No plagiarism allowed: see the handbook for students at <u>http://web.mit.edu/due/handbook.pdf</u> . On the other hand, you should feel free to consult as much as possible books and other educational material. Remember that the homework is primarily designed to give you a chance to gauge your understanding of the material – if you struggle with a concept, go back to the lecture notes, the textbook, the TAs, the instructor.

BONDING

1. Which of these (un-normalized) 2-electron wavefunctions is antisymmetric, and which is symmetric

    a. $\exp|\vec{r}_1 - \vec{r}_2|$

    b. $\exp|\vec{r}_1 + \vec{r}_2|$

    c. $(\vec{r}_1 - \vec{r}_2)\exp|\vec{r}_1 - \vec{r}_2|,|\vec{r}_1 - \vec{r}_2|\exp|\vec{r}_1 - \vec{r}_2|$

    d. $(\vec{r}_1 - \vec{r}_2)\exp[-(\vec{r}_1 - \vec{r}_2)^2]$

    e. $(\vec{r}_1 - \vec{r}_2)\exp[-(\vec{r}_1 + \vec{r}_2)^2]$

2. We have seen in class how we can approximate the Hartree-Fock wavefunction for H_2 as a LCAO of 1s orbitals centered on the two different protons in R_A and R_B:

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\begin{Vmatrix} \varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) \\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) \end{Vmatrix} = \frac{1}{\sqrt{2}}\left[\varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2) - \varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1) \right]$$

$$\varphi_\alpha(\vec{r}) = \left(c_1\Psi_{1s}(\vec{r} - \vec{R}_A) + c_2\Psi_{1s}(\vec{r} - \vec{R}_B) \right) \times (spin - up)$$

$$\varphi_\beta(\vec{r}) = \left(c_1\Psi_{1s}(\vec{r} - \vec{R}_A) + c_2\Psi_{1s}(\vec{r} - \vec{R}_B) \right) \times (spin - down)$$

    a. Can you write out explicitly 1) the 2-electron Hamiltonian in the presence of the Coulombic potential of the two separate nuclei, and the electron-electron interaction ? 2) the explicit expression for the energy functional E[ψ], i.e. all the integrals involved (consider the simpler case in which $c_1 = c_2$) ?

    b. If instead of having H_2 we had had He, what would have been a good choice for

        $\varphi_\alpha(\vec{r})$ and $\varphi_\beta(\vec{r})$

3. Let's expand a generic wavefunction $|\psi\rangle$ in the complete set of eigenfunctions $|\varphi_i\rangle$ (i=1,...,∞) of the Hermitian operator $\hat{A}$: $|\psi\rangle = \sum_i c_i |\varphi_i\rangle$. If someone tells us that $|\psi\rangle$ is orthogonal to $|\varphi_2\rangle$, what conclusions can we make on the values of c_1 and c_2 ? If I take an angular function $\Omega(\vartheta,\varphi)$ that is a normalized linear combination with arbitrary coefficients of $Y_1^0(\vartheta,\varphi)$ and $Y_2^0(\vartheta,\varphi)$ (i.e. the two spherical harmonics corresponding to l=1,m=0 and l=2,m=0), what will be the minimum value for $\langle\Omega|\hat{L}^2|\Omega\rangle$?

4. How would you order the boiling points of methane, ammonia, and water, and why ?

5. What are the orbitals for the electrons in the highest occupied molecular orbitals (HOMOs) for N_2 and for O_2 ? In each case, there are two electrons that have the same highest energy. Describe the space part of the orbital (draw it, and note its symmetries), and the spin of each orbital.

6. Use the applet at http://www.chem.ucalgary.ca/SHMO/ to calculate the HOMO-LUMO gap in benzene using Huckel theory (instructions are on the website). What will be the gap in naphthalene ? In anthracene ? What will happen as the molecule becomes longer ? (You can download the applet to your Java computer from http://quasiamore.mit.edu/SHMo2.zip). Can you try it for ethene, and solve the secular equation by hand ?

THERMODYNAMICS

1. **Free energy calculations.**

    a. Engel and Reid, problem 6.2.

    b. Engel and Reid, problem 6.3.

2. **Vapor-liquid equilibria.** Consider the experimental setup described in the cartoon below: We have a closed beaker containing either a quantity of pure liquid A or a solution of liquid A mixed with liquid B. The liquids are in equilibrium with the gas phase above them (pure gaseous A in the one case and a mixture of gaseous A and B in the other). The systems are equilibrated at constant temperature and pressure. Assuming the vapors can be modeled as ideal gases, answer the following questions:
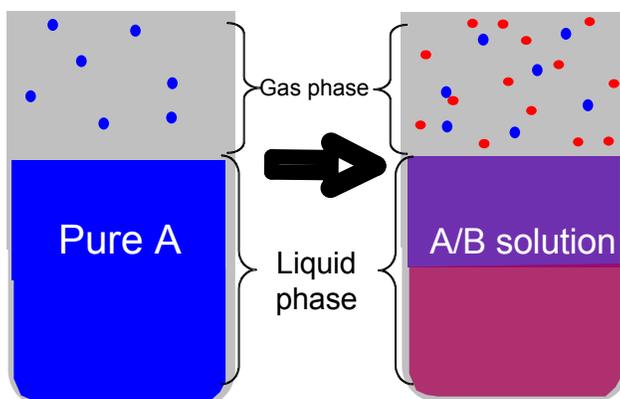
a. What is the equilibrium condition on the chemical potentials of A molecules in the case of pure A liquid in equilibrium with its gas? What is the condition on the chemical potential of A molecules for A molecules in the solution in equilibrium with the A/B gas mixture?

b. Show that at equilibrium, the difference between the standard state chemical potentials of the pure liquid A and pure A gas is:

$$\mu_i^{o,liquid}(T) - \mu_i^{o,gas}(T) = RT\ln\frac{P^*}{P_o}$$

…where P* is the vapor pressure of pure A (the pressure of pure A gas above pure A at the given temperature and pressure) and P_o is the reference pressure for the ideal gas.

c. Show that for the solution, the activity of A molecules is:

$$a_A^{solution} = \frac{P_i}{P^*}$$

…where P* is the vapor pressure of A above pure liquid A, as in part (b), and P_i is the partial pressure of A gas in the A/B gas mixture above the solution.

3. **Spontaneous formation of solutions.** Prove that if two pure liquids A and B are placed together in a container, formation of a solution from the two is always a spontaneous process if the pair form an ideal solution.
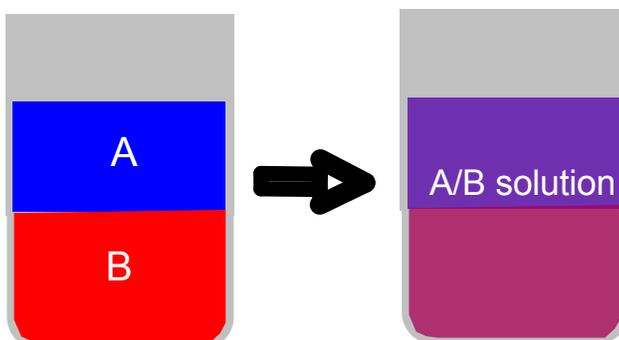
4. **Chemical reaction equilibria.**

   a. Consider the gas phase reaction of NO_2 shown below. At T = 700 K, the equilibrium constant K_p = 0.379. At a total pressure of 2 atm, the partial pressure of oxygen in the reaction is 0.378 atm at equilibrium. Determine the molar standard state free energy of reaction and the equilibrium composition of the gas mixture (final partial pressure of each component) for these conditions.

$$NO_{2(g)} \leftrightarrow NO_{(g)} + \frac{1}{2}O_{2(g)}$$
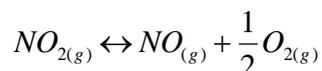
   b. We wish to mix an initial x moles $SO_3(g)$ and 1 mole $SO_2(g)$ to obtain a final partial pressure of oxygen equal to 0.05 atm in a reactor at 1100 K under a total pressure of 1.2 atm at equilibrium. Calculate x given:

$$SO_{2(g)} + \frac{1}{2}O_{2(g)} \leftrightarrow SO_{3(g)} \qquad \Delta \overline{G}_{rxn}^{o} = -94,560 + 89.37T \frac{J}{mole}$$

   (Modified from C.H.P. Lupis, *Chemical Thermodynamics of Materials*, problem V.6)

5. **Gas-solid reactions**.

   a. Engel and Reid problem 6.13.

b. Engel and Reid problem 6.29.