

INTERNATIONAL SCHOOL FOR ADVANCED STUDIES
1998 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

A chain of harmonic oscillators bounded to a plane.

A closed chain of N classical particles in dimension $d = 3$ is in equilibrium at temperature T . Between the i -th and the $i + 1$ -st particle there is a harmonic potential $k/2 (\vec{r}_i - \vec{r}_{i+1})^2$. Furthermore, each particle is bounded to the $z = 0$ plane by a harmonic potential $k_0/2 z_i^2$ and the first particle is constrained to lie on the z axis.

Calculate:

- i)* The free energy per particle of the system in the thermodynamic limit ($N \rightarrow \infty$) for $0 < T < \infty$.
- ii)* The specific heat per particle.
- iii)* The average potential energy per particle.
- iv)* The average square displacement per particle in the z direction and in the directions perpendicular to the z axis. Discuss the result in the $k_0 \rightarrow 0$ limit.

(hint: $1/2\pi \int_{-\pi}^{\pi} dk \ln [a + b \cos k] = \ln \left[\left(a + \sqrt{a^2 - b^2} \right) / 2 \right]$ if $a > |b| > 0$)

Problem 2

A simple toy molecule

Consider a perfect rigid hexagon made up of six hydrogen atoms, $i = 1, 2, \dots, 6$, (a toy model of benzene). Assuming an electrons in each atom i to hop quantum mechanically to its two neighboring atoms $i \pm 1$ with an amplitude $-t = \langle i | H | i \pm 1 \rangle$, so that $H = -t \sum_i |i\rangle \langle i+1|$, and neglecting further all overlaps, $\langle i | i \pm 1 \rangle = 0$:

i) Find all one-electrons orbitals of this system, their energy, and their degeneracy.

ii) Ignoring electron-electron repulsion, fill up the lowest orbitals, and describe the electronic ground state of the toy molecule (i.e. give the wavefunction, total spin, energy and degeneracy).

iii) In the same approximation, describe the first excited states with spin zero, and with spin one.

Now release the rigidity condition, and consider each atom to be kept at their equilibrium distance r_0 from its two neighbors by hard springs of stiffness K , described by $H_i = \frac{K}{2} \sum_i (|\mathbf{r}_i - \mathbf{r}_{i+1}| - r_0)^2$. Assuming here that $t \rightarrow t \exp[-\alpha(|\mathbf{r}_i - \mathbf{r}_{i+1}| - r_0)]$, with $\alpha > 0$,

iv) Discuss what the effect of K being large but finite will be on the ground state energy.

v) Now remove one electron, and discuss, at least qualitatively, the new five-electron ground state, and what will happen to the molecule geometry.

Problem 3

Vibrational spectrum of biatomic molecules

The interatomic potential of homopolar biatomic molecules can be modeled by the Morse potential, $U(x) = A [\exp(-2\alpha x) - 2\exp(-\alpha x)]$, with A and α positive constants.

The vibrational spectrum of this model is known exactly and is given by the continuum for positive energies and a finite number of bound states satisfying the relation: $\sqrt{-E_n} = \sqrt{A} \left[1 - \frac{\hbar\alpha}{\sqrt{2mA}} \left(n + \frac{1}{2} \right) \right]$, with integer n .

i) Consider the harmonic approximation around the minimum of the potential, and calculate the corresponding spectrum. Compare it with the exact one (ground state energy, spacing of the energy levels and number of bound states).

ii) Calculate by first order perturbation theory the ground state energy of the Morse oscillator.

iii) Calculate an improved variational value for the ground state energy considering gaussian trial wavefunctions.

iv) The following table gives the classical dissociation energy D_e and the vibrational frequency ν for first and second row dimers. From the exact spectrum, calculate the number of vibrational bound states and the anharmonic correction to the first excitation energy for each dimer.

	H_2	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2
D_e (eV)	4.75	1.06	0.11	3.08	6.31	9.91	5.23	1.66
ν (THz)	132	10.5	8.8	31.5	55.7	70.7	47.4	26.7

[hints: $h = 4.1357 \times 10^{-15} eVs$. Ground state wavefunction of the harmonic oscillator: $\phi_0(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \exp \left(-\frac{m\omega}{2\hbar} x^2 \right)$].

Problem 4

Classical antiferromagnet in a magnetic field

Assume a classical spin, \vec{n} , on each site R_i of a cubic lattice with L sites. The spins are represented by three dimensional unit vectors $\vec{n} = (n^x, n^y, n^z)$ subject to the constraint $|\vec{n}|^2 = 1$. At zero temperature the energy depends on the spin orientation at each lattice site by the following hamiltonian:

$$H = \sum_{\langle i,j \rangle} \left[J_z n_{R_i}^z n_{R_j}^z + J_{\perp} (n_{R_i}^x n_{R_j}^x + n_{R_i}^y n_{R_j}^y) \right] - H \sum_j n_{R_j}^z \quad (1)$$

where the symbol $\langle i, j \rangle$ denotes nearest neighbor summations. The cubic lattice sites can be subdivided in two compenetrated sublattices, A and B, such that nearest neighbor bonds connect atoms of different sublattices. For instance at $H = 0$ and $J_z > J_{\perp}$ the minimum energy is $E = -NJ_z$ and is obtained by an antiferromagnetic arrangement of the spins $n^z = 1$ in the A sublattice and $n^z = -1$ in the B one (or viceversa). In general the minimum energy is obtained when all the spins are parallel in each sublattice but not in all the lattice.

1. Find the spin arrangement which minimizes the hamiltonian as a function of H/J in the spin isotropic case $J_z = J_{\perp} = J$.
2. What happens for arbitrarily small H/J ?
3. and for large H/J ?
4. Consider the spin anisotropic case $J_{\perp} < J_z$, which stabilizes the antiferromagnetic solution along the z -direction for $H = 0$. How many transitions do you find as a function of H/J ?
5. Determine the possible order parameters in the various phases and the corresponding order of the transitions.

Problem 5

Simple singlet ground state of a particular spin-1/2 chain model

1. Consider three sites, 1, 2, and 3, each occupied by a spin-1/2 operator \vec{S}_i ($i = 1, 2, 3$) [here $\vec{S} = (1/2)\vec{\sigma}$ where $\vec{\sigma}$ are the Pauli matrices] and the three-site Hamiltonian

$$\begin{aligned} H_{1,2,3} &= \frac{J}{4}(\vec{S}_1 + \vec{S}_2 + \vec{S}_3)^2 \\ &= \frac{J}{2} \left(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_1 \cdot \vec{S}_3 + \frac{9}{8} \right), \end{aligned} \quad (1)$$

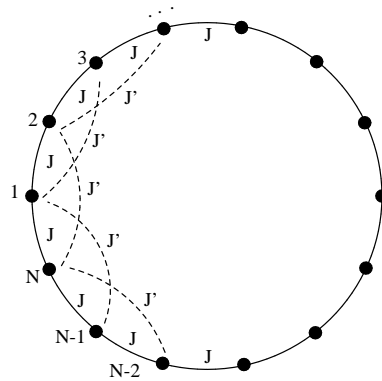
with $J > 0$.

By simple considerations of addition of angular momenta, determine the minimum eigenvalue of $H_{1,2,3}$ and the corresponding eigenstates.

2. Consider now a ring with an even number N of sites, and a spin-1/2 operator \vec{S}_i on each site $i = 1 \dots N$. Consider also the Hamiltonian

$$H_{JJ'}^{(N)} = J \sum_{i=1}^N \vec{S}_i \cdot \vec{S}_{i+1} + J' \sum_{i=1}^N \vec{S}_i \cdot \vec{S}_{i+2}, \quad (2)$$

with $J > 0$ and $J' > 0$. [Clearly, the ring geometry implies that one has to assume $\vec{S}_{N+1} = \vec{S}_1$ and $\vec{S}_{N+2} = \vec{S}_2$.]



- (2a) Determine the value of J' for which it is possible to rewrite $H_{JJ'}$ in terms of three-site Hamiltonians as follows:

$$H_{JJ'}^{(N)} = H_{1,2,3} + H_{2,3,4} + \dots + H_{N-1,N,1} + H_{N,1,2} + \text{const}. \quad (3)$$

- (2b) Fix from now on J' to the particular value, determined in (2a) above, for which Eq. 3 holds true. Using the fact that *for this particular value of J'* $H_{JJ'}^{(N)}$ is a sum of positive definite terms (the three-site $H_{i,i+1,i+2}$), of which one knows the

minimum energy states, show that the **ground state** $|\Psi^{(N)}\rangle$ of the Hamiltonian in Eq. 3 can be written as a product of $N/2$ *singlets* as follows:

$$|\Psi^{(N)}\rangle = (1,2)(3,4)\cdots(N-1,N), \quad (4)$$

where

$$(i, i+1) = \frac{1}{\sqrt{2}} (|\uparrow\rangle_i |\downarrow\rangle_{i+1} - |\downarrow\rangle_i |\uparrow\rangle_{i+1}).$$

(2c) Calculate the **ground state energy** of $|\Psi^{(N)}\rangle$.

(2d) Can you provide another simple ground state of $H_{JJ'}^{(N)}$ closely related to $|\Psi^{(N)}\rangle$?

Problem 6

Electronic Structure of 1,3-butadiene and ethylene.

In the Hückel formalism,

1) Calculates orbital energies of the π electrons of 1,3-butadiene and ethylene in terms of Coulomb and resonance integrals. Calculate also the orbital coefficients for the two molecules.

2) Calculate the stabilization due to delocalization of the π electrons in 1,3-butadiene relative to two molecules of ethylene.

3) In terms of π -bond orders, explain why the formula $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, which indicates two pure double bonds and one single bond, is not an adequate description of the π bonding in 1,3-butadiene.