Phys 231, Fall 2007, Homework 2, due Oct 22

(4 points per each problem)

1. Even closed-shell atoms such as Ne or Ar interact with each other via the van-der-Waals interaction, which is the interaction of two fluctuating electric dipoles ($1/R^6$), as opposed to the interaction of two static electric dipoles ($1/R^3$). This attraction, balanced by the hard-core repulsion, is the origin of the cohesive energy of van-der-Waals crystals. In this problem, let's try to understand how the $1/R^6$ attraction comes about. For simplicity, let's consider two hydrogen atoms, hydrogen atom 1 and hydrogen atom 2, placed at vector **R** from hydrogen 1, where |**R**| is much larger than the Bohr radius.
   (1) Suppose we take a snapshot measurement of positions of electrons 1 and 2, bound to atoms 1 and 2 respectively. We assume that protons 1 and 2 are at fixed positions, origin and **R** respectively. *Without* using any equations, explain why the lowest-order instantaneous Coulomb interaction between hydrogen 1 and hydrogen 2 is a dipole-dipole interaction.
   (2) Using known results of E&M, write down the form of this interaction energy in terms of **R**, $\mathbf{r_1}$ and $\mathbf{r_2}$, where $\mathbf{r_1}$ is the position of electron 1, and $\mathbf{r_2}$ is the position of electron 2, both measured relative to the position of their respective partner protons. Do not derive any formula. Simply use your favorite E&M book (or use Google) to find the electric field **E** due to a dipole, and use the fact that the energy of another dipole μ in that field **E** is $-\mu\cdot\mathbf{E}$. How does this energy depend on R?
   (3) The energy expression obtained in (2) gives the perturbation Hamiltonian operator H' of two weakly interacting hydrogen atoms. The unperturbed ground state wave function can be simply written as $|0\rangle = |1s\rangle_1|1s\rangle_2$, where the subscript 1 means hydrogen 1 etc. (In principle, the wave function should be written in ways to take into account of the identical nature of electrons 1 and 2, and all conclusions here remain true even if we do that, but here we for simplicity assume electrons 1 and 2 as non-identical.) Simply from the spherical symmetry of the 1s orbital, show that the first order perturbation correction to the energy eigenvalue vanishes.
   (4) Show that the 2nd order perturbation correction is finite, is negative and goes as $1/R^6$. In doing so, write down the wave function, or wave functions, of the first excited states that contribute to the 2nd order correction, in the bracket notation given above. Again, do this without doing any actual integral calculation for matrix elements of H', but only by noting symmetry of involved orbitals and H'.

   [Note: Although done for hydrogen atoms for simplicity, this proof of the form of van-der-Waals interaction is readily generalized for any neutral non-diploar objects interacting at a large distance.]

   [Hint: This is what is meant by the "symmetry property." As you learned from quantum mechanics or modern physics or introductory chemistry, an s orbital wave function depends on the radial distant r only, while wave functions for p orbitals, i.e. px, py, pz orbitals, depend on (r, x), (r, y), and (r, z), respectively. Thus, s orbitals remain unchanged by all reflection operations (e.g. reflection which is substitution by x -> -x), rotations or inversion. However, p orbitals do change under some of these operations. Consideration of changes of p orbitals under reflections (e.g. x->-x in the integral) or inversion would be sufficient to examine whether matrix elements in the perturbation expression vanishes or not.]

2. [Ewald Sums] Read, understand and summarize section 11.3.1 of Marder, i.e. show in detail how the Madelung constant α (eq. 11.22) is expressed in terms of numerically nice series (eq. 11.21) starting from numerically not-so-nice series (eq. 11.14).

3. We work with s and p orbitals belonging to the same principal quantum number in this problem. (1) By linear combinations of s, p_x and p_y orbitals, show that one can construct a new orthonormal basis consisting of three orbitals that are identical in shape (sketch it), and at 120 degree with respect to each other in the xy plane. These are the sp^2 orbitals in graphene, responsible for the strong in-plane covalent bonding between carbon atoms. The remaining p_z orbital gives a weak bonding between carbon atoms, and is the most important one for the electronic/thermal properties. (2) Consider a tetrahedron and suppose that the origin is at the center of the tetrahedron. Now, by linear combinations of all s and p orbitals, show that one can construct a new orthonormal basis consisting of orbitals that are identical in shape (sketch it) and point to the four vertices of the tetrahedron. These are the sp^3 orbitals found in diamond, Si, Ge, GaAs, ZnS etc. [Hint: For both (1) and (2), it may be the easiest to construct the p orbitals that point in the desired directions first. Of course, these p orbitals are not yet orthogonal to each other, but show that, by adding the same amount of s orbital to them, thus keeping the shape of orbitals the same, they can be made orthogonal to each other.]

4. It is known that in ice oxygen ions form crystals of tetrahedra, but hydrogen ions are disordered. This is due to the fact that the hydrogen to oxygen bond length is much like that in water molecule, but that this bond length is much shorter than half of oxygen-oxygen bond length. Thus each hydrogen ion has to decide which oxygen ion it “likes” to belong to, and this decision making gives rise to a disorder and a residual entropy. The “ice rules” summarize the situation. (1) The water molecule in ice resembles the water molecule in the gas phase. (2) Each water molecule is oriented so that its two hydrogen atoms are directed approximately toward two of the four oxygen atoms which surround it tetrahedrally, forming hydrogen bonds. (3) Only one hydrogen atom is positioned between each neighbouring oxygen–oxygen pair. Show that the entropy per hydrogen ion under these conditions is $(1/2)k_B\ln(3/2)$. Show that this residual entropy amounts to 1.68 J per mole per K. [To read more about this and spin ice, see Ramirez et al., Nature vol. 399, 333 (1999); Also use the web to find more information.]

5. Problem 20.4 of A&M