Physics 140A-Introduction to Solid State Physics
Winter, 2016
Problem Set 1--Due January 26th

Bonding in Solids--Basic Concepts:

[1] Think about the kind of bonding involved in transition metals with d electrons.

(a) Show that the five 3d electron wave functions given in the table handed out in lecture can be converted to real form so as to lead to functions (atomic orbitals) that can be described as $3d_{z^2}$, $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{yz}$, and $3d_{xz}$.

(b) If you wanted to make a tight-binding (or linear combination of atomic orbitals) molecular orbital in a solid in which Fe is surrounded by six nearest-neighbor O atoms in an "octahedron", that is, with the oxygens located at equal distances along the ±x, ±y, and ±z axes, which of the above real orbitals on Fe would be involved and why? Illustrate your answer with a sketch, including the types of O 2p orbitals involved and how they might overlap to form a good bonding wave functions.

[2] Consider the He atom with ground-state electronic configuration of $1s^2$ as a concrete example of a two-electron system. An approximate wave function for this atom can be written in a determinant form as:

$$\Psi(\vec{r}_1,s_1;\vec{r}_2,s_2) \approx \Phi(\vec{r}_1,s_1;\vec{r}_2,s_2) \equiv \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_{1s}(\vec{r}_1)\alpha(s_1) & \varphi_{1s}(\vec{r}_1)\beta(s_1) \\ \varphi_{1s}(\vec{r}_2)\alpha(s_2) & \varphi_{1s}(\vec{r}_2)\beta(s_2) \end{vmatrix}$$

where φ_{1s} is the appropriate one-electron wave function of the space coordinate $\vec{r}$ = r,θ,ϕ, α and β here represent spin-up (m_S = 1/2) and spin-down (m_S = -1/2) states, respectively, and s_i is the spin coordinate (or really just spin label).

(a) Show that this wave function is anti-symmetric, such that an interchange of the electron labels 1 and 2 changes the sign of the overall function, as required for all electrons.

(b) Multiply out the determinant and show that, although it represents having both electrons in a 1s orbital, we cannot tell whether electron 1 is spin up or spin down or whether electron 2 is spin up or spin down. The electrons are in this sense indistinguishable.

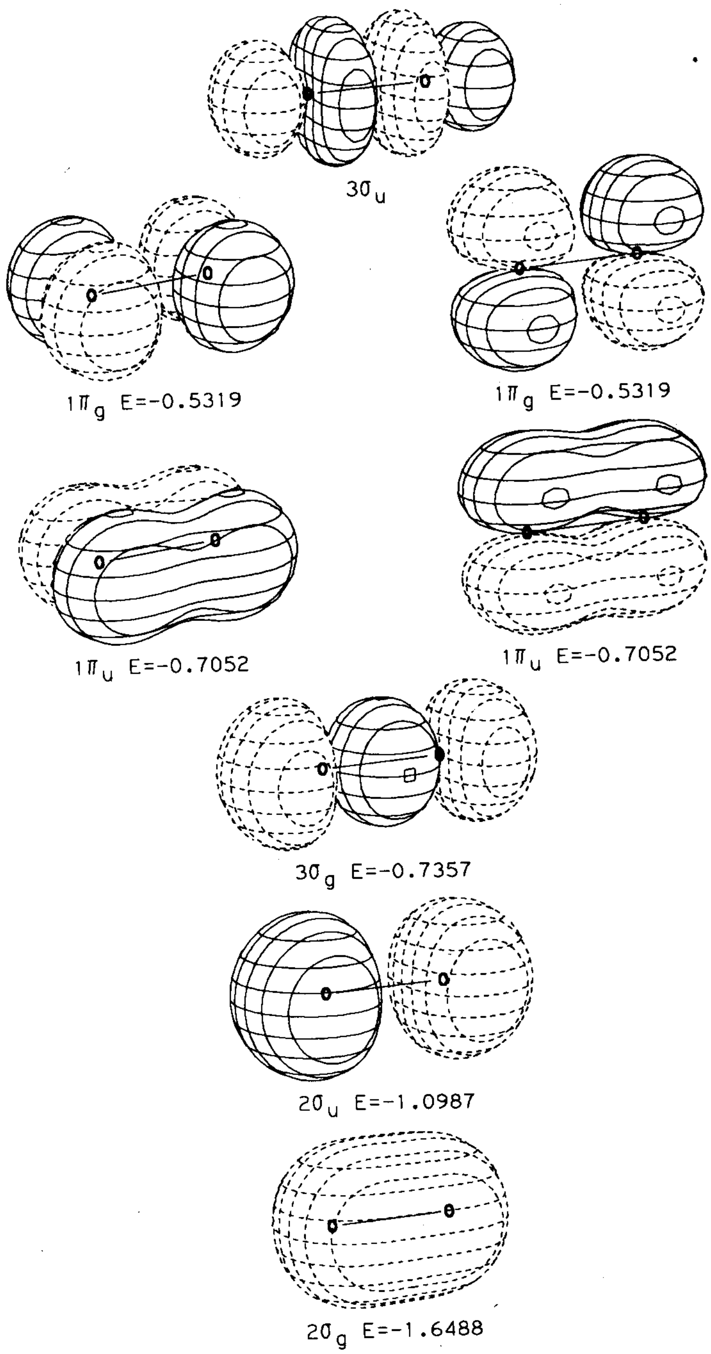
(c) Now replace $\varphi_{1s}(r_i)\beta(s_i)$ with $\varphi_{2s}(r_i)\alpha(s_i)$ (i = 1,2) so as to represent an excited state with configuration $1s^1 2s^1$ with both spins parallel. Show that the probablility of finding both electrons at the same point in space ($r_1 = r_2$; $s_1 = s_2$), as given by $|\Psi|^2$, is zero. This is the origin of the energy-lowering "exchange interaction" that is responsible for magnetism in solids and the first of Hund's rules for filling electronic states.

[3] With the example of CO discussed in lecture as a guide, fill the molecular orbitals of the oxygen molecule (O_2) (as shown on the attached figure and including also the 1s core electrons on each atom *A* and *B*) each with a maximum of two electrons (the Pauli Principle) until you run out of electrons and write down the overall electron configuration as $1s_A^2 1s_B^2 2\sigma_g^2$... Using the same rule for spin pairing in atoms discussed in lecture, can you explain why this molecule has a net spin, and is thus termed "paramagnetic"? Now, try to characterize each orbital as bonding, antibonding, or non-bonding.

[4] Calculate the Madelung constant for an infinite linear ionic chain consisting of alternating positive and negative charges of equal magnitude $q_- = -q_+$ and with equal spacing *a* along the chain.

[5] Problem 1.14 in Omar. Note that there is an error in this problem statement, in that the correct values for the binding energies of the crystal are 183.3 kcal/mole (incorrect) and 7.95 eV/molecule (correct).

For Problem 3--Molecular orbitals for the O_2 molecule: E = the approximate energies of electrons in these orbitals (in atomic units = a.u., with 1 a.u. = 27.21 eV) and the quantum symmetry designations σ_g, σ_u, π_g, and π_u being those appropriate to this linear molecule with two identical atoms.



…plus core electrons $1\sigma_g$ on O atom A at left and $1\sigma_u$ O atom B at right