University of Regensburg Summer Term 2014

Applications of Group Theory

PD Dr. Andrea Donarini

Lectures 9.2.01, Mondays, 14:15

Exercises H34, Wednesdays, 14:00

Sheet 7

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1. Benzene molecule

The Hueckel model of the benzene molecule only considers the p_z orbitals associated to its carbon atoms. In second quantization this Hamiltonian reads:

$$H = \sum_{i=1\ldots6,\,\sigma} \varepsilon c^\dagger_{i\sigma} c_{i\sigma} + t c^\dagger_{i+1\sigma} c_{i\sigma} + t^* c^\dagger_{i\sigma} c_{i+1\sigma}$$

where $c^\dagger_{i\sigma}$ creates and electron of spin σ in a p_z orbital centered around the position $\vec{R}_i$ with

$$\vec{R}_i = a_0 \begin{pmatrix} \cos\left(\frac{2\pi}{6}(i-1)\right) \\ \sin\left(\frac{2\pi}{6}(i-1)\right) \\ 0 \end{pmatrix},$$

and $a_0 = 1.42$Å, ε represents the on-site energy, t the hopping amplitudes between neighboring sites.

1. Identify the symmetry elements of the Hamiltonian and the associated point groups in the case that t is real and also if t has an imaginary component. Neglect in both cases the contribution of the spin.
2. Construct the characters of the representation associated to the single particle Hilbert space for the benzene Hamiltonian. Reduce the six dimensional representation associated to each of the two spin sectors.
3. Construct the basis states that transform like the irreducible representation of the point groups identified in points 1) and 2).
4. Find the eigenvalues and the eigenvectors of H and the associated degeneracies.

2. Hypothetical CH_4 molecule

Consider the hypothetical molecule CH_4 where the four H atoms are at the corner of a square $(\pm a, 0, 0)$ and $(0, \pm a, 0)$ while the C atom is at $(0, 0, z)$, where $z < a$. What are the symmetry elements?

1. Identify the proper character table.
2. Using the basis functions in the character table, write down a set of (2×2) matrices which provide a representatzion for the two-dimensional irreducible representation of this group.

3. Find the four linear combinations of the four H orbitals (assume identical s-functions at each H site) that transform as the irreducible representations of the group. What are their symmetry types?

4. What are the basis functions that generate the irreducible representations?

5. Check that xz forms a proper basis function for the two-dimensional representation of this point group and find its partner.

6. What are the irreducible representations and partners of the following basis functions in the point group (remenber that the four hydrogen lie in the xy plane): i) xyz, ii) x^2y, iii) x^2z. iv) $x + \mathrm{i}y$.

7. What additional symmetry operations result in the limit that all H atoms are coplanar with atom C? What is now the appropriate group and character table? Draw the corresponding stereogram.

Frohes Schaffen!