

## Spring 2006 - 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: Interaction of two distant atoms

Two hydrogen atoms A and B, a large distance  $R_{AB} = |\mathbf{R}_A - \mathbf{R}_B|$  apart, are described by the Hamiltonian  $H = H_0^A + H_0^B + V$ , where  $H_0^A = -\frac{\hbar^2}{2m}\nabla_1^2 - e^2/r_{1A}$  and  $H_0^B = -\frac{\hbar^2}{2m}\nabla_2^2 - e^2/r_{2B}$  describe the two separate atoms, with  $r_{1A} = |\mathbf{r}_1 - \mathbf{R}_A|$  and  $r_{2B} = |\mathbf{r}_2 - \mathbf{R}_B|$  their respective electron-proton distances. The interaction term is, with obvious notation:

$$V = \frac{e^2}{R_{AB}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} \quad (1)$$

1. For large  $R_{AB}$ , express the perturbation  $V$  in a simplified form (obtained by expansion), and interpret the physical significance of the leading term.

Treating the protons as classical, and calling  $E(R_{AB})$  the total ground state energy when the atoms are at distance  $R_{AB}$ , consider the interaction energy  $U(R_{AB}) = E(R_{AB}) - E(\infty)$  and, in particular, its calculation by perturbation theory:

2. Beginning with the unperturbed ground state  $\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \phi_{100}(\mathbf{r}_1)\phi_{100}(\mathbf{r}_2)$  of  $H_0^A + H_0^B$  use simple symmetry arguments to derive the qualitative analytical form of  $U(R_{AB})$  and its sign. Do the atoms attract or repel?
3. Carry out the explicit (approximate) perturbation calculation of  $U(R_{AB})$ . In place of the true excited state spectrum of the atom, assume a single  $2p$  excited state for each hydrogen atom. Evaluate numerically the interaction energy  $U(R_{AB})$ , preferably expressed in Hartree or in eV [1 Hartree =  $\frac{e^2}{a_B} = 27.2$  eV] when  $R_{AB} = 10 a_B \approx 5 \text{ \AA}$  apart.

Hint: Use  $\phi_{100}(\mathbf{r}) = \frac{1}{a_B\sqrt{\pi a_B}}e^{-(r/a_B)}$ ,  $\phi_{210}(\mathbf{r}) = \frac{1}{a_B\sqrt{32\pi a_B}}(z/a_B)e^{-(r/2a_B)}$ .

## Problem 2: The number of singlets in a correlated model

Consider a finite one dimensional model within a simple tight-binding scheme. The electrons can occupy atomic orbitals located in a finite number  $L$  of lattice sites. For simplicity we assume that on each site there is only one orbital orthogonal to the remaining  $L - 1$  ones. Each orbital can be occupied at most by two electrons with opposite spins. In the following  $N_{\uparrow}$  and  $N_{\downarrow}$  indicate the number of electrons with spin up or spin down along the  $z$ -direction, respectively.

1. Compute the total number of many-electron states with given total spin along the  $z$  axis  $S^z = (N_{\uparrow} - N_{\downarrow})/2$  and total electron number  $N = N_{\uparrow} + N_{\downarrow}$ .

Hint: recall that the number of possible combinations of  $q$  indistinguishable objects in  $p$  states is given by the combinatorial coefficient  $C(p, q) = \frac{p!}{q! \times (p-q)!}$ .

2. By using the above result, compute the total number of possible  $N$ -electron states with vanishing total spin (singlets).
3. As above, compute the total number of singlets with the constraint that two electrons of opposite spin cannot occupy the same orbital (e.g. due to the strong repulsion).

### Problem 3: Vibrational spectrum of the ammonia molecule

The equilibrium structure of the ammonia molecule,  $NH_3$ , is a pyramidal. All the  $HH$  bond lengths are equal to  $a_{HH} = 1.62 \text{ \AA}$ , whereas the  $NH$  bond lengths are  $a_{NH} = 1.01 \text{ \AA}$ . One of the vibrational modes of the molecule can be described to a high accuracy with the variation of the height,  $z$ , of the pyramid.

1. Assuming that the potential energy for this normal mode can be described by a function:

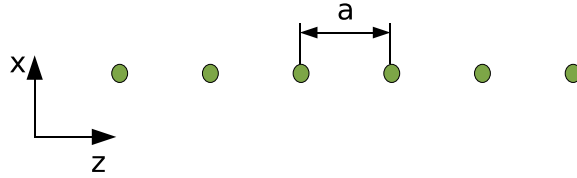
$$V(z) = Az^2 + Bz^4,$$

determine the value of the  $A$  and  $B$  constants in such a way that the corresponding vibrational frequency is  $\omega = 950 \text{ cm}^{-1}$  (The atomic weight of Nitrogen is  $A_N = 14$ ).

2. Show that in the harmonic approximation the vibrational ground state is doubly degenerate.
3. Show that anharmonic effects lift the degeneracy found in (2) and find an approximate value for the tunneling splitting. [Hint: consider the linear combinations of the two degenerate harmonic ground states that satisfy the symmetry requirements of the Hamiltonian]
4. Calculate the effects of an isotopic substitution ( $H \rightarrow D$ ) on the vibrational frequency and tunneling splitting.

# Problem 4: Relativistic electronic structure of a monatomic wire

Let us consider an infinite monatomic wire with atoms at distance  $a$ :



and assume that each atom has three atomic  $p$  orbitals:  $p_1, p_0, p_{-1}$ . The atomic wavefunctions can be written as:  $\phi_{p_m}(\mathbf{r}) = \phi_p(r)Y_{1,m}(\Omega_{\mathbf{r}})$  where  $(r, \Omega_{\mathbf{r}})$  are the spherical coordinates of  $\mathbf{r}$  and  $Y_{1,m}(\Omega_{\mathbf{r}})$  are the spherical harmonics with  $l = 1$ .

1. Use a tight-binding model to calculate the electronic band structure of the wire for Bloch wave-vectors  $\mathbf{k} = (0, 0, k_z)$  with  $-\frac{\pi}{a} \leq k_z \leq \frac{\pi}{a}$ . Assume that the matrix elements of the Hamiltonian between orbitals centered on the same atom are:

$$\int \phi_{p_m}^*(\mathbf{r}) H_0 \phi_{p_m}(\mathbf{r}) d^3r = \epsilon_p,$$

while the hopping integrals between orbitals centered on nearest-neighbor atoms are:

$$\int \phi_{p_m}^*(\mathbf{r}) H_0 \phi_{p_m}(\mathbf{r} \pm a\hat{\mathbf{z}}) d^3r = \begin{cases} -t & \text{for } m = \pm 1 \\ t_0 & \text{for } m = 0 \end{cases}$$

where  $t$  and  $t_0$  are positive numbers and  $t_0 > t$ . The matrix elements between orbitals with different  $m$  or between orbitals of atoms more distant than the first nearest-neighbor are zero. Orbitals on the same site are orthogonal while overlaps between orbitals centered on different sites are neglected.

2. Now consider an additional term in the Hamiltonian which represents the intra-atomic spin-orbit coupling,  $H_{so} = \alpha \mathbf{L} \cdot \mathbf{S}$ , where  $\mathbf{L}$  is the orbital angular momentum and  $\mathbf{S}$  is the spin angular momentum.  $\alpha$  is a parameter which measures the spin-orbit coupling strength. Consider a tight-binding model with six atomic orbitals per atom. Take for instance  $\phi_{p_m}(\mathbf{r})\chi_{\uparrow}$  and  $\phi_{p_m}(\mathbf{r})\chi_{\downarrow}$  where  $\chi_{\uparrow}, \chi_{\downarrow}$  are the eigenfunctions of the spin operator. Write the  $6 \times 6$  matrix which represents  $H_{so}$  in this basis.
3. Calculate and plot the electronic band structure in presence of spin-orbit coupling, by diagonalizing the total Hamiltonian  $H_0 + H_{so}$ . Discuss the two limiting cases  $\alpha \ll t$  and  $\alpha \gg t_0$ .

Hint: In this problem  $J_z = L_z + S_z$  is conserved so that states with different values of  $J_z$  cannot mix.

## Problem 5: Electronic states of a finite linear chain of alkali atoms

Consider a regularly spaced linear chain formed by  $N$  alkali atoms (Li, Na, K,..) with atomic electronic configuration  $[core]ns^1$  and assume that only the outer  $ns$  electron is relevant for the valence properties addressed here.

The valence electronic states of the system can be calculated with good approximation expressing the wave-functions of the system as linear combinations of atomic orbitals:

$$\psi(x) = \sum_{i=1}^N c_i \phi_{ns}^{at}(x - x_i)$$

and assuming that the only non-vanishing matrix elements in the single-particle Hamiltonian of the system are the on-site energy,  $\langle \phi_i | H | \phi_i \rangle = \varepsilon_{ns}$ , and the nearest-neighbor hopping,  $\langle \phi_i | H | \phi_{i+1} \rangle = -t$ .

1. Consider the simplest cases with  $N = 2, 3, 4$  and determine the corresponding electronic states (eigenvalues and eigenvectors up to a normalization constant) exploiting the symmetry of the system to simplify the problem.
2. Make a schematic drawing of the corresponding wave-functions in the different cases and compare them with the solutions that can be obtained for a particle in a finite box with hard wall at 0 and  $L$ .
3. Based on the analogy of the solutions in the two systems, write down the solution of the linear chain problem for general value of  $N$  (again provide eigenvalues and eigenvectors up to a normalization constant).
4. Assuming one electron per site and the independent electron approximation give the expression for the binding energy per site of the system ( $E_B = N^{-1}E_{tot}(N) - \varepsilon_{ns}$ ) and evaluate it explicitly in the  $N = 2, 3, 4$  cases and in the limit for  $N \rightarrow \infty$ .