# **Chapter 6: Approximation Methods for Stationary States**

### 6.1. Introduction

The exact solution of Schrödinger equation can be found for only a limited number of problems, such as square wells, harmonic oscillator, hydrogen atom etc. A majority of problems in quantum mechanics can usually be solved using a wide variety of approximate methods. In this chapter, we will consider approximation methods that deal with stationary states corresponding to the time-independent Hamiltonians: time independent perturbation theory (non-degenerate and degenerate) and variational methods.

## 6.2. Time independent perturbation theory

### 6.2.1. Non-degenerate system

Perturbation theory is developed to deal with small corrections to problems which we have solved exactly, like the harmonic oscillator and the hydrogen atom. We will make a series expansion of the energies and eigenstates for cases where there is only a small correction to the exactly soluble problem.

Suppose that the Hamiltonian for our system can be written as

$$\hat{H} = \hat{H}_{0} + \hat{H}_{1}$$
 .....(6-2-1)

Where  $\hat{H}_{o}$  is the dominant unperturbed Hamiltonian part (the part that we can solve exactly i.e., we know exactly its eigenvectors and eigenvalues), and  $\hat{H}_{1}$  is the perturbed Hamiltonian part (the part that we cannot solve, provided  $H_{1} \ll H_{o}$ ).

It is then assumed that the solutions to the unperturbed eigenvalue problem:

are known, in which we have labeled the unperturbed energy by  $\overset{(0)}{E_k}$  and the corresponding unperturbed eigenket by  $\begin{vmatrix} i \\ k \end{vmatrix}$ . By non-degenerate we mean that there is only one eigenket  $\begin{vmatrix} i \\ k \end{vmatrix}$  associated with each eigenvalue  $\overset{(0)}{E_k}$ . The eigenkets  $\begin{vmatrix} i \\ k \end{vmatrix}$  form a complete orthonormal set:

$$\left<\!\!\! \begin{pmatrix} ^{(0)} \\ k \\ k' \\ \end{pmatrix} \!\! = \! \delta_{kk'}$$

Since  $\hat{H}_1$  is small, the eigenstate  $|k\rangle$  for the total problem do not differ greatly from the eigenstate  $\begin{vmatrix} 0 \\ k \end{vmatrix}$  for the unperturbed problem, so

$$\left< \begin{matrix} ^{(0)} \\ k \end{matrix} \right| k \right> = 1$$

The corresponding Schrödinger equation of the full Hamiltonian given in eq. (6-2-1) is:

$$\hat{H}|k\rangle = E_k|k\rangle$$
 .....(6-2-3)

cannot be solved to obtain the energy eigenvalue  $E_k$  and the eigenkets  $|k\rangle$  exactly. However, it could be possible to reduce the full Hamiltonian  $\hat{H}$  into independent parts, the full Hamiltonian can be written as

Where  $\lambda$  is an arbitrary parameter (0 $\rightarrow$ 1) which can be later taken equal to unity to obtain desired solution.

It is possible to expand the eigenkets and the corresponding eigenvalues of the full Hamiltonian in power series of  $\lambda$ .

Substitute equations (6-2-5) and (6-2-4) into equation (6-2-3)

$$\begin{split} & \left(\hat{H}_{o} + \lambda \hat{H}_{1} \left( \begin{vmatrix} 0 \\ k \end{pmatrix} + \lambda \begin{vmatrix} 1 \\ k \end{pmatrix} + \lambda^{2} \begin{vmatrix} 2 \\ k \end{pmatrix} + ... \right) = \left( \stackrel{(0)}{E}_{k} + \lambda \stackrel{(1)}{E}_{k} + \lambda^{2} \stackrel{(2)}{E}_{k} + ... \right) \left( \begin{vmatrix} 0 \\ k \end{pmatrix} + \lambda \begin{vmatrix} 1 \\ k \end{pmatrix} + \lambda^{2} \begin{vmatrix} 2 \\ k \end{pmatrix} + ... \right) (6-2-6) \\ & \hat{H}_{o} \begin{vmatrix} 0 \\ k \end{pmatrix} + \lambda \left( \hat{H}_{1} \begin{vmatrix} 0 \\ k \end{pmatrix} + \hat{H}_{o} \begin{vmatrix} 1 \\ k \end{pmatrix} \right) + \lambda^{2} \left( \hat{H}_{1} \begin{vmatrix} 1 \\ k \end{pmatrix} + \hat{H}_{o} \begin{vmatrix} 2 \\ k \end{pmatrix} \right) + ... = E_{o} \begin{vmatrix} 0 \\ k \end{pmatrix} \\ & + \lambda \left( \stackrel{(1)}{E}_{k} \begin{vmatrix} 0 \\ k \end{pmatrix} + \stackrel{(0)}{E}_{k} \begin{vmatrix} 1 \\ k \end{pmatrix} \right) + \lambda^{2} \left( \stackrel{(1)}{E}_{k} \begin{vmatrix} 1 \\ k \end{pmatrix} + \stackrel{(0)}{E}_{k} \begin{vmatrix} 2 \\ k \end{pmatrix} + \stackrel{(0)}{E}_{k} \begin{vmatrix} 2 \\ k \end{pmatrix} + \dots (6-2-7) \\ & \dots (6-2-7) \end{split}$$

Because of linear dependence of terms in a power series, this can only be satisfied for arbitrary  $\lambda$  if all terms with the same power of  $\lambda$  cancel independently.

Equate coefficient of like power of  $\boldsymbol{\lambda}$ 

$$\lambda^{0} \rightarrow \hat{H}_{o} \begin{vmatrix} 0 \\ k \end{pmatrix} = E_{k} \begin{vmatrix} 0 \\ k \end{vmatrix} \qquad \dots (6-2-8)$$

The zeroth order energy (eigenvalue of the unperturbed Hamiltonian) is

$$\lambda^{1} \rightarrow \hat{H}_{1} \begin{vmatrix} 0 \\ k \end{vmatrix} + \hat{H}_{0} \begin{vmatrix} 1 \\ k \end{vmatrix} = E_{k} \begin{vmatrix} 0 \\ k \end{vmatrix} + E_{k} \begin{vmatrix} 1 \\ k \end{vmatrix} + \dots (6-2-10)$$

$$\lambda^{2} \rightarrow \hat{H}_{1} \begin{vmatrix} (1) \\ k \end{vmatrix} + \hat{H}_{0} \begin{vmatrix} (2) \\ k \end{vmatrix} = E_{k} \begin{vmatrix} (1) \\ k \end{vmatrix} + E_{k} \begin{vmatrix} (0) \\ k \end{vmatrix} + E_{k} \begin{vmatrix} (2) \\ k \end{vmatrix} + E_{k} \begin{vmatrix} (0) \\ k \end{vmatrix} \qquad \dots (6-2-11)$$

At this point, the parameter  $\lambda$  has done its work and is not needed any more.

#### First order correction to energy eigenvalue

Reorder equation (6-2-10) in the following form:

$$\left(\hat{H}_{o} - \hat{E}_{k}^{(0)}\right) \begin{vmatrix} 1 \\ k \end{vmatrix} = -\left(\hat{H}_{1} - \hat{E}_{k}^{(1)}\right) \begin{vmatrix} 0 \\ k \end{vmatrix} \qquad \dots (6-2-12)$$

Scalar product with  $\left< \begin{matrix} (0) \\ k \end{matrix} \right|$ 

The first order correction to the energy eigenvalue is

## First order correction to the energy eigenket

Expand  $\begin{vmatrix} 1 \\ k \end{vmatrix}$  in terms of the unperturbed function  $\begin{vmatrix} 0 \\ n \end{vmatrix}$ , where  $k \neq n$ 

$$\begin{vmatrix} {}^{(1)} \\ {}^{k} \end{pmatrix} = \sum_{n} c_{n} \begin{vmatrix} {}^{(0)} \\ {}^{n} \end{pmatrix}$$
 .....(6-2-17)

Insert equation (6-2-17) into equation (6-2-12)

$$\left(\hat{H}_{o} - \hat{E}_{k}^{(0)}\right) \sum_{n} c_{n} \left| \stackrel{(0)}{n} \right\rangle = -\left(\hat{H}_{1} - \hat{E}_{k}^{(1)}\right) \left| \stackrel{(0)}{k} \right\rangle \qquad \dots (6-2-18)$$

Scalar product with  $\left< egin{smallmatrix} ^{(0)} n \end{bmatrix}$ 

#### Second order correction to the energy eigenvalue

Rewrite equation (6-2-11) in the following form:

$$\left(\hat{H}_{o} - E_{k}^{(0)}\right) \begin{vmatrix} 2 \\ k \end{vmatrix} = -\left(\hat{H}_{1} - E_{k}^{(1)}\right) \begin{vmatrix} 1 \\ k \end{vmatrix} + E_{k}^{(2)} \begin{vmatrix} 0 \\ k \end{vmatrix} \qquad \dots (6-2-22)$$

Scalar product with  $\begin{pmatrix} 0 \\ k \end{pmatrix}$ 

$$\begin{pmatrix} {}^{(0)} & {}^{(0)} \\ E_{k} - E_{k} \end{pmatrix} \begin{pmatrix} {}^{(0)} & {}^{(2)} \\ k \end{pmatrix} = - \begin{pmatrix} {}^{(0)} & {}^{(1)} \\ k \end{pmatrix} + E_{k} \begin{pmatrix} {}^{(0)} & {}^{(1)} \\ k \end{pmatrix} + E_{k} \begin{pmatrix} {}^{(0)} & {}^{(0)} \\ k \end{pmatrix} + E_{k} \begin{pmatrix} {}^{(0)} & {}^{(0)} \\ k \end{pmatrix} \end{pmatrix} \dots (6-2-24)$$

Where  $\begin{pmatrix} 0 \\ k \\ k \end{pmatrix} = 0$  ,  $\begin{pmatrix} 0 \\ k \\ k \end{pmatrix} = 0$ 

Substitute equation (6-2-21) into equation (6-2-25)

**EX.** A diatomic molecule has permanent dipole moment  $\vec{P}$  along the direction connecting the two atoms. If such a molecule is placed in a uniform electric field  $\vec{\varepsilon}$ . Treat the molecule as a rigid rotator with unperturbed Hamiltonian  $H_0 = L^2/2I$ , where I is the moment of inertia of the molecule. If the perturbed Hamiltonian is  $\hat{H}_1 = -\vec{P} \cdot \vec{\varepsilon}$  which represent the interaction energy between the dipole moment and the electric field. Find:

- a) The first order energy shift of the ground state.
- b) The first order correction to the ground state wavefunction.
- c) The second order energy correction of the ground state.

Soln.

**a)** 
$$\hat{H}_{o} \begin{vmatrix} 0 \\ k \end{vmatrix} = E_{k} \begin{vmatrix} 0 \\ k \end{vmatrix} \longrightarrow \frac{L^{2}}{2I} \begin{vmatrix} 0 \\ k \end{vmatrix} = \frac{\ell(\ell+1)\hbar^{2}}{2I} \begin{vmatrix} 0 \\ k \end{vmatrix}$$

The eigenfunction of L<sup>2</sup> is  $Y_{\ell}^{m}(\theta, \phi)$ , so that the eigenfunction of  $H_{0}$  is also  $Y_{\ell}^{m}(\theta, \phi) = |\ell m\rangle$ 

The eigenfunction of the ground state =  $Y_0^0(\theta, \varphi) = |00\rangle = \frac{1}{\sqrt{4\pi}}$ 

Where  $\hat{H}_1 = -\vec{P} \cdot \vec{\varepsilon} = -P \varepsilon \cos \theta$ 

b) Using equation (6-2-21) 
$$\rightarrow \left| \stackrel{(1)}{k} \right\rangle = \sum_{n \neq k} \frac{\left\langle \stackrel{(0)}{n} \middle| \hat{H}_1 \middle| \stackrel{(0)}{k} \right\rangle}{\left( \stackrel{(0)}{E_k} - \stackrel{(0)}{E_n} \right)} \left| \stackrel{(0)}{n} \right\rangle$$

$$\begin{vmatrix} {}^{(0)}_{\mathbf{k}} \\ {}^{(0)}$$

$$\left\langle {{}^{(0)}_{n}} \middle| \hat{H}_{1} \middle| {{}^{(0)}_{k}} \right\rangle = \left\langle \ell m \middle| \hat{H}_{1} \middle| 00 \right\rangle = \frac{-P\varepsilon}{\sqrt{3}} \int Y_{\ell}^{m^{*}} Y_{1}^{0} d\Omega$$

Using the orthonormality condition  $\int Y_{\ell}^{m^*} Y_{\ell'}^{m'} d\Omega = \delta_{\ell\ell'} \delta_{mm'}$ 

$$\begin{pmatrix} {}^{(0)}\\n \end{pmatrix} \hat{\mathbf{H}}_{1} \begin{pmatrix} {}^{(0)}\\k \end{pmatrix} = \langle \ell m | \hat{\mathbf{H}}_{1} | 00 \rangle = \frac{-\mathbf{P}\varepsilon}{\sqrt{3}} \int \mathbf{Y}_{\ell}^{m^{*}} \mathbf{Y}_{1}^{0} d\Omega = \frac{-\mathbf{P}\varepsilon}{\sqrt{3}} \delta_{\ell 1} \delta_{m 0}$$

$$\begin{pmatrix} {}^{(0)}\\n \end{pmatrix} = | 10 \rangle = \mathbf{Y}_{1}^{0}(\theta, \varphi) \quad \Rightarrow \quad \mathbf{E}_{n}^{(0)} = \frac{\hbar^{2}}{\mathbf{I}}$$

$$\begin{pmatrix} {}^{(0)}\\k \end{pmatrix} = \frac{\mathbf{P}\varepsilon}{\sqrt{3}\hbar^{2}} \mathbf{Y}_{1}^{0} = \frac{1}{\sqrt{4\pi}} \frac{\mathbf{P}\varepsilon}{\hbar^{2}} \cos \theta$$

$$\begin{pmatrix} {}^{(0)}\\n \end{pmatrix} \hat{\mathbf{H}}_{1} \begin{pmatrix} {}^{(0)}\\k \end{pmatrix} \end{pmatrix}^{2}$$

c) Using equation (6-2-26)  $\rightarrow E_{k}^{(2)} = \sum_{n \neq k} \frac{\left|\left\langle n \left| \mathbf{H}_{1} \right| k \right\rangle\right|}{\left( \mathbf{E}_{k}^{(0)} - \mathbf{E}_{n}^{(0)} \right)} \rightarrow E_{o}^{(2)} = -\frac{\mathbf{I}}{3} \left( \frac{\mathbf{P}\varepsilon}{\hbar} \right)^{2}$ 

**EX.** Consider one dimensional anharmonic oscillator with full Hamiltonian  $\hat{H} = \frac{p^2}{2m} + \frac{1}{2}kx^2 + ax^4$ , where  $ax^4$  is small, if the unperturbed wavefunction of the ground state is  $\psi_o(x) = \left(\frac{k}{\pi\hbar\omega}\right)^{1/4} \cdot e^{\left(\frac{-kx^2}{2\hbar\omega}\right)}$ .

a) Find the first order energy shift for the ground state.

b) **(H.W)** Find the zeroth order energy eigenvalue, and the total energy of the ground state up to first order correction.

c) **(H.W)** Find the first order energy correction for the first excited state if the unperturbed wavefunction of the first excited state is given by:  $\psi_1(\mathbf{x}) = \left(\frac{\mathbf{k}}{\pi\hbar\omega}\right)^{1/4} \cdot \left(\frac{2\mathbf{k}}{\hbar\omega}\right)^{1/2} \cdot \mathbf{x} \cdot \mathbf{e}^{\left(\frac{-\mathbf{kx}^2}{2\hbar\omega}\right)}$ .

Soln.

$$\begin{vmatrix} {}^{(0)}_{k} \\ k \end{vmatrix} = \begin{vmatrix} {}^{(0)}_{0} \\ k \end{vmatrix} = \psi_{o}^{(0)} (x) = \left(\frac{k}{\pi \hbar \omega}\right)^{1/4} \cdot e^{\left(\frac{-kx^{2}}{2\hbar \omega}\right)}$$
$$\hat{H}_{o} = \frac{p^{2}}{2m} + \frac{1}{2}kx^{2}$$
$$\hat{H}_{1} = ax^{4}$$

a) Using equation (6-2-16)  $\rightarrow \tilde{E}_{k} = \left\langle \begin{pmatrix} 0 \\ k \end{pmatrix} \hat{H}_{1} \middle| \begin{matrix} 0 \\ k \end{pmatrix} \rightarrow \tilde{E}_{0} = \left\langle \begin{pmatrix} 0 \\ 0 \end{pmatrix} \hat{H}_{1} \middle| \begin{matrix} 0 \\ 0 \end{pmatrix} = \left( \frac{a^{2}k}{\pi \hbar \omega} \right)^{1/2} \int_{-\infty}^{\infty} e^{\left( \frac{-kx^{2}}{\hbar \omega} \right)} \cdot x^{4} dx$ 

$$\int_{-\infty}^{\infty} e^{\left(\frac{-kx^2}{\hbar\omega}\right)} \cdot x^4 dx = \frac{3}{4} \left(\frac{\hbar\omega}{k}\right)^{5/2} \sqrt{\pi}$$
$$E_o^{(1)} = \frac{3}{4} a \left(\frac{\hbar\omega}{k}\right)^2$$

**H.W.** Calculate the first order correction to the energy of the n<sup>th</sup> state of a harmonic oscillator whose center of potential has been displaced from 0 to a distance L.

**EX.** An electron of charge (-e) moves in a one-dimensional harmonic oscillator potential, the unperturbed Hamiltonian is  $\hat{H}_o = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2$ . A weak, uniform electric field  $\vec{\varepsilon}$  is applied in the positive x-direction. Thus, the potential energy due to the electric field is  $e_{\mathcal{E}x}$  (a) Write down the perturbation Hamiltonian  $\hat{H}_1$  in terms of  $\hat{a}^+$ ,  $\hat{a}^-$  and other quantities. (b) Find the first-order correction to the ground state energy. (c) Find the second-order correction to the ground state energy.

Soln.

$$\begin{aligned} \mathbf{a} ) \quad \hat{\mathbf{x}} = \sqrt{\frac{\hbar}{2m\omega}} \left( \hat{\mathbf{a}}^{+} + \hat{\mathbf{a}}^{-} \right) \quad \Rightarrow \quad \hat{\mathbf{H}}_{1} = \mathbf{e}\varepsilon\mathbf{x} = \mathbf{e}\varepsilon\sqrt{\frac{\hbar}{2m\omega}} \left( \hat{\mathbf{a}}^{+} + \hat{\mathbf{a}}^{-} \right) \\ \mathbf{b} ) \quad \hat{\mathbf{E}}_{\mathbf{k}}^{(1)} = \left\langle \begin{pmatrix} \mathbf{0} \\ \mathbf{k} \\ \mathbf{$$

The only allowed transition is where n=1 and so we find

$$\overset{(2)}{\mathcal{E}_{o}} = (\mathbf{e}\varepsilon)^{2} \cdot \frac{\hbar}{2m\omega} \cdot \frac{1}{\left(\frac{1}{2}\hbar\omega - \frac{3}{2}\hbar\omega\right)} = -\frac{(\mathbf{e}\varepsilon)^{2}}{2m\omega^{2}}$$

#### 6.2.2. Degenerate system

Consider a degenerate system such that the zeroth order Hamiltonian has  $\nu\,$  states with energy  $\stackrel{_{(0)}}{E_k}$  . These zeroth order states satisfy

$$\hat{H}^{(0)} \begin{vmatrix} 0 \\ k \\ \alpha \end{vmatrix} = \stackrel{(0)}{E}_{k,\alpha} \begin{vmatrix} 0 \\ k \\ \alpha \end{vmatrix} \qquad \alpha = 1, 2, 3, ..., \nu$$
 .....(6-2-27)

where now we use two indices to represent each state: the first index k runs over the different energy eigenvalues while the second index  $\alpha$  runs over the  $\nu$  degenerate states for a particular energy eigenvalue. Since we have  $\nu$  degenerate states of energy  $\stackrel{(0)}{E_k}$ , any linear combination of these states is also a valid state of energy  $\stackrel{(0)}{E_k}$ .

Let expand 
$$\begin{vmatrix} 0 \\ k \end{vmatrix}$$
 in terms of the degenerate unperturbed function  $\begin{vmatrix} 0 \\ k \\ \alpha \end{vmatrix}$   
 $\begin{vmatrix} 0 \\ k \end{pmatrix} = \sum_{\alpha=1}^{\nu} c_{\alpha} \begin{vmatrix} 0 \\ k \\ \alpha \end{pmatrix}$  .....(6-2-28)

Insert the above equation into equation (6-2-12)

$$\left(\hat{H}^{(0)} - \hat{E}_{k}^{(0)}\right) \left| \substack{k}{k} \right\rangle = -\sum_{\alpha=1}^{\nu} c_{\alpha} \left( \hat{H}^{(1)} - \hat{E}_{k}^{(1)} \right) \left| \substack{k, \alpha \\ k, \alpha \right\rangle} \qquad \dots (6-2-29)$$

Scalar product with  $\left< egin{smallmatrix} ^{\scriptscriptstyle (0)} k, eta \end{matrix} 
ight|$ 

In matrix form

Trivial solution, if  $c_{\alpha} = 0$ , (reject this solution because it has no physical meaning).

Nontrivial solution if and only if 
$$det\left(H_{\beta\alpha}^{(1)} - E_k^{(1)} \delta_{\beta\alpha}\right) = 0$$
, i.e.

	${ m H}_{13}^{(1)}$	${ m H}_{12}^{(1)}$	$H_{11}^{(1)} - \overset{(1)}{E_k}$
= 0	${ m H}_{23}^{(1)}$	$H_{22}^{(1)}\!-\! \overset{(1)}{E_k}$	${ m H}_{21}^{(1)}$
	$H_{33}^{(1)} - E_k^{(1)}$	${ m H}_{32}^{(1)}$	$H_{31}^{(1)}$
•	•	•	:

## 6.2.3. The Stark effect

The effect that an external electric field has on the energy levels of an atom is called the Stark effect.

**EX.** Consider the Stark effect in Hydrogen atom, where an external uniform weak electric field  $\mathcal{E}$  directed along the positive z-axis. Find the first order energy correction for the ground and first excited state.

## Soln.

In the absence of an electric field, the unperturbed Hamiltonian of the hydrogen atom is:

$$\hat{H}^{(0)} = \frac{\hat{p}^2}{2m} - \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r}$$

When the electric field is turned on, the interaction between the atom and the electric field generates a term  $e\vec{r} \cdot \vec{\mathcal{E}}$  that needs to be added to  $\hat{H}^{(0)}$ . i.e., the perturbed Hamiltonian is:

 $\hat{\mathbf{H}}^{(1)} = \mathbf{e}\vec{\mathbf{r}}\cdot\vec{\mathcal{E}} = \mathbf{e}r\mathcal{E}\cos\theta = \mathbf{e}\mathcal{E}\mathbf{z}$ 

The eigen state of  $\,\hat{H}^{(0)}\,\text{is}\,\,\left|n\ell m\right\rangle$ 

where n is the principal quantum number,  $\ell\,$  is the orbital quantum number and  $\,m\,$  is the magnetic quantum number.

1-For the ground state, n=1,

 $\ell = 0$  and  $m = 0 \rightarrow |100\rangle$ , this corresponds to "1s" configuration. This state is non-degenerate, so we use non-degenerate perturbation theory.

The first order correction to the ground state energy eigenvalue  $\stackrel{(i)}{E_{o}}$  is:

 $\overset{(1)}{\mathbf{E}_{\mathbf{k}}} = \left\langle \overset{(0)}{\mathbf{k}} \middle| \overset{(1)}{\mathbf{k}} \middle| \overset{(0)}{\mathbf{k}} \right\rangle \quad \Rightarrow \quad \overset{(1)}{\mathbf{E}_{\mathbf{0}}} = \mathbf{e}\mathcal{E}\left\langle \overset{(0)}{\mathbf{100}} \middle| \overset{(1)}{\mathbf{z}} \middle| \overset{(0)}{\mathbf{100}} \right\rangle \quad \Rightarrow \quad \overset{(1)}{\mathbf{E}_{\mathbf{0}}} = \mathbf{e}\mathcal{E}\int \mathbf{z} \left| \boldsymbol{\psi}_{\mathbf{100}}^{(0)} \right|^{2} \mathbf{d}\tau$ 

Because the function z has odd parity and the square of the wave function  $|\psi_{100}^{(0)}|^2$  has even parity. The resultant integrand has odd parity and so yields zero when integrated over all space.

$$\overset{(1)}{E}_{0} = 0$$

There is no first-order (i.e., linear) Stark effect occurs in the ground state of hydrogen.

The absence of a linear Stark effect in the ground state implies that the atom does not have a permanent electric dipole moment in its ground state.

2-For first excited state, n=2.

The n=2 state of the hydrogen atom is 4-fold degenerate, with one 2s state and three 2p states, i.e.  $|200\rangle$ ,  $|210\rangle$ ,  $|21-1\rangle$  and  $|211\rangle$ .

Let us denote the unperturbed first excited state as  $\begin{vmatrix} 0 \\ 1 \end{vmatrix}$  , then

$$\begin{vmatrix} {}^{(0)}_{\mathbf{k}} \end{pmatrix} = \sum_{\alpha=1}^{\nu} \mathbf{c}_{\alpha} \begin{vmatrix} {}^{(0)}_{\mathbf{k}}, \alpha \end{pmatrix} \rightarrow \begin{vmatrix} {}^{(0)}_{\mathbf{k}} \end{pmatrix} = \begin{vmatrix} {}^{(0)}_{\mathbf{k}} \end{pmatrix} \mathbf{c}_{1} + \begin{vmatrix} {}^{(0)}_{\mathbf{k}} \end{pmatrix} \mathbf{c}_{2} + \begin{vmatrix} {}^{(0)}_{\mathbf{k}} \end{pmatrix} \mathbf{c}_{3} + \begin{vmatrix} {}^{(0)}_{\mathbf{k}} \end{pmatrix} \mathbf{c}_{4}$$

We construct the matrix of the perturbation  $H^{(1)}$  in the n=2 degenerate subspace,

Reduction of the size of the matrix:

1- Since 
$$[\hat{L}_{z}, \hat{H}^{(1)}] = 0 \Rightarrow e\mathcal{E}[\hat{L}_{z}, z] = 0$$
  
 $e\mathcal{E}\langle n\ell m | [\hat{L}_{z}, z] | n\ell'm' \rangle = e\mathcal{E}\langle n\ell m | [\hat{L}_{z}z - z\hat{L}_{z}] | n\ell'm' \rangle = 0$   
 $e\mathcal{E}(\langle n\ell m | \hat{L}_{z}z | n\ell'm' \rangle - \langle n\ell m | z\hat{L}_{z} | n\ell'm' \rangle) = 0$   
 $e\mathcal{E}\hbar(m - m')\langle n\ell m | z | n\ell'm' \rangle = 0$   
 $\langle n\ell m | z | n\ell'm' \rangle = 0$  if  $m \neq m'$ 

According to the above condition, the following matrix elements in the determinant of eq. (1) will vanish

$$\left\langle 200 \middle| \hat{\mathbf{H}}^{(1)} \middle| 21-1 \right\rangle = \left\langle 200 \middle| \hat{\mathbf{H}}^{(1)} \middle| 211 \right\rangle = \left\langle 210 \middle| \hat{\mathbf{H}}^{(1)} \middle| 21-1 \right\rangle = \left\langle 210 \middle| \hat{\mathbf{H}}^{(1)} \middle| 211 \right\rangle = \left\langle 21-1 \middle| \hat{\mathbf{H}}^{(1)} \middle| 211 \right\rangle = 0$$

Eq. (1) becomes:

$$\mathbf{H}^{(1)} = \begin{pmatrix} \left\langle 200 \middle| \hat{\mathbf{H}}^{(1)} \middle| 200 \right\rangle & \left\langle 200 \middle| \hat{\mathbf{H}}^{(1)} \middle| 210 \right\rangle & 0 & 0 \\ \left\langle 210 \middle| \hat{\mathbf{H}}^{(1)} \middle| 200 \right\rangle & \left\langle 210 \middle| \hat{\mathbf{H}}^{(1)} \middle| 210 \right\rangle & 0 & 0 \\ 0 & 0 & \left\langle 210 \middle| \hat{\mathbf{H}}^{(1)} \middle| 210 \right\rangle & 0 & 0 \\ 0 & 0 & \left\langle 210 \middle| \hat{\mathbf{H}}^{(1)} \middle| 210 \right\rangle & 0 & 0 \\ 0 & 0 & \left\langle 210 \middle| \hat{\mathbf{H}}^{(1)} \middle| 210 \right\rangle & 0 & 0 \\ 0 & 0 & 0 & \left\langle 210 \middle| \hat{\mathbf{H}}^{(1)} \middle| 210 \right\rangle & 0 \\ 0 & 0 & 0 & \left\langle 211 \middle| \hat{\mathbf{H}}^{(1)} \middle| 211 \right\rangle \end{pmatrix} \end{pmatrix}$$
 .....(2)

2- Using parity condition:

The parity  $\hat{\Pi}$  of the hydrogen atom wave functions is determined as

 $\hat{\Pi}\Psi_{\mathrm{n}\ell\mathrm{m}}(\vec{\mathrm{r}}) = (-1)^{\ell}\Psi(\vec{\mathrm{r}})$ 

The Hamiltonian for the perturbation has odd parity, so the matrix elements between states of the same parity give an integrand that is odd and hence a zero integral. The only nonzero matrix elements are those between states of different parity, which are the s and p states.

i.e., the only nonzero matrix element  $\langle n\ell m | \hat{H}^{(1)} | n\ell'm' \rangle \neq 0$ , only if  $\ell + \ell' = odd$ . Eq. (2) becomes:

Thus, the only nonvanishing matrix elements of the perturbation are those connecting the 2s  $2s \equiv |200\rangle$  and  $2p_0 \equiv |210\rangle$  states; the  $2p_{\pm 1} \equiv |21\pm 1\rangle$  states are not affected by the perturbation and their energies are unchanged and the linear homogeneous equations reduce to a set of two equations.

$$\mathbf{H}^{(1)} = \begin{pmatrix} 0 & \left\langle 200 \middle| \hat{\mathbf{H}}^{(1)} \middle| 210 \right\rangle \\ \left\langle 210 \middle| \hat{\mathbf{H}}^{(1)} \middle| 200 \right\rangle & 0 \end{pmatrix} \dots (4)$$

Now we need to calculate the matrix element  $\left< \frac{0}{200} \middle| \hat{H}^{(1)} \middle| \frac{0}{210} \right>$ 

$$\begin{split} & \begin{vmatrix} 0 \\ 200 \\ 200 \\ \end{vmatrix} = \psi_{200}^{(0)}(\mathbf{r}, \theta, \varphi) = \mathbf{R}_{20}(\mathbf{r}) \mathbf{Y}_{0}^{0}(\theta, \varphi) \\ & \mathbf{R}_{20}(\mathbf{r}) = \mathbf{R}_{2s}(\mathbf{r}) = \frac{1}{2\sqrt{2}} \left( \mathbf{a}_{0} \right)^{-(3/2)} \left( 2 - \frac{\mathbf{r}}{\mathbf{a}_{0}} \right) \cdot \mathbf{e}^{\left( \frac{-\mathbf{r}}{2\mathbf{a}_{0}} \right)} \quad , \qquad \mathbf{Y}_{0}^{0}(\theta, \varphi) = |00\rangle = \frac{1}{\sqrt{4\pi}} \\ & \begin{vmatrix} 0 \\ 200 \\ 200 \\ \end{vmatrix} = \mathbf{R}_{20}(\mathbf{r}) \cdot \mathbf{Y}_{0}^{0}(\theta, \varphi) = \mathbf{R}_{2s}(\mathbf{r}) \cdot \mathbf{Y}_{0}^{0}(\theta, \varphi) = \frac{1}{4\sqrt{2\pi}} \left( \mathbf{a}_{0} \right)^{-(3/2)} \left( 2 - \frac{\mathbf{r}}{\mathbf{a}_{0}} \right) \cdot \mathbf{e}^{\left( \frac{-\mathbf{r}}{2\mathbf{a}_{0}} \right)} \\ & \begin{vmatrix} 210 \\ 210 \\ \end{vmatrix} = \psi_{210}^{(0)}(\mathbf{r}, \theta, \varphi) = \mathbf{R}_{21}(\mathbf{r}) \mathbf{Y}_{1}^{0}(\theta, \varphi) \\ & \mathbf{R}_{21}(\mathbf{r}) = \mathbf{R}_{2p}(\mathbf{r}) = \frac{1}{2\sqrt{6}} \left( \mathbf{a}_{0} \right)^{-(5/2)} \cdot \mathbf{r} \cdot \mathbf{e}^{\left( \frac{-\mathbf{r}}{2\mathbf{a}_{0}} \right)} \quad , \qquad \mathbf{Y}_{1}^{0} = \sqrt{\frac{3}{4\pi}} \cos \theta \\ & \begin{pmatrix} 0 \\ \psi_{210}^{(0)}(\mathbf{r}, \theta, \varphi) = \frac{\cos \theta}{4\sqrt{2\pi}} \left( \mathbf{a}_{0} \right)^{-(5/2)} \cdot \mathbf{r} \cdot \mathbf{e}^{\left( \frac{-\mathbf{r}}{2\mathbf{a}_{0}} \right)} \\ & \left\langle 200 \\ 200 \\ \dot{\mathbf{H}^{(1)}} \\ 210 \\ \dot{\mathbf{2}} = \mathbf{e}\mathcal{E} \left\langle 200 \\ 200 \\ \dot{\mathbf{r}} \cos \theta \\ \end{vmatrix} \right|_{210}^{-(5/2)} \cdot \mathbf{r} \cdot \mathbf{e}^{\left( \frac{-\mathbf{r}}{2\mathbf{a}_{0}} \right)} \\ & \left\langle 200 \\ \dot{\mathbf{H}^{(1)}} \\ \end{vmatrix} \right|_{210}^{(0)} \\ &= \mathbf{e}\mathcal{E} \left\langle 200 \\ 200 \\ \dot{\mathbf{r}} \cos \theta \\ \end{vmatrix} \right|_{210}^{-(5/2)} \cdot \mathbf{r} \cdot \mathbf{e}^{\left( \frac{-\mathbf{r}}{2\mathbf{a}_{0}} \right)} \\ & \left\langle 200 \\ \dot{\mathbf{H}^{(1)}} \\ \end{vmatrix} \right|_{210}^{(0)} \\ &= \mathbf{e}\mathcal{E} \left\langle 200 \\ 200 \\ \dot{\mathbf{r}} \cos \theta \\ \\ & \left\langle 200 \\ \mathbf{h}^{(1)} \\ \end{vmatrix} \right|_{210}^{(0)} \\ &= \mathbf{e}\mathcal{E} \left\langle 200 \\ \dot{\mathbf{r}} \cos \theta \\ \\ \\ & \left\langle 9 \\ \mathbf{h}^{-\mathbf{r}} \right\rangle \\ &= \mathbf{e}\mathcal{E} \left\langle 200 \\ \mathbf{h}^{-\mathbf{r}} \\ \\ & \left\langle 9 \\ \mathbf{h}^{-\mathbf{r}} \\ \\ & \left\langle 9 \\ \mathbf{h}^{-\mathbf{r}} \\ \\ & \left\langle 9 \\ \mathbf{h}^{-\mathbf{r}} \\ \\ \\ & \left\langle 9 \\ \mathbf{h}^{-\mathbf{r}} \\ \\ \\ & \left\langle 9 \\ \mathbf{h}^{-\mathbf{r}} \\ \\ \\ & \left\langle 9 \\ \mathbf{h}^{-\mathbf{r}} \\ \\ & \left\langle 9 \\ \mathbf{$$

and

$$\int_{0}^{\pi} \int_{0}^{2\pi} \mathbf{Y}_{0}^{0} \cos \theta \mathbf{Y}_{1}^{0} \sin \theta \mathrm{d}\theta \mathrm{d}\varphi = \frac{1}{\sqrt{4\pi}} \cdot \sqrt{\frac{3}{4\pi}} \cdot \int_{0}^{2\pi} \mathrm{d}\varphi \int_{0}^{\pi} \cos^{2} \theta \sin \theta \mathrm{d}\theta = \frac{1}{\sqrt{4\pi}} \cdot \sqrt{\frac{3}{4\pi}} \cdot 2\pi \cdot \frac{2}{3} = \frac{1}{\sqrt{3}} \cdot \frac{1}{\sqrt{3}}$$

Eq. (4) becomes

$$\mathbf{H}^{(1)} = \begin{pmatrix} 0 & -3\mathbf{a}_{o}\mathbf{e}\mathcal{E} \\ -3\mathbf{a}_{o}\mathbf{e}\mathcal{E} & 0 \end{pmatrix} \qquad \dots \dots (5)$$

We diagonalize the perturbation Hamiltonian to get the energies and states:

$$\begin{vmatrix} -\mathbf{E}_{1} & -3\mathbf{a}_{o}\mathbf{e}\mathcal{E} \\ -3\mathbf{a}_{o}\mathbf{e}\mathcal{E} & -\mathbf{E}_{1} \end{vmatrix} = \mathbf{0}$$
$$\begin{pmatrix} \mathbf{E}_{1} \\ \mathbf{E}_{1} \end{pmatrix}^{2} = (3\mathbf{a}_{o}\mathbf{e}\mathcal{E})^{2}$$
$$\therefore \quad \mathbf{E}_{1}^{(1)} = \pm 3\mathbf{e}\mathcal{E} \mathbf{a}_{o}$$

The perturbed energy states are shown in Fig.1. Note that the perturbation has lifted some of the degeneracy, but not all of it; two states remain degenerate. The  $2p_{\pm 1}$  states are not shifted, and those eigenstates remain the same. The 2s and  $2p_0$  states are mixed by the perturbation



Fig(1): Stark effect in the hydrogen n=2 state.

H.W. Find the eigenstates of the perturbation Hamiltonian in the above equations.

EX. A two-dimensional isotropic oscillator has the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{2} k (1 + bxy) (x^2 + y^2)$$

a) If b=0, write down the energies of the three lowest levels, stating the degeneracy in each case.

b) If b is small positive number such that b<<1, find the first perturbation corrections to the energy of the three lowest states. Where the zeroth order wavefunction of the three lowest states are given below, respectively:

$$\psi_0^{(0)}(\mathbf{x}) = \left(\frac{\mathbf{k}}{\pi\hbar\omega}\right)^{1/4} \cdot \mathbf{e}^{\left(\frac{-\mathbf{kx}^2}{2\hbar\omega}\right)} , \quad \psi_1^{(0)}(\mathbf{x}) = \left(\frac{\mathbf{k}}{\pi\hbar\omega}\right)^{1/4} \left(\frac{2\mathbf{k}}{\hbar\omega}\right)^{1/2} \mathbf{x} \cdot \mathbf{e}^{\left(\frac{-\mathbf{kx}^2}{2\hbar\omega}\right)} , \quad \psi_2^{(0)}(\mathbf{x}) = \left(\frac{\mathbf{k}}{\pi\hbar\omega}\right)^{1/4} \frac{1}{\sqrt{2}} \left(\frac{2\mathbf{k}}{\hbar\omega}\mathbf{x}^2 - 1\right) \cdot \mathbf{e}^{\left(\frac{-\mathbf{kx}^2}{2\hbar\omega}\right)}$$

Soln.

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{2} k \left( x^2 + y^2 \right) \quad , \qquad \hat{H}^{(1)} = \frac{1}{2} k b \left( x^3 y + x y^3 \right)$$

a) If b=0  $\rightarrow \hat{H}^{(1)} = 0$ 

$$\hat{\mathbf{H}}^{(0)} \begin{vmatrix} \mathbf{0} \\ \mathbf{k} \end{vmatrix} = \mathbf{E}_{\mathbf{n}} \begin{vmatrix} \mathbf{0} \\ \mathbf{k} \end{vmatrix} \quad \Rightarrow \quad \hat{\mathbf{H}}^{(0)} \begin{vmatrix} \mathbf{0} \\ \mathbf{n}_{\mathbf{x}} \\ \mathbf{n}_{\mathbf{y}} \end{vmatrix} = \mathbf{E}_{\mathbf{n}} \begin{vmatrix} \mathbf{0} \\ \mathbf{n}_{\mathbf{x}} \\ \mathbf{n}_{\mathbf{y}} \end{vmatrix}$$

The energy of the 2-Dimensional harmonic oscillator is given by:

$$\overset{(0)}{E}_{n_{x}n_{y}} = \hbar \omega \left( n_{x} + \frac{1}{2} + n_{y} + \frac{1}{2} \right) \equiv \overset{(0)}{E}_{n} = \hbar \omega (n+1)$$

1-For ground state n=0  $\rightarrow \overset{\scriptscriptstyle(0)}{\mathrm{E}_0} = \hbar \omega$  non-degenerate state

2-For first excited state n=1  $\rightarrow E_1^{(0)} = 2\hbar\omega$  two-fold degenerate (double degenerate) state

<u>n</u> x	<u>n</u> y	<u>n</u>
0	1	1
1	0	1

3-For second excited state n=2  $\rightarrow \dot{E}_2^{(0)} = 3\hbar\omega$  three-fold degenerate (triply degenerate) state

<u>n</u>x <u>n</u>y <u>n</u> 2 0 2 1 1 2 0 2 2

## b) If b<<1

1-For the ground state, n=0, the first order correction to the energy is:

$$\begin{split} E_{k}^{(1)} &= \left\langle \stackrel{(0)}{k} \middle| \hat{H}^{(1)} \middle| \stackrel{(0)}{k} \right\rangle \\ E_{n}^{(1)} &= \frac{1}{2} k b \left\langle \stackrel{(0)}{n_{x}} \stackrel{(0)}{n_{y}} \middle| x^{3} y + x y^{3} \middle| \stackrel{(0)}{n_{x}} \stackrel{(0)}{n_{y}} \right\rangle = \frac{1}{2} k b \left\langle \stackrel{(0)}{n_{x}} \middle| x^{3} \middle| \stackrel{(0)}{n_{x}} \right\rangle \left\langle \stackrel{(0)}{n_{y}} \middle| y \middle| \stackrel{(0)}{n_{y}} \right\rangle + \frac{1}{2} k b \left\langle \stackrel{(0)}{n_{x}} \middle| x \middle| \stackrel{(0)}{n_{x}} \right\rangle \left\langle \stackrel{(0)}{n_{y}} \middle| y^{3} \middle| \stackrel{(0)}{n_{y}} \right\rangle \\ E_{0}^{(1)} &= \left\langle \stackrel{(0)}{0} \left( \stackrel{(0)}{h} \right) \left| \stackrel{(0)}{0} \stackrel{(0)}{0} \right\rangle = \frac{1}{2} k b \left\langle \stackrel{(0)}{0} \middle| x^{3} y + x y^{3} \middle| \stackrel{(0)}{0} \stackrel{(0)}{0} \right\rangle = \frac{1}{2} k b \left\langle \stackrel{(0)}{0} \middle| x^{3} \middle| \stackrel{(0)}{0} \right\rangle \left\langle \stackrel{(0)}{0} \middle| y \middle| \stackrel{(0)}{0} \right\rangle + \frac{1}{2} k b \left\langle \stackrel{(0)}{0} \middle| x \middle| \stackrel{(0)}{0} \right\rangle \left\langle \stackrel{(0)}{0} \middle| y^{3} \middle| \stackrel{(0)}{0} \right\rangle = 0 \end{split}$$

# 2-For the first excited state, n=1,

$$\begin{split} &|\stackrel{(0)}{1} \rangle = \begin{vmatrix} \stackrel{(0)}{1} \stackrel{(0)}{0} \rangle c_{1} + \begin{vmatrix} \stackrel{(0)}{0} \stackrel{(0)}{1} \rangle c_{2} \\ &| \begin{pmatrix} \stackrel{(0)}{1} \stackrel{(0)}{0} & | \hat{H}^{(1)} & | \stackrel{(0)}{1} \stackrel{(0)}{0} \rangle - E_{1} & \begin{pmatrix} \stackrel{(0)}{1} \stackrel{(0)}{0} & | \hat{H}^{(1)} & | \stackrel{(0)}{0} \stackrel{(0)}{1} \rangle \\ &| \begin{pmatrix} \stackrel{(0)}{0} \stackrel{(0)}{0} & | \hat{H}^{(1)} & | \stackrel{(0)}{1} \stackrel{(0)}{0} \rangle \rangle - E_{1} & \begin{pmatrix} \stackrel{(0)}{0} \stackrel{(0)}{0} & | \hat{H}^{(1)} & | \stackrel{(0)}{0} \stackrel{(0)}{1} \rangle - E_{1} \\ &| \begin{pmatrix} \stackrel{(0)}{0} \stackrel{(0)}{0} & | \hat{H}^{(1)} & | \stackrel{(0)}{1} \stackrel{(0)}{0} \rangle = \begin{pmatrix} \stackrel{(0)}{0} \stackrel{(0)}{0} & | \hat{H}^{(1)} & | \stackrel{(0)}{0} \stackrel{(0)}{1} \rangle = 0 & (Why) \\ &| \stackrel{(1)}{1} = \pm \begin{pmatrix} \stackrel{(0)}{1} \stackrel{(0)}{0} & | \hat{H}^{(1)} & | \stackrel{(0)}{0} \stackrel{(0)}{1} \rangle = \pm \frac{1}{2} k b \left[ \begin{pmatrix} \stackrel{(0)}{1} & | x^{3} & | \stackrel{(0)}{0} \rangle \begin{pmatrix} \stackrel{(0)}{0} & | y & | \stackrel{(0)}{1} \rangle + \begin{pmatrix} \stackrel{(0)}{1} & | x & | \stackrel{(0)}{0} \rangle \begin{pmatrix} \stackrel{(0)}{0} & | y^{3} & | \stackrel{(0)}{1} \rangle \\ &| \stackrel{(0)}{0} & | y^{-1} & | \stackrel{(0)}{1} \rangle = \left( \frac{k}{\pi \hbar \omega} \right)^{1/4} \cdot e^{\left( \frac{-kx^{2}}{2\hbar \omega} \right) , & \stackrel{(0)}{\psi_{1}} x = \left( \frac{k}{\pi \hbar \omega} \right)^{1/4} \left( \frac{2k}{\hbar \omega} \right)^{1/2} x \cdot e^{\left( \frac{-kx^{2}}{2\hbar \omega} \right)} \\ &| \begin{pmatrix} \stackrel{(0)}{0} & | y & | \stackrel{(0)}{0} \rangle = \left( \frac{k}{\pi \hbar \omega} \right)^{1/2} \left( \frac{2k}{\hbar \omega} \right)^{1/2} \int_{-\infty}^{\infty} e^{\left( \frac{-kx^{2}}{\hbar \omega} \right)} \cdot x^{4} dx = \frac{3}{\sqrt{8}} \left( \frac{\hbar \omega}{k} \right)^{\frac{3}{2}} \\ &| \begin{pmatrix} \stackrel{(0)}{0} & | y & | \stackrel{(0)}{1} \rangle = \left( \frac{k}{\pi \hbar \omega} \right)^{1/2} \left( \frac{2k}{\hbar \omega} \right)^{1/2} \int_{-\infty}^{\infty} e^{\left( \frac{-ky^{2}}{\hbar \omega} \right)} \cdot y^{2} dy = \frac{1}{\sqrt{2}} \left( \frac{\hbar \omega}{k} \right)^{1/2} \end{split}$$

$$\begin{pmatrix} {}^{(0)}\\1 \\ x \\ \end{pmatrix} = \left(\frac{k}{\pi\hbar\omega}\right)^{1/2} \left(\frac{2k}{\hbar\omega}\right)^{1/2} \int_{-\infty}^{\infty} e^{\left(\frac{-kx^2}{\hbar\omega}\right)} \cdot x^2 dx = \frac{1}{\sqrt{2}} \left(\frac{\hbar\omega}{k}\right)^{1/2}$$

$$\begin{pmatrix} {}^{(0)}\\0 \\ y^3 \\ \end{pmatrix} = \left(\frac{k}{\pi\hbar\omega}\right)^{1/2} \left(\frac{2k}{\hbar\omega}\right)^{1/2} \int_{-\infty}^{\infty} e^{\left(\frac{-ky^2}{\hbar\omega}\right)} \cdot y^4 dy = \frac{3}{\sqrt{8}} \left(\frac{\hbar\omega}{k}\right)^{\frac{3}{2}}$$

$$\stackrel{(1)}{E_1} = \pm \frac{1}{2} kb \left[ \left(\frac{3}{\sqrt{8}} \left(\frac{\hbar\omega}{k}\right)^{\frac{3}{2}}\right) \left(\frac{1}{\sqrt{2}} \left(\frac{\hbar\omega}{k}\right)^{1/2}\right) + \left(\frac{1}{\sqrt{2}} \left(\frac{\hbar\omega}{k}\right)^{1/2}\right) \left(\frac{3}{\sqrt{8}} \left(\frac{\hbar\omega}{k}\right)^{\frac{3}{2}}\right) \right] = \pm \frac{3}{4} \frac{b\hbar^2\omega^2}{k}$$

## 3-For the second excited state n=2

$$\begin{vmatrix} \begin{pmatrix} (0) & (0) \\ 2 & 0 \\ \end{pmatrix} \hat{\mathbf{H}}^{(1)} \begin{vmatrix} (0) & (0) \\ 2 & 0 \\ \end{pmatrix} - \hat{\mathbf{E}}_{2} & \begin{pmatrix} (0) & (0) \\ 2 & 0 \\ \end{pmatrix} \hat{\mathbf{H}}^{(1)} \begin{vmatrix} (0) & (0) \\ 1 & 1 \\ \end{pmatrix} & \begin{pmatrix} (0) & (0) \\ 1 & 1 \\ \end{pmatrix} - \hat{\mathbf{E}}_{2} & \begin{pmatrix} (0) & (0) \\ 1 & 1 \\ \end{pmatrix} \hat{\mathbf{H}}^{(1)} \begin{vmatrix} (0) & (0) \\ 0 & 2 \\ \end{pmatrix} \\ \begin{pmatrix} (0) & (0) \\ 0 & 2 \\ \end{pmatrix} \hat{\mathbf{H}}^{(1)} \begin{vmatrix} (0) & (0) \\ 2 & 0 \\ \end{pmatrix} & \begin{pmatrix} (0) & (0) \\ 1 & 1 \\ \end{pmatrix} \hat{\mathbf{H}}^{(1)} \begin{vmatrix} (0) & (0) \\ 1 & 1 \\ \end{pmatrix} - \hat{\mathbf{E}}_{2} & \begin{pmatrix} (0) & (0) \\ 1 & 1 \\ \end{pmatrix} \hat{\mathbf{H}}^{(1)} \begin{vmatrix} (0) & (0) \\ 0 & 2 \\ \end{pmatrix} \\ \begin{pmatrix} (0) & (0) \\ 0 & 2 \\ \end{pmatrix} \hat{\mathbf{H}}^{(1)} \begin{vmatrix} (0) & (0) \\ 0 & 2 \\ \end{pmatrix} & \begin{pmatrix} (0) & (0) \\ 0 & 2 \\ \end{pmatrix} \hat{\mathbf{H}}^{(1)} \begin{vmatrix} (0) & (0) \\ 0 & 2 \\ \end{pmatrix} - \hat{\mathbf{E}}_{2} \\ = 0$$

Similarly,

$$\begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 2 & 0 \\ \end{pmatrix} \hat{\mathbf{H}}^{(1)} \begin{vmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 2 & 0 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 1 & 1 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)}_{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{(0)} {}^{(0)} \\ 0 & 2 \\ \end{pmatrix} = \begin{pmatrix} {}^{(0)}_{($$

$$\begin{vmatrix} -E_{2} & \langle 2 & 0 & | \hat{H}^{(1)} & | 1 & 1 \\ \langle 2 & 0 & | \hat{H}^{(1)} & | 1 & 1 \\ \rangle & 0 \\ \langle 1 & 1 & | \hat{H}^{(1)} & | 2 & 0 \\ \rangle & -E_{2} & \langle 1 & 1 & | \hat{H}^{(1)} & | 2 & 0 \\ \rangle & -E_{2} & \langle 1 & 1 & | \hat{H}^{(1)} & | 2 & 0 \\ \rangle & 0 & \langle 0 & 2 & | \hat{H}^{(1)} & | 1 & 1 \\ \rangle & -E_{2} \end{vmatrix} = 0$$

$$\stackrel{(1)}{E_{2}} \left( \begin{cases} (1) \\ E_{2} - & | \langle 0 & 2 & | \hat{H}^{(1)} & | 1 & 1 \\ \rangle & 1 & 1 \end{pmatrix} \right)^{2} - & | \langle 0 & 0 & | \hat{H}^{(1)} & | 1 & 1 \\ 2 & 0 & | \hat{H}^{(1)} & | 1 & 1 \\ \rangle & - & E_{2} \end{vmatrix} = 0$$

There are three eigenvalues: 
$$E_2^{(1)} = \pm \left( \left| \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2 & 1 \end{pmatrix}^2 + \left| \begin{pmatrix} 0 & 0 & 0 \\ 2 & 0 & 1 \end{pmatrix}^2 + \left| \begin{pmatrix} 0 & 0 & 0 \\ 2 & 0 & 1 \end{pmatrix}^2 \right|^2 + \left| \begin{pmatrix} 0 & 0 & 0 \\ 2 & 0 & 1 \end{pmatrix}^2 \right|^2 \right)^{1/2}$$
 and  $E_2^{(1)} = 0$ 

**H.W.** Determine 
$$\mathbf{E}_{2}^{(1)} = \pm \left( \left| \left\langle \begin{matrix} 0 & 0 \\ 0 & 2 \end{matrix} \right| \hat{\mathbf{H}}^{(1)} \left| \begin{matrix} 0 & 0 \\ 1 & 1 \end{matrix} \right|^{2} + \left| \left\langle \begin{matrix} 0 & 0 \\ 2 & 0 \end{matrix} \right| \hat{\mathbf{H}}^{(1)} \left| \begin{matrix} 0 & 0 \\ 1 & 1 \end{matrix} \right|^{2} \right)^{1/2} \right|^{1/2}$$

### 6.3. Variational method

Variational principle which is also called Rayleigh-Ritz method, states that the expectation value of a given Hamiltonian  $\hat{H}$  in any state using any trial (approximate) wave function  $\psi$  is always greater or equal to the exact ground-state energy  $\mathcal{E}_0$ .

$$\frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \ge \mathcal{E}_0$$
.....(6-3-1)

The equality condition in equation (6-3-1) holds if  $\psi$  is the exact ground state.

The variational method is particularly useful for determining the ground state energy and its eigenstate without explicitly solving the Schrödinger equation.

In general, we do not know the exact ground state energy  $\mathcal{E}_0$ , and wish to find an approximation for its value.

To prove equation (6-3-1), we assume that we know the exact solutions  $\Phi_i$  to the Schrödinger's equation,

$$\hat{H}\Phi_{i} = \mathcal{E}_{i}\Phi_{i}$$
, i=0, 1, 2, ...,  $\infty$  .....(6-3-2)

Expand the trial wave function  $\psi$  in terms of the exact eigenstates  $\Phi_i$  of  $\hat{H}$ .

$$\psi = \sum_{i} C_{i} \Phi_{i} \qquad \dots \dots (6-3-3)$$

The expectation value of the Hamiltonian  $\hat{H}$  in the trial wave function  $\psi$  is:

Subtract both sides of equation (6-3-4) from  $\mathcal{E}_{_0}$ 

$$E - \mathcal{E}_{0} = \frac{\sum_{i} |C_{i}|^{2} \mathcal{E}_{i}}{\sum_{i} |C_{i}|^{2}} - \mathcal{E}_{0} \qquad \dots \dots (6-3-5)$$

Since  $|C_i|^2$  always positive or zero, and  $\mathcal{E}_i \geq \mathcal{E}_0$  for non-degenerate bound systems, we have,

 $\mathbf{E} \ge \mathcal{E}_0 \tag{6-3-6}$ 

Or can be written as

$$\frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \ge \mathcal{E}_0$$
.....(6-3-7)

By the variational principle, our approximation  $\langle \hat{H} \rangle$  using any trial wavefunction  $\psi$  will always be greater than the exact ground value  $\mathcal{E}_0$ . Hence, the lower the expectation value  $\langle \hat{H} \rangle$  (i.e., the closer to the exact value), the better the trial wave function.

A typical varitaional calculation is as follows:

1- We first choose a trial wavefunction with a few variational (adjustable) parameters  $\alpha_1, \alpha_2, \ldots$  i.e  $\psi(\alpha_1, \alpha_2, \ldots)$ 

2- Calculate the expectation value of  $\hat{H}$  in the  $\psi(\alpha_1, \alpha_2, ...)$ , this yields an expression which depends on the parameters  $\alpha_1, \alpha_2, ...$ :

$$E(\alpha_{1}, \alpha_{2}, ...) = \frac{\int \psi^{*}(\alpha_{1}, \alpha_{2}, ...) \hat{H} \psi(\alpha_{1}, \alpha_{2}, ...) d\tau}{\int \psi^{*}(\alpha_{1}, \alpha_{2}, ...) \psi(\alpha_{1}, \alpha_{2}, ...) d\tau}$$
.....(6-3-8)

3- Using (6-3-8) to search for the minimum of  $E(\alpha_1, \alpha_2, ...)$  by varying the adjustable parameters  $\alpha_1, \alpha_2, ...$  until E is minimized.

$$\delta E(\alpha_1, \alpha_2, ...) = 0$$
 .....(6-3-9)

or

This gives the values of  $\alpha_1, \alpha_2, \dots$  that minimize E.

4- Substitute these values of  $\alpha_1, \alpha_2, ...$  into (6-3-8) to obtain the approximate value of the energy. The value E that obtained provides an upper bound for the exact state energy. The exact eigenstate will then be approximated by the state  $\psi(\alpha_1, \alpha_2, ...)$ .

Now, we can prove that the using of method of linear variations is equivalent to the construction of the matrix formulation  $\mathbf{H}\mathbf{C} = \mathbf{E}\mathbf{C}$  of the Schrödinger equation  $\hat{\mathbf{H}}\psi = \mathbf{E}\psi$ .

Let us assume that a set of basis functions  $\{\Phi_i, i=1, 2, ...n\}$  has been chosen, in which  $\Phi_i$  are linearly independent, but not necessarily orthogonal or normalized. The trial wave function  $\psi$  can be written as

$$\psi = \sum_{i}^{n} C_{i} \Phi_{i}$$
(6.3.11)

The energy expectation value of  $\psi$ ,

$$E = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau}$$
(6.3.12)

or can be written as

$$\mathbf{E} = \frac{\mathbf{C}^{\dagger} \mathbf{H} \mathbf{C}}{\mathbf{C}^{\dagger} \mathbf{S} \mathbf{C}} \tag{6.3.13}$$

where,  $\mathbf{H}$  and  $\mathbf{S}$  are the Hamiltonian matrix and the overlap matrix, respectively, their elements given by:

$$H_{ij} = \int \Phi_i^* \hat{H} \Phi_j d\tau$$
(6.3.14)

and

$$\mathbf{S}_{ij} = \int \Phi_i^* \Phi_j \mathrm{d}\tau \tag{6.3.15}$$

, and  $\boldsymbol{C}$  is the column vector of the expansion coefficient C.

In order to minimize E, we wish to ensure that

$$\frac{\partial E}{\partial C_i^*} = 0 \tag{6.3.16}$$

carrying out the above condition into Eq. (6.3.13) gives

$$\left(\frac{\partial \mathbf{E}}{\partial \mathbf{C}_{i}^{*}}\right)\left(\mathbf{C}^{\dagger}\mathbf{S}\mathbf{C}\right) + \mathbf{E}\frac{\partial}{\partial \mathbf{C}_{i}^{*}}\left(\mathbf{C}^{\dagger}\mathbf{S}\mathbf{C}\right) = \frac{\partial}{\partial \mathbf{C}_{i}^{*}}\left(\mathbf{C}^{\dagger}\mathbf{H}\mathbf{C}\right)$$
(6.3.17)

however,

$$\frac{\partial}{\partial C_{i}^{*}} \left( \mathbf{C}^{\dagger} \mathbf{S} \mathbf{C} \right) = \frac{\partial}{\partial C_{i}^{*}} \left( \sum_{i}^{n} \sum_{j}^{n} C_{i}^{*} \mathbf{S}_{ij} C_{j} \right) = \sum_{j}^{n} S_{ij} C_{j}$$
(6.3.18)

and similarly,

$$\frac{\partial}{\partial C_{i}^{*}} \left( \mathbf{C}^{\dagger} \mathbf{H} \mathbf{C} \right) = \frac{\partial}{\partial C_{i}^{*}} \left( \sum_{i}^{n} \sum_{j}^{n} C_{i}^{*} \mathbf{H}_{ij} C_{j} \right) = \sum_{j}^{n} \mathbf{H}_{ij} C_{j}$$
(6.3.19)

Substitute the results of Eqs. (6.3.18) and (6.3.19) into Eq. (6.3.17), and applying the condition in Eq. (6.3.16), then Eq (6.3.17) becomes

$$E\sum_{j}^{n} S_{ij}C_{j} = \sum_{j}^{n} H_{ij}C_{j}$$

$$\sum_{j}^{n} (H_{ij} - ES_{ij})C_{j} = 0, \qquad j=1, 2, ...n$$
(6.3.20)

We may rewrite the above equation in matrix form,

$$\mathbf{HC} = \mathbf{ESC} \tag{6.3.21}$$

**EX:** Use the variational method to estimate the energies of (a) the ground state, and (b) the first excited state for a one-dimensional harmonic oscillator. Hint: take the trial function for the ground state and first excited state to be Gaussian function i.e.,  $\psi_0(x, \alpha) = Ae^{-\alpha x^2}$  and  $\psi_1(x, \alpha) = B \cdot x \cdot e^{-\alpha x^2}$  respectively, where A and B are normalization constants. Soln.

a) Using 
$$\int_{-\infty}^{\infty} |\psi_0(\mathbf{x}, \alpha)|^2 d\mathbf{x} = 1 \text{ to find the normalization constant}$$

$$A^2 \int_{-\infty}^{\infty} e^{-2\alpha x^2} d\mathbf{x} = 1$$

$$A^2 \frac{\sqrt{\pi}}{(2\alpha)^{1/2}} = 1 \rightarrow A^2 = \frac{(2\alpha)^{1/2}}{\sqrt{\pi}} \rightarrow A = \left(\frac{2\alpha}{\pi}\right)^{1/4}$$

$$\therefore \quad \psi_0(\mathbf{x}, \alpha) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2}$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

$$E_0(\alpha) = \int_{-\infty}^{\infty} \psi_0^*(\mathbf{x}, \alpha) \hat{H} \psi_0(\mathbf{x}, \alpha) d\mathbf{x} = \left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right) e^{-\alpha x^2} d\mathbf{x}$$

$$E_0(\alpha) = \frac{\hbar^2}{2m} \alpha + \frac{m\omega^2}{8\alpha}$$

$$\frac{\partial E_0(\alpha)}{\partial \alpha} = \frac{\partial}{\partial \alpha} \left(\frac{\hbar^2}{2m} \alpha + \frac{m\omega^2}{8\alpha}\right) = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0 \rightarrow \alpha = \frac{m\omega^2}{2\hbar}$$

$$E_0 = \frac{1}{2}\hbar\omega \quad \text{and} \quad \psi_0(\mathbf{x}) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \cdot e^{\left(\frac{-m\omega x^2}{2\hbar}\right)}$$

The ground state energy and wave function obtained by the variational method are identical to their exact counterparts.

b) 
$$\psi_{1}(x) = Bxe^{-\alpha x^{2}}$$
  
Using  $\int_{-\infty}^{\infty} |\psi_{1}(x,\alpha)|^{2} dx = 1$  to find the normalization constant  
 $B = \left(\frac{32\alpha^{2}}{\pi}\right)^{1/4}$ ,  $\psi_{1}(x,\alpha) = \left(\frac{32\alpha^{3}}{\pi}\right)^{1/4} xe^{-\alpha x^{2}}$   
 $E_{1}(\alpha) = \int_{-\infty}^{\infty} \psi_{1}^{*}(x,\alpha)\hat{H}\psi_{1}(x,\alpha)dx = \left(\frac{32\alpha^{3}}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} e^{-\alpha x^{2}}x\left(-\frac{\hbar^{2}}{2m}\frac{d^{2}}{dx^{2}} + \frac{1}{2}m\omega^{2}x^{2}\right)xe^{-\alpha x^{2}}dx$   
 $= \left(\frac{32\alpha^{3}}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} e^{-\alpha x^{2}}x\left(-\frac{\hbar^{2}}{2m}\frac{d}{dx}\frac{d}{dx}\left(xe^{-\alpha x^{2}}\right) + \frac{1}{2}m\omega^{2}x^{3}e^{-\alpha x^{2}}\right)dx$   
 $= \left(\frac{32\alpha^{3}}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} e^{-\alpha x^{2}}x\left(-\frac{\hbar^{2}}{2m}\frac{d}{dx}\left(e^{-\alpha x^{2}} - 2\alpha x^{2}e^{-\alpha x^{2}}\right) + \frac{1}{2}m\omega^{2}x^{3}e^{-\alpha x^{2}}\right)dx$   
 $= \left(\frac{32\alpha^{3}}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} e^{-\alpha x^{2}}x\left(-\frac{\hbar^{2}}{2m}\left(-2\alpha xe^{-\alpha x^{2}} - 2\alpha\left(2xe^{-\alpha x^{2}} - 2\alpha x^{3}e^{-\alpha x^{2}}\right)\right) + \frac{1}{2}m\omega^{2}x^{3}e^{-\alpha x^{2}}\right)dx$   
 $= \left(\frac{32\alpha^{3}}{\pi}\right)^{1/2}\left(-\frac{\hbar^{2}}{2m}\left(-2\alpha\int_{-\infty}^{\infty} x^{2}e^{-2\alpha x^{2}} - 4\alpha\int_{-\infty}^{\infty} x^{2}e^{-2\alpha x^{2}} + 4\alpha^{2}\int_{-\infty}^{\infty} x^{4}e^{-2\alpha x^{3}}\right) + \frac{1}{2}m\omega^{2}\int_{-\infty}^{\infty} x^{4}e^{-2\alpha x^{2}}\right)dx$   
 $= \left(\frac{32\alpha^{3}}{\pi}\right)^{1/2}\left(-\frac{\hbar^{2}}{2m}\left(-12\alpha\int_{0}^{\infty} x^{2}e^{-2\alpha x^{2}} + 8\alpha^{2}\int_{0}^{\infty} x^{4}e^{-2\alpha x^{2}}\right) + m\omega^{2}\int_{0}^{\infty} x^{4}e^{-2\alpha x^{2}}\right)dx$   
 $E_{1}(\alpha) = \frac{3\hbar^{2}}{2m}\alpha + \frac{3m\omega^{2}}{8\alpha}$ 

The minimization of  ${}_{\mathrm{E}_1}(\alpha)$  with respect to  $\alpha$  , i.e

$$\frac{\partial E_{1}(\alpha)}{\partial \alpha} = \frac{\partial}{\partial \alpha} \left( \frac{\hbar^{2}}{2m} \alpha + \frac{m\omega^{2}}{8\alpha} \right) = \frac{3\hbar^{2}}{2m} - \frac{m\omega^{2}}{8\alpha^{2}} = 0 \quad \rightarrow \quad \alpha = \frac{m\omega^{2}}{2\hbar}$$

$$E_{1} = \frac{3}{2}\hbar\omega \quad \text{and} \quad \psi_{1}(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \left(\frac{2m\omega}{\hbar}\right)^{1/2} x \cdot e^{\left(\frac{-m\omega x^{2}}{2\hbar}\right)} = \left(\frac{4m^{3}\omega^{3}}{\pi\hbar^{3}}\right)^{1/4} x \cdot e^{\left(\frac{-m\omega x^{2}}{2\hbar}\right)}$$