

Chem 2430: HW #10

1. If there are two perturbations to H° , 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° .

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 $1/R^2$ 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 $\left(v + \frac{1}{2}\right)J(J+1)$.

