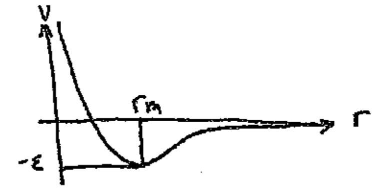
CHEMISTRY 551 KEY

PROBLEM SET IV

1) a) EXPAND $V(r)$ IN A TAYLOR SERIES ABOUT $r = r_m$



$$V(r) = -\varepsilon + \tfrac{1}{2}V''(r_m)(r-r_m)^2 + \tfrac{1}{3!}V'''(r_m)(r-r_m)^3 + O(r^4)$$

THE FIRST TWO TERMS CORRESPOND TO A HARMONIC OSCILLATOR POTENTIAL, AND THE LAST TERM TO A SMALL PERTURBATION H' (NEGLECTING r^4 TERMS)

$$\begin{aligned} H_0 &= -\hbar^2/2\mu\, d^2/dr^2 - \varepsilon + \tfrac{1}{2}V''(r_m)\cdot(r-r_m) \\ &= -\varepsilon + \hbar\omega/2\left\{-\hbar/\mu\omega\, d^2/dr^2 + 1/\hbar\omega\cdot V''(r_m)\cdot(r-r_m)^2\right\} \\ &= -\varepsilon + \hbar\omega/2\left\{\left(i\sqrt{\hbar/\mu\omega}\, d/dr\right)^2 + \mu\omega/\hbar\cdot(r-r_m)^2\right\} \\ &= -\varepsilon + \hbar\omega/2\left\{\hat{p}^2 + \hat{r}^2\right\} \end{aligned}$$

μ IS THE REDUCED MASS OF THE SYSTEM.

SETTING $\omega^2 = V''(r_m)/\mu$

$\hat{p} = i\sqrt{\hbar/\mu\omega}\, d/dr \qquad \hat{r} = \sqrt{\mu\omega/\hbar}\,(r-r_m)$

$$\begin{aligned} H' &= \tfrac{1}{6}V'''(r_m)(r-r_m)^3 \\ &= \sigma\hbar\omega\hat{r}^3 \end{aligned}$$

WHERE $\sigma = V'''(r_m)/(6\omega^2\mu)\cdot\sqrt{\hbar/\mu\omega}$

b) DEFINING $a \equiv 1/\sqrt{2}\,(\hat{r} + i\hat{p}) \qquad a^+ = 1/\sqrt{2}\,(\hat{r} - i\hat{p}) \qquad \Rightarrow \quad \hat{r} = 1/\sqrt{2}\,(a + a^+)$

$$\begin{aligned} H' = \sigma\hbar\omega\hat{r}^3 &= (\sigma\hbar\omega/\sqrt{8})\cdot(a+a^+)^3 \\ &= (\sigma\hbar\omega/\sqrt{8})\cdot(a^2 + \{a,a^+\} + a^{+2})(a+a^+) \\ &= (\sigma\hbar\omega/\sqrt{8})\cdot(a^3 + a^{+3} + (2N+1)(a+a^+) + a^2a^+ + a^{+2}a) \\ &= (\sigma\hbar\omega/\sqrt{8})\cdot(a^3 + a^{+3} + (2N+1)(a+a^+) + a(N+1) + a^+N) \\ &= (\sigma\hbar\omega/\sqrt{8})\cdot(a^3 + a^{+3} + (2N+1)(a+a^+) + (N+2)a + (N-1)a^+) \\ &= (\sigma\hbar\omega/\sqrt{8})\cdot(a^3 + a^{+3} + 3(N+1)a + 3Na^+) \end{aligned}$$

$aa^+ = N+1 \qquad a^+a = N$

$\{a,a^+\} = aa^+ + a^+a = 2N+1$

$aN = (N+1)a$

$a^+N = (N-1)a^+$

c)
$$\begin{aligned} \langle m|H'|n\rangle &= (\sigma\hbar\omega/\sqrt{8})\,\langle m|(a^3 + a^{+3} + 3(N+1)a + 3Na^+)|n\rangle \\ &= (\sigma\hbar\omega/\sqrt{8})\left\{\sqrt{n(n-1)(n-2)}\,\langle m|n-3\rangle + 3\sqrt{n}\,\langle m|(N+1)|n-1\rangle + 3\sqrt{n+1}\,\langle m|N|n+1\rangle + \sqrt{(n+1)(n+2)(n+3)}\,\langle n|n+3\rangle\right\}. \\ &= (\sigma\hbar\omega/\sqrt{8})\left\{\sqrt{n(n-1)(n-2)}\,\delta_m^{n-3} + 3n^{3/2}\delta_m^{n-1} + 3(n+1)^{3/2}\delta_m^{n+1} + \sqrt{(n+1)(n+2)(n+3)}\,\delta_m^{n+3}\right\} \end{aligned}$$

$\therefore\ \langle m|H'|n\rangle = 0$ UNLESS $m = n \pm 1$ OR $m = n \pm 3$

THE FIRST ORDER PERTURBATION $W_1 = \langle n|H'|n\rangle = 0$

d) THE SECOND ORDER PERTURBATION.

$$W_2 = \sum_{m \neq n} \frac{|\langle m|H'|n\rangle|^2}{E_n - E_m}$$

To zeroth order the energy difference is
$E_n - E_m = ((n+\tfrac{1}{2})\hbar\omega - \varepsilon) - ((m+\tfrac{1}{2})\hbar\omega - \varepsilon)$
$= (n-m)\hbar\omega$

$$W_2 = \frac{(\sigma\hbar\omega)^2}{8}\{n\cdot(n-1)(n-2)/(3\hbar\omega) + 9n^3/\hbar\omega + 9(n+1)^3/(-\hbar\omega) + (n+1)(n+2)(n+3)/(-3\hbar\omega)\}$$
$$= -\tfrac{1}{8}\sigma^2\hbar\omega\{30n^2+30n+11\}$$

So, to second order, the energy of level n is $\underline{E_n^{(2)} = (n+\tfrac{1}{2})\hbar\omega - \frac{\sigma^2\hbar\omega}{8}\{30n^2+30n+11\}}$

e) THE ELECTRIC DIPOLE COUPLING IS PROPORTIONAL TO $\langle i|\hat{r}|f\rangle$. FOR THE UNPERTURBED HAMILTONIAN

$$\langle 0|\hat{r}|2\rangle = 1/\sqrt{2}\ \langle 0|(a+a^{\dagger})|2\rangle = 0$$

To zeroth order
∴ THERE IS NO TRANSITION PROBABILITY FROM THE GROUND STATE TO THE SECOND EXCITED STATE. WHEN THE PERTURBATION H' IS INTRODUCED TO FIRST ORDER:

$|\psi_1\rangle = \sum_{n\neq m} a_n|n\rangle$ WHERE $a_n = \langle m|H'|n\rangle / (E_m - E_n)$

$$|0'\rangle = |0\rangle + \sigma\hbar\omega/\sqrt{8}\{(3/(E_0-E_1))|1\rangle + (\sqrt{6}/(E_0-E_3))|3\rangle\}$$
$$= |0\rangle + \sigma\{-(3/\sqrt{8})|1\rangle - (1/2\sqrt{3})|3\rangle\}$$

$$|2'\rangle = |2\rangle + \sigma\hbar\omega/\sqrt{8}\{(3(2)^{3/2}/(E_2-E_1))|1\rangle + (3(3)^{3/2}/(E_2-E_3))|3\rangle + ((5\cdot4\cdot3)^{1/2}/(E_2-E_5))|5\rangle\}$$
$$= |2\rangle + \sigma\{3|1\rangle - (9\sqrt{3/8})|3\rangle - (\sqrt{5/6})|5\rangle\}$$

AND
$$\langle 0'|\hat{r}|2'\rangle = 1/\sqrt{2}\{\langle 0'|(a+a^{\dagger})|2'\rangle\}$$
$$= \sigma/\sqrt{2}\{3\langle 0|a|1\rangle - (3/\sqrt{8})\langle 1|a|2\rangle - (1/2\sqrt{3})\langle 3|a^{\dagger}|2\rangle\} = \sigma/\sqrt{2}$$

∴ THE FIRST ORDER PERTURBATION H' PREDICTS A NON-ZERO $\langle 0'|\hat{r}|2'\rangle$ COUPLING.

f) THE FREQUENCY BETWEEN THE $|0'\rangle$ AND $|2'\rangle$ STATES $\omega_2' = (E_2' - E_0')/\hbar$ CAN BE CALCULATED FROM THE WAVEFUNCTIONS FOUND IN e) OR THE PERTURBATION FROM d)

$$\omega_2' = 1/\hbar\ ((E_2 + W_2(n=2)) - (E_0 + W_2(n=0)))$$
$$= 1/\hbar\ (2\hbar\omega - 1/8\ \sigma^2\hbar\omega(-191-11))$$
$$= 2\omega - 45/2\cdot\sigma^2\omega$$

IN TERMS OF $V'''(r_m)$ AND $V''(r_m)$: $\omega_2' = 2\sqrt{V''/\mu} + 5/8\cdot\hbar\,(V'''/V'')^2/\mu$

2) a) A HAMILTONIAN $H_0 = aJ_z + b/\hbar \cdot J_z^2$ ACTS ON THE SPACE SPANNED BY $j=1$

$H_0|1\rangle = \hbar(a+b)$
$H_0|0\rangle = 0$
$H_0|-1\rangle = \hbar(-a+b)$

THE $|j=1, m\rangle$ BASIS IS AN EIGEN BASIS OF H_0. THERE WILL BE DEGENERACIES IF $b/a = 1$; $H_0|0\rangle = H_0|-1\rangle = 0$ OR IF $b/a = -1$; $H_0|1\rangle = H_0|0\rangle = 0$ OR IF $b/a \to \pm\infty$; $H_0|1\rangle = H_0|-1\rangle = \pm b\hbar$

b) A PERTURBATION $W = \omega_0 J_u = \omega_0 \left(J_z \cos\theta + J_x \sin\theta \cos\phi + J_y \sin\theta \sin\phi \right)$

$$W = \omega_0 \hbar \left\{ \cos\theta \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \frac{\sin\theta\cos\phi}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} + \frac{\sin\theta\sin\phi}{\sqrt{2}} \begin{bmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{bmatrix} \right\} = \frac{\omega_0\hbar}{\sqrt{2}} \begin{bmatrix} \sqrt{2}\cos\theta & \sin\theta\, e^{-i\phi} & 0 \\ \sin\theta\, e^{i\phi} & 0 & \sin\theta\, e \\ 0 & \sin\theta\, e^{i\phi} & -\sqrt{2}\cos \end{bmatrix}$$

c) FOR $a=b$, $H_0|1\rangle = 2a\hbar$, $H_0|0\rangle = H_0|-1\rangle = 0$. TAKING $W = \omega_0 J_x$,

$E_{01} = H_0|1\rangle + \langle 1|W|1\rangle = 2a\hbar$ SINCE $\langle 1|J_x|1\rangle = 0$

THE PERTURBED ENERGIES OF THE DEGENERATE SUBSPACE ARE THE EIGENVALUES OF

$$\omega_0 \begin{bmatrix} \langle 0|J_x|0\rangle & \langle 0|J_x|1\rangle \\ \langle 1|J_x|0\rangle & \langle 1|J_x|1\rangle \end{bmatrix} = \omega_0 \begin{bmatrix} 0 & \hbar/\sqrt{2} \\ \hbar/\sqrt{2} & 0 \end{bmatrix}$$

WHICH HAS EIGENVALUES $W_\pm = \pm\omega_0\hbar/\sqrt{2}$ AND EIGENVECTORS $v_+ = \frac{1}{\sqrt{2}}(|0\rangle + |-1\rangle)$, $v_- = \frac{1}{\sqrt{2}}(|0\rangle - |-1\rangle)$

$\therefore$ THE EIGENVECTORS AND THE ENERGIES OF THE PERTURBED SYSTEM ARE:
$\{ |1\rangle, \frac{1}{\sqrt{2}}(|0\rangle + |-1\rangle), \frac{1}{\sqrt{2}}(|0\rangle - |-1\rangle) \}$ WITH CORRESPONDING ENERGIES $\{2a\hbar, \omega_0\hbar/\sqrt{2}, -\omega_0\hbar/\sqrt{2}$

d) FOR $b=2a$, $H_0|1\rangle = 3a\hbar$, $H_0|0\rangle = 0$, $H_0|-1\rangle = a\hbar$. THE FIRST ORDER PERTURBED GROUND STATE $|0'\rangle$ IS

$$|0'\rangle = |0\rangle + \sum_{m \neq n} \left(\frac{\langle m|W|n\rangle}{E_n - E_m} \right) |m\rangle$$

WHERE $n=0$, $E_n = 0$ AND $m = \pm 1$

$$|0'\rangle = |0\rangle - \left(\langle 1|W|0\rangle / (3a\hbar) \right) |1\rangle - \left(\langle -1|W|0\rangle / (a\hbar) \right) |-1\rangle$$

$$= |0\rangle - \omega_0 \sin\theta / \sqrt{2}\, a \left(e^{i\phi} |-1\rangle + \tfrac{1}{3} e^{-i\phi} |1\rangle \right)$$