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October 2008 - Entrance Examination: Condensed Matter

Solve 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: Benzene diamagnetism

[Preamble. Graphene – a single graphite sheet made of carbon atoms arranged in a 2-dimensional honeycomb lattice – is currently a hot subject. One notable property of graphite is its diamagnetism, namely an increase of energy in presence of a magnetic field, attributed to orbital currents in the special graphene lattice. The present problem is a cartoon inspired by the orbital diamagnetism of graphene, and to that, closely related, of benzene C_6H_6].

Consider an idealized hexagonal molecule made up of six identical atomic sites $i = 1, ..., 6$. Each site has a nondegenerate, orthonormal orbital $|i\rangle$ and a single electron. Electrons can hop from each site $|i\rangle$ to the two neighboring sites $|i-1\rangle$ and $|i+1\rangle$ with hopping energy $-t$, with $t > 0$. The Hamiltonian is $H_0 = -t \sum_i |i\rangle\langle i+1|$.

1. Calculate the electron levels e_n of this molecule, their degeneracy g_n, and their wavefunction expressed as a linear combination of the $|i\rangle$ orbitals. (Hint: treat as a "tight binding" linear chain with periodic boundary conditions)

2. Filling these levels with six electrons and Pauli's principle, calculate the total (non-interacting) electron energy $E_0 = \sum_n e_n g_n f_n$ where $f_n = 2$ for an occupied level, zero otherwise.

Add now a magnetic field B perpendicular to the hexagon, and vary its magnitude so that the molecule is threaded by a flux $\Phi = BA$ (A is the hexagon's area). Ignoring the Zeeman coupling to electron spin, the simplest way to include the field is to change nothing, but pick eigenfunctions of H_0 so that they no longer obey periodic boundary conditions, and must instead accommodate a phase shift $\exp[i2\pi(\Phi/\Phi_0)]$, where $\Phi_0 = hc/e$ is the flux quantum.

3. Calculate the new levels, and discuss the new total energy for arbitrary flux Φ/Φ_0.

4. For small flux, describe the total energy dependence upon Φ/Φ_0, and discuss whether and why that may describe diamagnetism or not.

Problem 2: Spin-orbit coupling in a cylindrically symmetric potential

Let us consider a spin 1/2 electron in a cylindrically symmetric potential $V(\rho)$. We assume that the spin of the electron is coupled to the electric field through a spin-orbit term so that the Hamiltonian in cylindrical coordinates (ρ, ϕ, z) is given by:

$$H = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial z^2}\right] + \frac{1}{2m^2c^2}\mathbf{S}\cdot\Big(\nabla V(\rho)\times\mathbf{p}\Big) + V(\rho), \qquad (1)$$

where $\mathbf{p} = -i\hbar\nabla$ is the momentum of the electron that in cylindrical coordinates reads $\mathbf{p} = -i\hbar\left(\frac{\partial}{\partial\rho}, \frac{1}{\rho}\frac{\partial}{\partial\phi}, \frac{\partial}{\partial z}\right)$ and $\mathbf{S} = \frac{\hbar}{2}\boldsymbol{\sigma}$ is the spin angular momentum written using Pauli matrices.

1. Express the spin-orbit term in cylindrical coordinates using the fact that the potential depends only on ρ.

2. Show that this Hamiltonian commutes with the z component of the total angular momentum $J_z = L_z + S_z$, where L_z is the z component of the orbital angular momentum $\mathbf{L} = \mathbf{r}\times\mathbf{p}$.

3. Show that the eigenstates of the Hamiltonian have the form

$$\phi_{n,m_j}(\rho,\phi,z) = f_{n,m_j}(\rho,z)\left(Ae^{im\phi}\chi_1 + Be^{i(m+1)\phi}\chi_{-1}\right), \qquad (2)$$

   where $m_j = m + \frac{1}{2}$, χ_s is an eigenstate of σ_z and $s = \pm 1$ indicates the corresponding eigenvalue. A and B are two constants.

Problem 3: Roto-vibrational lines of a diatomic molecule

The roto-vobrational levels of a diatomic molecule in one of its electronic levels (say, the ground state) can be described by an effective interatomic potential that, including a centrifugal barrier, reads:

$$\begin{aligned} V_l(r) &= V_0(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} \\ &\approx V_0(r_0) + \frac{1}{2}V_0''(r_0)(r-r_0)^2 + \frac{\hbar^2 l(l+1)}{2\mu r_0^2}, \end{aligned}$$

where r_0 is the interatomic equilibrium distance defined by the relation $V_0'(r_0) = 0$, μ is the reduced mass, and the centrifugal potential has been approximated by a constant, so as to decouple the vibrational motion from the rotational one.

1. Discuss the accuracy of the approximation of the centrifugal barrier as a constant, in terms of the properties of the molecule.

2. Show that the roto-vibrational levels of the molecule can be described by the formula: $E_{\nu,l} = E_{00} + A\nu + Bl(l+1)$, and indicate how E_{00} can be calculated from first principles (*i.e.* by solving the Schrödinger equation for the system of interacting electrons and nuclei: no general treatise, here - just a few lines of explanation of the general concepts).

The experimental data for the molecules HF, HCl, and HBr can be described by the following values of the A and B constants (data are in cm^{-1} : $1\ \mathrm{cm}^{-1} = 1.24 \times 10^{-4}$eV; the atomic masses of F, Cl, and Br are 19, 35, and 80 amu, respectively)

	A	$2B$
HF	4003	41.1
HCl	2907	20.8
HBr	2575	16.7

3. Estimate the values of the equilibrium interatomic distances for the three given molecules and the amplitude of the nuclear zero-point motion. Can you give an estimate of the molecular dissociation energy?

4. Calculate the wavelength of the first purely rotational line ($E_{00} \mapsto E_{01}$) and of the first roto-vibrational one ($E_{00} \mapsto E_{11}$) for the three molecules. Which regions of the electromagnetic spectrum do they belong to? Discuss the possibility of observing the $E_{00} \mapsto E_{10}$ transition in an optical absorption experiment.

5. Calculate the A and B constants for the DCl molecule, where D (*deuterium*) is the hydrogen isotope with nuclear mass equal to 2 amu.

Useful constants

$\hbar = 1.0546 \times 10^{-34}$ m^2 Kg sec^{-1}

Electron mass:
$m_e = 9.1094 \times 10^{-31}$ Kg

amu:
amu $= 1.66054 \times 10^{-27}$ Kg
amu $= 1822.89\ m_e$

Bohr radius:
1 $a_0 = 0.52918$ Å

Energy:
1 Hartree $= 27.2114$ eV
1 eV $= 1.602 \times 10^{-19}$ Joules