Exe 6: Excercises for (Physical and) Theoretical Chemistry
WS 2002/03 1^{st} Master semester Excercises No. 6
hand out: Fr., 22.11.02, return: Wed., Nov. 27, mail-box, AR-K6 left side wall.

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22) Inner and outer, core and valence orbitals. Order the n=5, 6, 7 orbitals of the U atom according to their spatial extensions. Order the n=5, 6, 7 orbitals of the U atom according to their energy levels. Which are inner and outer (criterion: smaller or $\geq$ 6s) core and valence (criterion lower or $\geq$ 5f) orbitals?

23) Hybridization. Hybridize two p-orbitals $p_x = f(r,z) \cdot \cos\phi, p_y = f(r,z) \cdot \sin\phi$: $p = \cos\gamma \cdot p_x + \sin\gamma \cdot p_y$. Show that the hybrid orbital p has the same (r,z)-dependence as p_x and p_y and that it has the same ϕ dependence as p_x, except being rotated by some angle.

24) Hybridization and density. Given an s-orbital $s(r)$ and a p_z-Orbital $p(r,\theta)$, and the two sp-hybrides $h_+ = (s+p)/\sqrt{2}$ and $h_- = (s-p)/\sqrt{2}$. Compare the densities of the two original orbitals, $\rho_{orig} = s^2 + p^2$, and of the two hybrides, $\rho_{hyb} = h_+^2 + h_-^2$.

25) d-s paradoxy of transition metal atoms. Discuss a virtual atom with two valence electrons 1 and 2. The total atomic energy is $E_{12} = h_1 + h_2 + g_{12}$, where h means the nuclear attraction energy (strongly negative) of one electron plus its kinetic energy (positive), and g is the interelectronic repulsion (positive). We apply the serious orbital approximation, where the two-electron state function $\Psi(1,2)$ is modeled as a product of two quasi-independent one-electron functions (orbitals) $\phi_a(1), \phi_b(1), \phi_a(2), \phi_b(2)$. Second we introduce the frozen ortibal approximation, where we assume that the state function of quasi-independent electron 1 in orbital a is independent of the state of electron 2.
Discuss the three two-electron states and the two one-electron states:

$d^2 : E_{12} = 2H_d + G_{dd}$ $\quad \epsilon_d = H_d + G_{dd}$
$ds : E_{12} = H_d + H_s + G_{ds}$ $\quad \epsilon_d = H_d + G_{ds}, \epsilon_s = H_s + G_{ds}$
$s^2 : E_{12} = 2H_s + G_{ss}$ $\quad \epsilon_s = H_s + G_{ss}$
$d^1 : E_1 = \epsilon_d = H_d$
$s^1 : E_1 = \epsilon_s = H_s$

Assume $H_s - 12\,\text{eV}$; $H_d = -14\,\text{eV}$; $G_{dd} = +6\,\text{eV}$; $G_{ss} = +4\,\text{eV}$; $G_{ds} = +2\,\text{eV}$.
a) Which two-electron and which one-electron configuration is the most stable, which one is the least stable? Draw a total energy level scheme for the five systems, all E's one above the other.
b) Determine the one-electron energies ϵ. Draw 5 orbital energy level schemes for the five systems, one besides the other one.