PHY 556 Spring 2007 Homework #3 due Monday Feb. 26, 2007

Character table for group T_d

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	+1	-	$x^2+y^2+z^2$	xyz
A_2	+1	+1	+1	-1	-1	-	-	-
E	+2	-1	+2	0	0	-	$(2z^2-x^2-y^2, x^2-y^2)$	-
T_1	+3	0	-1	+1	-1	(R_x, R_y, R_z)	-	$[x(z^2-y^2), y(z^2-x^2), z(x^2-y^2)]$
T_2	+3	0	-1	-1	+1	(x, y, z)	(xy, xz, yz)	(x^3, y^3, z^3) $[x(z^2+y^2), y(z^2+x^2), z(x^2+y^2)]$

1. Consider ordinary 3d Cartesian space, containing the vectors $\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$. Write 3 x 3 matrices for a representative case of a C_3, C_2, S_4, and σ_d operation. Use this information to confirm that this space transforms according to the representation T_2 of the group T_d.

2. Consider the space spanned by the four functions $\psi_s(r-r_i)$, $i=1,\ldots 4$, of *s*-functions on each of 4 atoms on the corners of a regular tetrahedron. These functions are the basis for a (reducible) representation of T_d (called the "permutation representation.") According to what irreducible representations does this space transform? Find new basis functions which transform according to these irreducible representations.

3. The atom displacements of a tetrahedral molecule (e.g. Na_4) are a 12-dimensional space which is the product space of the permutation space and the Cartesian 3-vector space. Find the irreducible representations that correspond to the vibrational eigenstates of the Na_4 molecule. Which representations remain after you dismiss the 3 uniform translations and the 3 uniform rotations? After doing this, symmetry alone can reduce the dynamical matrix to diagonal form, independent of spring constants. Sketch some representative vibrational eigenvectors and indicate the corresponding representation.

4. Another 12-dimensional space is spanned by *p*-functions on each atom. This space is isomorphic to the space of displacements, and generates the same 12-dimensional reducible representation of T_d. In one-electron approximation, Na_4 can be approximated as having 4 valence electrons whose single-particle wavefunctions are built from atomic-like *3s* and *3p* orbitals. These 4 electrons go into molecular orbitals with Hund's rules being not very important. The lowest energy orbital is singly degenerate (not counting spin, of course) and the next orbital is triply degenerate. What can you reasonably say about the nature of these wavefunctions or molecular orbitals?