

## Solution of homework # 7

### Exercise 1

Using the Auf-bau filling scheme we obtained that the electronic configuration for Li is  $1s^2 2s^1$ . There are two possible Slater determinants:

$$\Psi_1 \rightarrow \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_{1s}(\mathbf{r}_1)\alpha(1) & \psi_{1s}(\mathbf{r}_1)\beta(1) & \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{1s}(\mathbf{r}_2)\alpha(2) & \psi_{1s}(\mathbf{r}_2)\beta(2) & \psi_{2s}(\mathbf{r}_2)\alpha(2) \\ \psi_{1s}(\mathbf{r}_3)\alpha(3) & \psi_{1s}(\mathbf{r}_3)\beta(3) & \psi_{2s}(\mathbf{r}_3)\alpha(3) \end{vmatrix}, \quad (1)$$

$$\Psi_2 \rightarrow \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_{1s}(\mathbf{r}_1)\alpha(1) & \psi_{1s}(\mathbf{r}_1)\beta(1) & \psi_{2s}(\mathbf{r}_1)\beta(1) \\ \psi_{1s}(\mathbf{r}_2)\alpha(2) & \psi_{1s}(\mathbf{r}_2)\beta(2) & \psi_{2s}(\mathbf{r}_2)\beta(2) \\ \psi_{1s}(\mathbf{r}_3)\alpha(3) & \psi_{1s}(\mathbf{r}_3)\beta(3) & \psi_{2s}(\mathbf{r}_3)\beta(3) \end{vmatrix}, \quad (2)$$

where  $\alpha$  and  $\beta$  are the spin-up and spin-down eigenstates of the  $z$  component of spin ( $\hat{S}_z$ ), respectively. The difference between the two Slater determinants is the last column, in which the  $2s$  electron can have the spin up or spin down. It is instructive to explicate one of the Slater determinants, e.g. the first one, which reads:

$$\begin{aligned} \Psi_1 &= \frac{1}{\sqrt{6}} \psi_{1s}(\mathbf{r}_1)\alpha(1) \left[ \psi_{1s}(\mathbf{r}_2)\beta(2)\psi_{2s}(\mathbf{r}_3)\alpha(3) - \psi_{1s}(\mathbf{r}_3)\beta(3)\psi_{2s}(\mathbf{r}_2)\alpha(2) \right] \\ &- \frac{1}{\sqrt{6}} \psi_{1s}(\mathbf{r}_1)\beta(1) \left[ \psi_{1s}(\mathbf{r}_2)\alpha(2)\psi_{2s}(\mathbf{r}_3)\alpha(3) - \psi_{1s}(\mathbf{r}_3)\alpha(3)\psi_{2s}(\mathbf{r}_2)\alpha(2) \right] \\ &+ \frac{1}{\sqrt{6}} \psi_{2s}(\mathbf{r}_1)\alpha(1) \left[ \psi_{1s}(\mathbf{r}_2)\alpha(2)\psi_{1s}(\mathbf{r}_3)\beta(3) - \psi_{1s}(\mathbf{r}_3)\alpha(3)\psi_{1s}(\mathbf{r}_2)\beta(2) \right]. \end{aligned} \quad (3)$$

**Exercise 2**

1. Let us write the Hamiltonian of the system in the basis of the atomic orbitals of H and Li:

$$H = \begin{pmatrix} H_{11} & 0 & H_{13} \\ 0 & H_{22} & 0 \\ H_{31} & 0 & H_{33} \end{pmatrix}, \quad (4)$$

where we have used the following notations:

$$H_{11} = \langle \psi_{1s}^H | \hat{H} | \psi_{1s}^H \rangle,$$

$$H_{22} = \langle \psi_{1s}^{Li} | \hat{H} | \psi_{1s}^{Li} \rangle,$$

$$H_{33} = \langle \psi_{2s}^{Li} | \hat{H} | \psi_{2s}^{Li} \rangle,$$

$$H_{13} = \langle \psi_{1s}^H | \hat{H} | \psi_{2s}^{Li} \rangle,$$

$$H_{31} = \langle \psi_{2s}^{Li} | \hat{H} | \psi_{1s}^H \rangle.$$

Note that  $H_{13} = (H_{31})^*$ , which is consistent with the Hamiltonian operator being Hermitian. The matrix element  $H_{11}$  is the ground-state energy of the hydrogen atom, which as you know from the lectures is equal to  $H_{11} = -\frac{1^2}{2 \cdot 1^2} = -0.5 \text{ Ha} = -13.6 \text{ eV}$ . The matrix elements  $H_{22}$  and  $H_{33}$  are the energies of the  $1s$  and  $2s$  electrons of Li, which are equal to:

$$H_{22} = -\frac{3^2}{2 \cdot 1^2} = -4.5 \text{ Ha} = -122.4 \text{ eV},$$

$$H_{33} = -\frac{(3-2)^2}{2 \cdot 2^2} = -0.125 \text{ Ha} = -3.4 \text{ eV}.$$

The matrix elements  $H_{13}$  and  $H_{31}$  are equal and are set to  $-2.0 \text{ eV}$ . Note that besides the neglect of the electron-electron repulsion, the values of  $H_{13}$  and  $H_{31}$  were fixed arbitrarily, so the result of this exercise cannot be expected to be quantitatively predictive.

2. Within the hypothesis of a diagonal overlap matrix between atomic orbitals of H and Li, solving the variational problem amounts to diagonalizing the Hamiltonian matrix. Thus, we need to diagonalize the matrix Eq. (4), i.e. to find its eigenvalues  $\lambda$ . Hence, we need to construct a determinant and find the solutions of

$$\begin{vmatrix} H_{11} - \lambda & 0 & H_{13} \\ 0 & H_{22} - \lambda & 0 \\ H_{31} & 0 & H_{33} - \lambda \end{vmatrix} = 0, \quad (5)$$

which translates into the following equation:

$$[(H_{11} - \lambda)(H_{33} - \lambda) - H_{31}H_{13}](H_{22} - \lambda) = 0. \quad (6)$$

This equation has three solutions:

$$\lambda_1 = \frac{1}{2} \left( H_{11} + H_{33} + \sqrt{(H_{11} + H_{33})^2 - 4(H_{11}H_{33} - H_{31}H_{13})} \right) = -3.02 \text{ eV}, \quad (7)$$

$$\lambda_2 = \frac{1}{2} \left( H_{11} + H_{33} - \sqrt{(H_{11} + H_{33})^2 - 4(H_{11}H_{33} - H_{31}H_{13})} \right) = -13.98 \text{ eV}, \quad (8)$$

$$\lambda_3 = H_{22} = -122.4 \text{ eV}. \quad (9)$$

Therefore, the diagonalized Hamiltonian has the form:

$$\text{diag}(H) = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}. \quad (10)$$

3. By diagonalizing the Hamiltonian we have found three energy levels that correspond to the three eigenvalues  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$ . These states need to accommodate the 4 electrons of the LiH molecule (two electrons with different spin will occupy each level). The electronic ground-state corresponds to the state where the levels with lowest energy are progressively filled. The lowest energy level, with eigenvalue  $\lambda_3 = H_{22} = \langle \psi_{1s}^{Li} | \hat{H} | \psi_{1s}^{Li} \rangle$ , is the first to be filled, and it corresponds to the lithium 1s orbital. The other two states  $\varphi_1$  and  $\varphi_2$ , with eigenvalues  $\lambda_1$  and  $\lambda_2$ , correspond to hybridized hydrogen-1s and lithium-2s orbitals. Since  $\varphi_2$  has lower energy, it will be filled next. Therefore, the total electronic energy of the LiH molecule is the sum of the energy of the state  $\varphi_2$  and the energy of the lithium-1s core state:

$$E_{\text{LiH}} = 2\lambda_3 + 2\lambda_2 = 2(-122.4 - 13.98) \text{ eV} = -272.76 \text{ eV} . \quad (11)$$

The factor 2 here is due to the fact that there are two electrons with opposite spin in each level.

4. The binding energy of the molecule is:

$$E_{\text{binding}} = E_{\text{LiH}} - E_{\text{H}} - E_{\text{Li}} , \quad (12)$$

where  $E_{\text{LiH}}$  is the ground-state total energy of the LiH molecule given by Eq. (11),  $E_{\text{H}} = H_{11} = -13.6 \text{ eV}$  is the ground-state total energy of the hydrogen atom, and  $E_{\text{Li}}$  is the ground-state total energy of the lithium atom. Since we are neglecting the electron-electron repulsion, we have  $E_{\text{Li}} = 2H_{22} + H_{33} = -248.2 \text{ eV}$  (two times the energy of the Li 1s orbital plus the energy of the 2s orbital). Therefore, we obtain:

$$E_{\text{binding}} = (-272.76 + 13.6 + 248.20) \text{ eV} = -10.96 \text{ eV} . \quad (13)$$

It is important to note that the interaction between the atomic orbitals of H and Li is what allows the formation of the bond and the lowering of energy through “sharing” electrons on molecular states.

**Exercise 3 – Helium atom**

1. When neglecting the electron-electron interaction term, the Hamiltonian can be recasted in the following way

$$\begin{aligned} H &= -\frac{\nabla_1^2}{2} - \frac{Z}{r_1} - \frac{\nabla_2^2}{2} - \frac{Z}{r_2} \\ &= H_1 + H_2, \end{aligned} \tag{14}$$

where  $H_i = -\frac{\nabla_i^2}{2} - \frac{Z}{r_i}$  are hydrogen-like Hamiltonians, in the sense that they have the same structure of the Hamiltonian for the Hydrogen atom with the only difference of the atomic number  $Z$  (of course in the case of Hydrogen  $Z = 1$ ).

This two Hamiltonians act on different Hilbert spaces:  $H_1$  acts only on the Hilbert space defined by the coordinates  $\mathbf{r}_1$  and it does not affect quantities dependent only on  $\mathbf{r}_2$  (it acts like the identity over this Hilbert space), and  $H_2$  acts only on the Hilbert space defined by the coordinates  $\mathbf{r}_2$  and it does not concern quantities dependent only on  $\mathbf{r}_1$ . In this sense the action of  $H$  over the wavefunction  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$  becomes:

$$\begin{aligned} H\Psi(\mathbf{r}_1, \mathbf{r}_2) &= (H_1 + H_2)\psi_{n_1 l_1 m_1}(\mathbf{r}_1)\psi_{n_2 l_2 m_2}(\mathbf{r}_2) \\ &= (E_{n_1} + E_{n_2})\psi_{n_1 l_1 m_1}(\mathbf{r}_1)\psi_{n_2 l_2 m_2}(\mathbf{r}_2) \\ &= \left( -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2} \right) \psi_{n_1 l_1 m_1}(\mathbf{r}_1)\psi_{n_2 l_2 m_2}(\mathbf{r}_2), \end{aligned} \tag{15}$$

and then  $E = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2}$ . Here we have exploited the fact that  $\psi_{nlm}(\mathbf{r})$  is an eigenstate of the hydrogen-like Hamiltonian.

2. The ground state energy is obtained for  $n_1 = n_2 = 1$ , that is:

$$E_0 = -Z^2 \text{ Ha} = -4 \text{ Ha} = -108.8 \text{ eV}.$$

Compared to the exact value  $E_0^{\text{exact}} = -2.90 \text{ Ha}$ , we are committing an error of about 40%, so neglecting the electron-electron interaction term cannot be considered as a good approximation.

3. If we replace  $Z$  with  $\tilde{Z} = 1.70$  we obtain a ground state energy:

$$E_0 = -\tilde{Z}^2 \text{ Ha} = -2.90 \text{ Ha},$$

so we recover the exact value. By neglecting the electron-electron interaction term, we are representing a system where two independent electrons interact with the nucleus without feeling the presence of each other. Since the electron charge is negative, the presence of the other electron would “screen” the positive charge of the nucleus. In this sense  $\tilde{Z}$  represents an effective charge given by the effect of screening of the other electron on the nucleus. From this argument, it is obvious that this effective charge  $\tilde{Z}$  cannot be larger than the original charge  $Z$ .

4. Now we want to calculate the ground state including also the electron-electron interaction term  $V_{ee} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$ :

$$\begin{aligned}
 E_0 &= \langle \psi_{100}\psi_{100} | H_1 + H_2 + V_{ee} | \psi_{100}\psi_{100} \rangle \\
 &= \langle \psi_{100}\psi_{100} | H_1 + H_2 | \psi_{100}\psi_{100} \rangle + \langle \psi_{100}\psi_{100} | V_{ee} | \psi_{100}\psi_{100} \rangle \\
 &= \left( -\frac{Z^2}{2} - \frac{Z^2}{2} \right) + \frac{Z^6}{\pi^2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{e^{-2Z(r_1+r_2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} \\
 &= -Z^2 + \frac{5}{8}Z = -2.75 \text{ Ha.}
 \end{aligned} \tag{16}$$

So we get a better estimation of the ground state density but we still do not recover the exact value. The reason is that to calculate the expectation value of the Hamiltonian we have used a wavefunction which does not represent the real ground state. The wavefunctions  $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{n_1 l_1 m_1}(\mathbf{r}_1) \psi_{n_2 l_2 m_2}(\mathbf{r}_2)$  are the eigenstates of the Hamiltonian when the electron-electron interaction term is neglected, and in particular  $\psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2)$  is the ground state. When including also  $V_{ee}$ , there is no reason to think that they are still eigenfunctions of the Hamiltonian (actually they are not!) and so the relative expectation value cannot be correct. Moreover, from the variational principle we know that the calculated energy cannot be lower than the exact one, and indeed we get a higher energy.

5. In order to make the wavefunction  $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{n_1 l_1 m_1}(\mathbf{r}_1) \psi_{n_2 l_2 m_2}(\mathbf{r}_2)$  either symmetric or antisymmetric, we can simply sum or subtract the same product with the two particle interchanged, that is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_{n_1 l_1 m_1}(\mathbf{r}_1) \psi_{n_2 l_2 m_2}(\mathbf{r}_2) \pm \psi_{n_1 l_1 m_1}(\mathbf{r}_2) \psi_{n_2 l_2 m_2}(\mathbf{r}_1)], \tag{17}$$

where the factor  $\frac{1}{\sqrt{2}}$  ensures the usual normalization condition. If we want a symmetric function then we take the sum, if we want an antisymmetric function we take the difference. Since we are dealing with fermions, the whole wavefunction  $\Phi(\zeta_1, \zeta_2)$  must be antisymmetric under exchange of particles. On the other hand, there is no particular restriction on the symmetry of the spatial part (which can also be symmetric), provided that the whole wavefunction  $\Phi(\zeta_1, \zeta_2)$  is still antisymmetric. In the ground state, indeed, the spatial part of the wavefunction is found to be symmetric and so it takes the following form:

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) + \psi_{100}(\mathbf{r}_2) \psi_{100}(\mathbf{r}_1)]. \tag{18}$$

6. (**Advanced**) In the case of  $\chi_1$  and  $\chi_3$  it is trivial to show that they are both symmetric. By exchanging the particles, *i.e.* switching the two spins, we recover exactly the same wavefunction. Let's see what happens in the case of  $\chi_2$  and  $\chi_4$ :

$$\chi_2(s_1, s_2) \longrightarrow \chi_2(s_2, s_1) = \frac{1}{\sqrt{2}} [|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle] = \chi_2(s_1, s_2), \tag{19}$$

$$\begin{aligned}
 \chi_4(s_1, s_2) \longrightarrow \chi_4(s_2, s_1) &= \frac{1}{\sqrt{2}} [|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle] \\
 &= -\frac{1}{\sqrt{2}} [|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle] = -\chi_4(s_1, s_2).
 \end{aligned} \tag{20}$$

So  $\chi_2$  is symmetric too, while  $\chi_4$  is the only one to be antisymmetric. In the ground state the spatial part is symmetric, so in order to have an antisymmetric total wavefunction,

the only possible choice is choosing  $\chi_4$  for the spin part of the wavefunction:

$$\begin{aligned}\Phi_0(\zeta_1, \zeta_2) &= \Psi_0(\mathbf{r}_1, \mathbf{r}_2) \cdot \chi_4(s_1, s_2) \\ &= \frac{1}{\sqrt{2}} [\psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) + \psi_{100}(\mathbf{r}_2)\psi_{100}(\mathbf{r}_1)] \frac{1}{\sqrt{2}} [|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle].\end{aligned}\tag{21}$$