Exe 7: Excercises for (Physical and) Theoretical Chemistry
WS 2002/03 1^{st} Master semester Excercises No. 7
hand out: Fr., 29.11.02, return: Wed., Dec. 4, discuss: Fr., Dec. 6. 14 hct.

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26) Given two orthonormal orbital functions $a(r)$ and $b(r)$. What are the permutational symmetry types of the two-particle position functions: $\psi_1 = a(r_1) \cdot a(r_2)$, $\psi_2 = a(r_1) \cdot b(r_2)$, $\psi_3 = a(r_1) \cdot b(r_2) + b(r_1) \cdot a(r_2)$, $\psi_4 = a(r_1) \cdot b(r_2) - b(r_1) \cdot a(r_2)$. Which product functions are permitted a) for a two-boson (spin-zero) system, b) for a two-electron system with pseudoparallel spins, c) for a two-electron system with antiparallel spins, d) for two different particles 1 and 2?

27) Discuss the 2-equal particle functions $\psi_3(1,2)$ and $\psi_4(1,2)$. a) Determine the particle density $\rho(r_1) = \int dr_2 \cdot \psi^*(r_1,r_2) \cdot \psi(r_1,r_2)$. b) Determine the pair-probablity $P(r_1,r_2) = 1/2 \cdot \psi^*(r_1,r_2) \cdot \psi(r_1,r_2)$ for the case $r_1 = r_2 = r$, i.e. two particles at the same position.

28) Let the energy of two independent atoms be modeled as $E_{ats} = t_a/r^2 - Z_{eff}/r + C/r$, where r means the radius of the free atoms. Typical energies are obtained with kinetic energy parameter $t_a = 3.0$, nuclear attraction parameter $Z_{eff} = 4.0$ and electron-electron Coulomb repulsion parameter $C = 1.0$. Make a table with 1) optimized r_a from $dE_{ats}/dr = 0$, 2) resulting $T = t_a/r^2$, 3) $V = -Z_{eff}/r$, 4) $G = c/r$, 5) total potential energy $E_{pot} = V + G$, 6) total energy $E = T + E_{pot}$. In the next two columns discuss the case of molecular pure covalency by electron sharing; the electron delocalization results in relatively reduced kinetic energy: $t_a \rightarrow t_m = 2.6$. First keep the atomic radius; second optimize the radius of the atoms in the molecule and redetermine T, V, G, E_{pot}, E. Then discuss in the next two columns the case of polar ionic bonding by charge transfer; electrons go from the atom with lower electronegativity to the one with higher electronegativity: $t = 3, Z_{eff} = 4.2, C = 1$. Again at first keep the atomic radius r_a fixed, then calculate the energies for optimised atomic radius in the molecule, r_m. (By the way, the "valence bonding" and the dispersion forces are caused by avoiding the near approach of two electrons, electron correlation, of two overlapping, and respectively of two nonoverlapping, electron 'clouds': $C_a \rightarrow C_m = 0.8$)
Always give the atomic-molecular energy changes (i.e. bond energy terms) behind the molecular energies, in parentheses. Which columns obey the virial theorem? Which columns give reasonable total binding energies? Which columns display the "physical origin of the bond energy mechnism"?