Spring 2002 – Entrance Examination: Condensed Matter

Solve at least one of the following problems. Write out solutions clearly and concisely. State each approximation used. Diagrams welcome. Number page, problem, and question clearly. Do not write your name on the problem sheet, but use extra envelope.

Problem 1: Two coupled rotors

Consider two planar rotors, characterized by a fixed radius r, and angle ϕ_1 and ϕ_2, with Hamiltonian

$$h_i = \left(\frac{i\hbar}{r} \frac{\partial}{\partial \phi_i} \right)^2 \qquad i = 1, 2$$

1) Describe the energy spectrum and the eigenfunctions of each rotor, in the lack of interactions.

2) Consider next a coupling between the two rotors, of the form

$$V = -J \cos(\phi_1 - \phi_2) \qquad J > 0 .$$

Taking now $H = h_1 + h_2 + V$, discuss the effect of the coupling on the low-energy part of the spectrum in the two opposite limits a) very small J; b) very large J.

Problem 2: Vibrational-rotational spectrum of heteropolar molecules

The infrared spectrum of a heteropolar diatomic molecule is sketched in the figure as a function of the angular frequency ω.
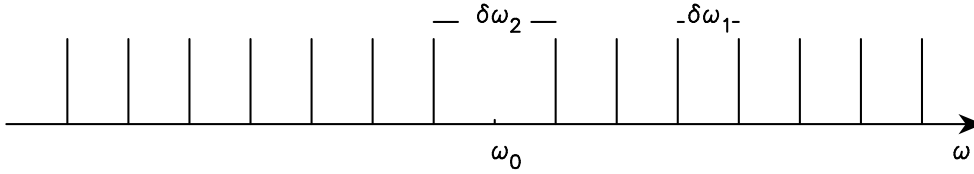
This spectrum can be interpreted by considering the vibrational-rotational motion of the two nuclei about the center of mass (The electrons are assumed to be in their ground state). Indicating with $\mathbf{r}$ the vector joining the two nuclei, one can write an approximate Hamiltonian for the relative motion:

$$H = -\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) + \frac{L^2}{2\mu r_0^2} + \frac{1}{2}\mu\omega_0(r - r_0)^2 - V_0 \tag{1}$$

Here $r = |\mathbf{r}|$ is the distance between the nuclei, μ their reduced mass, r_0 their equilibrium distance, L is the angular momentum operator acting on the θ and ϕ coordinates of $\mathbf{r}$, ω_0 is the angular frequency indicated in the figure, and V_0 is the depth of the potential well.

a) Write the exact Hamiltonian for the relative motion of the two nuclei with interaction potential energy $V(r)$ and describe the approximations leading to Eq.1.

b) Solve the eigenvalue problem for the Hamiltonian in Eq.1. Show that the solutions depend on three integer indices ν, l, m. Write the eigenvalues $E_{\nu,l,m}$ and the eigenvectors $\psi_{\nu,l,m}(\mathbf{r})$.

Let's consider the transitions between energy levels induced by electromagnetic infrared radiation. The coupling Hamiltonian is $\Delta H = -D(r)E\cos\theta$. Here $D(r)$ is the magnitude of the dipole moment of the molecule as a function of the distance between the nuclei, E is the (time dependent) electric field of the electromagnetic radiation assumed parallel to the z direction and θ is the angle between the molecular axis and the electric field.

c) Let's take $D(r) = d_0 + d_1(r - r_0)$, linear in $r - r_0$ with constant d_0 (equilibrium dipole moment) and d_1. Find the selection rules for the vibrational-rotational transitions by examining the matrix elements $\langle\psi_{\nu,l,m}|\Delta H|\psi_{\nu',l',m'}\rangle$.

d) Explain the spectrum shown in the figure and express $\delta\omega_1$ and $\delta\omega_2$ in terms of the Hamiltonian parameters.

e) Explain the missing line at $\omega = \omega_0$.

Hint: The following formula might be useful:

$$\cos\theta\, Y_l^m(\theta, \phi) = \sqrt{\frac{l^2 - m^2}{4l^2 - 1}}Y_{l-1}^m(\theta, \phi) + \sqrt{\frac{(l+1)^2 - m^2}{4(l+1)^2 - 1}}Y_{l+1}^m(\theta, \phi)$$

Problem 3: The benzene molecule

The benzene molecule C_6H_6 can be thought of as a ring of 6 sites, on each of which a C atom is placed. Each C atom shares one electron in delocalized p_z (out-of plane) orbitals, which can be roughly described with the tight-binding model

$$H = -t \sum_{i=1}^{6} \sum_{\sigma=\uparrow,\downarrow} (c_{i,\sigma}^{\dagger} c_{i+1,\sigma} + H.c.) , \qquad (2)$$

where $c_{i,\sigma}^{\dagger}$ creates an electron in the p_z orbital at the carbon site $i = 1 \ldots 6$, and $c_{7,\sigma}$ has to be understood to coincide with $c_{1,\sigma}$. The energy of excitation to the lowest excited state is observed, experimentally, at 2.0 eV.

1. Draw a single-particle energy diagram for these delocalized electronic states.

2. Fill the 6 lowest spin-orbital states with the electrons provided by the C atoms: compute the ground-state total energy.

3. Draw the lowest excited 6-electron state, by promoting one electron to the lowest empty state. Compute the energy of this first excited state and its excitation energy referred to the ground state. By comparison to the experimental data, determine t.

4. Determine the excitation energies referred to the ground state of the 2nd and 3rd excited states.