22.5.4: iv. Problem Solutions

Q1

a. $T_{nm} \approx \dfrac{|\langle n|V|m\rangle|^2}{\hbar^2\omega_{nm}^2}$

evaluating $\langle 1s|V|2s\rangle$ (using only the radial portions of the 1s and 2s wavefunctions since the spherical harmonics will integrate to unity) where V = (e^2, r) :

$$\langle 1s|V|2s\rangle = \int 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{\frac{-Zr}{a_0}} \frac{1}{r}\frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(1-\frac{Z_r}{2a_0}\right) e^{\frac{-Zr}{2a_0}} r^2 dr \tag{22.5.4.1}$$

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^3\left[\int r e^{\frac{-3Zr}{2a_0}} dr - \int \frac{Zr^2}{2a_0} e^{\frac{-3Zr}{2a_0}} dr\right] \tag{22.5.4.2}$$

Using integral equation 4 for two integration we obtain:

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^3\left[\frac{1}{\left(\frac{3Z}{2a_0}\right)^2} - \left(\frac{Z}{2a_0}\right)\frac{2}{\left(\frac{3Z}{2a_0}\right)}\right] \tag{22.5.4.3}$$

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^3\left[\frac{2^2a_0^2}{3^2Z^2} - \frac{2^3a_0^2}{3^3Z^2}\right] \tag{22.5.4.4}$$

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^3\left[\frac{(3)2^2a_0^2 - 2^3a_0^2}{3^3Z^2}\right] = \frac{8Z}{\sqrt{2}27a_0} \tag{22.5.4.5}$$

$$Now, \tag{22.5.4.6}$$

$$E_n = -\frac{Z^2e^2}{n^2 2a_0}, E_{1s} = -\frac{Z^2e^2}{2a_0}, E_{2s} = -\frac{Z^2e^2}{8a_0}, E_{2s} - E_{1s} = \frac{3Z^2e^2}{8a_0} \tag{22.5.4.7}$$

$$So, \tag{22.5.4.8}$$

$$T_{mn} = \frac{\left(\frac{8Z}{\sqrt{2}27a_0}\right)^2}{\left(\frac{3Z^2}{8a_0}\right)} = \frac{2^6Z^2 2^6a_0^2}{(2)3^8a_0^2Z^4} = \frac{2^{11}}{3^8Z^2} = 0.312(\text{ for Z} = 1) \tag{22.5.4.9}$$

b. $\varphi_m(r) = \varphi_{1s} = 2\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}} e^{\frac{-Zr}{a_0}} Y_{00}$

The orthogonality of the spherical harmonics results in only s-states having non-zero values for A_{nm}. We can then drop the Y_{00} (integrating this term will only result in unity) in determining the value of $A_{1s,2s}$.

$$\psi_n(r) = \psi_{2s} = \frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(1-\frac{Zr}{2a_0}\right) e^{\frac{-Zr}{2a_0}} \tag{22.5.4.10}$$

Remember for $\varphi_{1s}Z = 1$ and or $\psi_{2s}Z = 2$ (22.5.4.11)

$$A_{nm} = \int 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{\frac{-Zr}{a_0}} \frac{1}{\sqrt{2}}\left(\frac{Z+1}{a_0}\right)^{\frac{3}{2}}\left(1-\frac{(Z+1)r}{2a_0}\right) e^{\frac{-(Z+1)r}{2a_0}} r^2 dr \tag{22.5.4.12}$$

$$A_{nm} = \frac{2}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{Z+1}{a_0}\right)^{\frac{3}{2}}\int e^{\frac{-(3Z+1)r}{2a_0}}\left(1-\frac{(Z+1)}{2a_0}\right) r^2 dr \tag{22.5.4.13}$$

$$A_{nm} = \frac{2}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{Z+1}{a_0}\right)^{\frac{3}{2}}\left[\int r^2 e^{\frac{-(3Z+1)}{2a_0}} dr - \int \frac{(Z+1)r^3}{2a_0} e^{\frac{-(3Z+1)r}{2a_0}} dr\right] \tag{22.5.4.14}$$

Evaluating these integrals using integral equation 4 we obtain:

$$A_{nm} = \frac{2}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left[\frac{2}{\left(\frac{3Z+1}{2a_0}\right)^3} - \left(\frac{Z+1}{2a_0}\right)\frac{(3)(2)}{\left(\frac{3Z+1}{2a_0}\right)^4}\right] \tag{22.5.4.15}$$

$$A_{nm} = \frac{2}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{Z+1}{a_0}\right)^{\frac{3}{2}}\left[\frac{2^4 a_0^3}{(3Z+1)^3} - (Z+1)\frac{(3)2^4 a_0^3}{(3Z+1)^4}\right] \tag{22.5.4.16}$$

$$A_{nm} = \frac{2}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{Z+1}{a_0}\right)^{\frac{3}{2}}\left[\frac{-2^5 a_0^3}{(3Z+1)^4}\right] \tag{22.5.4.17}$$

$$A_{nm} = -2\frac{[2^3 Z(Z+1)]^{\frac{3}{2}}}{(3Z+1)^4} \tag{22.5.4.18}$$

The transition probability is the square of this amplitude:

$$T_{nm} = \left(-2\frac{[2^3 Z(Z+1)]^{\frac{3}{2}}}{(3Z+1)^4}\right)^2 = \frac{2^{11} Z^3 (Z+1)^3}{(3Z+1)^8} = 0.25 \text{ (for Z} = 1).$$

The difference in these two results (parts a. and b.) will become negligible at large values of Z when the perturbation becomes less significant as in the case of Z = 1.

Q2

$\vec{\varepsilon}$ is along Z (lab fixed), and $\vec{\mu}$ is along z (the C-I module fixed bond). The angle between Z and z is β:

$$\vec{\varepsilon}\dot{\vec{\mu}} = \varepsilon\mu Cos\beta = \varepsilon\mu D_{00}^{1*}(\alpha\beta\gamma)$$

So,

$$I = \langle D^{J'}_{M'K'} | \vec{\varepsilon}\vec{\mu} | D^{J}_{MK} \rangle = \int D^{J'}_{M'K'} \vec{\varepsilon}\vec{\mu} D^{J}_{MK} Sin\beta d\beta d\gamma d\alpha \tag{22.5.4.19}$$

$$= \varepsilon\mu \int D^{J'}_{M'K'} D^{1*}_{00} D^{J}_{MK} Sin\beta d\beta d\gamma d\alpha. \tag{22.5.4.20}$$

Now use: (22.5.4.21)

$$D^{J'*}_{M'n'} D^{1*}_{00} = \sum_{jmn} \langle J'M'10|jm\rangle^* D^{j*}_{mn} \langle jn|J'K'10\rangle^*, \tag{22.5.4.22}$$

to obtain: (22.5.4.23)

$$I = \varepsilon\mu \sum_{jmn} \langle J'M'10|jm\rangle * \langle jn|J'K'10\rangle * \int D^{j*}_{mm} D^{J}_{MK} Sin\beta d\beta d\gamma d\alpha. \tag{22.5.4.24}$$

Now use: (22.5.4.25)

$$\int D^{j*}_{mm} D^{J}_{MK} Sin\beta d\beta d\gamma d\alpha = \frac{8\pi^2}{2J+1} \delta_{Jj} \delta_{Mm} \delta_{Kn}, \tag{22.5.4.26}$$

to obtain: (22.5.4.27)

$$I = \varepsilon\mu \frac{8\pi^2}{2J+1} \sum_{jmn} \langle J'M'10|jm\rangle * \langle jn|J'K'10\rangle * \delta_{Jj} \delta_{Mm} \delta_{Kn} \tag{22.5.4.28}$$

$$= \varepsilon\mu \frac{8\pi^2}{2J+1} \langle J'M'10|JM\rangle \langle JK|J'K'10\rangle. \tag{22.5.4.29}$$

We use: (22.5.4.30)

$$\langle JK|J'K'10\rangle = \sqrt{2J+1}(-i)^{J'-1+K) } \begin{pmatrix} J' & 1 & J \\ K' & 0 & K \end{pmatrix} \tag{22.5.4.31}$$

and, (22.5.4.32)

$$\langle J'M'10|JM\rangle = \sqrt{2J+1}(-i)^{(J'-1+M)} \begin{pmatrix} J' & 1 & J \\ M' & 0 & M \end{pmatrix} \tag{22.5.4.33}$$

to give: (22.5.4.34)

$$I = \varepsilon\mu \frac{8\pi^2}{2J+1} \sqrt{2J+1}(-i)^{(J'-1+M)} \begin{pmatrix} J' & 1 & J \\ M' & 0 & M \end{pmatrix} \sqrt{2J+1}(-i)^{(J'-1+K)} \begin{pmatrix} J' & 1 & J \\ K' & 0 & K \end{pmatrix} \tag{22.5.4.35}$$

$$= \varepsilon\mu 8\pi^2 (-i)^{(J'-1+M+J'-1+K)} \begin{pmatrix} J' & 1 & J \\ M' & 0 & M \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ K' & 0 & K \end{pmatrix} \tag{22.5.4.36}$$

$$= \varepsilon\mu 8\pi^2 (-i)^{(M+K)} \begin{pmatrix} J' & 1 & J \\ M' & 0 & M \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ K' & 0 & K \end{pmatrix} \tag{22.5.4.37}$$

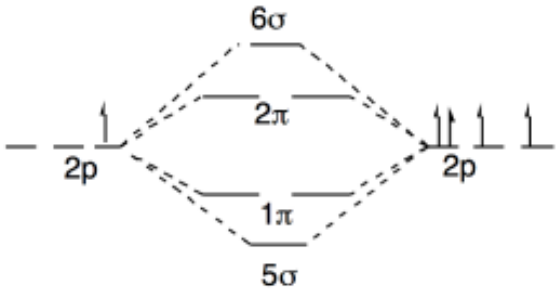
The 3-J symbols vanish unless: K' + 0 = K and M' + 0 = M.
So,

$$I = \varepsilon\mu 8\pi^2 (-i)^{(M+K)} \begin{pmatrix} J' & 1 & J \\ M & 0 & M \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ K & 0 & K \end{pmatrix} \delta_{M'M} \delta_{K'K}$$

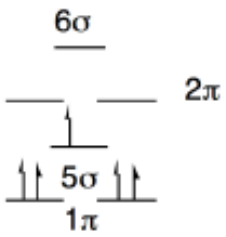
b. $\begin{pmatrix} J' & 1 & J \\ M & 0 & M \end{pmatrix}$ and $\begin{pmatrix} J' & 1 & J \\ K & 0 & K \end{pmatrix}$ vanish unless J' = J + 1, J, J - 1.$\therefore \Delta J = \pm 1, 0$
The K quantum number can not change because the dipole moment lies along the molecule's C_3 axis and the light's electric field thus can exert no torque that twists the molecule about this axis. As a result, the light can not induce transitions that excite the molecule's spinning motion about this axis.

Q3

a. B atom: $as^2 2s^2 2p^1$, ^2P ground state L = 1, S = $\frac{1}{2}$, gives degeneracy ((2L + 1)(2S + 1)) of 6.
O atom: $1s^2 2s^2 2p^4$, ^2P ground state L = 1, S = 1, gives a degeneracy ((2L + 1)(2S + 1)) of 9.
The total number of states formed is then (6)(0) = 54.
b. We need only consider the p orbitals to find the low lying molecular states:



Which, in reality look like this:



This is the correct ordering to give a $^2\sum^+$ ground state. The only low-lying electron configurations are $1\pi^3 5\sigma^2$ or $1\pi^4 5\sigma^1$. These lead to $^2\Pi$ and $^2\backslash\mathrm{Sum}^+$ states, respectively.

c. The bond orders in both states are $2\frac{1}{2}$.

d. The $^2\sum$ is + and g/u cannot be specified since this is a heteronuclear molecule.

e. Only one excited state, the $^2\Pi$, is spin-allowed to radiate to the $^2\sum^+$. Consider symmetries of transitio moment operators that arise in the E1, E2 and M1 contributions to the transition rate

Electric dipole allowed: $z \rightarrow \sum^+, x, y \rightarrow \Pi, \therefore$ the $^2\Pi \rightarrow ^2\sum^+$ is electric dipole allowed via a perpendicular band.

Magnetic dipole allowed: $R_z \rightarrow \sum^-, R_{x,y} \rightarrow \Pi, \therefore$ the $^{\Sigma}/rightarrow^2\sum^+$ is magnetic dipole allowed.

Electric quadrupole allowed: $x^2+y^2, z^2 \rightarrow \sum^+, xy, yz \rightarrow \Pi, x^2-y^2, xy \rightarrow \Delta \therefore$ the $^2\Pi \rightarrow ^2\sum^+$ is electric quadrupole allowed as well.

f. Since ionization will remove a bonding electron, the BO^+ bond is weaker than the BO bond.

g. The ground state BO^+ is $^1\sum^+$ corresponding to a $^1\pi^4$ electron configuration. An electron configuration of $1\pi^3 5\sigma^1$ leads to a $^3\Pi$ and a $^1\Pi$ state. The ^3Pi will be lower in energy. A $1\pi^2 5\sigma^2$ confirmation will lead to higher lying states of $^3\sum^-, ^1\Delta,$ and $^1\sum^+$.

h. There should be 3 bands corresponding to formation of BO^+ in the $^1\sum^+, ^3\Pi,$ and $^{\Pi}$ states. Since each of these involves removing a bonding electron, the Franck-Conden integrals will be appreciable for several vibrational levels, and thus a vibrational progression should be observed.

Q4

a. The bending (π) vibration is degenerate.

b.

$$H--C \equiv N \tag{22.5.4.38}$$
$$\Uparrow \tag{22.5.4.39}$$
$$\text{bending fundamental} \tag{22.5.4.40}$$

c.

$$H--C \equiv N \tag{22.5.4.41}$$
$$\Uparrow \tag{22.5.4.42}$$
$$\text{stretching fundamental} \tag{22.5.4.43}$$

d. CH stretch (ν_3 in figure) is σ CN stretch is σ and HCN (ν_2 in figure) bend is π.

e. Under z (σ)light the CN stretch and the CH stretch can be exited, since $\psi_0 = \sigma, \psi_1 = \sigma$ and $z = \sigma$ provides coupling.

f. Under x,y (π) light the HCN bend can be excited, since $\psi_0 = \sigma, \psi_1 = \pi$ and x,y = π provides coupling.

g. The bending vibration is active under (x,y) perpendicular polarized light. $\Delta J = 0, \pm 1$ are the selection rules for $\perp$ transitions. The CH stretching vibration is active under (z) $\parallel$ polarized light. $\Delta J = \pm 1$ are the selection rules for $\parallel$ transitions.