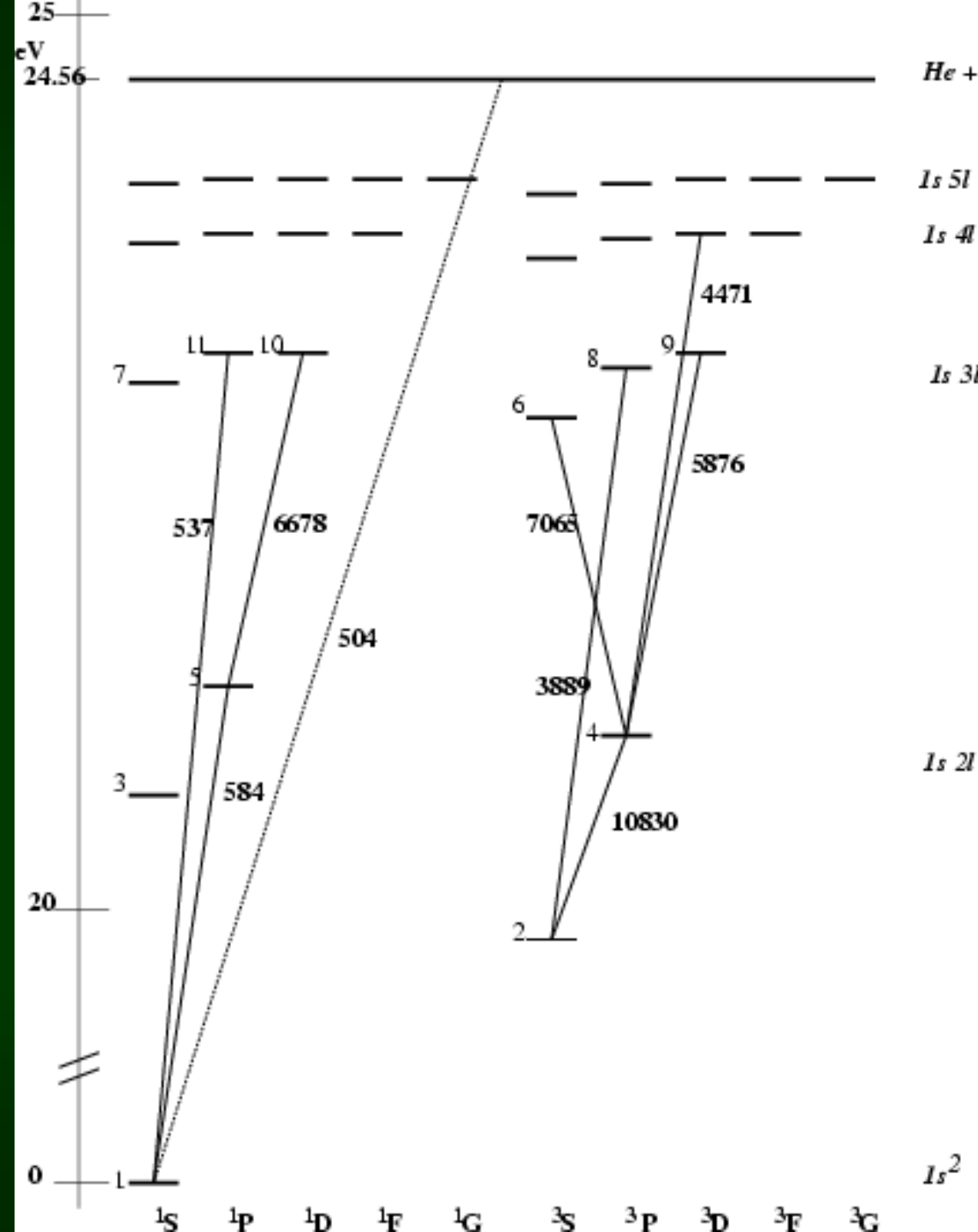


The Helium atom

Excited states



Excited states

Beside the energy minimization we have to impose additionally the orthogonality condition to the ground state, and to all states with lower energy.

In many cases orthogonality comes from the different symmetry properties of the wavefunctions.

2^3S triplet state

spin dependent part – symmetric

spacial part – antisymmetric

$$\phi_{2^3S}(r_1, r_2) = N[u_{1s}(r_1)v_{2s}(r_2) - v_{2s}(r_1)u_{1s}(r_2)], \quad (15)$$

Typical trial functions

$$u_{1s}(r) = e^{-\alpha r} \quad (16)$$

$$v_{2s}(r) = \left(1 - \frac{\beta r}{2}\right) e^{-\frac{\beta r}{2}}. \quad (17)$$

The energy function

$$E(\alpha, \beta) = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \quad (18)$$

Variational conditions

$$\frac{\partial E}{\partial \alpha} = 0; \quad \frac{\partial E}{\partial \beta} = 0. \quad (19)$$

We obtain $\alpha = 2,01$ and $\beta = 1,53$

Similar situation with 2^1P and 2^3P states

$$\phi_{2^{1,3}P}(\mathbf{r}_1, \mathbf{r}_2) = N_{\pm} [u_{1s}(r_1)v_{2pm}(\mathbf{r}_2) \pm v_{2pm}(\mathbf{r}_1)u_{1s}(r_2)]. \quad (20)$$

with $m = 0, \pm 1$.

$$u_{1s}(r) = e^{-\alpha r} \quad (21)$$

$$v_{2pm}(\mathbf{r}) = r e^{-\frac{\beta r}{2}} Y_{1m}(\hat{\mathbf{r}}). \quad (22)$$

2^1P - $\alpha = 2,00$ and $\beta = 0,97$,

2^3P - $\alpha = 1,99$ and $\beta = 1,09$.

In case of the 2^1S state we have to impose orthogonality to the ground state.

We take the trial function

$$\phi'_{2^1S}(r_1, r_2) = N [u_{1s}(r_1)v_{2s}(r_2) + v_{2s}(r_1)u_{2s}(r_2)] \quad (23)$$

and orthogonalize it

$$\phi_{2^1S} = \phi'_{2^1S} - \phi_{1^1S} \langle \phi_{1^1S} | \phi'_{2^1S} \rangle \quad (24)$$

The perturbational method

The Hamiltonian is split into two parts

$$H^0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2}, \quad (11)$$

$$H' = \frac{1}{r_{12}}. \quad (12)$$

$$\Psi(r_1, r_2) = \psi_{1s}(r_1)\psi_{1s}(r_2). \quad (13)$$

$$H^0 = H_1^0 + H_2^0, \quad (14)$$

a

$$H^0\Psi = E_0\Psi \quad (15)$$

The Schrödinger-equation can be separated

$$H_i^0\psi_{1s}(r_i) = E_i\psi_{1s}(r_i); \quad i = 1, 2 \quad (16)$$

or

$$\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right)\psi_{1s}(r_i) = E_i\psi_{1s}(r_i); \quad i = 1, 2. \quad (17)$$

hydrogenlike ion

$$E_i = -\frac{Z^2}{2} \quad (18)$$

$$\psi_{1s}(r_i) = \sqrt{\frac{Z^3}{\pi}} e^{-Zr_i}. \quad (19)$$

0th order

$$E_0 = E_1 + E_2 = -Z^2 \quad (20)$$

1st order

$$\begin{aligned} E^{(1)} &= \langle \Psi(r_1, r_2) | H' | \Psi(r_1, r_2) \rangle \\ &= \langle \psi_{1s}(r_1) \psi_{1s}(r_2) | \frac{1}{r_{12}} | \psi_{1s}(r_1) \psi_{1s}(r_2) \rangle. \end{aligned} \quad (21)$$

Result:

$$E^{(1)} = \frac{5}{8}Z \quad (22)$$

$$E = -Z^2 + \frac{5}{8}Z = -2,750 \text{ hartree} = -74,83 \text{ eV} \quad (23)$$

Experimental: $-2,90372$ hartree

The excited states

$$\Psi_k(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2). \quad (24)$$

Parahelium ($S = 0$) the spin part is antisymmetric, the spatial wavefunction is symmetric

Orthohelium ($S = 1$) the spin part is symmetric, the spatial wavefunction is antisymmetric

The unperturbed wavefunction

$$\Psi_k^+(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)]; \quad S = 0 \quad (25)$$

$$\Psi_k^-(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)]; \quad S = 1, \quad (26)$$

ψ_a and ψ_b hydrogenlike functions

$$E_{n_a n_b}^0 = -\frac{Z^2}{2} \left(\frac{1}{n_a^2} + \frac{1}{n_b^2} \right). \quad (27)$$

$$n_a = 1, n_b \equiv n$$

$$E_n^0 = -\frac{Z^2}{2} \left(1 + \frac{1}{n^2} \right). \quad (28)$$

$2n^2$ times degenerated unperturbed states

$$H' = 1/r_{12}$$

$$\det(\langle \Psi_{nlm}^\pm | H' | \Psi_{nl'm'}^\pm \rangle - \delta_{ll'} \delta_{mm'} \delta_{\pm\pm} E_n^{(1)}) = 0. \quad (29)$$

All nondiagonal elements will be zero

$$\begin{aligned} \langle \Psi_{nlm}^+ | \frac{1}{r_{12}} | \Psi_{nl'm'}^- \rangle &= \\ &= \frac{1}{2} [\langle \psi_{100} \psi_{nlm} | \frac{1}{r_{12}} | \psi_{100} \psi_{nl'm'} \rangle + \langle \psi_{nlm} \psi_{100} | \frac{1}{r_{12}} | \psi_{100} \psi_{nl'm'} \rangle \\ &\quad - \langle \psi_{100} \psi_{nlm} | \frac{1}{r_{12}} | \psi_{nl'm'} \psi_{100} \rangle - \langle \psi_{nlm} \psi_{100} | \frac{1}{r_{12}} | \psi_{nl'm'} \psi_{100} \rangle] \\ &= 0, \end{aligned} \quad (30)$$

and

$$\begin{aligned} \langle \Psi_{nlm}^\pm | \frac{1}{r_{12}} | \Psi_{nl'm'}^\pm \rangle &= \langle \psi_{100} \psi_{nlm} | \frac{1}{r_{12}} | \psi_{100} \psi_{nl'm'} \rangle \\ &\quad \pm \langle \psi_{100} \psi_{nlm} | \frac{1}{r_{12}} | \psi_{nl'm'} \psi_{100} \rangle, \end{aligned} \quad (31)$$

different from 0 only, if $l = l'$ and $m = m'$

The corrections are obtained by the diagonal elements

$$\begin{aligned}
 E_{nl\pm}^{(1)} &= \langle \Psi_{nlm}^{\pm} | H' | \Psi_{nl'm'}^{\pm} \rangle \\
 &= \langle \psi_{100} \psi_{nlm} | \frac{1}{r_{12}} | \psi_{100} \psi_{nlm} \rangle \\
 &\quad \pm \langle \psi_{nlm} \psi_{100} | \frac{1}{r_{12}} | \psi_{nlm} \psi_{100} \rangle \\
 &= J_{nl} \pm K_{nl}.
 \end{aligned} \tag{32}$$

J_{nl} Coulomb term

K_{nl} exchange term

$$J_{nl} = \int_0^{\infty} dr_2 r_2^2 R_{nl}^2(r_2) \int_0^{\infty} dr_1 r_1^2 R_{10}^2(r_1) \frac{1}{r_{>}} \tag{33}$$

$$\begin{aligned}
 K_{nl} &= \frac{1}{2l+1} \int_0^{\infty} dr_2 r_2^2 R_{10}(r_2) R_{nl}(r_2) \\
 &\quad \times \int_0^{\infty} dr_1 r_1^2 R_{10}(r_1) \frac{r_{<}^l}{r_{>}^{l+1}} R_{nl}(r_1),
 \end{aligned} \tag{34}$$

Finally

$$E_{nl\pm} = -\frac{Z^2}{2} \left(1 + \frac{1}{n^2} \right) + J_{nl} \pm K_{nl} \tag{35}$$

The energy of the ortho (triplet) state will be lower than the energy of the para (singlet) state

The Hartree method

General method for multielectron atoms

IEA – instead the real Hamiltonian

$$H = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j} \frac{1}{r_{ij}} \quad (25)$$

we take a sum of one-electron Hamiltonians

$$H_{\text{IE}} = \sum_{i=1}^N \left[-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + V(\mathbf{r}_i) \right]. \quad (26)$$

$V(\mathbf{r}_i)$ – screening potential created by the other electrons.

If we write the Schrödinger equation in this approximation

$$H_{\text{IE}} \phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E_{\text{IE}} \phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (27)$$

the equation can be separated into N one-electron equations

$$\left[-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + V(\mathbf{r}_i) \right] u_{a_i}(\mathbf{r}_i) = \epsilon_i u_{a_i}(\mathbf{r}_i), \quad (28)$$

with

$$\phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = u_{a_1}(\mathbf{r}_1) u_{a_2}(\mathbf{r}_2) \cdots u_{a_N}(\mathbf{r}_N). \quad (29)$$

In order to find the wavefunctions and the energy we use the variational method

$$\begin{aligned} E[\phi] &= \langle \phi | H | \phi \rangle \\ &= \langle u_{a_1}(\mathbf{r}_1) u_{a_2}(\mathbf{r}_2) \cdots u_{a_N}(\mathbf{r}_N) | \left[\sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j} \frac{1}{r_{ij}} \right] \right. \\ &\quad \left. \times | u_{a_1}(\mathbf{r}_1) u_{a_2}(\mathbf{r}_2) \cdots u_{a_N}(\mathbf{r}_N) \rangle. \end{aligned} \quad (30)$$

The wavefunctions are normalized

$$\langle u_{a_i}(\mathbf{r}) | u_{a_i}(\mathbf{r}) \rangle = 1; \quad i = \overline{1, N}. \quad (31)$$

We can write

$$\begin{aligned} E[\phi] &= \sum_{i=1}^N \langle u_{a_i}(\mathbf{r}_i) | \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) | u_{a_i}(\mathbf{r}_i) \rangle \\ &\quad + \sum_{i<j} \langle u_{a_i}(\mathbf{r}_i) u_{a_j}(\mathbf{r}_j) | \frac{1}{r_{ij}} | u_{a_i}(\mathbf{r}_i) u_{a_j}(\mathbf{r}_j) \rangle \\ &= \sum_i I_{a_i} + \sum_{i<j} J_{a_i a_j}. \end{aligned} \quad (32)$$

Where

$$I_{a_i} = \langle u_{a_i}(\mathbf{r}_i) | \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) | u_{a_i}(\mathbf{r}_i) \rangle, \quad (33)$$

one-electron integral, and

$$J_{a_i a_j} = \langle u_{a_i}(\mathbf{r}_i) u_{a_j}(\mathbf{r}_j) | \frac{1}{r_{ij}} | u_{a_i}(\mathbf{r}_i) u_{a_j}(\mathbf{r}_j) \rangle. \quad (34)$$

Coulomb-integral.

We have to find the minimum of the functional with a supplementary condition

$$\delta E[\phi] = 0; \quad \langle u_{a_i} | u_{a_i} \rangle = 1. \quad (35)$$

Using the Lagrange multiplier method

$$\delta(E[\phi] - \sum_i E_{a_i} \langle u_{a_i} | u_{a_i} \rangle) = 0. \quad (36)$$

E_{a_i} – Lagrange coefficients As we have shown in the first chapter, it is sufficient to make the variations for the bra vectors

$$\begin{aligned}
& \sum_i \left[\langle \delta u_{a_i} | \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) | u_{a_i} \rangle \right. \\
& \quad + \sum_{j>i} \langle \delta u_{a_i} u_{a_j} | \frac{1}{r_{ij}} | u_{a_i} u_{a_j} \rangle + \sum_{j>i} \langle u_{a_i} \delta u_{a_j} | \frac{1}{r_{ij}} | u_{a_i} u_{a_j} \rangle \\
& \quad \left. - E_{a_i} \langle \delta u_{a_i} | u_{a_i} \rangle \right] = 0. \quad (37)
\end{aligned}$$

Changing i and j in the second sum of the Coulomb-integral, one can write

$$\sum_i \langle \delta u_{a_i} | \left[-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + \sum_{j \neq i} \langle u_{a_j} | \frac{1}{r_{ij}} | u_{a_j} \rangle - E_{a_i} \right] | u_{a_i} \rangle = 0. \quad (38)$$

This should be valid for any δu_{a_i} , so we obtain

$$\left[-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + \sum_{j \neq i} \langle u_{a_j} | \frac{1}{r_{ij}} | u_{a_j} \rangle \right] u_{a_i}(\mathbf{r}_i) = E_{a_i} u_{a_i}(\mathbf{r}_i), \quad (39)$$

where $i = \overline{1, N}$

– Hartree equations

Electron i is moving in the field of the nucleus $-Z/r_i$ and the field created by the other electrons $\sum_{j \neq i} \langle u_{a_j} | 1/r_{ij} | u_{a_j} \rangle$. So E_{a_i} is the energy of electron i in state a_i .

Solving this system is much more complicated than solving the usual Schrödinger equation. The potential depends on the u_{a_j} functions, so these integro-differential equations are coupled.

Solution: self-consistent field method

- calculating the potential using some $u_{a_j}^0$ trial functions
- solving the equations using these potentials obtaining $u_{a_j}^1$
- repeating the procedure until the equations become self-consistent

The Hartree method is not consistent with the Pauli exclusion principle because the (29) function is not antisymmetric.

Because different electrons generally move in different potentials, the Hartree functions usually are not orthogonal to each other.