

BONDING

1. What are the quantum numbers used to describe the wavefunction of an electron in a central potential ?
2. Summarize the conceptual steps that led us to the solutions of the Schrödinger equation for an electron in a central potential.
3. Sketch the radial part and the angular part of one of the 3p wavefunctions for the hydrogen atom, and describe the nodal surfaces (i.e. where it goes to zero).
4. We want to understand if a hydrogen atom and a proton are stable together (i.e. they bind) as a charged molecular ion. Describe the attractive and repulsive interactions at work, and write down the Hamiltonian \hat{H} for this problem (use atomic units). What will determine the stability of this system ?
5. Determine the ground state wavefunction for the electron in this molecular ion. Use a trial wavefunction $|\psi_{trial}\rangle = c_1|\psi_{1s,A}\rangle + c_2|\psi_{1s,B}\rangle$, where $|\psi_{1s,A}\rangle$ is a 1s-like hydrogen wavefunction centered on one nucleus, $|\psi_{1s,B}\rangle$ is a 1s-like hydrogen wavefunction centered on the other nucleus. Assume that $\langle\psi_{1s,A}|\hat{H}|\psi_{1s,A}\rangle = \langle\psi_{1s,B}|\hat{H}|\psi_{1s,B}\rangle = 1$ (atomic units), $\langle\psi_{1s,A}|\hat{H}|\psi_{1s,B}\rangle = \langle\psi_{1s,B}|\hat{H}|\psi_{1s,A}\rangle = -1$ (atomic units), and that $|\psi_{1s,A}\rangle$ and $|\psi_{1s,B}\rangle$ are orthogonal and normalized to one (i.e. $\langle\psi_{1s,A}|\psi_{1s,B}\rangle = \delta_{A,B}$).
6. If the wavefunction for an electron in a central potential has a principal quantum number $n=4$ and angular momentum quantum number $l=2$, what will be the possible values for the magnetic quantum number m ?
7. How many nodes will characterize the radial wavefunction for the above electron ?
8. The energy needed to break apart a Li_2 dimer is larger than the energy needed to break a Be_2 dimer – explain why (remember, Li is the third atom in the periodic table, and Be is the fourth one).
9. What is the ground state energy for an electron in a hydrogen atom ? Suppose that we apply a magnetic field to such atom, but we do not allow the wavefunction to change. What will be the new ground state energy ? (The Hamiltonian in a strong magnetic field along the z axis has an added term $\frac{\mu_B}{\hbar} B_z (\hat{L}_z + 2\hat{S}_z)$, where $\frac{\mu_B}{\hbar} B_z$ is just a constant and \hat{L}_z and \hat{S}_z are the

operators for the z-component of the angular momentum and for the z-projection of the electron spin.

10. Describe the different hybridized orbitals that carbon can have in a molecule, and which geometry they enforce for the bonds around the carbon atom.

THERMODYNAMICS

1. **Flory-Huggins Theory.** We introduced a simple lattice model for polymer solutions in lectures 24 and 25. The Flory-Huggins model for polymer solutions is a close relative of the regular solution model of small-molecule binary solutions, and the free energy of mixing per lattice site in the Flory-Huggins model looks somewhat like the expression for the regular solution:

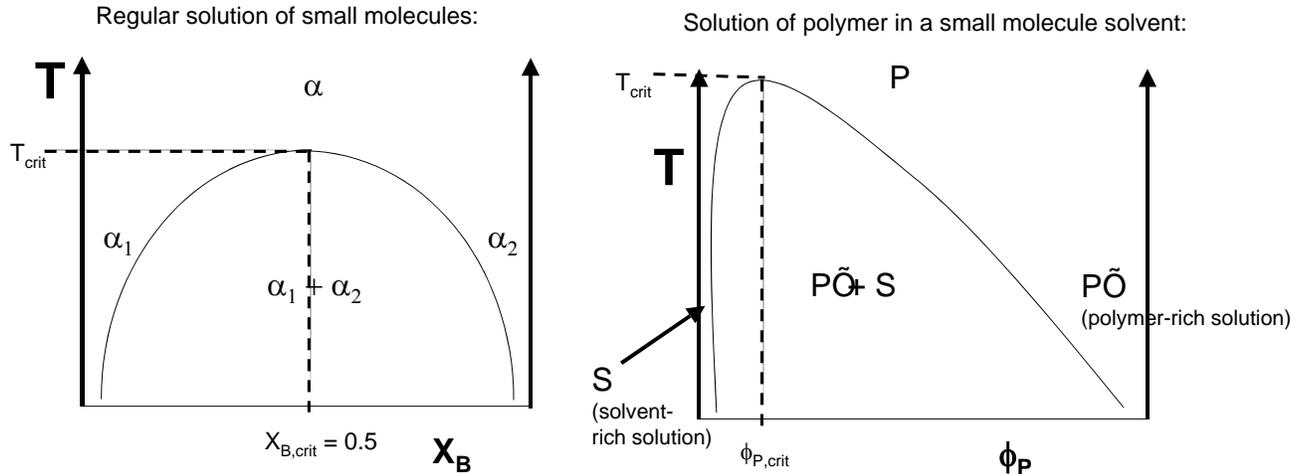
$$\frac{\Delta \bar{G}^{mix}}{M} = \chi kT \phi_p \phi_s + kT [\phi_p \ln \phi_p + \phi_s \ln \phi_s]$$

...where χ is the Flory-Huggins interaction parameter and ϕ_s and ϕ_p are the volume fractions of solvent and polymer, respectively.

- a. We showed earlier that the critical temperature in the regular solution model is $T_{crit} = \Omega/2R$. We obtained this result by determining the value of T when the second derivative of the free energy of mixing with respect to composition is equal to zero, at

the composition $X_B = 0.5$ ($\left. \frac{\partial^2 \Delta \bar{G}^{mix}}{\partial X_B^2} \right|_{X_B=0.5} = 0$). In this case we knew the miscibility

gap would first appear at $X_B = 0.5$ because the enthalpy and entropy of mixing functions in the regular solution are *symmetric* about $X_B = 0.5$. However, these functions are **not** symmetric about $\phi_p = 0.5$ in the Flory-Huggins model. (This is why the miscibility gap on the polymer solution phase diagram is 'canted' strongly toward the $\phi_p = 0$ vertical axis for long-chain polymers.) The Flory-Huggins model thus has both a critical temperature and a critical volume fraction (illustrated below).



Typically, instead of calculating a critical temperature for polymer solutions, one instead calculates χ_{crit} , the critical value of the interaction parameter at the onset of the miscibility gap (which, as you can see by looking at the definition of χ , is inversely proportional to the critical temperature). In order to determine the critical volume fraction, we use an additional condition on the free energy: The critical point is located at the temperature and composition where the following two criteria are met:

$$\frac{\partial^2 (\Delta \bar{G}^{mix} / M)}{\partial \phi_P^2} = 0$$

$$\frac{\partial^3 (\Delta \bar{G}^{mix} / M)}{\partial \phi_P^3} = 0$$

(We use here the free energy change on mixing per lattice site). Use these equations to determine the critical volume fraction $\phi_{P,crit}$ and χ_{crit} for the Flory-Huggins model, and show how they depend on N , the number of segments in the polymer chains.

- b. We showed in class how the entropy change on mixing a polymer with a small-molecule solvent, $\Delta \bar{S}^{mix}$, is obtained. Use this information to derive an expression for the entropy change on mixing a polymer A with chains each comprised of N_A segments with a *second polymer B*, which has chains comprised of N_B segments.

2. **The ideal solution as a lattice model.** We can derive the free energy of mixing for ideal solutions using a lattice model similar to the Flory-Huggins theory- but simpler. Suppose components A and B of the solution both occupy one lattice site each (and are the same size). Following the conceptual procedure we used in class (determining the entropy S from the number of configurations for the system W), answer the following questions:
- What is the entropy of the **unmixed** system of pure A molecules + pure B molecules?
 - What is the entropy of the homogeneously mixed system of A + B?
 - Using these two results, what is the molar entropy change on mixing for this model system? Compare your answer to the ideal solution entropy of mixing we gave earlier in class.
3. **Practice with the partition function.** In class, we gave a number of useful relationships that allow you to directly determine thermodynamic quantities from the partition function. An example is the expression for the internal energy:

$$U = \langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} = kT^2 \frac{\partial \ln Q}{\partial T}$$

Show that this expression is equivalent to the ensemble average of the internal energy:

$$U = \langle E \rangle = \sum_{i=1}^W E_i p_i$$

4. **Practice with the Boltzmann distribution.** Consider an imaginary crystal where a collection of 3 atoms vibrate as simple 1D harmonic oscillators, and each atoms has access only to the first 4 energy levels (the ground state and the first 3 excited states). The energies of the 4 states are 75k, 225k, 375k, and 525k from the ground state to the higher energy states (where k is the Boltzmann constant). The atoms are identical and distinguishable.
- What is the probability of finding **one atom** of the system in each possible energy level at T = 200K?
 - Compute the probability of observing the **system** with a total energy of 225k.
 - Compute the probability of observing the **system** with a total energy of 375k.

- d. Explain why it is more probable to find the **system** with an energy greater than the ground state energy (all atoms in the ground state energy level), despite the fact that the probabilities of finding **one atom** of the system in an excited state (part a) decrease with increasing energy.