

HW # 10

$$1. \quad \frac{1}{R^2} = \frac{1}{(R-R_e+R_e)^2} = \frac{1}{R_e^2 \left[1 + \frac{R-R_e}{R_e}\right]^2}$$

$$\approx \frac{1}{R_e^2} - \frac{2(R-R_e)}{R_e^3} = \frac{1}{R_e^2} - \frac{2x}{R_e^3}$$

$$\text{So } \frac{J(J+1)}{2\mu R^2} \approx \frac{J(J+1)}{2\mu} \left[\frac{1}{R_e^2} - \frac{2x}{R_e^3} \right]$$

The wavefunctions for the vibrational-rotational problem are of the form $|\psi_J \psi_n\rangle$ where J and n are the rotational and vibrational quantum numbers, respectively.

Neither the above term nor the other perturbation, δx^3 , change the rotational quantum #, so actually we only need to consider explicitly the vibrational degree of freedom.

The cross term is then of the form.

$$\delta \frac{J(J+1)}{2\mu R_e^3} \sum_{j \neq i} \frac{\langle i | x | j \rangle \langle j | x^3 | i \rangle}{E_i - E_j}$$

Note, here I have used the fact that the $\frac{J(J+1)}{2\mu R_e^2}$ term in the Taylor

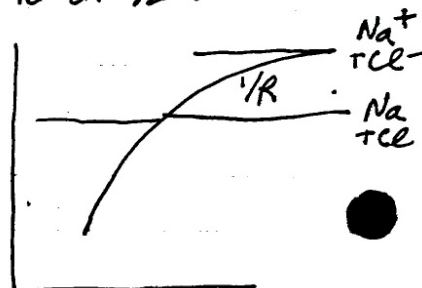
series cannot couple different vibrational levels.

To go further you could consider the case of $i=0, i=1, i=2$, to see what pattern appears.

Note: $i=0$ will couple to $j=1$
 $i=1$ will couple to $j=0, 2$
 $i=2$ will couple to $j=1, 3$

When the matrix elements are evaluated using ladder operators, you'll see that they are proportional to $i + \frac{1}{2}$.

2. IP Na = 5.1 eV
 EA Cl = 3.6 eV
 $\Delta E = 5.1 - 3.6 = 1.5 \text{ eV}$
 $= .055 \text{ au}$



$E_{\text{ion}} = .055 - 1/R$
 $E_{\text{ov}} \approx 0$

So the crossing is when $1/R = .055$
 i.e. 18.2 au or $\approx 9 \text{ \AA}$

3. $\sigma_g \pi_u^2$

$\pi_u^2 \rightarrow {}^1\Sigma_g, {}^3\Sigma_g, {}^1\Delta_g$

Now couple in the σ_g electron

${}^1\Sigma_g \rightarrow {}^2\Sigma_g, {}^3\Sigma_g \rightarrow {}^2\Sigma_g, {}^4\Sigma_g$
 ${}^1\Delta_g \rightarrow {}^2\Delta_g$