# Homework # 7

## Exercise 1

Consider the Li atom. In the previous set of exercises you found the electronic configuration of its ground state using the Auf-bau filling scheme.

- Write all the possible Slater determinants compatible with the electronic configuration you determined (don't forget about the spin!).

## Exercise 2

Suppose you want to determine the electronic structure (the wave function and the energy) of an isolated LiH molecule using the LCAO method. In a very rough approximation you can restrict your basis set to only three orbitals: the $1s$ orbital of the H atom and the $1s$ and $2s$ orbitals of the Li atom. Neglect the electron-electron repulsion.

1. Write the matrix representation of the Hamiltonian in the considered basis.

   For the diagonal matrix elements ($\langle\psi_{1s}^{H}|\hat{H}|\psi_{1s}^{H}\rangle$, $\langle\psi_{1s}^{Li}|\hat{H}|\psi_{1s}^{Li}\rangle$ and $\langle\psi_{2s}^{Li}|\hat{H}|\psi_{2s}^{Li}\rangle$) use the results for hydrogen-like atoms: $E_n = -\frac{Z_{eff}^2}{2n^2}$. Assume that $Z_{eff} \equiv Z$ for the $1s$ electrons of the two atoms, while $Z_{eff} \equiv Z - 2$ for the $2s$ electrons, since the nucleus charge is partially screened by the two $1s$ electrons.

   Suppose that $\langle\psi_{2s}^{Li}|\hat{H}|\psi_{1s}^{H}\rangle$ and $\langle\psi_{1s}^{H}|\hat{H}|\psi_{2s}^{Li}\rangle$ are the only non-zero off-diagonal terms of the Hamiltonian, and take them both equal to $-2.0$ eV.

2. Diagonalize the LCAO Hamiltonian in the chosen basis set.

3. Determine the ground state electronic structure of the molecule (by placing the electrons on its energy levels) and the total energy of the electrons.

4. Evaluate the binding energy of the molecule (i.e. the difference between the total energy determined in the previous point and the sum of the energies of the isolated atoms).

## Exercise 3 – Helium atom

In systems with more than one electron the Schrödinger equation becomes too complicated to be solved exactly due to the effects of the electron-electron interaction. To describe this kind of systems it is then necessary to use approximated methods (e.g. Hartree-Fock, LCAO, etc.). This is already apparent in the helium atom which contains two electrons and a nucleus with two protons.

The Hamiltonian of the Helium atom is given in Hartree atomic units by:

$$H = -\frac{1}{2}\nabla_{\mathbf{r}_1}^2 - \frac{1}{2}\nabla_{\mathbf{r}_2}^2 - \frac{Z}{|\mathbf{r}_1|} - \frac{Z}{|\mathbf{r}_2|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{1}$$

where $Z$ is the atomic number of the nucleus and $\mathbf{r}_1$ and $\mathbf{r}_2$ are the positions of the two electrons.

1. The simplest approximation consists in neglecting the last term in $H$ which describes the repulsion between the two electrons. With this approximation, the Hamiltonian becomes separable and it can be split in two hydrogen-like Hamiltonians. Let's write now the spatial part of the two-electron wavefunction as a simple product of two one-electron wavefunctions:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{n_1 l_1 m_1}(\mathbf{r}_1) \cdot \psi_{n_2 l_2 m_2}(\mathbf{r}_2) \tag{2}$$

   where $\psi_{nlm}(\mathbf{r})$ are the eigenstates of the hydrogen-like Hamiltonian. Write down the eigenvalues for this approximated Hamiltonian. [*Hint: Remember that the eigenvalues of the hydrogen-like Hamiltonian are given by the following expression (in Hartree units):* $E_n = -\frac{Z^2}{2n^2}$*.*]

2. Calculate the ground state energy and comment the difference with the "exact" value: $E_0 = -2.90$ Ha $= -79.0$ eV. Is it a good approximation?

3. Calculate again the ground state energy substituting $Z$ with the effective atomic number $\tilde{Z} = 1.70$. Do we get a better result? Comment the physical meaning of $\tilde{Z}$ and why it is smaller than $Z$.

4. We recall the expression for the ground state hydrogen-like wavefunctions (*1s* orbitals), $\psi_{100}(\mathbf{r}) = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Zr}$. Find the corresponding ground state energy, that is the expectation value of the Hamiltonian also including the electron-electron interaction term, that we neglected in the beginning. Do we get a better estimation of the ground state energy? [*Hint: The following integral is needed:* $\frac{Z^6}{\pi^2} \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \frac{e^{-2Z(r_1+r_2)}}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \frac{5}{8} Z$*.*]

5. Since the Hamiltonian of Eq.(1) does not depend on the spin, it has been possible to separate the spatial and the spin part of the wavefunction

$$\Phi(\zeta_1, \zeta_2) = \Psi(\mathbf{r}_1, \mathbf{r}_2) \cdot \chi(s_1, s_2) \tag{3}$$

   where $\zeta_i = (\mathbf{r}_i, s_i)$. We know that the wavefunction of a system of fermions must be antisymmetric under the exchange of particles. In this sense, Eq.(2) is not the right expression for the spatial part of the 2-particle wavefunction. In the case of the ground state, it turns out that the spatial part of the ground state wavefunction is symmetric. Based on Eq.(2), rewrite it in order to get an expression which is symmetric under the exchange of particles.

6. (**Advanced**) Finally, for a 2-particle system we find 4 possible eigenfunctions of the total spin operator:

$$\chi_1(s_1, s_2) = |\uparrow\uparrow\rangle \tag{4}$$

$$\chi_2(s_1, s_2) = \frac{1}{\sqrt{2}} \Big( |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \Big) \tag{5}$$

$$\chi_3(s_1, s_2) = |\downarrow\downarrow\rangle \tag{6}$$

$$\chi_4(s_1, s_2) = \frac{1}{\sqrt{2}} \Big( |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \Big) \tag{7}$$

$$\tag{8}$$

   which ones are symmetric and which ones are antisymmetric under the exchange of particles? Which of these eigenfunctions can be coupled to the spatial symmetric eigenfunction calculated in the previous point, in order to get a total antysimmetric wavefunction $\Phi(\zeta_1, \zeta_2)$?