1.6. The Slater-determinant and the angular momentum

$\hat{\mathbf{L}}$ – the total orbital momentum of the electron system

$\hat{\mathbf{S}}$ – the total spin

$\hat{L}_z$ and $\hat{S}_z$ – the $0z$ components

The $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$ and $\hat{S}_z$operators commute with the nonrelativistic Hamiltonian of the system, so they have a common set of eigenstates.

As a consequence ϕ trial functions used in the Hartree-Fock method should be the eigenfunctions of these operators.

$$\begin{aligned}
\hat{L}^2\phi &= L(L+1)\phi && (1)\\
\hat{L}_z\phi &= M_L\phi && (2)\\
\hat{S}^2\phi &= S(S+1)\phi && (3)\\
\hat{S}_z\phi &= M_S\phi. && (4)
\end{aligned}$$

The Slater-determinants do not obey always these requirements. Because these ϕ_1 determinants have been constructed from the spin-orbitals of each electron, these are the eigenfunctions of the one-electron angular momentum operators.

$$\begin{aligned}
\hat{l}_i^2\phi_1 &= l_i(l_i+1)\phi_1 && (5)\\
\hat{l}_{iz}\phi_1 &= m_{il}\phi_1 && (6)\\
\hat{s}_i^2\phi_1 &= s_i(s_i+1)\phi_1 && (7)\\
\hat{s}_{iz}\phi_1 &= m_{is}\phi_1, && (8)
\end{aligned}$$

where $i = \overline{1,N}$ and N being the number of electrons.

We want to construct from the ϕ_1 Slater-determinants wavefunctions being eigenfunctions of the angular momentum operators for the whole electron system. To perform, we have to make a transformation from the one-electron angular momenta representation to the total angular momentum representation. This task can be done by the coupling of angular momenta.

Let's take a simple example of system formed by two particles with angular momenta l_1 and l_2, the total angular momentum being L. The angular momentum state of the system in the one-particle representation may be written with the vector $|l_1 m_{l1} l_2 m_{l2}\rangle$, which corresponds to the wavefunction. In the total angular momentum representation the system can be described by the $|l_1 l_2 L M_L\rangle$ vector, which usually cannot be expressed by a single Slater-determinant, but it obeys the (1)–(4) conditions. The relationship between the two different representations is the following

$$\begin{aligned}
|l_1 l_2 L M_L\rangle &= \sum_{m_{l1} m_{l2}} |l_1 m_{l1} l_2 m_{l2}\rangle\langle l_1 m_{l1} l_2 m_{l2}|l_1 l_2 L M_L\rangle \\
&= \sum_{m_{l1} m_{l2}} C^{LM_L}_{l_1 m_{l1} l_2 m_{l2}} |l_1 m_{l1} l_2 m_{l2}\rangle. && (9)
\end{aligned}$$

Here we have used that the sum of the projectors $|l_1 m_{l1} l_2 m_{l2}\rangle\langle l_1 m_{l1} l_2 m_{l2}|$ for every possible m_{l1} and m_{l2} magnetic quantum numbers with $m_{l1} + m_{l2} = M_L$ projects to the subspace generated by the $|l_1 l_2 L M_L\rangle$ vector, so it does not change this vector. The occurring overlap integrals are the $C^{LM_L}_{l_1 m_{l1} l_2 m_{l2}}$ Clebsch–Gordan coefficients.

If we take into account also the coupling of the spins, the transformation between the total angular momentum representation L and S and the one-electron representation may be done in the following way

$$\begin{aligned} |l_1 l_2 L S M_L M_S\rangle &= \sum_{m_{l1} m_{l2}} \sum_{m_{s1} m_{s2}} C^{LM_L}_{l_1 m_{l1} l_2 m_{l2}} C^{SM_S}_{s_1 m_{s1} s_2 m_{s2}} \\ &\quad \times |l_1 m_{l1} l_2 m_{l2} s_1 m_{s1} s_2 m_{s2}\rangle, \end{aligned} \tag{10}$$

where $s_1 = s_2 = 1/2$.

In case of the multielectron atoms the above coupling of the angular momenta has to be done several times. Finally, the state of the system will be described by a linear combination of the Slater-determinants. The coefficients of these determinants depend on the coupling of the angular momenta.

1.7. Multiconfiguration wavefunctions

The Hartree-Fock method has been an IEA method, each electron moving in a field created by the other electrons. The electron system could be characterized by a single configuration, meaning that one could tell the number of electrons in each one-electron state. The interaction between the electrons not included in the Hartree-Fock approximation is the correlation energy

$$E_{\text{corr}} = E_{\text{exact}} - E_{HF}. \tag{11}$$

This correlation energy has a negative value.

This correlation interaction has been taken into account in the Hylleras-type description of the helium atom. However, this method should be very complicated for many-electron atoms, because we would have $N(N-1)/2$ interactions between the electrons, if N is the number of the electrons.

In the case of atoms with more than 2 electrons is more practical to use a trial function written as the linear combination of more configurations, and the coefficients of these configurations are taken to be variational parameters.

The method is based on the principle that any wavefunction may be expanded in terms of a basis set

$$\Phi = \sum_i c_i \phi_i. \tag{12}$$

Usually the $\{\phi_i\}$ basis is formed by the eigenfunctions of an approximate Hamiltonian, which can be written as a sum of one-electron operators. The basis is usually infinite. In practice we choose a basis set for which the expansion is rapidly convergent, and the coefficients c_i are negligible for greater values of i.

Let's keep the first n terms

$$\Phi = \sum_{i=1}^{n} c_i \phi_i \tag{13}$$

The functional

$$E[\Phi] = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} \tag{14}$$

will depend on n linear parameters

$$E(c_1, c_2, \dots, c_n) = \frac{\langle \sum_i c_i \phi_i | H | \sum_j c_j \phi_j \rangle}{\langle \sum_i c_i \phi_i | \sum_j c_j \phi_j \rangle} = \frac{\sum_{i,j} c_i^* c_j H_{ij}}{\sum_{i,j} c_i^* c_j S_{ij}}. \tag{15}$$

Here we have introduced the

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \tag{16}$$

matrix elements and the

$$S_{ij} = \langle \phi_i | \phi_j \rangle \tag{17}$$

overlap integrals.

Using the Rayleigh–Ritz variational method we can write

$$\frac{\partial E}{\partial c_i^*} = \frac{\sum_j H_{ij} c_j (\sum_{i,j} c_i^* c_j S_{ij}) - \sum_j S_{ij} c_j (\sum_{i,j} c_i^* c_j H_{ij})}{(\sum_{i,j} c_i^* c_j S_{ij})^2} = 0, \tag{18}$$

where $i = \overline{1, n}$. Using the (15) formula we obtain

$$\sum_j c_j H_{ij} - \sum_j c_j S_{ij} E = 0, \tag{19}$$

or

$$\sum_j c_j (H_{ij} - S_{ij} E) = 0, \tag{20}$$

with $i = \overline{1, n}$. If we have an orthonormal basis set $S_{ij} = \delta_{ij}$, and the linear equation system reduces to an eigenvalue problem

$$\sum_j c_j (H_{ij} - \delta_{ij} E) = 0, \tag{21}$$

or in matrix form

$$\begin{bmatrix} H_{11} - E & H_{12} & \cdots & H_{1n} \\ H_{21} & H_{22} - E & \cdots & H_{2n} \\ \vdots & \vdots & & \vdots \\ H_{n1} & H_{n2} & \cdots & H_{nn} - E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix} = 0. \tag{22}$$

The system has nonzero solutions only if the determinant of the matrix is zero

$$\begin{vmatrix} H_{11}-E & H_{12} & \cdots & H_{1n} \\ H_{21} & H_{22}-E & \cdots & H_{2n} \\ \vdots & \vdots & & \vdots \\ H_{n1} & H_{n2} & \cdots & H_{nn}-E \end{vmatrix} = 0. \tag{23}$$

From this nth degree equation the E eigenvalues can be obtained. Introducing the energy values in the (21) system, one can get also the c_i coefficients and the eigenfunctions.

We remark, that in the(13) series one may have only those ϕ_i configurations which ave the same symmetry as the state a Φ, including the angular momentum state.

We take as an example the 1^1S_0 ground state of the helium atom. We construct the state only from configurations with zero total spin and angular momentum, and the wavefunction depending on the spacial coordinates is symmetric under the interchange of the two electrons. So we can exclude from the beginning the $1s2p$ and $2s2p$ configurations.

Let us take the state as a linear combination of 3 configurations

$$1^1S_0 = c_1(1s^2) + c_2(1s2s) + c_3(2p^2). \tag{24}$$

Each configuration has to be written in a way to have the symmetry, spin and orbital momentum of the state. The first configuration is simply

$$(1s^2) = 1s(r_1)1s(r_2). \tag{25}$$

The second one has to be symmetrized

$$(1s2s) = \frac{1}{\sqrt{2}}[1s(r_1)2s(r_2) + 2s(r_1)1s(r_2)]. \tag{26}$$

In the third case we have to find a linear combination of the products to obtain a total orbital momentum $L = 0$. Using the (9) expansion we obtain

$$|1100\rangle = C^{00}_{1\text{-}111}|1\text{-}111\rangle + C^{00}_{1010}|1010\rangle + C^{00}_{111\text{-}1}|111\text{-}1\rangle, \tag{27}$$

or including the numerical values of the Clebsch-Gordan coefficients

$$(2p^2) = \frac{1}{\sqrt{3}}[2p_{-1}(\mathbf{r_1})2p_{+1}(\mathbf{r_2}) - 2p_0(\mathbf{r_1})2p_0(\mathbf{r_2}) + 2p_{+1}(\mathbf{r_1})2p_{-1}(\mathbf{r_2})], \tag{28}$$

where the low index of the orbitals stand for the magnetic quantum number.

2. The stationary perturbation method

2.1. Electrostatic corrections to the Hartree-Fock method

These electrostatic corrections arise from the coupling of the orbital momenta and spins of the individual electrons to the total orbital momentum and spin of the atom. The orbit-orbit and spin-spin interactions have an electrostatic nature, while the spin-orbit interaction is a relativistic effect. We consider the Russel–Saunders (LS) coupling and neglect the spin-orbit interactions.

If we want to obtain the energy of the atom depending on the coupling of the angular momenta (or the values of L and S) we have to choose the wavefunction in order 0 to be the eigenfunctions of $\mathbf{L}^2$, $\mathbf{S}^2$, L_z and S_z. The first-order perturbational correction to the energy will be

$$E_k^{(1)} = \langle kl_1l_2\cdots l_NLSM_LM_S|H'|kl_1l_2\cdots l_NLSM_LM_S\rangle. \tag{29}$$

The H' perturbational potential contains the electron-electron interactions. The $|kl_1l_2\cdots l_NLSM_LM_S\rangle$ states may be expressed as a linear combination of Slater-determinants.

With these kind of perturbational calculations we can deduct the Hund's' rule, meaning that the energy of a given configuration decreases with the increasing value of S. Similarly, it can be shown, that for the same value of spin, the energy is decreasing for increasing value of L.

Let's apply this method for some of the excited states of the helium.

For a triplet state ($S=1$) we write the unperturbed wavefunction as

$$|0l_2L1M_LM_S\rangle = \sum_{m_{s1}m_{s2}} C^{1M_S}_{\frac{1}{2}m_{s1}\frac{1}{2}m_{s2}}|00l_2m_{l2}\tfrac{1}{2}m_{s1}\tfrac{1}{2}m_{s2}\rangle \tag{30}$$

Because $l_1 = m_{l1} = 0$, the total orbital momentum equals the orbital momentum of the excited electron $l_2 = L \equiv l$, $m_{l2} = M_L \equiv m$. Look first at the case $M_S = \pm 1$

$$\begin{aligned} |0ll1m_{l2}\pm 1\rangle &= C^{1\pm 1}_{\frac{1}{2}\pm\frac{1}{2}\frac{1}{2}\pm\frac{1}{2}}|00lm\tfrac{1}{2}\pm\tfrac{1}{2}\tfrac{1}{2}\pm\tfrac{1}{2}\rangle \\ &= |00lm\tfrac{1}{2}\pm\tfrac{1}{2}\tfrac{1}{2}\pm\tfrac{1}{2}\rangle. \end{aligned} \tag{31}$$

The sum over $m_{s1,2}$ reduces to one term, so the Slater-determinant has the required symmetry. Noting with χ the part of the orbitals depending on the spin, we obtain

$$\begin{aligned} \Psi_{1\pm 1}(q_1,q_2) &= \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_{100}(r_1)\chi_{\pm\frac{1}{2}}(1) & \psi_{nlm}(\mathbf{r_1})\chi_{\pm\frac{1}{2}}(1) \\ \psi_{100}(r_2)\chi_{\pm\frac{1}{2}}(2) & \psi_{nlm}(\mathbf{r_2})\chi_{\pm\frac{1}{2}}(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}}[\psi_{100}(r_1)\psi_{nlm}(\mathbf{r_2}) - \psi_{nlm}(\mathbf{r_1})\psi_{100}(r_2)] \\ &\quad \times\chi_{\pm\frac{1}{2}}(1)\chi_{\pm\frac{1}{2}}(2). \end{aligned} \tag{32}$$

If $M_S = 0$, we get

$$\begin{aligned}
|0ll1m0\rangle &= C^{10}_{\frac{1}{2},\frac{1}{2},\frac{1}{2},-\frac{1}{2}}|00lm\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle \\
&\quad + C^{10}_{\frac{1}{2},-\frac{1}{2},\frac{1}{2},\frac{1}{2}}|00lm\tfrac{1}{2}\text{-}\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\rangle \\
&= \frac{1}{\sqrt{2}}\left[|00lm\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle + |00lm\tfrac{1}{2}\ \text{-}\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle\right], \qquad (33)
\end{aligned}$$

where we have used the numerical values of the Clebsch–Gordan coefficients
Writing the Slater-determinants in detail

$$\begin{aligned}
\Psi_{10}(q_1,q_2) &= \frac{1}{2}\left[\begin{vmatrix} \psi_{100}(r_1)\chi_{+\frac{1}{2}}(1) & \psi_{nlm}(\mathbf{r_1})\chi_{-\frac{1}{2}}(1) \\ \psi_{100}(r_2)\chi_{+\frac{1}{2}}(2) & \psi_{nlm}(\mathbf{r_2})\chi_{-\frac{1}{2}}(2) \end{vmatrix}\right. \\
&\quad \left. + \begin{vmatrix} \psi_{100}(r_1)\chi_{-\frac{1}{2}}(1) & \psi_{nlm}(\mathbf{r_1})\chi_{+\frac{1}{2}}(1) \\ \psi_{100}(r_2)\chi_{-\frac{1}{2}}(2) & \psi_{nlm}(\mathbf{r_2})\chi_{+\frac{1}{2}}(2) \end{vmatrix}\right] \\
&= \frac{1}{\sqrt{2}}[\psi_{100}(r_1)\psi_{nlm}(\mathbf{r_2}) - \psi_{nlm}(\mathbf{r_1})\psi_{100}(r_2)] \\
&\quad \times \frac{1}{\sqrt{2}}[\chi_{+\frac{1}{2}}(1)\chi_{-\frac{1}{2}}(2) + \chi_{-\frac{1}{2}}(1)\chi_{+\frac{1}{2}}(2)]. \qquad (34)
\end{aligned}$$

As one may observe, the spin-dependent part of the wavefunction is symmetric.
For the singlet case ($S = 0$) we get for the expansion of the state

$$\begin{aligned}
|0ll1m00\rangle &= \sum_{m_{s1}m_{s2}} C^{00}_{\frac{1}{2}m_{s1}\frac{1}{2}m_{s2}}|00lm\tfrac{1}{2}m_{s1}\tfrac{1}{2}m_{s2}\rangle \\
&= C^{00}_{\frac{1}{2},\frac{1}{2},\frac{1}{2},-\frac{1}{2}}|00lm\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\ \text{-}\tfrac{1}{2}\rangle \\
&\quad + C^{00}_{\frac{1}{2},-\frac{1}{2},\frac{1}{2},\frac{1}{2}}|00lm\tfrac{1}{2}\ \text{-}\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle \\
&= \frac{1}{\sqrt{2}}\left[|00lm\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\ \text{-}\tfrac{1}{2}\rangle - |00lm\tfrac{1}{2}\ \text{-}\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle\right]. \qquad (35)
\end{aligned}$$

Detailing the Slater-determinants

$$\begin{aligned}
\Psi_{00}(q_1,q_2) &= \frac{1}{2}\left[\begin{vmatrix} \psi_{100}(r_1)\chi_{+\frac{1}{2}}(1) & \psi_{nlm}(\mathbf{r_1})\chi_{-\frac{1}{2}}(1) \\ \psi_{100}(r_2)\chi_{+\frac{1}{2}}(2) & \psi_{nlm}(\mathbf{r_2})\chi_{-\frac{1}{2}}(2) \end{vmatrix}\right. \\
&\quad \left. - \begin{vmatrix} \psi_{100}(r_1)\chi_{-\frac{1}{2}}(1) & \psi_{nlm}(\mathbf{r_1})\chi_{+\frac{1}{2}}(1) \\ \psi_{100}(r_2)\chi_{-\frac{1}{2}}(2) & \psi_{nlm}(\mathbf{r_2})\chi_{+\frac{1}{2}}(2) \end{vmatrix}\right] \\
&= \frac{1}{\sqrt{2}}[\psi_{100}(r_1)\psi_{nlm}(\mathbf{r_2}) + \psi_{nlm}(\mathbf{r_1})\psi_{100}(r_2)] \\
&\quad \times \frac{1}{\sqrt{2}}[\chi_{+\frac{1}{2}}(1)\chi_{-\frac{1}{2}}(2) - \chi_{-\frac{1}{2}}(1)\chi_{+\frac{1}{2}}(2)] \qquad (36)
\end{aligned}$$

So the spin-dependent part of the wavefunction is antisymmetric, while the spatial part is symmetric. The $\langle\Psi_{SM_S}|H'|\Psi_{SM_S}\rangle$ correction will depend on S. The higher the S, the lower will be the energy.

We give an example also for the dependence of the energy on L. Let's consider an atom with two p electrons on its outer shell. If these are equivalent (has the same principal and orbital quantum numbers), the possible terms are ${}^1S$, ${}^1D$ and ${}^3P$. Taking into account the previous discussions, the triplet state will have the lowest energy. We will compare the energy of the two singlet terms, in order to investigate the L-dependence

We may take only the spatial part of the wavefunctions

$$|11LM_L\rangle = \sum_{m_{l1},m_{l2}} C^{LM_L}_{1m_{l1}1m_{l2}} |1m_{l1}1m_{l2}\rangle. \tag{37}$$

If $L = 0$

$$|1100\rangle = \frac{1}{\sqrt{3}} \left[|111\text{-}1\rangle - |1010\rangle + |1\text{-}111\rangle \right]. \tag{38}$$

In the H' perturbational potential only the term containing the interaction of the two electrons $1/r_{12}$ will depend on L.

$$\begin{aligned} \langle 1100|\frac{1}{r_{12}}|1100\rangle &= \frac{1}{3}\Big[2\langle 111\text{-}1|\frac{1}{r_{12}}|111\text{-}1\rangle + \langle 1010|\frac{1}{r_{12}}|1010\rangle \\ &\quad +2\langle 111\text{-}1|\frac{1}{r_{12}}|1\text{-}111\rangle - 4\langle 1010|\frac{1}{r_{12}}|111\text{-}1\rangle \Big]. \end{aligned} \tag{39}$$

The matrix elements can be calculated with the known method. For the first two terms from the expansion of $1/r_{12}$ remain only $l = 0,\ 2,\ m_l = 0$ for the third term $l = 2$, $m_l = 2$, while for the last one $l = 2$, $m_l = 1$. Performing the calculations we get

$$\begin{aligned} \langle 1100|\frac{1}{r_{12}}|1100\rangle &= \int_0^\infty dr_1 r_1^2 R_p(r_1)^2 \int_0^\infty dr_2 r_2^2 R_p(r_2) \frac{1}{r_>} \\ &+ \frac{2}{5}\int_0^\infty dr_1 r_1^2 R_p(r_1)^2 \int_0^\infty dr_2 r_2^2 R_p(r_2) \frac{r_<^2}{r_>^3}. \end{aligned} \tag{40}$$

If $L = 2$, the form of the (37) expansion depends on the value of M_L. But the energy without any external field cannot depend on M_L, and we can choose a value, for example $M_L = 2$

$$|l_1 = 1, l_2 = 1, L = 2, M_L = 2\rangle = |l_1 = 1, m_{l1} = 1, l_2 = 1, m_{l2} = 1\rangle, \tag{41}$$

and the matrix element of $1/r_{12}$ will be

$$\begin{aligned} &\langle l_1 = 1, l_2 = 1, L = 2, M_L = 2|\frac{1}{r_{12}}|l_1 = 1, l_2 = 1, L = 2, M_L = 2\rangle = \\ &= \langle l_1 = 1, m_{l1} = 1, l_2 = 1, m_{l2} = 1|\frac{1}{r_{12}}|l_1 = 1, m_{l1} = 1, l_2 = 1, m_{l2} = 1\rangle \\ &= \int_0^\infty dr_1 r_1^2 R_p(r_1)^2 \int_0^\infty dr_2 r_2^2 R_p(r_2) \frac{1}{r_>} \\ &\quad + \frac{1}{25}\int_0^\infty dr_1 r_1^2 R_p(r_1)^2 \int_0^\infty dr_2 r_2^2 R_p(r_2) \frac{r_<^2}{r_>^3} \end{aligned} \tag{42}$$

All radial integrals are positive, so the energy of the $L = 2$ state will be lower than that with $L = 0$ because $1/25 < 2/5$.