

CHEMISTRY 531 EXAM I SOLUTIONS

1. Consider a particle of mass m in a two-dimensional box of dimensions $L_x = L_y = L$

a) Give the normalized wavefunctions in Cartesian coordinates, the energy eigenvalues, and the degeneracy of the first four energy levels.

$$\psi_{n_x, n_y}(x, y) = \frac{2}{L} \sin\left(\frac{n_x x}{L}\right) \sin\left(\frac{n_y y}{L}\right); \quad E_{n_x, n_y} = \frac{2\hbar^2}{2mL^2} (n_x^2 + n_y^2);$$

(1,1) $g = 1$; (1,2)=(2,1), $g = 2$; (2,2), $g = 1$; (3,1)=(3,1) $g = 2$.

b) Give the Hamiltonian in plane polar coordinates.

$$H = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) + V(r, \theta)$$

$$V(r, \theta) = 0, \quad 0 \leq r \leq L; \quad 0 \leq \theta \leq 2\pi \\ = \text{otherwise}$$

2. Consider a harmonic oscillator subjected to an external perturbation of the form ϵx .

a) Give the general expressions for the first and second order perturbation theory expressions for corrections to the energy eigenvalues.

b) Give explicit expressions for these corrections using the following

$$x |n\rangle = \left(\frac{\hbar}{2\mu}\right)^{1/2} (\sqrt{n} |n-1\rangle + \sqrt{n+1} |n+1\rangle),$$

where the $\{|n\rangle\}$ are the eigenfunctions of the harmonic oscillator Hamiltonian, $n = 0, 1, 2, \dots$

$$E_n^{(0)} = 0 \text{ because } \langle m|x|n\rangle = 0.$$

$$\langle m|x|n\rangle = \frac{\hbar}{2\mu} \left[\frac{\sqrt{n}}{\sqrt{n+1}} \delta_{m,n-1} + \frac{\sqrt{n+1}}{\sqrt{n}} \delta_{m,n+1} \right]$$

So, one infinite sum has two terms only, i.e.,

$$E_n^{(2)} = \frac{\hbar^2}{2\mu} \left[\frac{n}{\hbar} - \frac{n+1}{\hbar} \right] = -\frac{\hbar}{2\mu} \quad n = 0, 1, 2, \dots$$

3. The Hamiltonian for the linear rigid rotator is

$$H = \frac{L_{op}^2}{2I}; \quad \frac{1}{I} = \frac{1}{2\mu r_e^2}$$

a) What are the eigenfunctions of H?

$$Y_{\ell m}(\theta, \phi)$$

b) What are the eigenvalues of H?

$$\hbar^2 \ell(\ell + 1) / 2I = E_{\ell}$$

c) Show that these have units of energy.

$$\hbar = \text{angular momentum} = \text{mass} \cdot \text{distance}^2 / \text{time}$$

$$= \text{mass} \cdot \text{distance}^2 = \frac{\hbar^2}{\text{mass}} = \frac{\text{distance}^4 \cdot \text{mass}^2}{\text{mass} \cdot \text{distance}^2 \cdot \text{time}^{-2}}$$

$$= \frac{\text{distance}^2}{\text{time}^2} \cdot \text{mass}$$

$$= \text{energy}$$

$$\text{or } \hbar = \text{energy} \cdot \text{time}$$

d) What is the degeneracy of the energy eigenvalue?

$$g_{\ell} = 2\ell + 1 \quad (\text{since } -\ell \leq m \leq \ell)$$

4. Re-consider the full Hamiltonian given in problem 2. Set up the variational approach using an expansion of the wave function in terms of the basis $\{ |n\rangle \}$. Consider just two terms in this expansion $n = 0$ and 1 . Show that the Schrödinger equation becomes a 2×2 matrix equation. Give an explicit expression for the H-matrix. Diagonalize it and get the two eigenvalues. Compare those with the ones you get in second order from problem 2.

$$\begin{aligned} \psi &= c_0 |0\rangle + c_1 |1\rangle \\ H\psi &= \begin{pmatrix} \langle 0|H|0\rangle & \langle 0|H|1\rangle \\ \langle 1|H|0\rangle & \langle 1|H|1\rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \end{pmatrix} \\ \langle 0|H|0\rangle &= \frac{\hbar^2}{2\mu} + \langle 0|x|0\rangle = \frac{\hbar^2}{2\mu} \\ \langle 1|H|1\rangle &= \frac{\hbar^2}{2\mu} + \langle 1|x|1\rangle = \frac{3\hbar^2}{2\mu} \\ \langle 0|H|1\rangle &= \langle 0|x|1\rangle = \frac{\hbar^2}{2\mu} \end{aligned}$$

Eigenvalues obtained from secular equation

$$\det \begin{vmatrix} \langle 0|H|0\rangle - E & \langle 0|H|1\rangle \\ \langle 1|H|0\rangle & \langle 1|H|1\rangle - E \end{vmatrix} = 0$$

$$\left(\frac{\hbar^2}{2\mu} - E \right) \left(\frac{3\hbar^2}{2\mu} - E \right) - \frac{\hbar^4}{4\mu^2} = 0$$

$$E_{1,2} = \frac{E_0^{(0)} + E_1^{(0)}}{2} \pm \frac{1}{2} \sqrt{\left(E_1^{(0)} - E_0^{(0)}\right)^2 + 4V_{01}^2}$$

$$E_{1,2} = \hbar \omega \pm \frac{1}{2} \sqrt{(\hbar \omega)^2 + 4V_{01}^2} \frac{\hbar \omega}{2\mu}$$

$$= \hbar \omega \pm \frac{\hbar \omega}{2} \sqrt{1 + 4 \frac{V_{01}^2}{(\hbar \omega)^2}} = \hbar \omega \pm \frac{\hbar \omega}{2} \sqrt{1 + \frac{4V_{01}^2}{\mu^2 \hbar^2 \omega^2}}$$

Recall $(1+x)^{1/2} \approx 1 + \frac{1}{2}x$ of $x \ll 1$

if $x = 4V_{01}^2 / \mu^2 \hbar^2 \omega^2$

$$E_{1,2} = \hbar \omega \pm \frac{\hbar \omega}{2} \left(1 + \frac{4V_{01}^2}{\mu^2 \hbar^2 \omega^2}\right)^{1/2} = \hbar \omega \pm \frac{\hbar \omega}{2} \left(1 \pm \frac{2V_{01}^2}{\mu^2 \hbar^2 \omega^2}\right)$$

$$E_1 = \frac{\hbar \omega}{2} - \frac{2V_{01}^2}{2\mu^2 \hbar^2 \omega^2} \stackrel{?}{=} E_0^{(2)} \quad \text{yes}$$

$$E_2 = \frac{3\hbar \omega}{2} + \frac{2V_{01}^2}{2\mu^2 \hbar^2 \omega^2} \stackrel{?}{=} E_1^{(2)} \quad \text{no}$$

So, we are not getting an accurate excited state result, but we are getting an accurate ground state result.