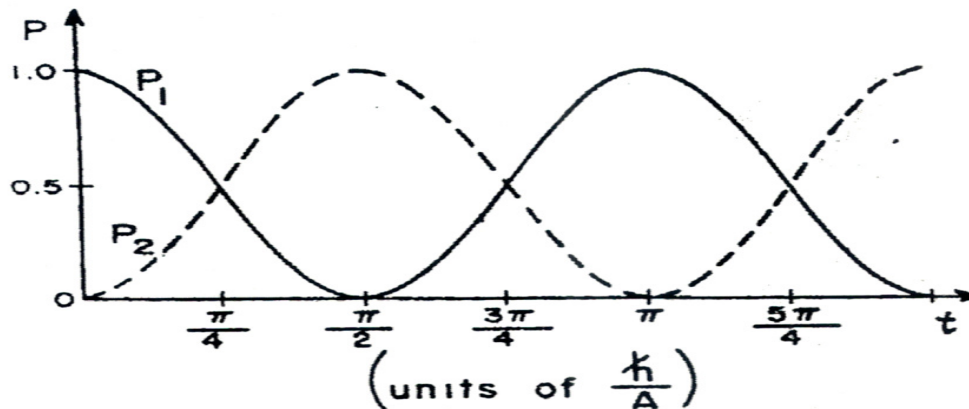


Fig 2: The probability P_1 that an ammonia molecule in state $|1\rangle$ at $t=0$ will be found in state $|1\rangle$ at t .

The probability P_2 that it will found in state $|2\rangle$.

The splitting of the energy levels of the ammonia molecule is, however, strictly a quantum mechanical effect. The splitting of the energy levels of the ammonia molecule has important practical applications. Here, have an example of a practical physical problem that we can understand with the quantum mechanics.

Next we want to know Hamiltonian for many state systems.

2.2 The Many-Body Schrodinger Equation

If we have N nuclei, we are dealing with a state of $N+ZN$ electromagnetically interacting particles. This is a many-state problem and because the particles are so light, quantum mechanics is needed: a quantum many state problems. The exact many-particle Hamiltonian for this system is:

$$H = -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{R}_i}^2}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{R}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} \quad (12)$$

The mass of the nucleus at R_i , is M_i , the electrons have mass one and are at r_i . The above equation can be written as,

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{ext} + \hat{V}_{ee} + \hat{V}_{nn} \quad (13)$$

where, \hat{T}_n , is the many-nucleus kinetic energy operator, \hat{T}_e is the many-electron kinetic energy operator, \hat{V}_{ext} , is the electron-nucleus interaction energy operator (external potential), \hat{V}_{ee} is the electron-electron interaction energy operator and \hat{V}_{nn} is the nucleus-nucleus interaction energy operator. The Schrodinger equation of this system is represented by

$$H \psi = E \psi \quad (14)$$

A macroscopic solid consists of $N=10^{23}$ electrons and nucleus/cm³, which makes equation (3) impossible to solve in realistic cases. Therefore several approximations need to be introduced.

3. Results and Discussion

The first approximation to solve the time independent Schrodinger equation for the above Hamiltonian is the Born-Oppenheimer approximation. This approximation is used to remove the nuclei from the system and treats them as in an adiabatic environment due to the fact that the nuclei are much heavier; hence move much slower than the electrons. In this approximation, the kinetic energy of the nuclei is neglected and the interaction between the nuclei can be handled classically. Thus, the original problem in equation (12) is reduced to one regarding a system of interacting electrons moving in an external potential $V_{ext}(r)$, formed by a frozen-in ionic configuration. Therefore we rewrite equation (13) formally as a problem of many electrons moving in an external potential V_{ext} generated by the stationary nuclei:

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{ee} \quad (15)$$

Therefore the Schrodinger equation of this system is

$$H \psi = \left[-\frac{1}{2} \sum_i \nabla^2 - \sum_{i,j} \frac{Z_j}{|r_i - R_j|} + \frac{1}{2} \sum_{i \neq j} \frac{Z_j}{|r_i - r_j|} \right] \psi = E \psi \quad (16)$$

In principle, this equation may solve to arbitrary accuracy by representing ψ as a direct product wave function and diagonalising the Hamiltonian. The total energy E can then be written as

$$E[\psi] = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \quad (17)$$

Other approximation and theories which are helpful in this regard are - Hartee-Fock-Approximation, Diversity Functional Theory, Thomas-Fermi Theory, Hohenberg-Kohn Thearerus etc.

4. Conclusion

As it is obvious from the above discussion that in many state systems or in many body problems knowing or calculating the Hamiltonian is a tough and complicated one. So, we will restrictourselves to the two state systems only.

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