Physics 880A20 — Winter 2003

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Answers To Assignment # 3

1.  $V = \frac{V_3}{2}(1-\cos 3\alpha_1) + \frac{V_3}{2}(1-\cos 3\alpha_2)$

$$F_1 = F_2 = \frac{h}{8\pi^2 c I_\alpha}$$

a)

$$\left[-F\frac{d^2}{d\alpha_1^2} - F\frac{d^2}{d\alpha_2^2} + V(\alpha_1,\alpha_2)\right]\psi(\alpha_1,\alpha_2) = E\,\psi(\alpha_1,\alpha_2)$$

Try $\psi(\alpha_1,\alpha_2) = \psi_1(\alpha_1)\psi_2(\alpha_2)$

$$-F\psi_2(\alpha_2)\frac{d^2\psi_1}{d\alpha_1^2} - F\psi_1(\alpha_1)\frac{d^2\psi_2}{d\alpha_2^2} + \psi_1\psi_2\frac{V_3}{2}(1-\cos 3\alpha_1)$$

$$+ \psi_1\psi_2\frac{V_3}{2}(1-\cos 3\alpha_2) = E\,\psi_1\psi_2$$

$$\frac{1}{\psi_1\psi_2}: \quad \underbrace{-\frac{F\psi_1''}{\psi_1} + \frac{V_3}{2}(1-\cos 3\alpha_1)}_{E_1} \underbrace{-\frac{F\psi_2''}{\psi_2} + \frac{V_3}{2}(1-\cos 3\alpha_2)}_{E_2} = E$$

$E = E_1 + E_2$

$$-F\frac{d^2\psi_1}{d\alpha_1^2} + \frac{V_3}{2}(1-\cos 3\alpha_1)\psi_1 = E_1\psi_1$$

$$-F\frac{d^2\psi_2}{d\alpha_2^2} + \frac{V_3}{2}(1-\cos 3\alpha_2)\psi_2 = E_2\psi_2$$

$V = 0$ Free Rotor - solved in class

$$E_1 = Fhm_1^2 \qquad \psi_1(\alpha_1) = 1/\sqrt{2\pi}\; e^{im_1\alpha_1}$$

$$E_2 = Fhm_2^2 \qquad \psi_2(\alpha_2) = 1/\sqrt{2\pi}\; e^{im_2\alpha_2}$$

$E = Fh(m_1^2 + m_2^2) \quad m_1, m_2 = 0, \pm 1, \pm 2, \ldots$

$$\psi_{m_1 m_2}(\alpha_1,\alpha_2) = \psi_{m_1}(\alpha_1)\psi_{m_2}(\alpha_2) = \frac{1}{2\pi}e^{im_1\alpha_1}e^{im_2\alpha_2}$$

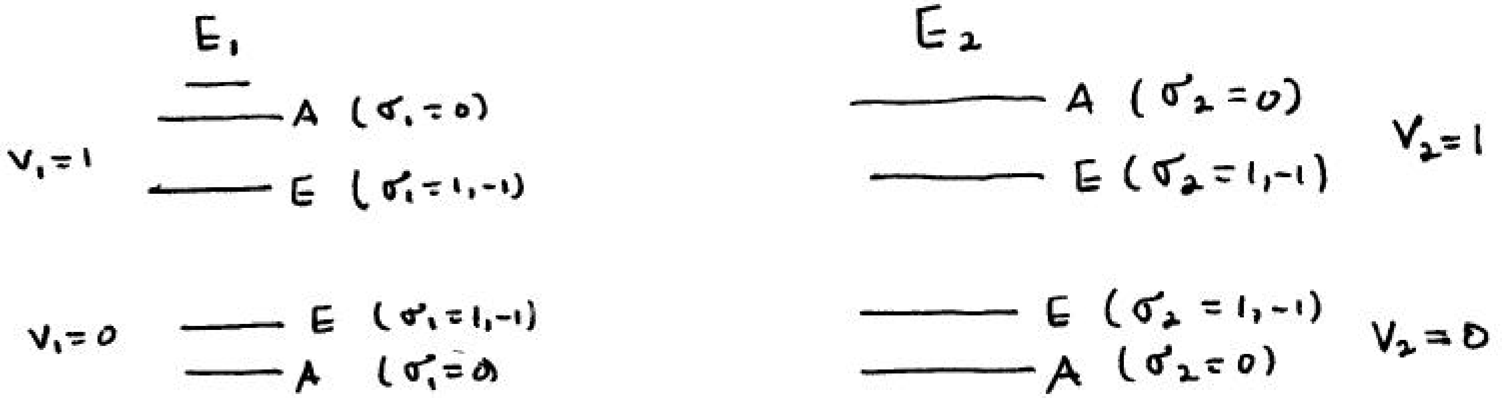
$$\langle 3k_1' + \sigma_1 | \mathcal{H}_1 | 3k_1 + \sigma_1 \rangle = \left[F(3k_1+\sigma_1)^2 + \frac{V_3}{2} \right] \delta_{k_1' k_1} - \frac{V_3}{4}\, \delta_{k_1'\, k_1 \pm 1}$$

Similarly

$$\langle 3k_2' + \sigma_2 | \mathcal{H}_2 | 3k_2 + \sigma_2 \rangle = \left[F(3k_2+\sigma_2)^2 + \frac{V_3}{2} \right] \delta_{k_2' k_2} - \frac{V_3}{4}\, \delta_{k_2'\, k_2 \pm 1}$$

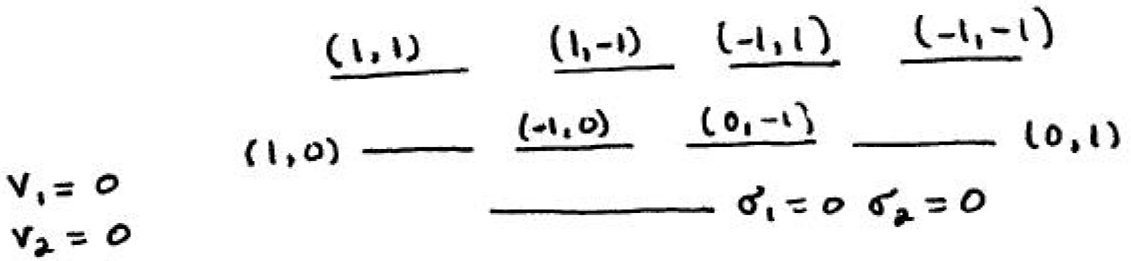
(c) $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 \qquad E = E_1 + E_2 \; ; \; E_{v_1\sigma_1, v_2\sigma_2} = E_{v_1\sigma_1} + E_{v_2\sigma_2}$

Since E_1 + E_2 are identical solutions, the computed energy levels are given by torsional quantum numbers v_1, v_2 and σ_1, σ_2. For a given torsional state, specified by v_1, v_2, one expects the following pattern for $E_1 + E_2$:



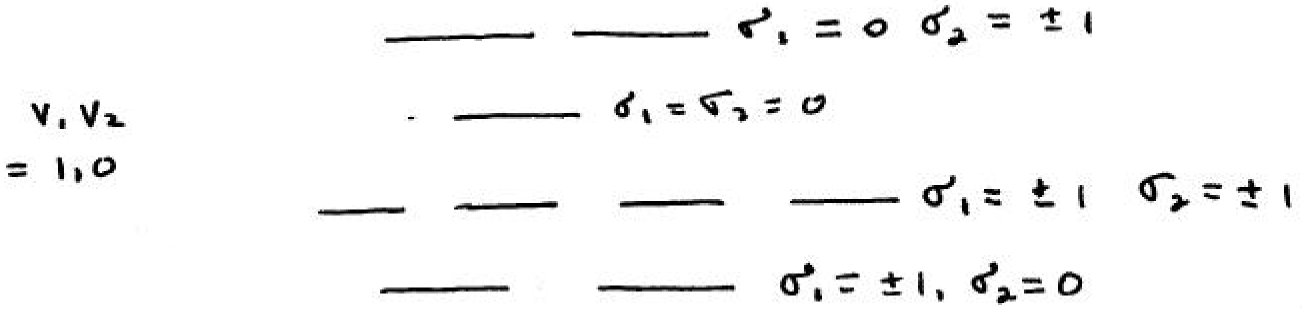
where the splitting increases as v increases.

$\Rightarrow$ Let us first consider the lowest torsional state, 0,0

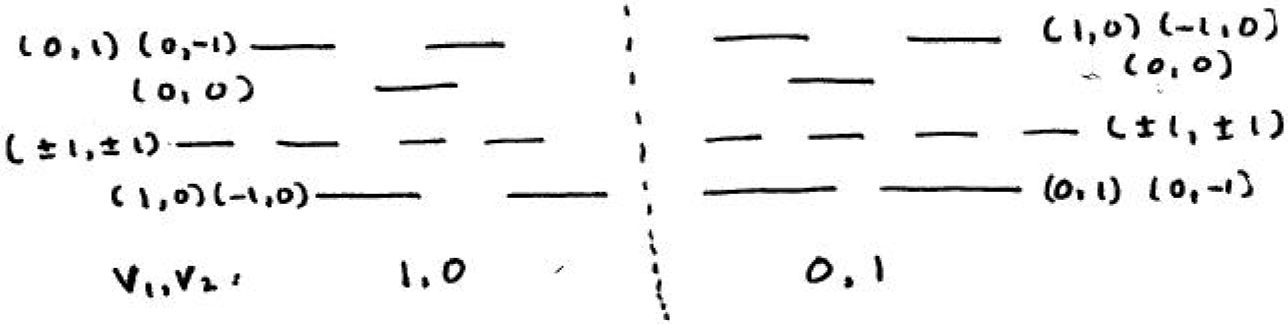


Thus, one expects 2 4-fold degenerate states and 1 non-degenerate state. In excited v_1, v_2 states, it is less clear what the order will be.

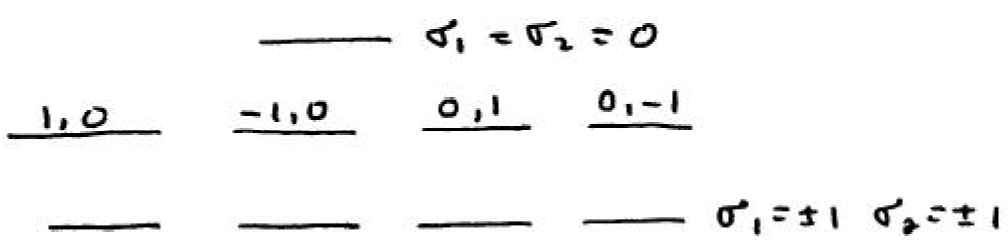
Consider the states v_{t1}, v_{t2} = 1,0 + 0,1. Assuming the $v = 1$ splitting of A + E to be the larger:



Of course, if one considers both degenerate states ($v_1 v_2$ = 1,0 + 0,1) the pattern is different:



Finally, for a state such as $v_{t1} = 1$, $v_{t2} = 1$:



Rational letter labels: AA $\sigma_1 = \sigma_2 = 0$

EE ($\sigma_1 = \pm 1$ $\sigma_2 = \pm 1$) AE ($\sigma_1 = 0$ $\sigma_2 = \pm 1$) EA ($\sigma_1 = \pm 1$, $\sigma_2 = 0$)

(NOT USED — SEE NEXT PAGE)

(d) It is unlikely that coupling terms can break the 4-fold degeneracy of states such as $(\pm1,0)$ $(0,\pm1)$ since the diagonal elements of $(1,0)$ & $(-1,0)$ are the same. The degeneracy breaking, if it does occur, will probably affect the $(\pm1,\pm1)$ states since a $(1,1)$ sub level and a $(1,-1)$ sublevel do not have very similar wave functions.

Detailed calculations were actually needed to determine that $V_{12}\cos 3\alpha_1 \cos 3\alpha_1$ does NOT reduce any degeneracy but $V_{12}'' \sin 3\alpha_1 \sin 3\alpha_2$ does.

The breaking leads to the following pattern for $V_1 = V_2 = 0$:

"EA" $(1,-1)$ $(-1,1)$ ——— ——— } order depends on sign of V_{12}'
"AE" $(1,1)$ $(-1,-1)$ ——— ———

$(\pm1,0)$ ——— ——— ——— ——— $(0,\pm1)$ "EE"

——— $\sigma_1=0$ $\sigma_2=0$ "AA"

Note the confusing letter designations, designed solely to get the degeneracy right; e.g. EE $= 2\times2 = 4$

2. $|v\sigma\rangle = \psi_{v\sigma}(\alpha)$ μ is not a function of α

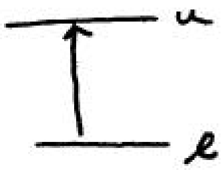
For methanol, both μ_a & μ_b are non-zero.

$i = a, b$

$$\mu_i \langle J' K_{-1}' K_1' \, v'\sigma' | \Phi_{iF} | J K_{-1} K_1 \, v\sigma \rangle$$

$$= \mu_i \underbrace{\langle J' K_{-1}' K_1' | \Phi_{iF} | J K_{-1} K_1 \rangle}_{a- \text{ \& } b-\text{type}} \underbrace{\langle v'\sigma' | v\sigma \rangle}_{\Delta\sigma = 0,\ \Delta v = 0}$$

This turns out to be not quite right because the $\mathcal{H}_{\rm tre}$ term mixes different torsional states, but not different σ. $\longrightarrow$ $\Delta v = 0$

3. 

$$\mathcal{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \qquad \Psi = \sum c_n(t)\, e^{-iE_n t/\hbar} |\varphi_n\rangle$$

$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'(t) \quad \mathcal{H}_0|\varphi_n\rangle = E_n|\varphi_n\rangle$

$$\mathcal{H}\Psi = (\mathcal{H}_0 + \mathcal{H}')\sum_n C_n(t) e^{-iE_nt/\hbar}|\varphi_n\rangle$$

$$= i\hbar\frac{d}{dt}\sum_n C_n(t)\, e^{-iE_nt/\hbar}|\varphi_n\rangle$$

$$\sum_n C_n(t)\, e^{-iE_nt/\hbar}\left[\mathcal{H}'|\varphi_n\rangle + E_n|\varphi_n\rangle\right]$$

$$= i\hbar\sum_n \dot{C}_n(t)\, e^{-iE_nt/\hbar}|\varphi_n\rangle$$

$$+ i\hbar\sum_n C_n(t)\left[-i\frac{E_n}{\hbar}\right]e^{-iE_nt/\hbar}|\varphi_n\rangle$$

Note: $i\hbar(-iE_n/\hbar) = E_n$ so that the $E_n|\varphi_n\rangle$ terms on both sides of the equation cancel.

$$\sum_n C_n(t)\, e^{-iE_nt/\hbar}\,\mathcal{H}'|\varphi_n\rangle$$

$$= i\hbar\sum_n \dot{C}_n\, e^{-iE_nt/\hbar}|\varphi_n\rangle$$

Mult. both sides by: $\langle\varphi_m| \times e^{+iE_mt/\hbar}$: $\langle\varphi_m|\varphi_n\rangle = \delta_{mn}$ "left multigrate"

$$\therefore \frac{dC_m(t)}{dt} = -\frac{i}{\hbar}\sum_n C_n(t)\, e^{-i(E_n - E_m)t/\hbar}(\mathcal{H}')_{mn}$$

$$\frac{dC_m(t)}{dt} = -\frac{i}{\hbar}\sum_n C_n(t)\, e^{-i\omega_{nm}t}(\mathcal{H}')_{mn}$$

Initial conditions $\quad C_\ell(t=0) = 1 \quad C_{n\neq\ell}(t=0) = 0$

Perturbation Approximation: $C_\ell(t) \approx 1$ at all t.

Let $m = u$

$$\frac{dC_u(t)}{dt} \cong -\frac{i}{\hbar}\, e^{-i\omega_{\ell u}t}(\mathcal{H}')_{u\ell}$$

$$c_n(t) = -\frac{i}{\hbar} \int_0^t e^{i\omega_{nl}\tau} (\mathcal{H}'(\tau))_{nl} \, d\tau$$