## Chem 2430: HW #10

1. If there are two perturbations to  $H^{\circ}$ , i.e.,  $H = H^{\circ} + H' + H''$  then there are two possible contributions to the first-order energy correction for state  $i \langle i | H' | i \rangle$  and  $\langle i | H'' | i \rangle$ .

The second order correct the energy of state *i* is then  $\sum_{j \neq i} \frac{\langle i | H' + H'' | j \rangle|^2}{E_i^\circ - E_j^\circ}$ 

Here and above  $|i\rangle$  and  $|j\rangle$  refer to eigenfunctions of  $H^{\circ}$ .

Assuming the integrals are real, there is the possibility of  $\langle i | H'' | j \rangle^2$ ,  $\langle i | H'' | j \rangle^2$  and  $\langle i | H' | j \rangle \langle j | H'' | i \rangle$  terms in the numerator.

For the vibrational-rotational Hamiltonian of a diatomic molecule, let H' denote the  $\gamma (r - r_e)^3$  correction to the harmonic potential, and H" denote the lowest order correction from expansion of  $\frac{1}{R^2}$  in the rotational part of the operator.

Show that the cross term in the second-order expression for the energy contributes to a correction involving the factor  $\left(v + \frac{1}{2}\right)J(J+1)$ .

2. Estimate the distance at which the potential energy curves corresponding to the Na + Cl and  $Na^+ + Cl^-$  diabatic states of sodium chloride cross.

3. How many electronic states are derived from the  $\sigma_g(\pi_u)^2$  configuration and what are the terms symbols? Which of these states can be described by using a single Slater determinant wave function?