

BONDING

1. (10 points) The variational principle states that for a given Hamiltonian the expectation value of the energy, calculated on any generic “trial” wavefunction, will always be larger or equal than the lowest energy eigenstate (i.e. the ground state for the Hamiltonian at hand). If it is equal, then the trial wavefunction must coincide with the ground state eigenfunction of the Schrödinger equation, and the expectation value of the energy will obviously be the ground state eigenvalue.

The variational principle has both practical and conceptual consequences; e.g. it allows us to find good approximate solutions to problems we would not be able to solve exactly if formulated as a differential equation. It also allows us to study most many-electron problems using trial wavefunctions that are simple linear combinations of atomic orbitals. It actually provides a justification for the concept of “hybridization” of atomic orbitals, and allows to explore ground and excited states of molecules and solids as simple linear combinations of atomic orbitals (LCAO for molecules, “tight-binding” for solids).

For this problem we’ll go back to the hydrogen atom, and will consider a trial wavefunction $\Psi_\alpha = C \exp(-\alpha r)$; different values of α will correspond to different shapes of Ψ_α (i.e. different decays towards large r). α can be considered a “tunable handle” that allows us to explore all possible wavefunctions in a class (here, that of simple decaying exponentials as a function of the polar coordinate r). Note that the only role of the multiplicative constant C is to “normalize” the solution, so that the integral over all space of the square modulus of the wavefunction is equal to 1 (i.e. we are 100% certain to find an electron somewhere). The expectation value of the energy, for this generic non-normalized trial solution Ψ_α , will be

$$E_\alpha = \frac{\langle \Psi_\alpha | \hat{H} | \Psi_\alpha \rangle}{\langle \Psi_\alpha | \Psi_\alpha \rangle}.$$

Here comes the question: Find analytically the value of the variational coefficient α that minimizes E_α , and compare the energy and wavefunction that you obtain with those that we have encountered when solving explicitly the Schrödinger equation for the hydrogen atom. All integrals can be done with Mathematica (available on Athena), Macsyma (public domain), or using the Mortimer tables; just in case, here is trickiest one (it involves a Laplacian, and that needs to be expressed in spherical coordinates):

$$\langle \Psi_\alpha | -\frac{1}{2} \nabla^2 | \Psi_\alpha \rangle = \pi \frac{C^2}{2\alpha}$$

2. (10 points) Draw the radial component of the 3s, 3p, and 3d orbitals for the hydrogen atom. For each of these orbitals, draw or describe the nodal surfaces and explain which ones are due to the radial component of the wavefunction, and which to the angular (spherical harmonics) component.

- (10 points) Describe the electronic structure of methane, ammonia, and water, highlighting similarities or differences. What are the factors determining the angles between atoms in these molecules ?
- (10 points) Explain how we can derive the energy levels of a conjugated molecule such as benzene using the Huckel method. Explain the steps involved.
- What are the typical distances between carbon atoms in ethane, ethane, and ethyne ? What are the different interactions that determine this distance ?

THERMODYNAMICS

- Phase separation of a regular solution.** Given below is thermodynamic data for an A-B solid solution that exhibits regular solution behavior, with a miscibility gap in the solid state. You have a sample with composition $X_B = 0.15$ which is cooled from very high temperatures to 250 K.

$$\mu_{A,o} = -2,000 \frac{J}{mole}$$

$$\mu_{B,o} = -1,000 \frac{J}{mole}$$

$$\Omega = 7,000 \frac{J}{mole}$$

As a reminder, you can derive the molar free energy of solution for the regular solution from the molar free energy of mixing and the molar free energy of the heterogeneous A-B mixture:

$$\Delta \bar{G}^{mix,rs} = \bar{G}^{RS} - \bar{G}^{heter}$$

$$\bar{G}^{RS} = \Delta \bar{G}^{mix,rs} + \bar{G}^{heter} = \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B] + \mu_{A,o} X_A + \mu_{B,o} X_B$$

- What is the critical temperature for this system?
- What are the locations (X_B values) of the spinodals and the phase boundaries (boundaries between the miscibility gap and pure α_1 , α_2 phases) for this regular solution at the given temperature?
- At the given temperature and composition, will this system phase separate by nucleation and growth or by spinodal decomposition? Show why.

2. **Two-state quantum systems.** Suppose you have a collection of N non-interacting molecules that are indistinguishable (and identical). Each molecule resides in one of two microstates: a ground state with energy 0 , and an excited state with energy ε_0 .
- What is the molecular partition function for this system?
 - What is the partition function of the entire system of N molecules?
 - What is the internal energy of this system as the temperature approaches infinity?
 - Using the molecular partition function, determine what temperature gives a probability for a molecule to reside in the excited state equal to $1/2$. (Hint: The answer will seem unusual- it is a unique property of a two-state system. But you should readily be able to solve for T !)
3. **Predicting molecular collapse of a polymer chain at cold temperatures.** Let's determine the thermodynamic properties of a 6-repeat unit polymer chain, modeled as a set of 6 connected beads. The links between each bead (covalent bonds in the real polymer) are flexible and allow the chain to reside in numerous possible microstates, which are enumerated in the figure below. Within these microstates, the internal energy of the chain is *greater* when there are no bead-bead contacts (contacts between beads which are *not* covalently linked to one another). The microstates have 3 different possible energies, based on the number of bead-bead contacts present: states with no contacts have an energy $2\varepsilon_0$, states with 1 bead-bead contact have an energy ε_0 , and states with 2 bead-bead contacts have an energy 0 . As shown in the figure below, there are 4 states with 2 contacts, 11 states with 1 contact, and 21 states with zero contacts. Use this simple model to answer the following questions:
- What is the partition function for this 6-unit polymer?
 - What is the probability of the polymer being in a state with energy 0 , ε_0 , or $2\varepsilon_0$? (Hint: you want to know the probability of being in *any of the states* with the energy of interest, not just the probability of being in *one specific state* of that energy).
 - Calculate the internal energy of the polymer chain as a function of temperature.
 - Calculate the value of the critical temperature T_c , where the polymer is 50% likely to be in one of the fully collapsed (2-contact) states. You do not need to solve the final

equation- simply reduce the required relationship as much as possible (a graphical/numerical solution is required to obtain the exact value of T_c).