

## UNIT 3

# Stationary perturbation theory

*Notes by L. Poudel, T. Papatheodore, and Y. Song*

### The Method

Perturbation theory applies to systems whose Hamiltonians may be expressed in the form

$$H = H_0 + W. \quad (1)$$

$H_0$  is called the unperturbed Hamiltonian and it is assumed to be time-independent. We already know the solution corresponding to  $H_0$ , which is to say that we already know its eigenvalues and eigenstates.

$$H_0 | E_{0,\dots} \rangle = E_0 | E_{0,\dots} \rangle \quad (2)$$

$E_0$  is degenerate in general and the  $0,\dots$  allows for the possibility of other quantum numbers if there is degeneracy.  $W$  is called the “perturbation”, which causes modifications to the energy levels and stationary states of the unperturbed Hamiltonian.  $W$  is assumed to be much smaller than  $H_0$  and for *stationary* perturbation theory it is also time-independent. In order to quantify the “smallness” of  $W$  we assume that it is proportional to a real, dimensionless parameter  $\lambda$  which is much smaller than 1:

$$W = \lambda \hat{W}, \quad (3)$$

where  $\lambda \ll 1$  and  $\hat{W}$  is an operator whose matrix elements are comparable to those of  $H_0$ . Now, substitution of (3) into (1) yields

$$H = H_0 + \lambda \hat{W}. \quad (4)$$

From (4) we can see that as  $\lambda \rightarrow 0$ ,  $H(\lambda) \rightarrow H_0$ , and we recover the unperturbed Hamiltonian.

## Approximate Solution of the Eigenvalue Equation

We want to find a solution to the eigenvalue equation

$$H(\lambda) | \psi(\lambda) \rangle = E(\lambda) | \psi(\lambda) \rangle \quad (5)$$

In order to approximate the solutions  $E(\lambda)$  and  $| \psi(\lambda) \rangle$  we assume that they can be expanded in powers of  $\lambda$ :

$$E(\lambda) = E_0 + \lambda E_1 + \lambda^2 E_2 + \dots \quad (6)$$

$$| \psi(\lambda) \rangle = | \psi_0 \rangle + \lambda | \psi_1 \rangle + \lambda^2 | \psi_2 \rangle + \dots \quad (7)$$

Substitution of (4), (6) and (7) into (5) yields

$$\begin{aligned} (H_0 + \lambda \hat{W})(| \psi_0 \rangle + \lambda | \psi_1 \rangle + \lambda^2 | \psi_2 \rangle + \dots) = \\ (E_0 + \lambda E_1 + \lambda^2 E_2 + \dots)(| \psi_0 \rangle + \lambda | \psi_1 \rangle + \lambda^2 | \psi_2 \rangle + \dots) \end{aligned} \quad (8)$$

Multiply equation (8) out and collect like terms of  $\lambda$ . Now, since  $\lambda$  is arbitrary we must equate the coefficients of successive powers of  $\lambda$  on both sides of the equation.

**0th Order Terms:**  $\lambda^0$

$$H_0 | \psi_0 \rangle = E_0 | \psi_0 \rangle \quad (9)$$

**1st Order Terms:**  $\lambda^1$

$$H_0 | \psi_1 \rangle + \hat{W} | \psi_0 \rangle = E_0 | \psi_1 \rangle + E_1 | \psi_0 \rangle \quad (10)$$

**2nd Order Terms:**  $\lambda^2$

$$H_0 | \psi_2 \rangle + \hat{W} | \psi_1 \rangle = E_0 | \psi_2 \rangle + E_1 | \psi_1 \rangle + E_2 | \psi_0 \rangle \quad (11)$$

Since equation (5) defines  $| \psi(\lambda) \rangle$  only to within a constant factor, we can choose its norm and phase. We assume  $| \psi(\lambda) \rangle$  to be normalized and choose its phase so that  $\langle \psi_0 | \psi(\lambda) \rangle$  is real.

Now, since  $\langle \psi(\lambda) | \psi(\lambda) \rangle = 1$  we obtain the following:

**To 0th Order**  $| \psi(\lambda) \rangle = | \psi_0 \rangle$

$$\implies \langle \psi(\lambda) | \psi(\lambda) \rangle = \langle \psi_0 | \psi_0 \rangle = 1 \quad (12)$$

**To 1st Order**  $| \psi(\lambda) \rangle = | \psi_0 \rangle + \lambda | \psi_1 \rangle$

$$\begin{aligned} \implies \langle \psi(\lambda) | \psi(\lambda) \rangle &= (\langle \psi_0 | + \lambda \langle \psi_1 |)(| \psi_0 \rangle + \lambda | \psi_1 \rangle) \\ &= \langle \psi_0 | \psi_0 \rangle + \lambda \langle \psi_0 | \psi_1 \rangle + \lambda \langle \psi_1 | \psi_0 \rangle + \lambda^2 \langle \psi_1 | \psi_1 \rangle = 1 \end{aligned} \quad (13)$$

We can drop the last term involving  $\lambda^2$  since we are only concerned with 1st order terms. Now we also know that  $\langle \psi_0 | \psi_0 \rangle = 1$  which then implies that  $\langle \psi_0 | \psi_1 \rangle + \langle \psi_1 | \psi_0 \rangle = 0$ . And, since  $\langle \psi_0 | \psi_1 \rangle$  is real we obtain

$$\langle \psi_0 | \psi_1 \rangle = \langle \psi_1 | \psi_0 \rangle = 0 \quad (14)$$

**To 2nd Order**  $| \psi(\lambda) \rangle = | \psi_0 \rangle + \lambda | \psi_1 \rangle + \lambda^2 | \psi_2 \rangle$

A similar argument for the 2nd order terms may be applied to obtain

$$\langle \psi_0 | \psi_2 \rangle = \langle \psi_2 | \psi_0 \rangle = -\frac{1}{2} \langle \psi_1 | \psi_1 \rangle \quad (15)$$

## Non-Degenerate Energy Level

We will now find the corrections to the energy levels and energy eigenstates of a non-degenerate level. Project the 1st order equation (10) onto the state  $|\psi_0\rangle$ :

$$\langle\psi_0|H_0|\psi_1\rangle + \langle\psi_0|\hat{W}|\psi_0\rangle = \langle\psi_0|E_0|\psi_1\rangle + \langle\psi_0|E_1|\psi_0\rangle \quad (16)$$

Now let  $H_0$  operate to the left on  $\langle\psi_0|$  in the first term and pull the constants out to obtain

$$E_0\langle\psi_0|\psi_1\rangle + \langle\psi_0|\hat{W}|\psi_0\rangle = E_0\langle\psi_0|\psi_1\rangle + E_1\langle\psi_0|\psi_0\rangle \quad (17)$$

From this equation we can see that since  $\langle\psi_0|\psi_0\rangle = 1$  from (12) and the first and third terms cancel we obtain the first order correction to the energy level:

$$E_1 = \langle\psi_0|\hat{W}|\psi_0\rangle \quad (18)$$

Now we want to find the first order correction,  $|\psi_1\rangle$ , to the eigenstate. Project the first order equation (10) onto the state  $\langle E'_0|$ , where  $\langle E'_0|$  is an eigenstate corresponding to any other energy level other than  $E_0$ . We obtain

$$E'_0\langle E'_0|\psi_1\rangle + \langle E'_0|\hat{W}|\psi_0\rangle = E_0\langle E'_0|\psi_1\rangle + E_1\langle E'_0|\psi_0\rangle \quad (19)$$

The last term,  $\langle E'_0|\psi_0\rangle$ , is equal to zero since the two terms of the inner product belong to different eigenvalues. Then we can solve for  $\langle E'_0|\psi_1\rangle$  to obtain

$$\langle E'_0|\psi_1\rangle = \frac{\langle E'_0|\hat{W}|\psi_0\rangle}{E_0 - E'_0} \quad (20)$$

Now expanding the state  $|\psi_1\rangle$  on the  $|E'_0\rangle$  basis we conclude that the correction to the energy eigenstate is

$$\begin{aligned} |\psi_1\rangle &= \sum_{E'_0} |E'_0\rangle \langle E'_0|\psi_1\rangle \\ &= \sum_{E'_0 \neq E_0} |E'_0\rangle \frac{\langle E'_0|\hat{W}|\psi_0\rangle}{E_0 - E'_0} + |E_0\rangle \langle E_0|\psi_1\rangle \\ &= \sum_{E'_0 \neq E_0} |E'_0\rangle \frac{\langle E'_0|\hat{W}|\psi_0\rangle}{E_0 - E'_0}, \end{aligned} \quad (21)$$

where the last equation follows since  $\langle E_0|\psi_1\rangle = 0$  due to the fact that the two states of the inner product belong to different eigenvalues.

Now we follow the same procedure for the 2nd order equation. In order to find the 2nd order correction to the energy level we project the 2nd order equation (11) onto the state  $|\psi_0\rangle$ :

$$E_0\langle\psi_0|\psi_2\rangle + \langle\psi_0|\hat{W}|\psi_1\rangle = E_0\langle\psi_0|\psi_2\rangle + E_1\langle\psi_0|\psi_1\rangle + E_2\langle\psi_0|\psi_0\rangle \quad (22)$$

Now, the first terms on each side of the equation cancel, the second term on the right side is zero since  $\langle \psi_0 | \psi_1 \rangle = 0$ , and  $\langle \psi_0 | \psi_0 \rangle = 1$  which yields the conclusion

$$E_2 = \langle \psi_0 | \hat{W} | \psi_1 \rangle \quad (23)$$

Now, plugging in equation (21) for  $|\psi_1\rangle$  gives the 2nd order correction to the energy level:

$$E_2 = \sum_{E'_0 \neq E_0} \langle \psi_0 | \hat{W} | E'_0 \rangle \frac{\langle E'_0 | \hat{W} | \psi_0 \rangle}{E_0 - E'_0} = \sum_{E'_0 \neq E_0} \frac{|\langle \psi_0 | \hat{W} | E'_0 \rangle|^2}{E_0 - E'_0} \quad (24)$$

The second order correction to the energy level,  $|\psi_2\rangle$  is to be found on your own at home following the same procedure as in the first order correction.

## Degenerate Energy Level

Now we allow for the energy  $E_0$  to be degenerate so that the corresponding states are denoted  $|E_{0,a}\rangle$ , where  $a$  is a quantum number. If we suppose that the degeneracy is 2, then  $a$  can take on two values:  $a = 1, 2$ .

We proceed in an analogous manner to the nondegenerate case except now we must project the first order equation onto both possible states  $|E_{0,a}\rangle$ . Doing so we see that

$$E_0 \langle E_{0,a} | \psi_1 \rangle + \langle E_{0,a} | W | \psi_0 \rangle = E_0 \langle E_{0,a} | \psi_1 \rangle + E_1 \langle E_{0,a} | \psi_0 \rangle \quad (25)$$

Notice that the first term on each side of the equation cancels leaving us with two equations; one for each case  $a = 1, 2$ :

$$\langle E_{0,a} | W | \psi_0 \rangle = E_1 \langle E_{0,a} | \psi_0 \rangle \quad (26)$$

### For a = 1

$$\langle E_{0,1} | W | \psi_0 \rangle = E_1 \langle E_{0,1} | \psi_0 \rangle \quad (27)$$

But generally  $|\psi_0\rangle$  must be written as a linear combination of the states  $|E_{0,a}\rangle$ :

$$|\psi_0\rangle = \alpha_1 |E_{0,1}\rangle + \alpha_2 |E_{0,2}\rangle \quad (28)$$

Plugging equation (28) into (27) we obtain

$$\alpha_1 \langle E_{0,1} | W | E_{0,1} \rangle + \alpha_2 \langle E_{0,1} | W | E_{0,2} \rangle = E_1 \alpha_1 \quad (29)$$

### For a = 2

$$\langle E_{0,2} | W | \psi_0 \rangle = E_1 \langle E_{0,2} | \psi_0 \rangle \quad (30)$$

Plugging equation (28) into (30) we obtain

$$\alpha_1 \langle E_{0,2} | W | E_{0,1} \rangle + \alpha_2 \langle E_{0,2} | W | E_{0,2} \rangle = E_1 \alpha_2 \quad (31)$$

Now, the operator  $W$  may be written in matrix form in the  $|E_{0,a}\rangle$  basis as

$$\begin{bmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{bmatrix}$$

so that equations (29) and (31) may be written as the matrix equation

$$W \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E_1 \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

The characteristic equation  $\det(W - E_1\mathbb{I}) = 0$  may then be solved in order to find the two eigenvalues and eigenstates.

## Example: 1D Harmonic Oscillator

Here we can see the method in action by proceeding with an example that we already know the answer to and then checking to see if our results match. The Hamiltonian for the 1-D harmonic oscillator is given by

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad (32)$$

Now, if the particle has a charge  $q$  we can turn on an electric field  $\vec{\varepsilon} = \varepsilon\hat{x}$  so that we introduce a perturbation  $W = -q\varepsilon x$ , and the total Hamiltonian then becomes

$$H = H_0 + W = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - q\varepsilon x \quad (33)$$

Recall that we have already solved this problem exactly in compliment  $F_V$  where we showed that

$$E'_n = (n + \frac{1}{2})\hbar\omega - \frac{q^2\varepsilon^2}{2m\omega^2} \quad (34)$$

$$\varphi'(x) = \varphi(x - \frac{q\varepsilon}{m\omega^2}) \quad (35)$$

We will now find the same results using perturbation theory.

### 1st order correction to the energy

$$E_n^{(1)} = \langle n | W | n \rangle = -q\varepsilon \langle n | x | n \rangle = 0 \quad (36)$$

The last equality follows since  $x = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a)$ , and hence there is no shift in the energy level to first order correction.

### 2nd order correction to the energy

$$E_n^{(2)} = \sum_{n' \neq n} \frac{|\langle n' | W | n \rangle|^2}{E_n - E'_n} \quad (37)$$

$$\langle n' | W | n \rangle = -q\varepsilon \langle n' | x | n \rangle = -q\varepsilon \sqrt{\frac{\hbar}{2m\omega}} \langle n' | a^\dagger + a | n \rangle \quad (38)$$

$$= -q\varepsilon \sqrt{\frac{\hbar}{2m\omega}} (\sqrt{n+1} \langle n' | n+1 \rangle + \sqrt{n} \langle n' | n-1 \rangle) \quad (39)$$

Therefore, the only nonzero contributions in equation (37) will come from  $n' = n+1$  and  $n' = n-1$ , yielding a second order correction to the energy term

$$E_n^{(2)} = q^2 \varepsilon^2 \frac{\hbar}{2m\omega} \left( -\frac{n+1}{\hbar\omega} + \frac{n}{\hbar\omega} \right) = -\frac{q^2 \varepsilon^2}{2m\omega^2} \quad (40)$$

Comparing equations (34) and (40) we notice that our second order correction to the energy level matches identically with the exact solution.

We now find the correction to the energy state:

$$| \psi_1 \rangle = \sum_{n' \neq n} \frac{\langle n' | W | n \rangle}{E_n - E_{n'}} | n' \rangle \quad (41)$$

$$= -q\varepsilon \sqrt{\frac{\hbar}{2m\omega}} \frac{1}{\hbar\omega} (-\sqrt{n+1} | n+1 \rangle + \sqrt{n} | n-1 \rangle) \quad (42)$$

$$= -q\varepsilon \sqrt{\frac{\hbar}{2m\omega}} \frac{1}{\hbar\omega} (-a^\dagger + a) | n \rangle \quad (43)$$

$$= -\frac{iq\varepsilon}{m\hbar\omega^2} p | n \rangle \quad (44)$$

Equation (42) follows from (39), equation (43) follows from the definitions of the creation and annihilation operators, and equation (44) follows from the definition of momentum as  $p = i\frac{m\hbar\omega}{2}(a^\dagger - a)$ . We can now check to see if equation (44) matches with the exact solution (35).

Taylor expand equation (35):

$$\varphi_n \left( x - \frac{q\varepsilon}{m\omega^2} \right) = \varphi_n(x) - \frac{q\varepsilon}{m\omega^2} \frac{d\varphi}{dx} + \dots \quad (45)$$

Now, since  $p = -i\hbar \frac{d}{dx}$ , we can see that equation (44) can be written as

$$\psi_1(x) = \langle x | \psi_1 \rangle = -\frac{q\varepsilon}{m\omega^2} \frac{d\varphi}{dx}, \quad (46)$$

and we can verify that our first order correction to the eigenstate does match the known exact solution.

## Ex-II: Harmonic oscillator with quadratic potential

Consider a harmonic oscillator with hamiltonian  $H_0$ , which is given by

$$H_0 = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad (47)$$

Let us add a quadratic potential to above oscillator. So, the perturbation is given by

$$W = \frac{1}{2}\lambda m\omega^2 x^2 \tag{48}$$

We assume  $\lambda \ll 1$ . In practice, this can be done by adding very weak spring with small spring constant. Now, the hamiltonian becomes,

$$H = H_0 + W = \frac{P^2}{2m} + \frac{1}{2}(\lambda + 1)m\omega^2 x^2 \tag{49}$$

The hamiltonian given by equation (49) is also the equation of harmonic oscillator with frequency  $\omega' = \omega\sqrt{1 + \lambda}$ , which can be solved exactly. So, the new energy levels is given by

$$E'_n = (n + \frac{1}{2})\hbar\omega' \tag{50}$$

Where,

$$\omega' = \omega\sqrt{(1 + \lambda)} \tag{51}$$

Using taylor expansion, we get different order correction in energy level

$$E'_n = (n + \frac{1}{2})\hbar\omega(1 + \frac{\lambda}{2} - \frac{\lambda^2}{8} + \dots) \tag{52}$$

But, this time we want to solve the problem using perturbation theory. First, we solve problem in  $H_0$ , the solution of which is

$$H_0 | n \rangle = E_n | n \rangle \tag{53}$$

Where

$$E_n = (n + \frac{1}{2})\hbar\omega \tag{54}$$

So, knowing that we can write expression for  $E'$ , which is general expression for any perturbation

$$E'_n = E_n + \lambda \langle n | W | n \rangle + \lambda^2 \sum_{n' \neq n} \frac{|\langle n' | W | n \rangle|^2}{E_n - E'_n} + \dots \tag{55}$$

The second term in equation (55) is average potential energy of harmonic oscillator, and therefore is exactly half of total energy of harmonic oscillator without perturbation. This is as expected from equation (52). We can also calculate it by using creation and annihilation operator.

$$\begin{aligned} \langle n | W | n \rangle &= \frac{1}{2}m\omega^2 \langle n | x^2 | n \rangle \\ &= \frac{1}{2}E_N \end{aligned} \tag{56}$$

To calculate the third term let us first calculate  $\langle n'|W|n\rangle$

$$\begin{aligned}\langle n'|W|n\rangle &= \frac{1}{2}m\omega^2 \frac{\hbar}{2m\omega} \langle n'|(a^\dagger + a)^2|n\rangle \\ &= \frac{\hbar\omega}{4} \langle n'|a^{\dagger 2} + a^2 + a^\dagger a + aa^\dagger|n\rangle \\ &= \frac{\hbar\omega}{4} [\sqrt{(n+1)(n+2)}\delta_{n',n+2} + \sqrt{n(n-1)}\delta_{n',n-2} + (2n+1)\delta_{n',n}]\end{aligned}\quad (57)$$

The first term contributes when  $n' = n + 2$ , second term contributes when  $n' = n - 2$ . But third contributes only when  $n' = n$ , which is excluded in our relation

$$\begin{aligned}\sum_{n' \neq n} \frac{|\langle n'|W|n\rangle|^2}{\hbar\omega(n' - n)} &= \frac{\hbar\omega}{16} \left[-\frac{1}{2}(n+1)(n+2) + \frac{1}{2}n(n-1)\right] \\ &= -\frac{1}{8}\hbar\omega\left(n + \frac{1}{2}\right)\end{aligned}\quad (58)$$

We get exactly same term as expected from equation (52). Similarly, we can calculate higher order terms.

### EX-3: Harmonic oscillator with cubic potential

This time we add cubic potential to the same hamiltonian.

$$W = x^3 \quad (59)$$

In this case there is no way to solve the problem as we did previous example. So, we must use perturbation theory to solve this problem. Here, the first term in energy will be original energy without perturbation. The second term in energy is also straightforward (i.e. zero since  $x^3$  is odd)

$$\langle n|x^3|n\rangle = 0 \quad (60)$$

The first correction in energy will be coefficient of  $\lambda^2$ . First we will evaluate  $\langle n'|W|n\rangle$ . Most of the terms of  $\langle n'|W|n\rangle$  are zero. The non zero terms are,

(i) When  $n' = n + 3$

$$\langle n+3|W|n\rangle = \left(\frac{\hbar}{2m\omega}\right)^{\frac{3}{2}} \langle n+3|(a^\dagger)^3|n\rangle \quad (61)$$

$$|\langle n+3|W|n\rangle|^2 = \left(\frac{\hbar}{2m\omega}\right)^3 (n+1)(n+2)(n+3) \quad (62)$$

(ii) When  $n' = n - 3$

$$|\langle n+3|W|n\rangle|^2 = \left(\frac{\hbar}{2m\omega}\right)^3 n(n-1)(n-2) \quad (63)$$



(iii) When  $n' = n + 1$

$$|\langle n + 3 | W | n \rangle|^2 = \left(\frac{\hbar}{2m\omega}\right)^{\frac{3}{2}} 9(n + 1)^3 \quad (64)$$

(iv) When  $n' = n - 1$

$$|\langle n + 3 | W | n \rangle|^2 = \left(\frac{\hbar}{2m\omega}\right)^{\frac{3}{2}} 9n^3 \quad (65)$$

Combining contributions from all these terms, we get

$$\sum_{n' \neq n} \frac{|\langle n' | W | n \rangle|^2}{\hbar\omega(n' - n)} = \left(\frac{\hbar}{2m\omega}\right)^{\frac{3}{2}} \frac{1}{\hbar\omega} \left[-\frac{1}{3}(n+1)(n+2)(n+3) + \frac{1}{3}n(n-1)(n-2) - 9(n+1)^3 + 9n^3\right] \quad (66)$$

With little effort in algebra

$$= -\frac{1}{8} \frac{\hbar^2}{m^3\omega^4} \left[30\left(n + \frac{1}{2}\right)^2 + \frac{7}{2}\right] \quad (67)$$

Finally, different between two successive energy level

$$E'_{n+1} - E'_n = \hbar\omega - \frac{15}{2} \frac{\lambda^2 \hbar^2}{m^3\omega^4} (n + 1) \quad (68)$$

In this case, separation in energy level is not equal but increases with increase in value of  $n$ . In realistic system, we never have only quadratic potential. Actually, if we expand potential around minimum, there will be higher order corrections. So, these cubic terms comes to play.

## Diatomic Molecule

Consider a molecule which consists of two atoms. Let us pretend that we don't know much about the molecule. First, we guess that when the atoms are very far away the force between them must be attractive, otherwise no molecule could be formed. However, at closer distances, they repel each other, since they are restricted to be at finite distance from Heisenberg Uncertainty principle. Hence, there must be an equilibrium distance, which is also the size of molecule. The potential energy at this point is the dissociation energy of the molecule. Also, we have bound states due to this potential.

Expanding potential(Figure 1) around minimum value of potential energy,

$$V(r) = V(r_0) + V'(r_0)(r - r_0) + \frac{1}{2}V''(r_0)(r - r_0)^2 + \frac{1}{6}V'''(r_0)(r - r_0)^3 + \dots \quad (69)$$

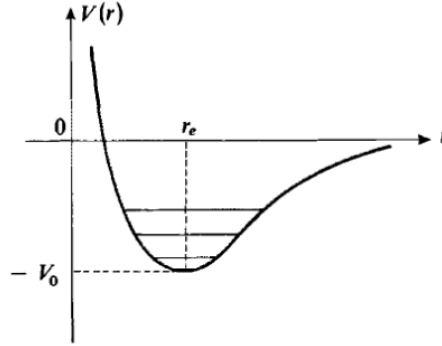


Figure 1: Potential of a diatomic molecule

The higher order terms are less significant.  $V'(r_0)$  will be zero, since potential is minimum at this point. If we call  $r - r_0 = x$ , then, the second order term corresponds to a harmonic oscillator and  $\frac{1}{6}V'''(r_0)$  is  $\lambda$  for a cubic potential in our formulation. Assume the system is in ground state, which is quite common at room temperature since thermal energy is much less than energy of harmonic oscillator ( $KT \ll \hbar\omega$ ) at room temperature. Now, we want to measure the possible transitions of the molecule by interacting with electromagnetic radiation. The dipole moment  $D$  couples to electromagnetic waves, thus for two states  $|\phi\rangle$  and  $|\psi\rangle$  to be able to transition from one to another the condition  $\langle\phi|D|\psi\rangle \neq 0$  has to be satisfied.

When a system goes from first excited state  $|\phi_1\rangle$  to ground state  $|\phi_0\rangle$  so that energy of system changes.

$$|\phi_1\rangle \rightarrow |\phi_0\rangle + \text{photon} \quad (70)$$

the frequency of photon is given by  $\omega_1 = \frac{E_1 - E_0}{\hbar} \approx \sqrt{\frac{V''(r_0)}{m}}$

This is what happens if we include only up till the second order term in the potential energy in equation (69). In this case the states  $|\phi_n\rangle$  become the harmonic oscillator states  $|n\rangle$ . To be more accurate, we need to consider the third order term of the potential energy in equation (69). So, the general expression for the ground state becomes

$$|\phi_0\rangle \rightarrow |0\rangle + \lambda|\psi\rangle + \dots \quad (71)$$

where  $|\psi\rangle$  is the first order correction

$$|\psi\rangle = \sum_{n \neq 0} \frac{\langle n|W|0\rangle|n\rangle}{n\hbar\omega} \quad (72)$$

So, the ground state becomes,

$$|\phi_0\rangle \rightarrow |0\rangle - \lambda \frac{\langle 1|W|0\rangle}{\hbar\omega} |1\rangle - \lambda \frac{\langle 3|W|0\rangle}{3\hbar\omega} |3\rangle \quad (73)$$

The ground state of the entire Hamiltonian is not only  $|0\rangle$  but  $|\phi_0\rangle$  with some higher order correction. We can think of higher states  $|\phi_n\rangle$  to be approximately states of the harmonic oscillator  $|n\rangle$ . So, to this approximation, we can see there can be transitions from  $|\phi_4\rangle, |\phi_2\rangle$  and  $|\phi_1\rangle$  to  $|\phi_0\rangle$  because the corresponding matrix elements  $\langle \phi_n|D|\phi_0\rangle \neq 0$ . When transition takes place from  $|\phi_3\rangle \rightarrow |\phi_0\rangle$ , frequency of photon is given as by applying our results for the cubic potential multiple times.

$$\omega_{3 \rightarrow 0} = \frac{E'_3 - E'_0}{\hbar} \quad (74)$$

$$= 3\omega - \frac{90}{2}\lambda^2 \frac{\hbar}{m^3\omega^4} \quad (75)$$

## Spin-Spin Interaction

Two spins interact because they correspond to magnetic moments which create magnetic fields. Let us consider two spin half particle. Let us switch on magnetic field  $\vec{B} = B\hat{z}$ . So the Hamiltonian can be written as

$$H_0 = \omega_1 S_{1z} + \omega_2 S_{2z} \quad (76)$$

where  $\omega_1$  and  $\omega_2$  are given by equations

$$\omega_1 = -\gamma_1 B_0 \quad (77)$$

$$\omega_2 = -\gamma_2 B_0 \quad (78)$$

where  $\gamma$  is the gyromagnetic ratio. We know the eigenstates of Hamiltonian, which are

$$H_0|++\rangle = \frac{\hbar}{2}(\omega_1 + \omega_2)|++\rangle \quad (79)$$

$$H_0|+-\rangle = \frac{\hbar}{2}(\omega_1 - \omega_2)|+-\rangle \quad (80)$$

$$H_0|-+\rangle = \frac{\hbar}{2}(-\omega_1 + \omega_2)|-+\rangle \quad (81)$$

$$H_0| - - \rangle = -\frac{\hbar}{2}(\omega_1 + \omega_2)| - - \rangle \quad (82)$$

we assume  $\omega_1 > \omega_2$ . In this way, we get four different energy levels. If we make transition from first energy level to second energy level, we get a photon of frequency  $\omega_2$ . Similarly, if we make transition between second and fourth energy level, we get photon of frequency  $\omega_1$ . Also, transition between first to third and third to fourth energy level gives photon of frequency  $\omega_1$  and  $\omega_2$  respectively.

We emphasize the transition with  $\omega_1$  and  $\omega_2$  since they are frequency they appear in the evolution of  $\langle S_x \rangle$ . Now, I am going to switch on small magnetic field  $B_1$  in  $\hat{x}$  direction. If We make this field oscillating with frequency  $\omega$  then we can keep tuning it to one of  $\omega_1$  or  $\omega_2$  to get resonance. To do this, make  $B_1$  time dependent  $B_1 = B_1 \hat{x} \cos(\omega t)$ . Then, we expect resonance when  $\omega$  matches with  $\omega_1$  or  $\omega_2$ . By tuning this  $B_1$  we can studying the transition of the system via resonances.

Consider two spin  $S_1$  and  $S_2$  at distance  $R = R\hat{n}$ . The magnetic moment corresponding to them will be  $\mu_1 = \gamma_1 S_1$  and  $\mu_2 = \gamma_2 S_2$ . Their interaction between these magnetic moment gives perturbation to hamiltonian which is given by

$$W = \frac{\mu_0}{4\pi} \gamma_1 \gamma_2 \left[ \frac{\vec{S}_1 \cdot \vec{S}_2 - 3\hat{n} \cdot \vec{S}_1 \hat{n} \cdot \vec{S}_2}{R^3} \right] \quad (83)$$

If we take  $\xi = -\frac{\mu_0 \gamma_1 \gamma_2}{4\pi R^3}$

In spherical coordinates,  $\hat{n}$  can be written as

$$\hat{n} = \begin{pmatrix} \sin\theta \cos\phi \\ \sin\theta \sin\phi \\ \cos\theta \end{pmatrix}$$

Finally,

$$\begin{aligned} W = & \xi \left[ -S_{1z} S_{2z} - \frac{1}{2} S_{1+} S_{2-} - \frac{1}{2} S_{1-} S_{2+} \right. \\ & + 3(S_{1z} \cos\theta + \frac{1}{2} e^{-i\phi} \sin\theta S_{1+} + \frac{1}{2} e^{i\phi} \sin\theta S_{1-}) \\ & \left. (S_{2z} \cos\theta + \frac{1}{2} e^{-i\phi} \sin\theta S_{2+} + \frac{1}{2} e^{i\phi} \sin\theta S_{2-}) \right] \end{aligned}$$

Applying first order perturbation theory, we find the corrections to each of the energy levels.

$$\langle ++ | W | ++ \rangle = \xi \left[ -\left(\frac{\hbar}{2}\right)^2 + 3\left(\frac{\hbar}{2} \cos\theta\right)^2 \right] = \xi \frac{\hbar^2}{4} [-1 + 3\cos^2\theta] = \hbar\Omega \quad (84)$$

For perturbation theory to work,  $\hbar\Omega \ll \hbar\omega_1, \hbar\omega_2$  has to be satisfied. Similarly we can determine the correction for the other states.

$$\langle -+ | W | -+ \rangle = -\hbar\Omega = \langle +- | W | +- \rangle, \langle -- | W | -- \rangle = \hbar\Omega \quad (85)$$

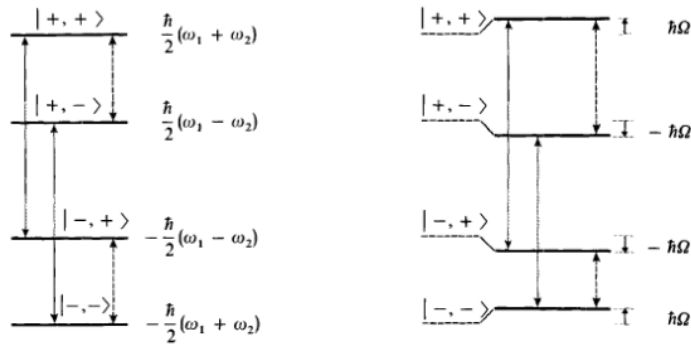


Figure 2: Energy corrections(non-degenerate)

From this correction we can find that the transition from  $|++\rangle$  to  $|--\rangle$  now has an energy of  $\hbar(\omega_1 + 2\Omega)$ , the transition from  $|++\rangle$  to  $|+-\rangle$  has an energy of  $\hbar(\omega_2 + 2\Omega)$ , transition from  $|+-\rangle$  to  $|--\rangle$  now has an energy of  $\hbar(\omega_1 - 2\Omega)$  and transition from  $|+-\rangle$  to  $|-\rangle$  now has an energy of  $\hbar(\omega_2 - 2\Omega)$ . We thus observe that the original two peaks in the spectrum split into two sets of twin peaks centered at  $\omega_1$  and  $\omega_2$  with the twin peaks separated by  $4\Omega$  (Figure 2 and Figure 3).

So far we considered  $\omega_1 > \omega_2$ , but as in some real materials such as gypsum ( $CaSO_4 \cdot 2H_2O$ ),  $\omega_1 = \omega_2 = \omega$ . In such cases we have to employ degenerate perturbation theory since the eigenvalues of  $H_0$  for  $|+-\rangle$  and  $|-\rangle$  are now the same.

We have already found  $\langle + - | W | + - \rangle$  and  $\langle - + | W | - + \rangle$ , it turns out the the matrix elements  $\langle + - | W | - + \rangle$  and  $\langle - + | W | + - \rangle$  are also  $-\hbar\Omega$ . Thus in the basis of  $|+-\rangle$  and  $|-\rangle$  the perturbation can be written as

$$W = -\hbar\Omega \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad (86)$$

Solving for the eigenvalues and eigenvectors of this system, we obtain in the

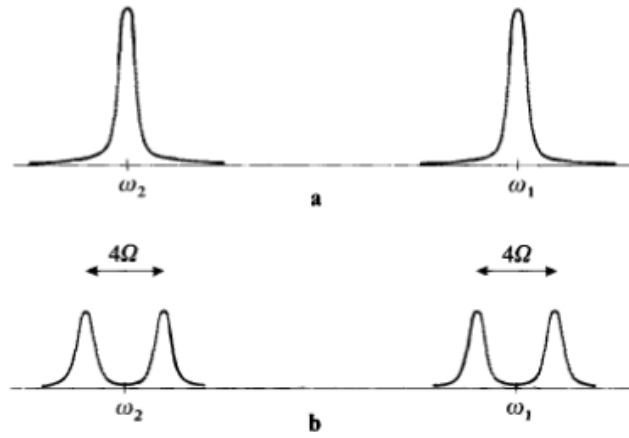


Figure 3: Split of resonance frequencies(non-degenerate)

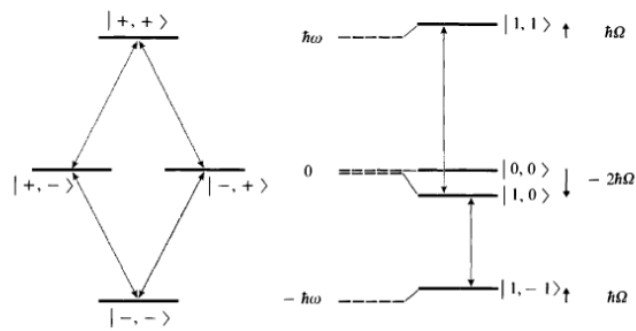


Figure 4: Energy corrections(degenerate)



Figure 5: Split of resonance frequencies(degenerate)

$|SM\rangle$  notation

$$|10\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} + \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}, |00\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} - \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (87)$$

The eigenvalues of  $W$  in the  $|+-\rangle$  and  $| - + \rangle$  basis are 0 and  $-2\hbar\Omega$  corresponding to the states  $|00\rangle$  and  $|10\rangle$  in the  $|SM\rangle$  notation. The other 2 nondegenerate states  $|++\rangle$  and  $|--\rangle$  corresponds to  $|11\rangle$  and  $|1-1\rangle$  in the  $|SM\rangle$  notation. Transitions only occur between states with the same  $L$ . The frequency of transition after correction from  $|11\rangle$  to  $|10\rangle$  is  $\omega + 3\hbar\Omega$  and the frequency for transition from  $|10\rangle$  to  $|1-1\rangle$  becomes  $\omega - 3\hbar\Omega$ . We can thus observe twin peaks centered at  $\omega$  that are separated by  $6\Omega$  (Figure 4 and 5).

## Volume Effect

In a hydrogen atom, we typically assume to have a potential of the form  $V(r) = -\frac{e^2}{r}$ , but with such an assumption we are treating the proton as a point which it really isn't. Thus this volume effect should show up in the spectrum of the atom. Assume the atom has a radius  $a_0$  which is the Bohr radius and the proton has a radius of  $r_0$ , satisfying  $r_0 \ll a_0$ . Also assume the charge of the proton is uniformly distributed in the volume of the sphere, we can find the potential for

both inside and outside the proton

$$V(r) = \begin{cases} -\frac{e^2}{r} & , r > r_0 \\ \frac{3e^2}{r_0} - \frac{e^2}{2r_0^3}r^2 & , r < r_0 \end{cases} \quad (88)$$

Contrasting this potential with the original potential for which we know the energy levels, we obtain that our perturbation for this problem

$$W = \begin{cases} 0 & , r > r_0 \\ \frac{e^2}{2r_0} \left[ \left( \frac{r}{r_0} \right)^2 + 2\frac{r_0}{r} - 3 \right] & , r < r_0 \end{cases} \quad (89)$$

With this correction the Hamiltonian of the hydrogen atom can be written as

$$H = H_0 + W \quad (90)$$

$H_0$  is the hamiltonian of the hydrogen atom treating the proton as fixed and as a point with  $H_0|nlm\rangle = E_n|nlm\rangle$  and  $E_n = -\frac{E_{ion}}{n^2}$ . Where  $E_{ion}$  is the ionizing energy. The energy levels  $|nlm\rangle$  are degenerate which means we need to employ degenerate perturbation theory to solve this problem.

Consider the subspace for a fixed  $n$  and  $W$  in that subspace. The matrix elements in this basis are

$$\begin{aligned} \langle nlm|W|nl'm'\rangle &= \int d^3r \phi_{nlm}^*(\vec{r})W(r)\phi_{nl'm'}(\vec{r}) \\ &= \int d\Omega Y_{lm}^* Y_{l'm'} \int dr r^2 R_{nl}^*(r)W(r)R_{nl'}(r) \\ &= \delta_{ll'}\delta_{mm'} \int dr r^2 W(r)|R_{nl}(r)|^2 \end{aligned} \quad (91)$$

Thus  $W$  in this basis has only diagonal elements which simplifies everything. Also,  $W$  is non-zero only within  $r_0$  thus within  $r_0$  we can approximate  $R_{nl}(r)$  by  $R_{nl}(0)$ . Thus the matrix elements are

$$\begin{aligned} \langle nlm|W|nlm\rangle &= \int dr r^2 W(r)|R_{nl}(r)|^2 \\ &\approx |R_{nl}(0)|^2 \int_0^{r_0} dr r^2 W(r) \\ &= |R_{nl}(0)|^2 \frac{e^2 r_0^2}{10} \end{aligned} \quad (92)$$

Thus we find the corrected energies are given by

$$E'_{nl} = E_n + |R_{nl}(0)|^2 \frac{e^2 r_0^2}{10} + \dots \quad (93)$$

Note that  $|R_{nl}(0)|^2$  is non-zero only when  $l = 0$ , thus only s-waves are affected by this effect (within this approximation) which can be verified by observation.



## Variational Method

Suppose we are given a certain hamiltonian

$$H|\psi\rangle = E|\psi\rangle \quad (94)$$

The expectation of the hamiltonian is given by

$$\langle H \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \quad (95)$$

Now we introduce a perturbation to  $|\psi\rangle$ ,

$$|\psi\rangle \rightarrow |\psi\rangle + \lambda|\delta\psi\rangle \quad (96)$$

Now  $\langle H \rangle$  becomes, to the first order of  $\lambda$ ,

$$\langle H \rangle \rightarrow \frac{\langle H \rangle + \lambda^* \langle \delta\psi | H | \psi \rangle + \lambda \langle \psi | H | \delta\psi \rangle + \dots}{\langle \psi | \psi \rangle + \lambda^* \langle \delta\psi | \psi \rangle + \lambda \langle \psi | \delta\psi \rangle + \dots} = \frac{N}{D} \quad (97)$$

Expand  $D^{-1}$  to first order of  $\lambda$  we obtain

$$D^{-1} = \langle \psi | \psi \rangle^{-1} [1 - \lambda^* \frac{\langle \delta\psi | \psi \rangle}{\langle \psi | \psi \rangle} - \lambda \frac{\langle \psi | \delta\psi \rangle}{\langle \psi | \psi \rangle} + \dots] \quad (98)$$

Plug this into the expression for  $\langle H \rangle$  we obtain

$$\langle H \rangle \rightarrow \frac{N}{D} = \langle H \rangle + \frac{1}{\langle \psi | \psi \rangle} \{ \lambda \langle \psi | H | \delta\psi \rangle - \lambda \langle H \rangle \langle \psi | \delta\psi \rangle + C.C. \} + O(\lambda^2) \quad (99)$$

When the original wavefunction  $|\psi\rangle$  is a eigenfunction of the Hamiltonian,  $H|\psi\rangle = E|\psi\rangle$ , the terms in curly brackets in the above equation becomes

$$\lambda E \langle \psi | \delta\psi \rangle - \lambda E \langle \psi | \delta\psi \rangle + C.C. = 0 \quad (100)$$

Thus in this case after introducing  $|\delta\psi\rangle$  to  $|\psi\rangle$ ,  $\langle H \rangle \rightarrow \langle H \rangle + O(\lambda^2)$ , which means any perturbation of first order to an eigenstate of the Hamiltonian will not change the expectation of the Hamiltonian to the first order.

Conversely, if  $\langle H \rangle$  is not changed by any  $|\delta\psi\rangle$  to first order, we can choose

$$|\delta\psi\rangle = \lambda^*(H - \langle H \rangle)|\psi\rangle \quad (101)$$

With this choice we plug it into the terms in curly brackets in Equation (99)

$$0 = \lambda \langle \psi | H | \delta\psi \rangle - \lambda \langle H \rangle \langle \psi | \delta\psi \rangle + C.C. \quad (102)$$

$$= |\lambda|^2 \langle \psi | (H - \langle H \rangle) (H - \langle H \rangle) | \psi \rangle + C.C. \quad (103)$$

$$= 2 \langle \delta\psi | \delta\psi \rangle \quad (104)$$

From this result and the choice of  $|\delta\psi\rangle$  we find that  $H|\psi\rangle = \langle H \rangle|\psi\rangle$  which means  $|\psi\rangle$  is an eigenvector. We see that the converse of our previous argument is also true.

## Example: Harmonic Oscillator

Consider a Harmonic oscillator, the hamiltonian of which is given by

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2x^2 \quad (105)$$

We want to figure out the ground state. We first want to guess the wave function. For the ground state, a good guess will be  $\psi = e^{-\alpha x^2}$ , where  $\alpha$  is an arbitrary parameter. Now, we need to calculate  $H$

First, the denominator

$$\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} dx e^{-2\alpha x^2} \quad (106)$$

The numerator, i. e. average of hamiltonian is given by

$$\begin{aligned} \langle \psi | H | \psi \rangle &= \int_{-\infty}^{\infty} dx \left[ \frac{\hbar^2}{2m} (\psi')^2 + \frac{1}{2} m \omega^2 x^2 \psi^2 \right] \\ &= \int_{-\infty}^{\infty} dx \left[ \frac{\hbar^2}{2m} (2\alpha x)^2 e^{-2\alpha x^2} + \frac{1}{2} m \omega^2 x^2 e^{-2\alpha x^2} \right] \\ &= \left( \frac{2\hbar^2 \alpha^2}{m} + \frac{1}{2} m \omega^2 \right) \int_{-\infty}^{\infty} dx x^2 e^{-2\alpha x^2} \\ &= \left( \frac{2\hbar^2 \alpha^2}{m} + \frac{1}{2} m \omega^2 \right) \left[ (-) \frac{x e^{-2\alpha x^2}}{4\alpha} \Big|_{-\infty}^{\infty} + \frac{1}{4\alpha} \int_{-\infty}^{\infty} dx e^{-2\alpha x^2} \right] \quad (107) \end{aligned}$$

The first term goes to zero when  $x \rightarrow \infty$  and only the second remains. Also, the integral inside the second term is exactly equal to  $\langle \psi | \psi \rangle$  and get cancels with the denominator. So

$$\begin{aligned} \langle H \rangle &= \left[ \frac{2\hbar^2 \alpha^2}{m} + \frac{1}{2} m \omega^2 \right] \frac{1}{4\alpha} \\ &= \frac{\hbar^2}{2m} \alpha + \frac{m\omega^2}{8\alpha} \quad (108) \end{aligned}$$

I have free parameter  $\alpha$  which we haven't specified. So we find the extremum of  $\langle H \rangle$  with respect to  $\alpha$ . i.e,

$$\frac{d\langle H \rangle}{d\alpha} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0 \quad (109)$$

This equation fixes  $\alpha$ , which is given by

$$\alpha = \frac{m\omega}{2\hbar} \quad (110)$$

For this  $\alpha$ ,

$$\begin{aligned}\langle H \rangle &= \frac{\hbar^2}{2m} \frac{m\omega}{2\hbar} + \frac{1}{8} m\omega^2 \frac{2\hbar}{m\omega} \\ &= \frac{\hbar}{4} + \frac{\hbar}{4} \\ &= \frac{\hbar\omega}{2}\end{aligned}\quad (111)$$

Which is precisely the ground state energy. Now, we see  $\psi$ , which is the ground state wave function, is given by

$$\psi = e^{-\frac{m\omega}{2\hbar}x^2} \quad (112)$$

This is exactly the same wave function that we obtain by solving the Schrodinger equation.

## Example II: Harmonic oscillator

Let us guess  $\psi$  which has peak at  $x \rightarrow 0$  and goes to zero smoothly at  $x \rightarrow \infty$ , as ground state of harmonic oscillator. For that we choose  $\psi = \frac{1}{(x^2 + \alpha^2)}$ . In the same way as before, we calculate the denominator.

$$\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} dx \frac{1}{(x^2 + \alpha^2)^2} \quad (113)$$

substitute  $x = \alpha \tan\theta$ , we get,

$$\begin{aligned}\langle \psi | \psi \rangle &= \frac{2}{\alpha^3} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} d\theta \cos^2 \theta \\ &= \frac{\pi}{2\alpha^3}\end{aligned}\quad (114)$$

Now, the numerator is

$$\langle \psi | H | \psi \rangle = \int_{-\infty}^{\infty} dx \left[ \frac{\hbar^2}{2m} \left( \frac{1}{(x^2 + \alpha^2)} \right)' ^2 + \frac{1}{2} m\omega^2 x^2 \frac{1}{(x^2 + \alpha^2)^2} \right] \quad (115)$$

making substitution  $x = \tan \theta$ , we get,

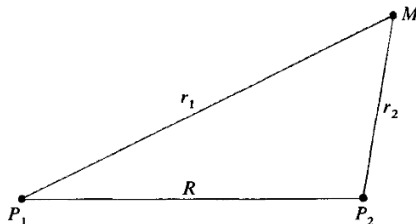
$$\langle \psi | H | \psi \rangle = \frac{\pi \hbar^2}{8m\alpha^5} + \frac{\pi m\omega^2}{4\alpha} \quad (116)$$

Therefore,

$$\langle H \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\hbar^2}{4m\alpha^2} + \frac{m\omega^2 \alpha^2}{2} \quad (117)$$

Taking  $\frac{d\langle H \rangle}{d\alpha} = 0$ , we obtain

$$-\frac{\hbar^2}{2m\alpha^3} + m\omega^2 \alpha = 0 \quad (118)$$

Figure 6:  $H_2^+$  ion

or,

$$\alpha^4 = \frac{\hbar^2}{2m^2\omega^2} \quad (119)$$

Looking at energy

$$\begin{aligned} \langle H \rangle &= \frac{\hbar\omega}{\sqrt{2}} \\ &\approx 0.7 \hbar\omega \end{aligned} \quad (120)$$

But, the correct answer is  $0.5 \hbar\omega$

## Chemical Bond of $H_2^+$ Ion

In this section we will study the “real life” example of the chemical bond in a  $H_2^+$  ion which consists of 2 protons which share an electron.

The geometry of the situation is shown in Figure 6 where  $r_1$  is the distance from proton 1 to the electron,  $r_2$  is the distance from proton 2 to the electron, and  $R$  is the distance from proton 1 to proton 2. The Hamiltonian for the system is given by

$$H = \frac{p^2}{2\mu} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} \quad (121)$$

where the last three terms in the Hamiltonian are the potential energies due to the particle interactions. Now consider the system when the electron is very close to proton 1. Referring to Figure 6 we see that  $r_2 \approx R$  which implies that

the last two terms in the Hamiltonian cancel leaving us with

$$H \approx \frac{p^2}{2\mu} - \frac{e^2}{r_1} \quad (122)$$

Recent work with the hydrogen atom allows us to recognize ground state solutions of the form

$$\varphi(\vec{r}_1) = Ae^{-\frac{r_1}{a_0}} = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r_1}{a_0}} \quad (123)$$

where the constant A was determined by normalization. We can make the same argument for the electron being very close to proton 2 which yields a solution

$$\varphi(\vec{r}_2) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r_2}{a_0}} \quad (124)$$

## The Variational Approach

Because the electron moves around in the real situation we cannot use these specific solutions to generally describe the motion. However, we may use a linear combination of the two solutions as our guess at the variational method

$$\psi = c_1\varphi(\vec{r}_1) + c_2\varphi(\vec{r}_2) \quad (125)$$

So we want to solve the equation

$$H\psi = E\psi \quad (126)$$

in order to find the eigenvalues and eigenfunctions. We use our guess and write the eigenvalue equation in the form

$$H|\psi\rangle = E|\psi\rangle \quad (127)$$

Projecting Equation (125) onto the state  $|1\rangle$  and using the expansion

$$|\psi\rangle = c_1|1\rangle + c_2|2\rangle \quad (128)$$

we obtain

$$c_1\langle 1|H|1\rangle + c_2\langle 1|H|2\rangle = Ec_1\langle 1|1\rangle + Ec_2\langle 1|2\rangle \quad (129)$$

Projecting Equation (125) onto the state  $|2\rangle$  and using Equation (126) we obtain

$$c_1\langle 2|H|1\rangle + c_2\langle 2|H|2\rangle = Ec_1\langle 2|1\rangle + Ec_2\langle 2|2\rangle \quad (130)$$

These two equations may be written in matrix form as

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad (131)$$

where

$$\langle i | H | j \rangle = H_{ij} \quad (132)$$

$$\langle i | j \rangle = S_{ij} \quad (133)$$

and  $i, j = 1, 2$ . Our job now is to analyze the equation

$$\det(H - ES) = 0 \quad (134)$$

We begin by constructing the matrix elements of  $H$  and  $S$  from Equation (131)

**For the matrix  $S$**  we have

$$S_{11} = \langle 1 | 1 \rangle \quad (135)$$

$$S_{12} = \langle 1 | 2 \rangle \quad (136)$$

$$S_{21} = \langle 2 | 1 \rangle \quad (137)$$

$$S_{22} = \langle 2 | 2 \rangle \quad (138)$$

We can simplify this by noting that  $\varphi_1$  and  $\varphi_2$  are both normalized so that  $S_{11} = S_{22} = 1$ . We also notice that since our two states are real  $S_{12} = S_{21} = s$ . Then we see that

$$s = \langle 1 | 2 \rangle = \langle 2 | 1 \rangle = \int d^3r_1 \varphi_1(r_1) \varphi_2(r_2) = \int d^3r_1 \varphi_1(r_1) \varphi_2(r_1 - R) \quad (139)$$

where the last equality comes from the relation between positions  $r_2 = r_1 - R$ . We obtain

$$s = \frac{1}{\pi a_0^3} \int_0^\infty \int_0^\pi \int_0^{2\pi} r_1^2 \cos\theta dr_1 d\theta d\phi e^{\frac{-r_1}{a_0}} e^{\frac{-|r_1-R|}{a_0}} \quad (140)$$

$$= e^{\frac{-R}{a_0}} \left[ 1 + \frac{R}{a_0} + \frac{1}{3} \frac{R^2}{a_0^2} \right] \quad (141)$$

**For the matrix  $H$**  we have

$$H_{11} = \langle 1 | H | 1 \rangle = \langle 1 | \frac{p^2}{2\mu} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} | 1 \rangle \quad (142)$$

The first two terms are simply the Hamiltonian corresponding to the hydrogen atom with  $r = r_1$  where  $H' | 1 \rangle = E' | 1 \rangle$ . Since this is the familiar ionization energy we may rewrite the equation as

$$H_{11} = -E_{ion} - \langle 1 | \frac{e^2}{r_2} | 1 \rangle + \frac{e^2}{R} \quad (143)$$

Now we determine  $\langle 1 | \frac{e^2}{r_2} | 1 \rangle$  as follows

$$\langle 1 | \frac{e^2}{r_2} | 1 \rangle = \int d^3r_1 \varphi^2(r_1) \frac{e^2}{|r_1 - R|} = \frac{1}{\pi a_0^3} \int d^3r_1 e^{\frac{-2r_1}{a_0}} \frac{e^2}{|r_1 - R|} \quad (144)$$

$$= E_{ion} \frac{2a_0}{R} [1 - e^{\frac{-2R}{a_0}} (1 + \frac{R}{a_0})] \quad (145)$$

The matrix element  $H_{12}$  is found in a similar manner to be

$$H_{12} = E_{ion} 2e^{\frac{-R}{a_0}} (1 + \frac{R}{a_0}) \quad (146)$$

But  $H_{11} = H_{22}$  since it does not matter whether you integrate over  $r_1$  or  $r_2$  and  $H_{12} = H_{21}$  since H is Hermitian so we have constructed the two matrices S and H.

### Solutions:

Now we find the determinant to obtain the eigenvalues.

$$\det(H - ES) = (H_{11} - E)^2 - (H_{12} - E)^2 = 0 \quad (147)$$

which yields the two solutions

$$E_+ = \frac{H_{11} + H_{12}}{1 + S} \quad (148)$$

$$E_- = \frac{H_{11} - H_{12}}{1 - S} \quad (149)$$

If the protons fly away from each other ( $R \rightarrow \infty$ ) what happens to these energies? Well, since both are dependent only on  $H_{11}$ ,  $H_{12}$ , and  $S$  we can look at the behavior of these quantities as  $R \rightarrow \infty$  to find out. Equations (143) and (145) imply that

$$\lim_{R \rightarrow \infty} H_{11} \rightarrow -E_{ion} \quad (150)$$

and equations (138) and (144) show that

$$\lim_{R \rightarrow \infty} S \rightarrow 0 \quad (151)$$

$$\lim_{R \rightarrow \infty} H_{12} \rightarrow 0 \quad (152)$$

Referring back to Equations (148) and (149) we see that

$$\lim_{R \rightarrow \infty} E_+ \rightarrow -E_{ion} \quad (153)$$

and

$$\lim_{R \rightarrow \infty} E_- \rightarrow -E_{ion} \quad (154)$$

So that the equations for  $E_+$  and  $E_-$  come together asymptotically as shown in Figure 7.

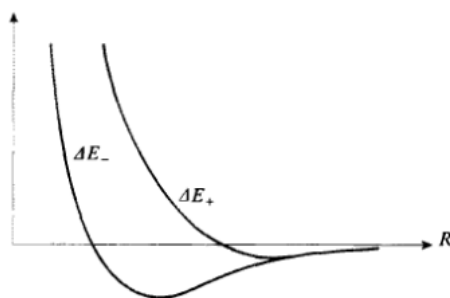


Figure 7:  $E_+$  and  $E_-$  converges to  $-E_{ion}$