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 problems sheet, but use extra envelope.

Problem 1
Three non-interacting electrons in one dimension

Consider the one-dimensional motion of three non-interacting "electrons" on a rigid segment of length L.

1) Suppose initially the segment to be closed onto itself in a large circle (periodic boundary conditions). Write down the eigenfunctions, the energy and the degeneracy of the three-electron ground state, for total spin S=1/2 and S=3/2 respectively. Do the same for the first and second excited states.

2) Next, imagine cutting the circle, so that the three electron now move on the same linear segment, but with open boundary conditions. By assuming electrons to flow into the new ground state, determine magnitude and sign of the "cutting energy" for S=1/2, and that for S=3/2.

Now return to closed boundary conditions, and allow for a hypothetical small periodic deformation of the circle in some unspecified external field, whose net result is an additional periodic potential

$$V(x) = v_0 \cos(Qx + \phi) ,$$

where x is the coordinate on the circle, and v_0 is the amplitude, ϕ the phase, and $2\pi/Q$ the periodicity (in principle arbitrary relative to L) of the new potential. Assume that the onset of such a deformation will cost an energy $\frac{1}{2}kv_0^2$, to be added to the total system energy (k is a positive stiffness constant).

3) Determine what value of Q is most effective in splitting the degeneracy of the ground state found at point 1, for either value of total spin. For that Q value, calculate and discuss the total energy change of the three electrons as a function of v_0 and ϕ. Determine in particular whether the total energy will be lower than that for $v_0 = 0$, and calculate by how much, assuming large k and small v_0.

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Problem 2

Two-spin system

Consider a simple model of two quantum spins of magnitude $S = 1/2$, whose Hamiltonian is

$$\hat{H} = J\vec{S}_1 \cdot \vec{S}_2 + \vec{v} \cdot \left(\vec{S}_1 + \vec{S}_2\right), \tag{1}$$

$\vec{v}$ being a vector providing a preferential direction of the spins.

1) Discuss the behavior of magnetic susceptibilities, entropy and specific heat as functions of the temperature, especially pointing out the role of the two energy scales present in Eq.(1), for the cases: (a) $J > 0$, (b) $J < 0$.

2) Suppose one has the possibility to perform a spin-polarized neutron scattering at zero temperature. In this experiment, an incoming beam of neutrons with a given spin-polarization $\alpha = \uparrow, \downarrow$ at a given wavevector $\vec{k}$ is scattered, and the detector can determine the intensity, the wavevector $\vec{k'}$ and the spin-polarization β of the outgoing beam. Is it possible by this experiment to estimate the sign of J, its strength, and the value and direction of $\vec{v}$?

In order to answer this question, assume that the scattering potential $\hat{V}(\vec{r})$ felt by a neutron is simply:

$$\hat{V}(\vec{r}) = U\left(\delta(\vec{r} - \vec{r}_1) + \delta(\vec{r} - \vec{r}_2)\right) + \vec{\sigma} \cdot \vec{B}(\vec{r}), \tag{2}$$

where $U > 0$, $\vec{\sigma}$ is the spin operator of the neutron, and $\vec{B}$ is the magnetic field generated by the magnetic dipoles $\vec{S}_1$ and $\vec{S}_2$. In terms of the spin density $\vec{S}(\vec{r})$ of the two-system, defined by

$$\vec{S}(\vec{r}) = \vec{S}_1 \delta(\vec{r} - \vec{r}_1) + \vec{S}_2 \delta(\vec{r} - \vec{r}_2), \tag{3}$$

the magnetic field is

$$\vec{B}(\vec{r}) = -\frac{\mu}{S}\vec{\nabla} \int d\vec{r}' \frac{\vec{S}(\vec{r}') \cdot (\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3}, \tag{4}$$

where μ is the magnetic moment of the spin S.

[*Hints:* To solve the point (2) make use of the Fermi golden rule to evaluate the transition probability $P_{i \to f}^{\alpha, \vec{k} \to \beta, \vec{k'}}$ that an incoming neutron with spin α and momentum $\vec{k}$ is scattered by the potential (2) into a state with spin β and momentum $\vec{k'}$, inducing in the spin system a transition from an initial state $|i\rangle$ to a final state $|f\rangle$.

You may find useful to work directly in Fourier space, i.e. with the Fourier components of Eqs.(3) and (4), and probably to know the following identity:

$$-\vec{\nabla}\frac{\vec{M} \cdot \vec{r}}{r^3} \equiv \vec{\nabla} \times \frac{\vec{M} \times \vec{r}}{r^3},$$

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as well as the Fourier transform of $\vec{r}/r^3$, which is $4\pi i\vec{q}/q^2$].

Problem 3
Rotating rod filled with benzene

Consider a rod (a very elongated, hollow cylinder), of length $L = 1\,\mathrm{m}$ and with an internal diameter of $1\,\mathrm{cm}$. The rod is filled with benzene (C_6H_6), and placed at a temperature $T_o = 6.4°C$ (1 degree above the melting point), and atmospheric pressure $P_o \simeq 0.1\,\mathrm{MPa}$ (NB: $1\,\mathrm{MPa} \equiv 10^6\,\mathrm{N/m^2} = 10\,\mathrm{bar} = 9.87\,\mathrm{atm} = 10^7\,\mathrm{dyne/cm^2} = 10^7\,\mathrm{erg/cm^3}$). T_o and P_o will remain constant throughout the experiment. One extremity of the rod is closed, while the other is open. The open extremity is connected to the axle of an engine, which puts the whole rod into rotation with angular speed ω, the closed extremity describing a circular trajectory with radius L.

1) Explain why solidification of benzene is expected to occur for a sufficiently high rotational speed, and where you expect it to begin.
2) Estimate the rotational speed required to start the solidification process. Assume a constant compressibility $\kappa_T = -(1/V)(\partial V/\partial P)_T = 8 \times 10^{-4}\mathrm{MPa^{-1}}$. Other useful data are the liquid density at P_o, $\rho_o = 0.90\,\mathrm{g/cm^3}$, the latent heat of melting, $L = 1.3 \times 10^9\,\mathrm{erg/g}$, and the volume change on melting, $\Delta V = V_{\mathrm{liq}} - V_{\mathrm{sol}} = 0.11\,\mathrm{cm^3/g}$.
3) Sketch a plot of the local Gibbs free energy along the rod when benzene is partly solid and partly liquid.
4) Explain what you expect to happen if benzene were replaced by water (with T_o still slightly above the melting point).

Problem 4
Crystal of molecular hydrogen

Consider a crystal of hydrogen molecules (H_2) at zero temperature. Assume that each molecules can be approximated with a one-dimensional harmonic oscillator of restoring constant k, independent of the hydrogen isotope. Neglect the interactions between the molecules, as well as internal rotations. The atomic mass of hydrogen is M_H.

1) Find the quantum zero-point energy of the system in the case where a fraction x of the molecules are isotopically substituted with deuterium molecules (D_2). The atomic mass of deuterium is $M_D = 2M_H$.
2) Find the zero-point energy of the system where a fraction x of the hydrogen atoms are randomly substituted with deuterium atoms (such a system will be composed by H_2, HD, and D_2 molecules). Show that the system is unstable against complete

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phase separation (i.e. against the formation of two separate isotopically pure crystals composed of H_2 and D_2, respectively).

3) Assuming that the entropy of the random crystal of point (2) is only determined by the number of configurations, calculate, for $x = 0.5$, the temperature T_c at which it becomes stable against *complete* phase separation. [Hint: $\log n! \simeq n \log n$]

Problem 5
Simple model with a transition

A quantum system of N degrees of freedom is in equilibrium at temperature T. The number of states with energy in the interval $(E, E + \Delta E)$ is $\exp[\Psi(E)] \, \Theta(\Psi(E)) \, \Delta E$ where $\Psi(E) = \alpha N - |E|/e_0$ ($\Theta(x)$ is the step function which is 0 for negative valves of the argument and 1 otherwise), and α and e_0 are given constants. Calculate:

1) The free energy of the system in the thermodynamic limit $(N \to \infty)$ for $0 < T < \infty$.
2) The latent heat at the transition point.
3) Repeat point 1 when $\Psi(E) = \alpha N - \frac{N}{e_0^2}(\frac{E}{N})^2$
4) The specific heat for case 3: is there still a transition?

[Hint: for point 3 use the following results $\int_a^b \exp(-Nf(x))dx \sim \exp(-N \, \text{Min}_{a \leq x \leq b} f(x))$ valid in the large N limit].

Problem 6
Ground-State of a modified harmonic oscillator

Consider the modified harmonic oscillator in one dimension:

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2 + \kappa(px + xp)$$

1) Calculate the ground-state energy of this hamiltonian by first- and second-order perturbation theory in the limit of $\kappa \to 0$.
2) Is the first order energy an upper bound to the true ground-state energy?
3) In general the second-order energy is not guaranteed to give an upper bound to the ground-state. Can you obtain an improved upper bound using the same ingredients?
4) (optional) Can you find the exact ground-state energy and wavefunction of this system?

Problem 7
Bose-Einstein condensation in a gas

Bose-Einstein condensation (BEC) has been recently observed in a dilute gas of trapped atoms. The condensate can be described by a common macroscopic one-body wavefunction

$$\Psi(\mathbf{r}, t) = \sqrt{\rho(\mathbf{r}, t)} \exp[i\theta(\mathbf{r}, t)] \tag{1}$$

normalized to the total number of atoms: $\int |\Psi|^2 d\mathbf{r} = N$.

For a weakly interacting BEC Ψ obeys the non-linear Schroedinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + [V_{ext} + U_0 \|\Psi\|^2] \Psi \qquad (2)$$

where V_{ext} is the external field due to the trap.

Let us consider the **one-dimensional** problem of bosons in a double-well trap given by

$$V_{ext}(x) = \frac{1}{2} m\omega^2 \, x^2 + V_0 \exp[-\frac{x^2}{\Lambda}], \ V_0 > 0. \qquad (3)$$

$V_{ext}(x)$ can be approximated by two symmetric harmonic wells A and B with a repulsive barrier between them.

Let us first consider the **non-interacting** boson gas ($U_0 = 0$).

1) Find the approximate eigenfunction $g_A(x)$ and the eigenvalue E_A of the ground state of the harmonic well A and similarly for the well B.

2) Assuming that $\int dx g_A(x)g_B(x) \sim 0$, find the wave functions $\Psi^+(x)$ and $\Psi^-(x)$ of the ground and first excited state for the full trap $V_{ext}(x)$ in terms of $g_A(x)$ and $g_B(x)$, and the corresponding energy expectation values. Discuss the results and the conditions on the parameters of $V_{ext}(x)$ which justify the ortogonality assumption.

3) Solve eq.(2) (with $U_0 = 0$), under the approximations which are consistent with g_A and g_B being roughly orthogonal. Take the initial conditions $N_A(t = 0) = N$, $N_B(t = 0) = 0$ and $\theta_A(t = 0) = \theta_B(t = 0)$.

[Hint: Write eq.(1) in the form $\Psi(x,t) = C(a_A(t)g_A(x) + a_B(t)g_B(x))$ (with $a_B(t) = \sqrt{N_B(t)}e^{i\theta_B(t)}$, $N_A(t)$ and $N_B(t)$ are the number of atoms at the time t in the well A,B respectively) and replace it in eq.(2) (setting $U_0 = 0$). Try to describe the dynamics as a two state problem (with a 2×2 hamiltonian acting on a two-components state-vector).]

4. Find the frequency of the oscillating flux.

5. (optional) Let us now switch on the **interaction** between atoms ($U_0 \neq 0$) in the eq.(2). How should the 2×2 hamiltonian be modified? Discuss qualitatively the effects of the non-linear term in the oscillating flux of bosons.

Problem 8
π orbitals of allyl radical.

1) Within the framework of Hückel theory, calculate the energies of the π molecular orbitals of the allyl radical: $[CH_2 = CH - CH_2]$.

Indicate the atomic orbitals as $|\mu\rangle$ and and $|\nu\rangle$. Set:
The Coulomb integral $\langle \mu|H|\mu\rangle = \alpha$.
The bond integral $\langle \mu|H|\nu\rangle = \beta$ if $|\nu\rangle = |\mu\rangle \pm 1$, $\langle \mu|H|\nu\rangle = 0$ otherwise.

The overlap integral $\langle \mu | \nu \rangle = \delta_{\mu\nu}$.

Recall that α and β are negative quantities.

2) The resonance energy ΔE_{res} is defined as the difference of the energy of a molecule of n delocalized double bonds and the energy of n noninteracting double bonds or ethylene units. In terms of ΔE_{res}, which ion is more stable?

(a) the allyl cation $[CH_2 = CH - CH_2]^+$.

(b) the allyl anion $[CH_2 = CH - CH_2]^-$.