J07Q.3 - Triangular Molecule

Problem

If a Na atom is represented by a singly occupied $3s$ orbital, the molecular orbitals of the triangular Na_3 *molecule* are given by the eigenstates $\psi_\nu(i) = \langle i|\psi_\nu\rangle$ of the one-electron Hamiltonian

$$h(\vec{t}) = \sum_{i=1}^{3} \epsilon_0 |i\rangle\langle i| - \sum_{i\neq j} t_{ij}|i\rangle\langle j|, \quad t_{ij} = t_{ji}, \quad \langle i|j\rangle = \delta_{ij}$$

with all t_{ij} real and positive, where $|i\rangle, i = 1, 2, 3$ is the $3s$ orbital on atom i. $\vec{t} = (t_{12}, t_{23}, t_{31})$ is a coordinate in a three-dimensional parameter space characterizing the molecular shape. For general values of $\vec{t}, h_{ij} = \langle i|h(\vec{t})|j\rangle$ is a generic 3×3 matrix, but when two or more of the t_{ij} are equal, symmetries of the eigenvectors make it easy to diagonalize (it is also easily diagonalized when any t_{ij} vanish).

a) FInd the three molecular orbitals $\psi_\nu(i)$ when $\vec{t} = (t, t, \lambda t)$. Classify them by symmetry, and sketch the energy levels $\epsilon_\nu(\lambda)$ as a function of $\lambda > 0$. How are they occupied in the Na_3 molecule ground state? What is special when $\lambda = 1$ (when all Na atoms are equivalent)?

The Born-Oppenheimer (BO) approximation determines molecular shape by minimizing the electronic energy as a function of fixed nuclear coordinates of the atoms. Your results in a) should imply that the BO energy has (at least) *three* distinct minima. Label them A,B and C. Tunneling of the molecular shape degrees of freedom between these minima restores the symmetry of the molecule, in which all three Na atoms are equivalent.

b) Model the molecular orbitals of A, B and C by those of $(t, 0, 0), (0, t, 0)$ and $(0, 0, t)$. The $\psi_\nu(i)$ can always be chosne real; if they change adiabatically as the shape evolves along the periodic path $A \to B \to C \to A, \psi_\nu(i) \to \eta_\nu\psi_\nu(i), \eta_\nu = \pm 1$. Determine η_ν for each orbital. (You may assume that the path from A to B passes through the configuration $(t/2, t/2, 0)$, and use this to fix the sign of $\psi_\nu(i)$ at B relative to that at A, *etc.*; only the *sign* ($\pm$ or 0) of $\psi_\nu(i)$ is important in this calculation.)

(Your results should imply that the BO ground state $|\psi_0\rangle$ of the Na_3 molecule evolves to $-|\psi_0\rangle$ along this path: this calculation was historically the first time that a "Berry Phase" was encountered.)