International School for Advanced Studies
1999 Entrance Examination: Condensed Matter

Solve one of the problems below. Write out solution 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. Free electrons in a channel

Consider electron motion in two dimensions (x, y), free but confined by infinitely hard walls to take place within a narrow "channel" of width d. Precisely, the potential is $V(|x| < d/2, y) = 0$, $V(|x| > d/2, y) = \infty$.

1. Solve Schroedinger's equation for one-electron motion inside this channel. Determine the spectrum of eigenfunctions and eigenvalues as a function of the appropriate quantum numbers. Along y, assume a large but finite channel lenght $L >> d$, and periodic boundary conditions $\psi(x, y = -L/2) = \psi(x, y = L/2)$.

2. Repeat for antiperiodic boundary conditions, meaning $\psi(x, y = -L/2) = -\psi(x, y = L/2)$. Point out the differences, and their reason, particularly concerning the ground state.

3. Assume filling the channel with N noninteracting electrons (linear density $n = N/L$). As n increases, derive the form of the total electron energy E^{tot}, and describe the evolution of the Fermi energy E^F and of the Fermi "surface". In particular, determine the first few critical values of n where singularities appear, both in E^{tot} and in E^F, and discuss why they happen.

4. Add a small external magnetic field B, chosen so that its effect on the eigenfunctions is negligible, the only remaining effect being the Zeeman coupling to the electron spins. Including now the small field-induced splitting between spin up and spin down electron states, obtain a new expression for the total electron energy. Using this, show at least qualitatively what kind of singularities the Pauli magnetic susceptibility would develop at the critical densities, and discuss their meaning.

Problem 2: A two-electron system

A two-electron system is described by the Hamiltonian $H_0 = 2J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \frac{1}{4})$, with $J > 0$ (no spatial degrees of freedom, all spins in units of $\hbar$).

1. The system is prepared initially in the state $\alpha\,|+,-\rangle + \beta\,|-,+\rangle$, with $|\alpha|^2 + |\beta|^2 = 1$. What is the average value of S_{1z}? Which probability is assigned with the occurrence of each of the S_{1z} values? Which state would describe properties of electron 1 only?

2. A perturbation H_1 is added to H_0, that couples the singlet $|s\rangle$ with any triplet state $|t_\alpha\rangle$, $\alpha = 1, 2, 3$, such that $\langle s|\, H_1\, |t_\alpha\rangle = W$, where W is a complex number. All the other matrix elements of H_1 are zero. Find all eigenstates and eigenvalues of $H_0 + H_1$.

3. With H_1 still present, let it be assumed that the state of the two electrons at $t = 0$ is $|s\rangle$. What is the probability $P_\alpha(t)$ to find the two-spin system in $|t_\alpha\rangle$ at a later time t? At what times is this transition probability maximum?

   The two electrons are now enclosed in a cubic box of volume L^3. H_1 has been switched off, so that the Hamiltonian reads as $H_0 + V(\mathbf{r}_1) + V(\mathbf{r}_2)$, where V is the confining potential.

4. Write down the new ground state of the system, its energy and degeneracy.

Problem 3: A simple model for strongly correlated electrons in a solid

A single electron in a solid is assumed to occupy (or not occupy) the highest energy orbital of the localized atoms. The atom positions are represented by a cubic crystalline lattice. The strong electron-electron Coulomb repulsion may be parameterized in the following way: on each site there is an energy cost U to host a pair of electrons with opposite spins. No electronic kinetic energy is assumed in this simple model. Try to answer to the following questions:

1. Compute the free energy per site $F = -1/(\beta L)\log\left(\mathrm{Tr}e^{-\beta H}\right)$ (L being the total number of sites) as a function of the inverse temperature $\beta = 1/k_B T$ and the chemical potential μ (the Hamiltonian is $H = UD - \mu N$, where N is the total number of electrons and D the total number of doubly occupied sites).

2. Compute the average number of electrons per site $< n >$ at a given temperature. For increasing $< n >$, show that for $\beta \to \infty$ there is a jump in the chemical potential when $< n >= 1$. Compute the value of this jump and discuss the metalic or insulating properties of the model at $< n >= 1$.

3. Compute the entropy for $\beta \to \infty$. Is the third "law" of thermodynamics (zero entropy at zero temperature) verified for $< n >= 1$?

4. Assume now that electrons can hop from an atom to a neighboring one with matrix element $t << U$. Do you expect qualitative changes of the above properties ?

Problem 4: Vibrational modes of a semi-infinite linear chain

Let us consider a semi-infinite linear harmonic chain of atoms of mass M, with spacing a and nearest neighbour interaction with force constant β.

1. Find the equations of motion of the system and solve them. Describe the normal modes of the system, and discuss the existence of a solution localized mainly on the first few atoms.

2. Modify the mass of the first atom to M_0, find the condition for the existence of a localized mode and determine its frequency.

3. Modify the force constant between the first and the second atom to β_0, keeping all the masses equal to M. Find the condition for the existence of a localized mode, and determine its frequency.

4. Change both the mass of the first atom to M_0 and the force constant between the first and second atom to β_0. Show that a localized mode exists provided that $\frac{\beta_0}{\beta} > f(\frac{M_0}{M})$. Give an expression for $f(\frac{M_0}{M})$.

Problem 5: An "Ideal Gas" of Classical Particles

Consider a gas of classical particles on a lattice of N sites. Let $n_i = 0, 1, 2, \ldots$ be the number of particles on site $i = 1, \ldots, N$. The Hamiltonian is given by

$$H = \mu \sum_{i=1}^{N} n_i + \epsilon \sum_{i=1}^{N} \delta_{n_i,0}$$

where μ is the chemical potential.

1. Discuss the ground state of H for *i)* $\epsilon > \mu > 0$, *ii)* $\mu > \epsilon > 0$. Then compute the Grand Canonical partition function, the free energy and from this show that the density $\rho \equiv \langle n \rangle$ of particles tends to 1 or 0 as the temperature vanishes if $\epsilon > \mu$ or $\epsilon < \mu$ respectively.

2. Consider now the Hamiltonian

$$H' = \mu \sum_{i=1}^{N} n_i + \epsilon \sum_{i=1}^{N} \log(n_i + 1)$$

where μ is again the chemical potential.

Find the free energy and discuss the behavior of the density $\rho = \langle n \rangle$ as a function of μ for *i)* $T > T_c \equiv \epsilon/2$ and for *ii)* $T < T_c$ (draw a qualitative graph).

3. Consider the same system as in point 2 at fixed density ρ. Show that for $T < T_c$ there is a critical density $\rho_c(T)$ such that the previously derived description holds only if $\rho < \rho_c(T)$. The critical density diverges as $\rho_c(T) \sim |T - T_c|^{-\gamma}$ when $T \to T_c^-$. Compute the exponent γ.

4. In order to understand what happens for $\rho > \rho_c(T)$, add a term $-\delta n_1$ to the Hamiltonian H' (note that this term breaks the symmetry between sites) and discuss qualitatively what happens in the limit $\delta \to 0$ when $T < T_c$. Discuss the similarity of your findings with Bose-Einstein condensation. (Hint: the number of particles in the system is ρN).

Problem 6: Statistical mechanics of a discrete model.

A physical system of N degrees of freedom has a configuration determined by

$$\vec{\sigma} = \{\sigma_1, \sigma_2, ..., \sigma_N\},$$

where each variable σ_i can assume the discrete values $0, 1, 2, \ldots, q$.

In terms of the variable $n = \{$ *number of σ's different from zero* $\}$, the energy of a configuration $\vec{\sigma}$ is

$$H(\vec{\sigma}) = un - \varepsilon \delta_{n,0} \quad u > 0,\ \varepsilon > 0.$$

Calculate:

1. the number of states with a given n;

2. the free-energy at temperature T and the equilibrium probability P_n^{eq}, to find the system in a state with a given n;

3. the free-energy per degrees of freedom in the limit $N \to \infty$ and $\varepsilon = vN$ with v fixed, and describe the possible phase transition and the behaviour of the thermal average of n/N as a function of T.

4. Consider again the case of finite N and fixed ε at equilibrium. The time evolution of the probability to be in a state with a given n, $P_n(t)$, is determined by the master equation

   $$\frac{dP_n}{dt} = P_{n-1}w(n-1 \to n) - P_n w(n \to n-1) + P_{n+1}w(n+1 \to n) - P_n w(n \to n+1)$$

   where $n \geq 0$ and $w(m \to m \pm 1)$ is the transition rate from a state m to the state $m \pm 1$ (and for $n = 0$ the terms involving $n - 1$ are missing).

   Given that $w(m \to n-1) = m \cdot k$ for $m > 0$, determine the remaining $w's$ by assuming that detailed balance holds.

   If ε is large enough one can assume that for all $n > 0$ $P_n(t)$ is proportional to $P_n(eq)$. Within this approximation show that $P_0(t) - P_0^{eq} \sim \exp(-t/\tau)$ and calculate τ.

Problem 7: δ-like potential barrier in one dimension

Consider the stationary Schrœdinger equation of a particle moving in one dimension in the presence of a δ-function potential centered at $x = 0$,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + U\delta(x)\psi(x) = E\psi(x),$$

where U can be either positive or negative.

1. Calculate the eigenfunctions and eigenvalues of the Hamiltonian, for both positive and negative U.

Suppose that at time $\tau = 0$, you prepare a wave packet $\Psi(x)$ centered around a wave vector $k_0 > 0$ and around the position $x_0 < 0$, that is

$$\Psi(x) = \int_{-\infty}^{\infty} dk\, f(k) \mathrm{e}^{i(k_0+k)(x-x_0)}, \tag{1}$$

where $f(k)$ is peaked at $k = 0$ and decays fast over an interval $\delta k \ll k_0$. Assume that

$$\frac{1}{\delta k} \ll |x_0| \ll \frac{k_0}{\delta k^2}.$$

Show qualitatively that this condition implies that the wave packet at the beginning is sufficiently far from the barrier, and that it will not spread too much in the time it will reach the barrier. Let this wave packet impinge on the potential barrier. Part of it will be transmitted on the right of the barrier. In a time τ, the trasmitted wave packet will be centered around position $0 < x_1 \ll k_0/\delta k^2$. In the absence of the barrier, the same wave packet arrives at x_1 in a time τ_1, so that $\tau - \tau_1 = \tau_W(k_0)$ can be considered as the delay time induced by the barrier (the so called Wigner delay time).

2. Calculate $\tau_W(k_0)$ as a function of k_0 both for positive and negative U and discuss the result. To simplify the analysis, asssume that the length

$$a = \frac{\hbar^2}{mU} \ll \frac{1}{\delta k}.$$

The following problem is suggested for candidates interested in the bio-simulation curriculum

Problem 8: Aromatic compounds

This problem is concerned with the π electrons of benzene, pyridine (C_5NH_5) and pyrazine ($C_4N_2H_4$) molecules in the Hückel (i.e., tight binding) approximation. Assume that i) the bond terms β are the same for carbon and nitrogen; ii) the atomic terms are α for carbon and $\alpha' = \alpha + K_N\beta$ for nitrogen, with $K_N = 0.5$.

1. Calculate the orbital energy levels and indicate the electron configuration for the neutral ground state.

2. In terms of delocalization energy, which molecule is the most stable?

3. Explain why K_N can be expected to be a positive number.