

① Because  $V(x)$  is an even function, the first excited state must be odd. Therefore, the simplest and most meaningful choice for  $f(x)$  is  $f(x) = x$ , i.e.

$$\psi(x) = A x e^{-\beta|x|}$$

The derivatives of this trial function are:

$$\frac{d\psi}{dx} = A \left( 1 - \frac{\beta x^2}{|x|} e^{-\beta|x|} \right) \quad \frac{d^2\psi}{dx^2} = A \left( -2\beta \frac{x}{|x|} + \beta^2 x \right) e^{-\beta|x|}$$

The overlap integral is

$$\langle \psi | \psi \rangle = A^2 \int_{-\infty}^{+\infty} x^2 e^{-2\beta|x|} dx = 2A^2 \int_0^{+\infty} x^2 e^{-2\beta x} dx = 2A^2 \frac{2}{(2\beta)^3} = \frac{A^3}{2\beta^3}$$

Kinetic energy:

$$\begin{aligned} \langle \psi | -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} | \psi \rangle &= A^2 \left( -\frac{\hbar^2}{2m} \right) \int_{-\infty}^{+\infty} e^{-2\beta|x|} \left( -2\beta \frac{x^2}{|x|} + \beta^2 x^2 \right) dx = \\ &= A^2 \left( -\frac{\hbar^2}{2m} \right) \int_{-\infty}^{+\infty} e^{-2\beta|x|} \left( -2\beta|x| + \beta^2 x^2 \right) dx = A^2 \left( -\frac{\hbar^2}{2m} \right) \left[ -\frac{1}{6} + \frac{1}{2\beta} \right] = A^2 \left( -\frac{\hbar^2}{2m} \right) \left( \frac{1}{2\beta} \right) \end{aligned}$$

Potential energy:

$$\begin{aligned} \langle \psi | g(|x|) | \psi \rangle &= A^2 g \int_{-\infty}^{+\infty} |x| x^2 e^{-2\beta|x|} dx = 2A^2 g \int_0^{+\infty} x^3 e^{-2\beta x} dx = 2A^2 g \frac{6}{(2\beta)^4} = \\ &= \frac{3}{4} A^2 g \frac{6}{\beta^4} \end{aligned}$$

The trial energy is then

$$E = \frac{\langle \psi | T + V | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\frac{\hbar^2}{2m} \frac{1}{2\beta} + \frac{3}{4} \frac{g}{\beta^4}}{1/(2\beta^3)} = \frac{\frac{\hbar^2 \beta^2}{2m}}{1/(2\beta^3)} + \frac{3}{2} \frac{g}{\beta^2}$$

Minimization with respect to parameter  $\beta$ :

$$\frac{\partial E}{\partial \beta} = \frac{\hbar^2 \beta}{m} - \frac{3}{2} \frac{g}{\beta^2} = 0 \Rightarrow \frac{\hbar^2 \beta^3}{m} = \frac{3}{2} g \Rightarrow \beta^3 = \frac{3mg}{2\hbar^2} \quad \beta = \left( \frac{3mg}{2\hbar^2} \right)^{1/3}$$

$$E = \frac{\hbar^2}{2m} \left( \frac{3mg}{2\hbar^2} \right)^{2/3} + \frac{3}{2} g \left( \frac{2\hbar^2}{3mg} \right)^{1/3} = \left( \frac{3}{2} \right)^{5/3} \cdot \left( \frac{\hbar^2 g^2}{m} \right)^{1/3}$$

(2) The solution to the unperturbed problem is

$$|n_x n_y\rangle = \frac{2}{a} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{a} \quad E_{n_x n_y} = \frac{\hbar^2 \pi^2}{2ma^2} (n_x^2 + n_y^2)$$

where  $n_x = 1, 2, 3, \dots$   $n_y = 1, 2, 3, \dots$

For the ground state  $n_x = n_y = 1$  (non-degenerate)

For the first excited state  $n_x = 1, n_y = 2$  or  $n_x = 2, n_y = 1$  (two-fold degenerate)

In the case of the ground state

$$E_{\text{gr}}^{(1)} = \langle 11 | C_{xy} | 11 \rangle = C \langle 11 | 11 \rangle \langle 11 | 11 \rangle = C \cdot \frac{a}{2} \cdot \frac{a}{2} = C \frac{a^2}{4}$$

For the first excited state we must use the degenerate perturbation theory. We need to find a proper basis in which the perturbation matrix  $W$  is diagonal.

$$W = \begin{pmatrix} \langle 21 | H' | 12 \rangle & \langle 21 | H' | 12 \rangle \\ \langle 12 | H' | 21 \rangle & \langle 21 | H' | 21 \rangle \end{pmatrix} = C \begin{pmatrix} \frac{a}{2} \cdot \frac{a}{2} & \left(-\frac{16a}{9\pi^2}\right)\left(-\frac{16a}{9\pi^2}\right) \\ \left(\frac{16a}{9\pi^2}\right)\left(-\frac{16a}{9\pi^2}\right) & \frac{a}{2} \cdot \frac{a}{2} \end{pmatrix} =$$

$$= Ca^2 \begin{pmatrix} \frac{1}{4} & \frac{256}{81\pi^4} \\ \frac{256}{81\pi^4} & \frac{1}{4} \end{pmatrix}$$

The eigenvalues of this matrix are

$$E_{\text{1st.ex.}}^{(1)} = Ca^2 \left( \frac{1}{4} \pm \frac{256}{81\pi^4} \right)$$

$$③ \quad S_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

The unperturbed Hamiltonian is  $H_0 = \alpha S_z^2 = \alpha \hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

The perturbation is  $H' = \beta \hbar^2 \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$

The eigenvalues and eigenstates of the unperturbed Hamiltonian are:

$$E_1^{(0)} = \alpha \hbar^2 \quad \psi_1^{(0)} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad E_2^{(0)} = 0 \quad \psi_2^{(0)} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad E_3^{(0)} = \alpha \hbar^2 \quad \psi_3^{(0)} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

State #2 is non-degenerate, so

$$E_2^{(1)} = \langle \psi_2^{(0)} | H' | \psi_2^{(0)} \rangle = H'_{22} = 0$$

$$E_2^{(2)} = \sum_{m \neq 2} \frac{|H'_{m2}|^2}{E_2^{(0)} - E_m^{(0)}} = \frac{|H'_{12}|^2}{-\alpha \hbar^2} + \frac{|H'_{32}|^2}{-\alpha \hbar^2} = -2\hbar^2 \frac{\beta^2}{\alpha}$$

States #1 and #3 are degenerate. We need to find a proper basis in which the perturbation submatrix is diagonal.

$$W = \begin{pmatrix} H'_{11} & H'_{13} \\ H'_{31} & H'_{33} \end{pmatrix} = \beta \hbar^2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{The eigenvalues are } E_1^{(1)} = \beta \hbar^2 \quad E_3^{(1)} = -\beta \hbar^2$$

$$\phi_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \quad \phi_3 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \quad \phi_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

Then the second order corrections to the energies of states #1 and #3 are

$$E_1^{(2)} = \sum_{m \neq 1} \frac{|\langle \phi_m | H' | \phi_1 \rangle|^2}{E_1^{(0)} - E_m^{(0)}} = \frac{|\langle \phi_2 | H' | \phi_1 \rangle|^2}{E_1^{(0)} - E_2^{(0)}} = \frac{|\langle \phi_2 | H' | \phi_1 \rangle|^2}{\alpha \hbar^2}$$

$$E_3^{(2)} = \sum_{m \neq 3} \frac{|\langle \phi_m | H' | \phi_3 \rangle|^2}{E_3^{(0)} - E_m^{(0)}} = \frac{|\langle \phi_2 | H' | \phi_3 \rangle|^2}{E_3^{(0)} - E_2^{(0)}} = \frac{|\langle \phi_2 | H' | \phi_3 \rangle|^2}{\alpha \hbar^2}$$

Now,

$$\langle \phi_2 | H' | \phi_1 \rangle = \frac{\beta \hbar^2}{\sqrt{2}} (0 \ 1 \ 0) \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \sqrt{2} \beta \hbar^2 \Rightarrow E_1^{(2)} = \frac{2 \hbar^2 \beta^2}{\alpha}$$

$$\langle \phi_2 | \mathcal{H} | \phi_1 \rangle = \frac{\beta t^2}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} = 0 \Rightarrow E_3^{(2)} = 0$$

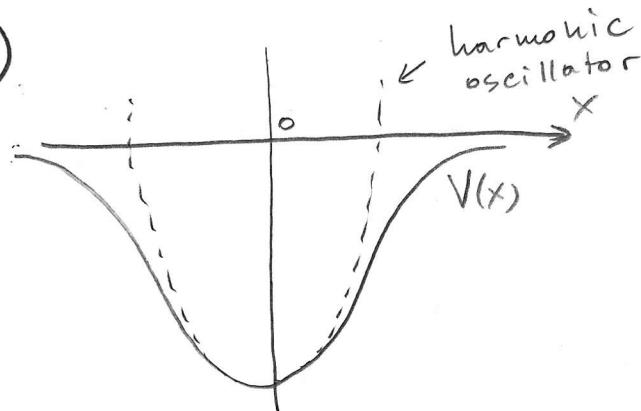
So the final result is:

$$E_1 = \alpha t^2 \left( 1 + \frac{\beta}{2} + 2 \frac{\beta^2}{\alpha^2} + \dots \right)$$

$$E_2 = \alpha t^2 \left( 0 + 0 - 2 \frac{\beta^2}{\alpha^2} + \dots \right)$$

$$E_3 = \alpha t^2 \left( 1 - \frac{\beta}{2} + 0 + \dots \right)$$

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a) At the bottom we can expand the potential in the Taylor series:

$$V(x) = -V_0 e^{-\beta x^2} \approx -V_0 \left(1 - \beta x^2 + \frac{\beta^2 x^4}{2} - \dots\right)$$

With that our Hamiltonian is

$$H = \underbrace{-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}}_{H_0} - V_0 + V_0 \beta x^2 - \underbrace{\frac{V_0 \beta^2}{2} x^4}_{H^1} + \dots$$

To determine how small  $\frac{V_0 \beta^2}{2}$  should be let us introduce natural units of length and energy (just as we do it for a harmonic oscillator), namely

$$y = \sqrt{2} x \quad E = \frac{E}{\hbar \omega} \quad \text{where } \alpha = \frac{m \omega}{\hbar} \quad \omega = \sqrt{\frac{2 V_0 \beta}{m}}$$

We then obtain

$$H = \underbrace{-\frac{1}{2} \frac{d^2}{dy^2} - \frac{V_0}{\hbar \omega} + \frac{1}{2} y^2}_{\text{an additive constant}} - \frac{1}{\hbar \omega} \frac{V_0 \beta^2}{2} \frac{\hbar^2}{m^2 \omega^2} y^2 + \dots$$

or

$$H = \underbrace{-\frac{1}{2} \frac{d^2}{dy^2} - \frac{V_0}{\hbar \omega} + \frac{1}{2} y^2}_{H_0} - \underbrace{\frac{1}{4} \sqrt{\frac{\beta \hbar^2}{2 m V_0}} y^4}_{H^1} + \dots$$

Apparently, the coefficient before  $y^4$  must be small, that is

$$\frac{1}{4} \sqrt{\frac{\beta \hbar^2}{2 m V_0}} \ll 1 \quad \text{or} \quad \frac{\beta \hbar^2}{m V_0} \ll 1$$

b) First order correction to the energy:

$$\mathcal{E}_0^{(1)} = \langle \Psi_0^{(0)} | H' | \Psi_0^{(0)} \rangle \quad \text{with} \quad \Psi_0^{(0)} = \frac{1}{\pi^{1/4}} e^{-\frac{y^2}{2}}$$

$$\begin{aligned} \mathcal{E}_0^{(1)} &= -\frac{1}{4} \sqrt{\frac{\beta \hbar^2}{2mV_0}} \langle \Psi_0^{(0)} | y^4 | \Psi_0^{(0)} \rangle = -\frac{1}{4} \sqrt{\frac{\beta \hbar^2}{2mV_0}} \int_{-\infty}^{+\infty} y^4 e^{-y^2} dy = \\ &= -\frac{1}{4} \sqrt{\frac{\beta \hbar^2}{2mV_0}} \cdot \frac{3}{4} \sqrt{\pi} = -\frac{3}{16} \sqrt{\frac{\beta \hbar^2}{2mV_0}} \end{aligned}$$

$$E_0^{(1)} = \hbar \omega \mathcal{E}_0^{(1)} = -\frac{3}{16} \hbar \sqrt{\frac{2V_0 \beta}{m}} \sqrt{\frac{\beta \hbar^2}{2mV_0}} = -\frac{3}{16} \frac{\hbar^2 \beta}{m}$$