Chemistry 441 Quantum Chemistry Problems on the Time Dependent SE revised 3/22/02

I. Selection rules for IR transitions

A. IR transitions (Harmonic oscillator wave functions):

Often it is possible to see that a particular integral $\int \psi_m s \psi_n ds = 0$ on the basis of symmetry.

1. For example, for $m = 0$ and $n = 2$, sketch the wave functions, multiply ψ_o first by s, next by ψ_2 and then plot the result. Use this plot to show that the integral over all values of s must be zero.

2. Plot $\psi_m s \psi_n ds$ for $m = 3$, $n = 5$ over a reasonable range of s values, and then make a statement about total area under the curve based upon the symmetry of your plot.

3. Sometimes the symmetry argument will not work. Plot $\psi_m s \psi_n ds$ for $m = 2$, $n = 5$ and then use numerical integration to show that the integral over a large range of s values is close to 0.

4. There is an important relationship between successive Hermite polynomials which is worked out on p. 79 of Pauling and Wilson:

$$H_{n+1}(s) - 2sH_n(s) + 2nH_{n-1}(s) = 0.$$

This formula allows one to substitute for sH_n in the integral $\int \psi_m s \psi_n ds$ and then use the orthogonality of ψ_m and ψ_m to derive a general rule for state transitions in a harmonic oscillator. Try doing this to show that $\int \psi_m s \psi_n ds = 0$ unless $m = n+1$ or $m = n-1$. This result is known as a selection rule.

5. Use the formula of problem 4 to show that in general,

$$s^k H_n = a_{n+k} H_{n+k} + a_{n+k-2} H_{n+k-2} + \ldots + a_{n-k+2} H_{n-k+2} + a_{n-k} H_{n-k}$$

(if the subscript is < 0, then the a coefficient is 0)

6. Try finding a "selection rule" for the integrals: $\int \psi_m s^2 \psi_n ds$ and $\int \psi_m s^3 \psi_n ds$ (Use the formula given in problem 5)

7. Here is the relevance of the previous problem: Consider the perturbed HO, with $V(x)$ given by a Morse-like potential: $V(x) = \frac{1}{2}kx^2 + a_3 x^3 + \ldots$ where the last term may be considered as a perturbing potential:

$$v(x) = a_3 x^3 + \ldots = a' s^3 + \ldots$$

This perturbing potential introduces modifications $\psi_m^{(1)}$ into the wavefunctions given by equation (39) from the perturbation theory section: $\psi_m^{(1)} = \sum_n \left[\frac{<\psi_n^{o*} v \psi_m^o>}{E_m^o - E_n^o} \right] \psi_n^o = a' \sum_n \left[\frac{<\psi_n^{o*} s^3 \psi_m^o>}{E_m^o - E_n^o} \right] \psi_n^o$ for $m \neq n$

If a summation term is not 0 for any particular n, then this formula "mixes" ψ_n^o into ψ_m^o.

a. Show that the $\psi_m^{(1)}$ correction "mixes" states $m+3$, $m+1$, $m-1$, and $m-3$ into ψ_m^o

b. Given this result, show that IR transitions with $n = m + 2$ or $m - 2$ are now "allowed". (If the a' term of the perturbation a's^3 is quite small, the transition probabilities are still very low).

B. Electronic transitions:

8. Use symmetry arguments to show that $\int \psi_{1s} x \psi_{2s} d\tau = 0$ and that $\int \psi_{1s} x \psi_{2p_x} d\tau$ will not be zero. (An extension of this leads to the selection rule $\Delta l = \pm 1$ for electronic transitions.)