Physics 880A20 Winter Quarter 2003
Dr. Herbst

<u>HOMEWORK ASSIGNMENT # 3</u>

DUE: Friday, 7 March

1. Consider the molecule dimethyl ether (CH_3OCH_3), which possesses two internally rotating methyl tops, each with a potential given by

$$V = \frac{V_3}{2}(1 - \cos 3\alpha).$$

a) Determine the eigenvalues and eigenfunctions for the internal rotation in the limit of free rotation (i.e. each V_3=0). You need not define the rotational constant F.
b) Write down a suitable basis set for the actual internal rotation problem based on free rotor functions in terms of σ_1=1,0,−1 and σ_2 = 1,0,−1. Derive the matrices that, upon diagonalization, solve the problem.
c) What would you expect the degeneracy structure to be for each torsional eigenvalue? Use reasonable labels similar to the *A*(degeneracy =1) and *E*(degeneracy=2) labels for the single methyl case.
d) Can you guess how the degeneracy pattern would change if there were a coupling term between the two rotors; e.g.

$$V' = V_{12}\cos 3\alpha_1 \cos 3\alpha_2$$

2. Show that the selection rule for transitions between torsional substates in the single methyl rotor problem is *A*-*A* and *E*-*E* only. Hint: consider how the dipole moment changes with torsional angle α as the methyl rotates.

3. Derive the formula used in class for the probability of a transition from a lower level to an upper level

$$P_{u\leftarrow l} = |c_u(t)|^2$$

$$\text{where } c_u(t) = \frac{-i}{\hbar}\int_0^t \exp(-iE_{ul}t'/\hbar)H'_{ul}\,dt'$$

via time-dependent perturbation theory.