

# Chapter 2: Approximate Methods for time-independent Schrödinger Equation

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# Summary of the Chapter

In this chapter we discuss two approaches for obtaining approximate solutions of time-independent Schrödinger equation. The first is a variational approach called Rayleigh-Ritz variational principle, while the other one is called perturbation theory. Noteworthy point is that both approaches are, in principle, applicable to problems which are exactly solvable along with those for which no exact solution is available. Next, we will discuss these approaches in detail.

# Rayleigh-Ritz variational Approach

- This approach is aimed at obtaining a solution to the ground state energy and wave function of the system.
- It involves taking a trial wave function for the problem, and then computing the energy of the system as expectation value of its Hamiltonian.
- In order to obtain its value, the energy is minimized with respect to the parameters in the wave function
- This leads us to equations for those parameters, which can be solved to obtain their values.
- For these values of the parameters, the wave function becomes the best possible solution, yielding the lowest ground state energy for all wave functions of that mathematical form.

# Upper Bound Condition

- Let  $H$  be a Hamiltonian whose exact eigenvalues and eigenfunctions are  $E_i$  and  $|\psi_i\rangle$  respectively.

$$H|\psi_i\rangle = E_i|\psi_i\rangle \quad (1)$$

- Let us consider another wave function  $|\psi\rangle$ , and examine the energy expectation value with respect to it

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \quad (2)$$

- because  $|\psi_i\rangle$  form a complete basis, therefore, we can expand  $|\psi\rangle$  in terms of them

$$|\psi\rangle = \sum_i c_i |\psi_i\rangle \quad (3)$$

## Upper Bound Condition(contd.)

- assuming that  $|\psi_i\rangle$  form an orthonormal set

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad (4)$$

- On substituting in Eq. 2, we have

$$E = \frac{\sum_{i,j} c_j^* c_i \langle \psi_j | H | \psi_i \rangle}{\sum_{i,j} c_j^* c_i \langle \psi_j | \psi_i \rangle}.$$

On using Eqs. 1 and 4, we obtain

$$E = \frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2} \geq \frac{E_0 (\sum_i |c_i|^2)}{(\sum_i |c_i|^2)} \geq E_0$$

- this argument holds because  $E_i \geq E_0$  (the true ground state energy) and because  $|c_i|^2 \geq 0$ .
- This means that the energy corresponding to an arbitrary wave function  $|\psi\rangle$  will always be greater than the true ground state of the system.
- The equality holds only if  $|\psi\rangle = |\psi_0\rangle$ .

## Upper Bound Condition(contd.)

- This means that the energy expectation value with respect to an arbitrary wave function serves as an upper bound for the ground state energy.
- This suggests a procedure for obtaining a decent approximation to the ground state energy.
- Choose a trial wave function with an unknown set of variational parameters (say  $\alpha_i, i = 1, \dots, m$ ).
- Next, compute the energy expectation value with respect to this trial wave function  $|\psi(\alpha_i)\rangle$

$$E(\alpha_i) = \frac{\langle \psi(\alpha_i) | H | \psi(\alpha_i) \rangle}{\langle \psi(\alpha_i) | \psi(\alpha_i) \rangle} \quad (5)$$

- Minimize  $E(\alpha_i)$ , with respect to  $\alpha_i$  using the condition

$$\frac{\partial E(\alpha_i)}{\partial \alpha_i} = 0, i = 1, \dots, m \quad (6)$$

- Solution of Eq.(6) will yield values of  $\alpha_i$ , which can be substituted in Eq.(5) to obtain  $E_{min} \geq E_0$ . We will demonstrate this by a few examples.

## Example(1): Simple Harmonic Oscillator

- Let us estimate the ground state of one-dimensional simple harmonic oscillator using the trial wave function of the form  $\psi(x) = ce^{-\alpha x^2}$
- Because this function is of the form of the exact wave function, the obtained energy should be the exact ground state energy  $\frac{\hbar\omega}{2}$ . Let us first normalize  $\psi(x)$

$$\langle\psi|\psi\rangle = c^2 \int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = 1$$

- Substitute  $t = \sqrt{2\alpha}x$

$$\Rightarrow \langle\psi|\psi\rangle = \frac{c^2}{\sqrt{2\alpha}} \int_{-\infty}^{\infty} e^{-t^2} dt = c^2 \sqrt{\frac{\pi}{2\alpha}} = 1$$

$$\Rightarrow c = \left(\frac{2\alpha}{\pi}\right)^{1/4}$$

- Above we used the value of the Gaussian integral  $\int_{-\infty}^{\infty} e^{-t^2} dt = \sqrt{\pi}$ .

# Simple Harmonic Oscillator(contd.)

- Now

$$E(\alpha) = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \sqrt{\frac{2\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha x^2} \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} e^{-\alpha x^2} + \frac{1}{2} m \omega^2 x^2 e^{-\alpha x^2} \right) dx$$

- But

$$\begin{aligned} \frac{d^2}{dx^2} \{ e^{-\alpha x^2} \} &= \frac{d}{dx} ( -2\alpha x e^{-\alpha x^2} ) \\ &= \left( -2\alpha e^{-\alpha x^2} + 4\alpha^2 x^2 e^{-\alpha x^2} \right) \end{aligned}$$

$$\Rightarrow E(\alpha) = \sqrt{\frac{2\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha x^2} \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} e^{-\alpha x^2} + \frac{1}{2} m \omega^2 x^2 e^{-\alpha x^2} \right) dx$$



# Simple Harmonic Oscillator(contd.)

- using the standard integral

$$\int_{-\infty}^{\infty} x^{2n} e^{-\frac{x^2}{a^2}} dx = \sqrt{\pi} \frac{a^{2n+1} (2n-1)!}{2^n}$$

- we have

$$\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx = \frac{\sqrt{\pi}}{2} \left( \frac{1}{\sqrt{2\alpha}} \right)^3$$

- so that

$$E(\alpha) = \left\{ \sqrt{\frac{2\alpha}{\pi}} 2\alpha \sqrt{\frac{\pi}{2\alpha}} \frac{\hbar^2}{2m} - \frac{\hbar^2}{2m} \sqrt{\frac{2\alpha}{\pi}} 4\alpha^2 \frac{\sqrt{\pi}}{2} \frac{1}{(2\alpha)^{3/2}} + \frac{1}{2} m\omega^2 \frac{\sqrt{\pi}}{2\sqrt{\pi}} \frac{\sqrt{2\alpha}}{(2\alpha)^{3/2}} \right\}$$

$$E(\alpha) = \left\{ \frac{\hbar^2}{2m} \alpha + \frac{m\omega^2}{8\alpha} \right\}$$

$$\frac{dE}{d\alpha} = 0 \Rightarrow \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0$$

# Simple Harmonic Oscillator(contd.)



$$\Rightarrow \alpha = \frac{m\omega}{2\hbar}$$

$$\Rightarrow E_{min} = \frac{\hbar^2}{2m} \frac{m\omega}{2\hbar} + \frac{m\omega^2}{8} \times \frac{m\omega}{2\hbar}$$

$$\Rightarrow \boxed{E_{min} = \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} = \frac{\hbar\omega}{2}} ,$$

which, as expected, is nothing but the exact value of the ground state energy!

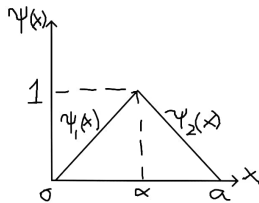
- Furthermore, for this value of  $\alpha$ , the wave function is also the exact ground state wave function

$$\boxed{\psi(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}} = \psi_0(x)}$$

- Thus, as expected, we recover the exact ground state energy and the wave function for this trial wave function

## Example(II): One-Dimensional Box

- Next, let us try to estimate the ground state energy of a particle of mass  $m$ , confined to move in a one dimensional box of length  $a$ , with infinite potential at the boundaries ( $x = 0, a$ ).
- We consider the trial function to be a linear function which is zero at  $x = 0$  and  $x = a$ , and is peaked at  $x = \alpha$ ,  $0 \leq \alpha \leq a$ , where  $\alpha$  is a variational parameter.



- Clearly, this trial wave function is given by

$$\psi(x) = \psi_1(x) = \frac{Nx}{\alpha} \text{ for } 0 \leq x \leq \alpha$$

$$\psi(x) = \psi_2(x) = \frac{N(a-x)}{(a-\alpha)} \text{ for } \alpha \leq x \leq a$$

$$\psi(x) = 0 \text{ elsewhere}$$

# One-Dimensional Box(contd.)

- Next, we obtain the normalization constant

$$\begin{aligned}\int_0^a \psi^2(x) dx &= \frac{N^2}{\alpha^2} \int_0^\alpha x^2 dx + \frac{N^2}{(a-\alpha)^2} \int_\alpha^a (a-x)^2 dx \\ &= \frac{N^2}{3} \alpha + \frac{N^2}{3} (a-\alpha) = 1\end{aligned}$$

$$\frac{N^2}{3} a = 1$$

$$N = \sqrt{\frac{3}{a}}$$

$$\Rightarrow \psi_1(x) = \sqrt{\frac{3}{a}} \frac{x}{\alpha}$$

$$\psi_2(x) = \sqrt{\frac{3}{a}} \frac{(a-x)}{(a-\alpha)}$$

# One-Dimensional Box(contd.)

- Now the standard form

$$E = \langle \psi | H | \psi \rangle = \int \psi^* \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V \right\} \psi d\tau$$

is not valid here because  $\psi'(x)$  is discontinuous at  $x = \alpha$ .

- For such cases one uses the alternative expression

$$E = \int \left\{ \frac{\hbar^2}{2m} (\vec{\nabla} \psi^*) \cdot (\vec{\nabla} \psi) + V \psi^* \psi \right\} d\tau$$

which can be obtained by integrating by parts the first term and using the fact that the wave function vanishes at infinity.

- For the present case  $\psi^* = \psi$  and  $V = 0$ , so that

$$\begin{aligned} E(\alpha) &= \frac{\hbar^2}{2m} \int_0^a \left( \frac{d\psi}{dx} \right)^2 dx \\ &= \frac{\hbar^2}{2m} \int_0^\alpha \left( \frac{d\psi_1}{dx} \right)^2 dx + \frac{\hbar^2}{2m} \int_\alpha^a \left( \frac{d\psi_2}{dx} \right)^2 dx \end{aligned}$$

# One-Dimensional Box(contd.)

- or

$$\begin{aligned} E(\alpha) &= \frac{\hbar^2}{2m} \left(\frac{3}{a}\right) \frac{1}{\alpha^2} \int_0^\alpha dx + \frac{\hbar^2}{2m} \left(\frac{3}{a}\right) \frac{1}{(a-\alpha)^2} \int_\alpha^a dx \\ &= \frac{\hbar^2}{2m} \left(\frac{3}{a}\right) \left\{ \frac{1}{\alpha} + \frac{1}{a-\alpha} \right\} \end{aligned}$$

$$\Rightarrow \frac{dE}{d\alpha} = \frac{\hbar^2}{2m} \left(\frac{3}{a}\right) \left\{ -\frac{1}{\alpha^2} + \frac{1}{(a-\alpha)^2} \right\} = 0$$

$$\Rightarrow a - \alpha = \pm \alpha$$

- The only meaningful solution is

$$2\alpha = a \Rightarrow \alpha = \frac{a}{2}$$

- And

$$E_{min} = \frac{\hbar^2}{2m} \left(\frac{3}{a}\right) \times \frac{4}{a} = \frac{6\hbar^2}{ma^2}$$

# One-Dimensional Box(contd.)

$$E_0(\text{exact}) = \frac{\hbar^2 \pi^2}{2a^2 m} \approx \frac{5\hbar^2}{ma^2} \Rightarrow E_{\min} > E_0$$

- If we plot the true ground state wave function  $\psi_0 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$  along with the approximate wave function  $\psi(x)$  is obtained above, we have

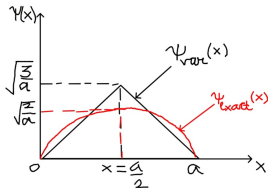


Figure: Comparison between Exact and Approximate wave function

- We note that  $\alpha = \frac{a}{2}$  obtained through variational principle ensures that the variational wave function peaks at the same  $x = \frac{a}{2}$ , as the exact wave function.



# Time-Independent Perturbation Theory

- Time-independent, or static, perturbation theory is another mathematical approach for obtaining approximate solutions of time-independent Schrödinger equation, if the Hamiltonian differs from an exactly solvable model by an additive term.
- Let us assume that the Hamiltonian in question is

$$H = H_0 + V \quad (7)$$

- For which the time independent Schrödinger equation has been solved

$$H_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle \quad (8)$$

- And our aim is to solve

$$H|\psi_n\rangle = E_n|\psi_n\rangle \quad (9)$$

- Approximately, because its exact solutions are unknown. The underlying argument behind perturbation theory is that if  $V$ (called perturbation) is small compared to  $H_0$ , then the solutions of Eq.(9) can be developed in terms of solutions of Eq.(8).

# Time Independent Perturbation Theory

- Because of the smallness of  $V$ ,  $E_n/|\psi_n\rangle$  are expected to be close to  $E_n^{(0)}/|\psi_n^{(0)}\rangle$ .
- It is mathematically helpful to introduce a real parameter  $\lambda(0 \leq \lambda \leq 1)$ , and consider the Hamiltonian

$$H = H_0 + \lambda V \quad (10)$$

- With this, one expects that as  $\lambda$  varies from  $\lambda = 0$  to  $\lambda = 1$ , the eigenvalues and eigenvectors will evolve smoothly from  $E_n^{(0)}/|\psi_n^{(0)}\rangle$  to  $E_n/|\psi_n\rangle$ .
- That will allow us to obtain eigenvalues and eigenvectors as a function of  $\lambda$ , and then we will set  $\lambda = 1$ , to obtain the desired solutions.
- We assume that eigenvalues and eigenvectors of the new Hamiltonian Eq.(10) can be expanded in the powers of  $\lambda$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots \quad (11)$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (12)$$

# Time Independent Perturbation Theory

- We can also assume that the wave function of the unperturbed Hamiltonian is properly normalised  $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$ , while for the perturbed wave function we assume the so-called intermediate normalization.

$$\langle \psi_n^{(0)} | \psi_n \rangle = 1 \quad (13)$$

- Eq.(11) to Eq.(13) yields

$$\langle \psi_n^{(0)} | \psi_n \rangle = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + \lambda \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \lambda^2 \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \dots = 1$$

- Using  $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$ , we have

$$\boxed{\langle \psi_n^{(0)} | \psi_n^{(i)} \rangle = 0 \text{ for } i = 1, 2, \dots} \quad (14)$$

- Next we substitute Eq.(11) and Eq.(12) in the perturbed eigenvalue problem (Eq. 9)

$$(H_0 + \lambda V) | \psi_n \rangle = E_n | \psi_n \rangle$$

# Time Independent Perturbation Theory

- and compare the coefficients on both sides of the same power of  $\lambda$

$$(H_0 + \lambda V) \{ |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots \} = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) \{ |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots \}$$

$$\Rightarrow H_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle \quad (15)$$

$$H_0 |\psi_n^{(1)}\rangle + V |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(1)}\rangle + E_n^{(1)} |\psi_n^{(0)}\rangle \quad (16)$$

$$H_0 |\psi_n^{(2)}\rangle + V |\psi_n^{(1)}\rangle = E_n^{(0)} |\psi_n^{(2)}\rangle + E_n^{(1)} |\psi_n^{(1)}\rangle + E_n^{(2)} |\psi_n^{(0)}\rangle \quad (17)$$

- Or, in general, on comparing coefficients of  $\lambda^i$  on both the sides we obtain

$$H_0 |\psi_n^{(i)}\rangle + V |\psi_n^{(i-1)}\rangle = E_n^{(0)} |\psi_n^{(i)}\rangle + E_n^{(1)} |\psi_n^{(i-1)}\rangle + \dots + E_n^{(i)} |\psi_n^{(0)}\rangle \quad (18)$$

# Time Independent Perturbation Theory

- On taking the inner product of Eq.(18) with  $|\psi_n^{(0)}\rangle$  and using Eq.(14) we obtain a recursive equation of  $E_n^{(i)}$

$$\boxed{E_n^{(i)} = \langle \psi_n^{(0)} | V | \psi_n^{(i-1)} \rangle} \quad (19)$$

- To obtain corrections to the wave function, we expand  $|\psi_n^{(i)}\rangle$  in terms of eigenvectors of  $H_0$ , which form a complete basis

$$|\psi_n^{(i)}\rangle = \sum_k c_{kn}^{(i)} |\psi_k^{(0)}\rangle$$

- because

$$\langle \psi_n^{(0)} | \psi_n^{(i)} \rangle = 0$$

- implies that the sum above must not include  $|\psi_n^{(0)}\rangle$  term which we indicate by a prime

$$|\psi_n^{(i)}\rangle = \sum_{k'} c_{kn}^{(i)} |\psi_k^{(0)}\rangle = \sum_{k \neq n} c_{kn}^{(i)} |\psi_k^{(0)}\rangle \quad (20)$$

# Time Independent Perturbation Theory

- To determine the unknown coefficients  $c_{jn}^{(i)}$ , we take the inner product of Eq.(18) with  $|\psi_j^{(0)}\rangle$

$$\begin{aligned}\langle \psi_j^{(0)} | H_0 | \psi_n^{(i)} \rangle + \langle \psi_j^{(0)} | V | \psi_n^{(i-1)} \rangle &= E_n^{(0)} \langle \psi_j^{(0)} | \psi_n^{(i)} \rangle + \\ &E_n^{(1)} \langle \psi_j^{(0)} | \psi_n^{(i-1)} \rangle + \\ &\dots + E_n^{(i)} \underbrace{\langle \psi_j^{(0)} | \psi_n^{(0)} \rangle}_{=0 \text{ because } j \neq n}\end{aligned}$$

- Using Eq.(20) and orthonormality condition of  $|\psi_j^{(0)}\rangle$ 's, i.e.  $\langle \psi_j^{(0)} | \psi_i^{(0)} \rangle = \delta_{ij}$  also

$$\langle \psi_j^{(0)} | H_0 = E_j^{(0)} \langle \psi_j^{(0)} |$$

- We have

$$\begin{aligned}E_j^{(0)} c_{jn}^{(i)} + \langle \psi_j^{(0)} | V | \psi_n^{(i-1)} \rangle &= E_n^{(0)} c_{jn}^{(i)} + \\ &E_n^{(1)} c_{jn}^{(i-1)} + E_n^{(2)} c_{jn}^{(i-2)} + \dots + E_n^{(i-1)} c_{jn}^{(1)}\end{aligned}$$

$$\begin{aligned}
 \Rightarrow (E_n^{(0)} - E_j^{(0)})c_{jn}^{(i)} &= \langle \psi_j^{(0)} | V | \psi_n^{(i-1)} \rangle - E_n^{(1)}c_{jn}^{(i-1)} + \\
 &\quad - \dots \quad E_n^{(i-1)}c_{jn}^{(i)} \\
 \Rightarrow c_{jn}^{(i)} &= \frac{1}{(E_n^{(0)} - E_j^{(0)})} \left\{ \langle \psi_j^{(0)} | V | \psi_n^{(i-1)} \rangle - E_n^{(1)}c_{jn}^{(i-1)} + \right. \\
 &\quad \left. - \dots \quad E_n^{(i-1)}c_{jn}^{(1)} \right\}
 \end{aligned} \tag{21}$$

- The equation is a recursive relation expressing i-th order correction to  $|\psi_n\rangle$  in terms of lower order correction.

# Time Independent Perturbation Theory

- Next, we self consistently iterate energy correction Eq.(19) and wave function correction Eq.(21), to obtain expressions for these corrections order by order
  - Substituting  $i = 1$ , Eq.(19) yields

$$E_n^{(1)} = \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle = \langle V \rangle_n^{(0)} \quad (22)$$

from Eq.(21) we have

$$\Rightarrow c_{jn}^{(1)} = \frac{\langle \psi_j^{(0)} | V | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_j^{(0)})} \quad (23)$$

$$\Rightarrow |\psi_n^{(1)}\rangle = \sum_{j \neq n} \frac{\langle \psi_j^{(0)} | V | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_j^{(0)})} |\psi_j^{(0)}\rangle \quad (24)$$

Eq.(22) implies that first order correction to the energy to the  $n$ -th level is nothing but the expectation value of the perturbing potential  $V$  with respect to unperturbed wave function.



## Time Independent Perturbation Theory

- For  $i = 2$ ,  $E_n^{(2)} = \langle \psi_n^{(0)} | V | \psi_n^{(1)} \rangle$ , using Eq.(24) we have

$$E_n^{(2)} = \sum_{j \neq n} \langle \psi_n^{(0)} | V | \left\{ \frac{\langle \psi_j^{(0)} | V | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_j^{(0)})} | \psi_j^{(0)} \rangle \right\}$$

$$\boxed{E_n^{(2)} = \sum_{j \neq n} \frac{|\langle \psi_n^{(0)} | V | \psi_j^{(0)} \rangle|^2}{(E_n^{(0)} - E_j^{(0)})}} \quad (25)$$

and

$$c_{jn}^{(2)} = \frac{1}{(E_n^{(0)} - E_j^{(0)})} \left\{ \langle \psi_j^{(0)} | V | \psi_n^{(1)} \rangle - E_n^{(1)} c_{jn}^{(1)} \right\}$$

# Time Independent Perturbation Theory

on substituting the values of  $|\psi_n^{(1)}\rangle$  and  $E_n^{(1)}$ , we have

$$c_{jn}^{(2)} = \frac{\sum_{k \neq n} \frac{\langle \psi_j^{(0)} | V | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | V | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_j^{(0)})(E_n^{(0)} - E_k^{(0)})} - \frac{\langle \psi_j^{(0)} | V | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_j^{(0)})^2}}{(E_n^{(0)} - E_j^{(0)})^2} \quad (26)$$

Substituting this in  $|\psi_n^{(2)}\rangle = \sum_{j \neq n} c_{jn}^{(2)} |\psi_j^{(0)}\rangle$ , we have

$$|\psi_n^{(2)}\rangle = \sum_{j \neq n} \sum_{k \neq n} \frac{\langle \psi_j^{(0)} | V | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | V | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_j^{(0)})(E_n^{(0)} - E_k^{(0)})} |\psi_j^{(0)}\rangle - \sum_{j \neq n} \frac{\langle \psi_j^{(0)} | V | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_j^{(0)})^2} |\psi_j^{(0)}\rangle \quad (27)$$

From Eq.(25) and Eq.(27), it is obvious that with increasingly higher orders, formulas of perturbation expansions, become

# Time Independent Perturbation Theory

more and more complex. For such orders, one normally uses computers to evaluate these corrections.

Points to be noted:

- 1 Because finally we set  $\lambda = 1$ , there is no guarantee that the perturbation series converges, unless the perturbation  $V$  is truly small with respect to  $H_0$ .
- 2 Perturbation series does not have variational property. That is, if we truncate the series at a given order, the obtained energy could be smaller than the true energy.
- 3 We note that if there are states  $E_j^{(0)} = E_n^{(0)}$ , i.e.,  $n$ -th level is degenerate, the corresponding

$$c_j^{(1)} = \frac{\langle \psi_j^{(0)} | V | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_j^{(0)}} \longrightarrow \infty$$

and perturbation theory will diverge. Thus, this approach is applicable only to non degenerate energy levels.

# Example (I): Charged 1D SHO in an Electric Field

- Let us assume that a particle of mass  $m$ , carrying a charge  $q$ , is executing simple harmonic motion of frequency  $\omega$ . Clearly its Hamiltonian is

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad (28)$$

- If we now apply an Electric Field  $\vec{E} = E_0 \hat{j}$ , where  $E_0$  has no position or time dependence, an additional potential  $V = -qE_0 x$  is introduced in the Hamiltonian, and the modified Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - qE_0 x \quad (29)$$

$$\Rightarrow H = H_0 + V \quad (30)$$

- Assuming that  $V$  is a weak perturbation compared to  $H_0$ , we can apply perturbation theory to this problem, treating  $H_0$  to be the unperturbed Hamiltonian.

## (a). Exact Solution

- However this problem can also be solved exactly, as shown next. Thus, this problem allows us to compare the exact solution with those obtained using the perturbation theory.
- We have to solve time dependent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi - qE_0 x\psi = E\psi \quad (31)$$

- Let us write the potential term as a “perfect square”

$$\begin{aligned} V' &= \frac{1}{2}m\omega^2 x^2 - qE_0 x \\ &= \frac{1}{2}m\omega^2 \left\{ x^2 - \frac{2qE_0}{m\omega^2} x \right\} \\ &= \frac{1}{2}m\omega^2 \left\{ \left( x - \frac{qE_0}{m\omega^2} \right)^2 - \frac{q^2 E_0^2}{m^2 \omega^4} \right\} \end{aligned}$$

- Or

$$V' = \frac{1}{2}m\omega^2 \left( x - \frac{qE_0}{m\omega^2} \right)^2 - \frac{q^2 E_0^2}{2m\omega^2} \quad (32)$$

- If we substitute this in Eq.(31) and make the transformation

$$x' = x - \frac{qE_0}{m\omega^2} \quad (33)$$

- And use

$$\frac{d}{dx} = \frac{dx'}{dx} \frac{d}{dx'} = \frac{d}{dx'}$$

$$\Rightarrow \frac{d^2}{dx^2} = \frac{d}{dx} \left( \frac{d}{dx} \right) = \left( \frac{d}{dx'} \right) \left( \frac{d}{dx'} \right) = \frac{d^2}{dx'^2}$$

- We have

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx'^2} + \frac{1}{2} m \omega^2 x'^2 \psi - \frac{q^2 E_0^2}{2m\omega^2} \psi = E \psi$$

- which leads to a new eigenvalue problem

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx'^2} + \frac{1}{2}m\omega^2 x'^2\psi = E'\psi \quad (34)$$

- where

$$E' = E + \frac{q^2 E_0^2}{2m\omega^2} \quad (35)$$

- Eq.(34) has the form of eigenvalue problem of a 1D SHO, therefore, it will have the same solutions

$$\psi_n(x') = 2^{-\frac{n}{2}} (n!)^{-\frac{1}{2}} \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x'^2} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x'\right) \quad (36)$$

- and

$$E'_n = E_n + \frac{q^2 E_0^2}{2m\omega^2} = \left(n + \frac{1}{2}\right) \hbar\omega$$

$$\Rightarrow \boxed{\begin{aligned} E_n &= \left(n + \frac{1}{2}\right) \hbar\omega - \frac{q^2 E_0^2}{2m\omega^2} \\ E_n &= E_n^{(0)} - \frac{q^2 E_0^2}{2m\omega^2} \end{aligned}} \quad (37)$$



## (b). Perturbation Theoretic Solution

- On treating  $V = -qE_0x$  as a small perturbation, with  $H_0$  as the reference Hamiltonian, we have

$$E_n^{(0)} = \left( n + \frac{1}{2} \right) \hbar\omega \quad (38)$$

$$\psi_n^{(0)}(x) = 2^{-\frac{n}{2}} (n!)^{-\frac{1}{2}} \left( \frac{m\omega}{\hbar\pi} \right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2} H_n \left( \sqrt{\frac{m\omega}{\hbar}} x \right) \quad (39)$$

Let's calculate perturbation corrections, order by order

- First Order correction

$$\begin{aligned} E_n^{(1)} &= \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle \\ &= -qE_0 \langle \psi_n^{(0)} | x | \psi_n^{(0)} \rangle \\ &= 0 \end{aligned}$$

# Perturbation Theoretic Solution

- Because  $\psi_n^{(0)}(x)$  have a definite parity w.r.t.  $x \rightarrow -x$ ;  
 $\psi_n^{(0)}(-x) = (-1)^n \psi_n^{(0)}(x)$  while  $x$  is an odd parity operator.  
Thus, the integrand is odd parity, leading to a zero integral.
- And, the first-order correction to the  $n$ -th eigenfunction is

$$\begin{aligned} |\psi_n^{(1)}\rangle &= \sum_{j \neq n} \frac{\langle \psi_j^{(0)} | V | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_j^{(0)})} |\psi_j^{(0)}\rangle \\ &= -qE_0 \sum_{j \neq n} \frac{\langle \psi_j^{(0)} | x | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_j^{(0)})} |\psi_j^{(0)}\rangle \end{aligned}$$

- For a 1D-SHO we know that

$$\langle \psi_j^{(0)} | x | \psi_n^{(0)} \rangle = \sqrt{\frac{\hbar}{2m\omega}} \left\{ \sqrt{n} \delta_{j,n-1} + \sqrt{n+1} \delta_{j,n+1} \right\}$$

with this we have

$$|\psi_n^{(1)}\rangle = -\frac{qE_0}{\hbar\omega} \sqrt{\frac{\hbar n}{2m\omega}} |\psi_{n-1}^{(0)}\rangle + \frac{qE_0}{\hbar\omega} \sqrt{\frac{\hbar(n+1)}{2m\omega}} |\psi_{n+1}^{(0)}\rangle$$

# Perturbation Theoretic Solution

- Second order correction:

$$\begin{aligned} E_n^{(2)} &= \sum_{j \neq n} \frac{|\langle \psi_n^{(0)} | V | \psi_j^{(0)} \rangle|^2}{(E_n^{(0)} - E_j^{(0)})} \\ &= q^2 E_0^2 \sum_{j \neq n} \frac{|\langle \psi_n^{(0)} | x | \psi_j^{(0)} \rangle|^2}{(E_n^{(0)} - E_j^{(0)})} \end{aligned}$$

- Using the previous result we have

$$\begin{aligned} E_n^{(2)} &= q^2 E_0^2 \left\{ \frac{\hbar}{2m\omega} \frac{n}{\hbar\omega} - \frac{\hbar}{2m\omega} \frac{n+1}{\hbar\omega} \right\} \\ &= -\frac{q^2 E_0^2}{2m\omega^2} \end{aligned}$$

- Which is nothing but the exact correction. We shall not consider the second order correction to the wave function  $|\psi_n^{(2)}\rangle$  because the calculation is tedious.

# Perturbation Theoretic Solution

- For  $n = 0$ , let us compare  $|\psi_n^{(1)}\rangle$  to the first order terms in the exact wave function  $\psi_{n=0}(x')$

$$\psi_0(x') = \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}\left(x - \frac{qE_0}{m\omega^2}\right)^2}$$

$$\psi_0(x') = \psi_0(x) e^{-\frac{q^2 E_0^2}{2\hbar\omega}} e^{\frac{qE_0 x}{\hbar\omega}}$$

to first order in  $E_0$

$$e^{-\frac{q^2 E_0^2}{2\hbar\omega}} \approx 1$$

$$e^{\frac{qE_0 x}{\hbar\omega}} \approx 1 + \frac{qE_0 x}{\hbar\omega}$$

$$\psi_0(x') \approx \psi_0(x) + \psi_0(x) \frac{qE_0}{\hbar\omega} x$$

$$x = \sqrt{\frac{\hbar}{m\omega}} \frac{1}{2} \left( 2\sqrt{\frac{m\omega}{\hbar}} x \right) = \frac{1}{2} \sqrt{\frac{\hbar}{m\omega}} H_1(\xi)$$

where  $\xi = x\sqrt{\frac{m\omega}{\hbar}}$

# Perturbation Theoretic Solution

- So

$$\psi_0(x) \frac{qE_0 x}{\hbar\omega} = \frac{qE_0}{\hbar\omega} \frac{1}{\sqrt{2}} \sqrt{\frac{\hbar}{2m\omega}} \psi_0(x) H_1(\xi)$$

but

$$\begin{aligned} \psi_0(x) H_1(\xi) &= \sqrt{2} \left( \frac{m\omega}{\hbar\pi} \right)^{\frac{1}{4}} \frac{1}{\sqrt{2}} e^{-\frac{m\omega}{\hbar^2} x^2} H_1\left(\sqrt{\frac{m\omega}{\hbar}} x\right) \\ &= \sqrt{2} \psi_1(x) \end{aligned}$$

with this

$$\psi_0(x') \approx \psi_0(x) + \frac{qE_0}{\hbar\omega} \sqrt{\frac{\hbar}{2m\omega}} \psi_1(x)$$

Thus the correction term

$$\Delta\psi_0(x) = \frac{qE_0}{\hbar\omega} \sqrt{\frac{\hbar}{2m\omega}} \psi_1(x)$$

agrees perfectly with  $|\psi_n^{(1)}\rangle$  for  $n = 0$ . One can prove this result for any value of  $n$ .

# Quadratic Stark Effect of Hydrogen Atom

- We know that the Hamiltonian of the hydrogen atom is

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} \quad (40)$$

- It satisfies the time independent Schrödinger equation

$$H_0|\psi_{nlm}\rangle = E_n^{(0)}|\psi_{nlm}\rangle \quad (41)$$

- If we apply a static electric field on the hydrogen atom, its energy levels get shifted, and the phenomena is called the **Stark effect**.
- As a matter of fact this phenomena is observed not just for hydrogen, rather for all atoms, molecules and solids.
- It is seen that for non degenerate levels, the energy level shift is proportional to square of strength of the E-field and the phenomena is called **Quadratic Stark effect**.

## Quadratic Stark Effect(contd.)

- For certain degenerate levels, one observes a shift linearly proportional to the field, and then the phenomenon is called **Linear Stark effect**.
- The ground state of the hydrogen atom is non degenerate (except for spin degeneracy, which plays no role here), therefore it will exhibit Quadratic Stark effect whose theory we will develop next.
- Let us suppose that the external electric field is in the z direction  $\vec{E} = E_0 \hat{k}$ , and electronic charge is  $q = -e$ , then the modified Hamiltonian will be

$$H = H_0 + eE_0 z \quad (42)$$

- Thus, the perturbation term is given by

$$V = eE_0 z \quad (43)$$

and the question is, can this be considered small ?

# Quadratic Stark Effect(contd.)

- Most electric fields produced in the lab are much smaller than the strength of internal electric fields, which are  $\sim 10^{11} \text{ V/m}$ .
- Therefore, the assumption of perturbation being much smaller than the original Hamiltonian is valid.
- For the  $n$ -th energy level, the correction up to second order in the electric field is

$$\begin{aligned} E_n &= E_n^{(0)} + \langle n|V|n\rangle + \sum_{k \neq n} \frac{|\langle n|V|k\rangle|^2}{E_n^{(0)} - E_k^{(0)}} \\ &= E_n^{(0)} + eE_0 \langle \psi_n^{(0)} | z | \psi_n^{(0)} \rangle + e^2 E_0^2 \sum_{k \neq n} \frac{|\langle \psi_n^{(0)} | z | \psi_k^{(0)} \rangle|^2}{(E_n^{(0)} - E_k^{(0)})} \end{aligned} \quad (44)$$

- Let us calculate perturbative corrections to the ground state of hydrogen atom, so that

$$|\psi_n^{(0)}\rangle = |1s\rangle \quad (45)$$



# Quadratic Stark Effect(contd.)

- Using this in Eq.(44)

$$E_{1s} = E_{1s}^{(0)} + eE_0 \langle 1s|z|1s \rangle + e^2 E_0^2 \sum_{k \neq n} \frac{|\langle 1s|z|\psi_k^{(0)} \rangle|^2}{(E_{1s}^{(0)} - E_k^{(0)})} \quad (46)$$

- But  $\langle 1s|z|1s \rangle = 0$  because a state has a definite parity, and  $z$  has odd parity.
- Thus, we will have corrections only in the second order of perturbation theory.
- Let us compute the second order terms which are non zero.
- All hydrogen atom eigenstates can be written in the form  $|nlm\rangle$ . Let us compute

$$\langle nlm|z|n'l'm' \rangle = \langle nlm|X_1^0|n'l'm' \rangle \quad (47)$$

# Quadratic Stark Effect(contd.)

- Using Wigner-Eckart theorem, and the short notation  $X_1 \equiv X$ , we have

$$\langle nlm|z|n'l'm'\rangle = \langle l'1m'0|l'1lm\rangle\langle nl||X||n'l'\rangle$$

- Clearly  $m' = m$  for non-vanishing CGC. Therefore, non zero matrix elements will correspond to

$$\langle nlm|z|n'l'm'\rangle = \langle l'1m0|l'1lm\rangle\langle nl||X||n'l'\rangle$$

- In our case  $nlm \equiv 100 \equiv 1s$

$$\begin{aligned}\Rightarrow \langle 1s|z|\psi_k^{(0)}\rangle &= \langle 100|X|n'l'm'\rangle \\ &= \langle l'100|l'100\rangle\langle 10||X||n'l'\rangle\end{aligned}$$

# Quadratic Stark Effect(contd.)

- As per selection rule  $\langle l'100|l'100\rangle$  is non zero only if  $l' = 1$ , and  $\langle 1100|1100\rangle = -\frac{1}{\sqrt{3}}$ .
- This means that  $\langle 1s|z|\psi_k^{(0)}\rangle$  will be non-zero only for p-type states with  $m = 0$ , i.e.

$$\begin{aligned}\langle 1s|z|\psi_k^{(0)}\rangle &= \langle 1s|z|n'pm' = 0\rangle \\ &= -\sqrt{\frac{1}{3}}\langle 10||X||n'p\rangle\end{aligned}$$

- Thus, apart from the restriction that sum is only over p-type states, we have no other way to truncate the sum.
- Thus, sum over  $k$  will include an infinite number of terms containing not just bound p states, but also positive energy continuum p-type states.

# Quadratic Stark Effect(contd.)

- There are several ways to tackle this problem:
  - 1 One can convert the second order energy correction infinite series into a differential equation which can be solved exactly.
  - 2 One can include a large number of terms in the series using a computer, and sum of them till a desired level of convergence achieved. The terms will decrease in magnitude with increasing  $k$  because  $E_{1s}^0 - E_k^0$  (the denominator) will increase.
  - 3 One can find an upper bound on the contribution of the second order term using a mathematical trick which we demonstrate next

$$\begin{aligned} E_n^{(2)} &= e^2 E_0^2 \sum_{k \neq 1s} \frac{|\langle \psi_{1s}^{(0)} | z | \psi_k^{(0)} \rangle|^2}{(E_{1s}^{(0)} - E_k^{(0)})} \\ &\leq e^2 E_0^2 \sum_k \frac{|\langle \psi_{1s}^{(0)} | z | \psi_k^{(0)} \rangle|^2}{(E_{1s}^{(0)} - E_{2p}^{(0)})} \end{aligned}$$

# Quadratic Stark Effect(contd.)

- But

$$E_{1s}^{(0)} - E_{2p}^{(0)} = \frac{e^2}{2a_0} \left[ \frac{1}{4} - 1 \right] = -\frac{3e^2}{8a_0}$$

where  $a_0 \equiv$  Bohr radius

- Now numerator is

$$\sum_k |\langle \psi_{1s}^{(0)} | z | \psi_k^{(0)} \rangle|^2 = \sum_k \langle \psi_{1s}^{(0)} | z | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | z | \psi_{1s}^{(0)} \rangle$$

- $k$  also includes the contribution of the  $1s$  term, and also terms corresponding to  $l \neq 1$  orbitals because  $\langle \psi_{nlm}^{(0)} | z | \psi_{nlm}^{(0)} \rangle = 0$ .
- Using the fact that  $\sum_k |\psi_k^{(0)}\rangle \langle \psi_k^{(0)}| = I$ , we obtain

$$\sum_k |\langle \psi_{1s}^{(0)} | z | \psi_k^{(0)} \rangle|^2 = \langle \psi_{1s}^{(0)} | z^2 | \psi_{1s}^{(0)} \rangle$$

- It can be shown

$$\langle \psi_{1s}^{(0)} | z^2 | \psi_{1s}^{(0)} \rangle = a_0^2$$



$$\begin{aligned} E_{1s}^{(2)} &< -\frac{e^2 E_0^2 8 a_0}{3 e^2} a_0^2 \\ \Rightarrow E_{1s}^{(2)} &< -\frac{8 E_0^2 a_0^3}{3} \end{aligned}$$

- Because the leading term correction to energy is  $\propto E_0^2$ , this effect is called **Quadratic Stark Effect**.

# Wave Function Renormalization

- So far we have assumed that the perturbed wave function is intermediate normalized

$$\langle \psi_n^{(0)} | \psi_n \rangle = 1$$

- However, if we want to normalize  $|\psi_n\rangle$ , we have to compute the quantity  $\langle \psi_n | \psi_n \rangle$ , and then multiply the wave function by its inverse square root, to obtain the normalized wave function  $|\bar{\psi}_n\rangle$

$$|\bar{\psi}_n\rangle = Z^{1/2} |\psi_n\rangle \quad (48)$$

where

$$Z = \frac{1}{\langle \psi_n | \psi_n \rangle} \quad (49)$$

- Let us compute  $Z$  to the second order

$$\langle \psi_n | \psi_n \rangle = \langle \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots | \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots \rangle$$

# Wave Function Renormalization(contd.)

- Using the fact that

$$\langle \psi_n^{(0)} | \psi_n^{(i)} \rangle = 0$$

- We obtain to second order in  $\lambda^2$

$$\begin{aligned} \langle \psi_n | \psi_n \rangle &= 1 + \lambda^2 \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \dots \\ &= 1 + \lambda^2 \sum_{k'} \frac{|\langle \psi_n^{(0)} | V | \psi_k^{(0)} \rangle|^2}{(E_n^{(0)} - E_k^{(0)})^2} \end{aligned} \quad (50)$$

- Thus, we note that  $|\psi_n\rangle$  is normalized to first order in  $\lambda$ .
- Now, for small  $\lambda$ , to second order

$$\begin{aligned} Z &= \frac{1}{\langle \psi_n | \psi_n \rangle} = 1 - \lambda^2 \sum_{k'} \frac{|\langle \psi_n^{(0)} | V | \psi_k^{(0)} \rangle|^2}{(E_n^{(0)} - E_k^{(0)})^2} \\ &= \frac{\partial}{\partial E_n^{(0)}} \left\{ E_n^{(0)} + \lambda \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle + \lambda^2 \sum_{k'} \frac{|\langle \psi_n^{(0)} | V | \psi_k^{(0)} \rangle|^2}{(E_n^{(0)} - E_k^{(0)})} \right\} \end{aligned}$$



or

$$Z = \frac{\partial E_n}{\partial E_n^{(0)}} \quad (51)$$

- Although we have derived this result to second order, but it is an exact result true to any order.
- Note that  $Z = |\langle \psi_n^{(0)} | \bar{\psi}_n \rangle|^2$ , that is the probability of finding the  $n$ -th unperturbed state, in the perturbed state.

# Degenerate Perturbation Theory

- Let us assume that the  $n$  –  $th$  energy level of the unperturbed Hamiltonian is  $g$ -fold degenerate

$$H_0|\psi_{ni}^{(0)}\rangle = E_n^{(0)}|\psi_{ni}^{(0)}\rangle \text{ where } i = 1, 2, \dots, g \quad (52)$$

- If we try to calculate the first-order wave function correction, or the second-order energy correction, we have

$$|\psi_{ni}^{(1)}\rangle = \sum_{j \neq i} \frac{|\langle \psi_{nj}^{(0)} | V | \psi_{ni}^{(0)} \rangle|^2}{(E_n^{(0)} - E_n^{(0)})} |\psi_{nj}^{(0)}\rangle + \sum_{k \neq n} \frac{|\langle \psi_k^{(0)} | V | \psi_n^{(0)} \rangle|^2}{(E_n^{(0)} - E_k^{(0)})} |\psi_k^{(0)}\rangle \quad (53)$$

and

$$E_n^{(2)} = \sum_{j \neq i} \frac{|\langle \psi_{nj}^{(0)} | V | \psi_{ni}^{(0)} \rangle|^2}{(E_n^{(0)} - E_n^{(0)})} + \sum_{k \neq n} \frac{|\langle \psi_k^{(0)} | V | \psi_n^{(0)} \rangle|^2}{(E_n^{(0)} - E_k^{(0)})} \quad (54)$$

# Degenerate Perturbation Theory

- Note that in order to compute the corrections  $|\psi_{ni}^{(1)}\rangle$  and  $E_n^{(2)}$ , we have to perform summation over  $g-1$  degenerate levels (see first terms of Eq.(53) and Eq.(54)) leading to vanishing denominators and divergent contributions.
- The way to handle this problem mathematically is to make the divergent first terms of Eq.(53) and Eq.(54) vanish, by ensuring that  $\langle \psi_{nj}^{(0)} | V | \psi_{ni}^{(0)} \rangle = 0$ ; i.e., by making the numerators also vanish.
- The straightforward way to achieve this is to diagonalize  $V$  within the  $g$ -dimensional subspace, and then use the eigen functions of  $V$  as the new wave functions instead of  $|\psi_{ni}^{(0)}\rangle$ . Let us see how this works.
- Let the representation of  $V$  within degenerate subspace defined as

$$V_{ij}^{(n)} = \langle \psi_{nj}^{(0)} | V | \psi_{ni}^{(0)} \rangle \quad (55)$$

# Degenerate Perturbation Theory

- Then the  $g \times g$  dimensional Matrix  $V^{(n)}$  defined as

$$V^{(n)} = \begin{pmatrix} V_{11}^{(n)} & \cdots & V_{1g}^{(n)} \\ \vdots & \vdots & \vdots \\ V_{g1}^{(n)} & \cdots & V_{gg}^{(n)} \end{pmatrix} \quad (56)$$

is clearly hermitian because  $V$  is a Hermitian operator.

- Thus  $V^{(n)}$  is diagonalizable with the real eigenvalues and mutually orthogonal eigenvectors

$$V^{(n)}|\psi_{n\alpha}^{(0)}\rangle = V_{n\alpha}|\psi_{n\alpha}^{(0)}\rangle \quad (57)$$

and

$$\langle \psi_{n\alpha}^{(0)} | \psi_{n\beta}^{(0)} \rangle = \delta_{\alpha\beta} \text{ for } \alpha, \beta = 1, 2, \dots, g \quad (58)$$

where eigen vectors  $|\psi_{n\alpha}^{(0)}\rangle$  are clearly linear combination of  $|\psi_{ni}^{(0)}\rangle$ 's.

$$|\psi_{n\alpha}^{(0)}\rangle = \sum_{i=1}^g C_{i\alpha}^{(n)} |\psi_{ni}^{(0)}\rangle \quad (59)$$

- where coefficients  $C_{i\alpha}^{(n)}$  are eigenvectors of matrix  $V^{(n)}$

$$\begin{pmatrix} V_{11}^{(n)} & \cdots & V_{1g}^{(n)} \\ \vdots & \ddots & \vdots \\ V_{g1}^{(n)} & \cdots & V_{gg}^{(n)} \end{pmatrix} \begin{pmatrix} C_{1\alpha}^{(n)} \\ \vdots \\ C_{g\alpha}^{(n)} \end{pmatrix} = V_{n\alpha}^{(1)} \begin{pmatrix} C_{1\alpha}^{(n)} \\ \vdots \\ C_{g\alpha}^{(n)} \end{pmatrix} \quad (60)$$

- using Eq.(57) and Eq.(58), it is obvious that

$$\begin{aligned} \langle \psi_{n\beta}^{(0)} | V | \psi_{n\alpha}^{(0)} \rangle &= \langle \psi_{n\beta}^{(0)} | V^{(n)} | \psi_{n\alpha}^{(0)} \rangle \\ &= V_{n\alpha}^{(1)} \langle \psi_{n\beta}^{(0)} | \psi_{n\alpha}^{(0)} \rangle \\ &= V_{n\alpha}^{(1)} \delta_{\alpha\beta} \end{aligned}$$

# Degenerate Perturbation Theory

- Now, if for computing the perturbation theoretic corrections to the  $n$ -th level we use the kets  $|\psi_{n\alpha}^{(0)}\rangle, \alpha = 1, \dots, g$  instead of  $|\psi_{ni}^{(0)}\rangle$ , we have

$$\begin{aligned} H_0 |\psi_{n\alpha}^{(0)}\rangle &= \sum_j C_{j\alpha}^{(n)} H_0 |\psi_{nj}^{(0)}\rangle \\ &= \sum_j C_{j\alpha}^{(n)} E_n^{(0)} |\psi_{nj}^{(0)}\rangle \\ &= E_n^{(0)} \left( \sum_j C_{j\alpha}^{(n)} |\psi_{nj}^{(0)}\rangle \right) \end{aligned}$$

or

$$\boxed{H_0 |\psi_{n\alpha}^{(0)}\rangle = E_n^{(0)} |\psi_{n\alpha}^{(0)}\rangle} \quad (61)$$

- Thus  $|\psi_{n\alpha}^{(0)}\rangle$ , just like  $|\psi_{ni}^{(0)}\rangle$  are still eigenvectors of the unperturbed Hamiltonian  $H_0$ , with the same eigenvalue  $E_n^{(0)}$ .

# Degenerate Perturbation Theory

- The first order perturbation correction to the energy will be

$$E_{n\alpha}^{(1)} = \langle \psi_{n\alpha}^{(0)} | V | \psi_{n\alpha}^{(0)} \rangle = V_{n\alpha} \quad (62)$$

- Using Eq.(53) and Eq.(54) to compute  $|\psi_{n\alpha}^{(1)}\rangle$  and  $E_n^{(2)}$ , we have

$$|\psi_{n\alpha}^{(1)}\rangle = \sum_{\beta \neq \alpha} \frac{\langle \psi_{n\beta}^{(0)} | V | \psi_{n\alpha}^{(0)} \rangle}{(E_n^{(0)} - E_{n\beta}^{(0)})} |\psi_{n\beta}^{(0)}\rangle + \sum_{k \neq n} \frac{\langle \psi_k^{(0)} | V | \psi_{n\alpha}^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} |\psi_k^{(0)}\rangle$$

but both the numerator and denominator of the first term vanish, so we take that to be zero, leading to

$$|\psi_{n\alpha}^{(1)}\rangle = \sum_{k \neq n} \frac{\langle \psi_k^{(0)} | V | \psi_{n\alpha}^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} |\psi_k^{(0)}\rangle \quad (63)$$

and

$$|\psi_{n\alpha}\rangle = |\psi_{n\alpha}^{(0)}\rangle + \lambda |\psi_{n\alpha}^{(1)}\rangle + \dots \quad (64)$$

- Similarly we will have

$$\begin{aligned} E_{n\alpha}^{(2)} &= \sum_{\beta \neq \alpha} \frac{|\langle \psi_{n\beta}^{(0)} | V | \psi_{n\alpha}^{(0)} \rangle|^2}{(E_n^{(0)} - E_n^{(0)})} + \sum_{k \neq n} \frac{|\langle \psi_k^{(0)} | V | \psi_{n\alpha}^{(0)} \rangle|^2}{(E_n^{(0)} - E_k^{(0)})} \\ &= \sum_{k \neq n} \frac{|\langle \psi_k^{(0)} | V | \psi_{n\alpha}^{(0)} \rangle|^2}{(E_n^{(0)} - E_k^{(0)})} \end{aligned} \quad (65)$$

and

$$E_{n\alpha} = E_n^{(0)} + \lambda V_{n\alpha} + \lambda^2 \sum_{k \neq n} \frac{|\langle \psi_k^{(0)} | V | \psi_{n\alpha}^{(0)} \rangle|^2}{(E_n^{(0)} - E_k^{(0)})} \quad (66)$$

- Note that Eq.(63) and Eq.(64) do not involve summations over the states of degenerate subspace( $|\psi_{n\beta}\rangle$ ) because of vanishing numerator, therefore, the sums will not be divergent.



# Degenerate Perturbation Theory

- In case the eigenvalues of  $V$  matrix ( $V_{n\alpha}$ ) in the degenerate subspace still have some degeneracies then it is not clear to which  $|\psi_{n\alpha}^{(0)}\rangle$  will the perturbed wave function reduce in the limit  $\lambda \rightarrow 0$ .
- Apart from this ambiguity, rest of the problems related to the divergences have been resolved in this theory.

## Example: Linear Stark Effect for $n=2$ (H-atom)

- If the electric field of strength  $E_0$  has been applied in the  $z$  direction, then as discussed earlier in the context of **Quadratic Stark effect**, the perturbation term in the Hamiltonian will be given by

$$V = eE_0z$$

- Ignoring the spin,  $n = 2$  level of the hydrogen is  $2^2 = 4$ -fold degenerate with the unperturbed degenerate states  $|2s\rangle, |2p_0\rangle, |2p_1\rangle, |2p_{-1}\rangle$ , where subscripts associated with the  $p$  orbitals indicate the  $m$  values. For this Subspace we define the order basis as

$$\begin{aligned} |1\rangle &= |2s\rangle \\ |2\rangle &= |2p_0\rangle \\ |3\rangle &= |2p_1\rangle \\ |4\rangle &= |2p_{-1}\rangle \end{aligned} \tag{67}$$

# Linear Stark Effect for $n=2$ (H-atom)

- Now we have to construct and diagonalize the  $V$  operator in this basis.
- Because all are our basis States have definite parity, so as discussed earlier the diagonal Matrix elements with respect them will vanish

$$V_{ii} = \langle i|V|i\rangle = 0 \text{ for } i = 1, \dots, n$$

- Additionally, using the Wigner-Eckart theorem

$$\begin{aligned}\langle 1|V|3\rangle &= \sqrt{\frac{4\pi}{3}} eE_0 \langle 1100|1100\rangle \langle 20||r|21\rangle \\ &= 0 \text{ (CGC vanishes)}\end{aligned}$$

- For the same reason, the following matrix elements also vanish

$$\langle 1|V|4\rangle = \langle 2|V|3\rangle = \langle 2|V|4\rangle = 0$$

# Linear Stark Effect for $n=2$ (H-atom)

- Thus the only off-diagonal matrix elements of  $V$  which do not vanish are

$$\langle 1|V|2\rangle = \langle 2|V|1\rangle = \sqrt{\frac{4\pi}{3}} eE_0 \langle 1100|1100\rangle \langle 20||r|21\rangle$$

- On computing the CGC, and the reduced matrix element, one obtains

$$\boxed{\langle 1|V|2\rangle = \langle 2|V|1\rangle = -3eE_0 a_0} \quad (68)$$

- Thus the  $V$  matrix is obtained to be

$$V \equiv \begin{pmatrix} 0 & -3eE_0 a_0 & 0 & 0 \\ -3eE_0 a_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

# Linear Stark Effect for $n=2$ (H-atom)

- Clearly only first two eigenvalues of the matrix will be non zero which can be obtained by diagonalizing the smaller Matrix

$$V \equiv \begin{pmatrix} 0 & -3eE_0 a_0 \\ -3eE_0 a_0 & 0 \end{pmatrix}$$

which has eigenvalues

$$\lambda_{1,2} = \pm 3eE_0 a_0$$

with the eigenvectors

$$|\lambda_1\rangle = |\psi_{n1}^{(0)}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \left\{ |2s\rangle + |2p_0\rangle \right\}$$

$$|\lambda_2\rangle = |\psi_{n2}^{(0)}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}} \left\{ |2s\rangle - |2p_0\rangle \right\}$$

# Linear Stark Effect for $n=2$ (H-atom)

- So the four-fold degeneracy of  $n = 2$  level is lifted as below

$$E_{21}^{(1)} = E_2^{(0)} + 3eE_0 a_0$$

$$E_{22}^{(1)} = E_2^{(0)} - 3eE_0 a_0$$

$$E_{23}^{(1)} = E_{2n}^{(1)} = E_2^{(0)}$$

- Thus the degeneracy of two levels  $|2s\rangle$  and  $|2p_0\rangle$  is lifted, while the other two levels  $|2p_1\rangle$  and  $|2p_{-1}\rangle$  are still degenerate as shown
- However with these states one can do second order perturbation theory because in the new basis all off-diagonal Matrix elements of  $V$  vanish. The new basis is

$$|\lambda_1\rangle = \frac{1}{\sqrt{2}} \left\{ |2s\rangle + |2p_0\rangle \right\}$$

$$|\lambda_2\rangle = \frac{1}{\sqrt{2}} \left\{ |2s\rangle - |2p_0\rangle \right\}$$

$$|\lambda_3\rangle = |2p_1\rangle$$

$$|\lambda_4\rangle = |2p_{-1}\rangle$$

# Linear Stark Effect for $n=2$ (H-atom)

- This phenomena is called **Linear Stark effect** because the lowest order energy shifts are proportional to  $E_0$ , as against  $E_0^2$  for the state  $|1s\rangle$ . This linear shift will be larger in magnitude because  $E_0$  is small. Note that linear shift is possible in this case only because of degeneracy of the  $n = 2$  level.