Continuation of the simple variational method for the He

The matrix element can be calculated as

$$\langle \psi_{1s}(\mathbf{r_1})\psi_{1s}(\mathbf{r_2})|H|\psi_{1s}(\mathbf{r_1})\psi_{1s}(\mathbf{r_2})\rangle = -\frac{\alpha^2}{2} - \frac{\alpha^2}{2}$$

$$-(Z-\alpha)\int_0^\infty r_1^2 dr_1 \frac{1}{r_1}R_{1s}^2(r_1) - (Z-\alpha)\int_0^\infty r_2^2 dr_2 \frac{1}{r_2}R_{1s}^2(r_2)$$

$$+\int_0^\infty dr_1 r_1^2 R_{1s}^2(r_1)\int_0^\infty dr_2 r_2^2 \frac{1}{r_>}R_{1s}^2(r_2), \tag{1}$$

We obtain R_{1s} from the ψ_{1s} by separating the $Y_{00} = 1/\sqrt{4\pi}$ orbital part.

$$R_{1s}(r) = 2\alpha^{3/2}e^{-\alpha r}. \tag{2}$$

Introducing this function, for the $E(\alpha)$ we obtain

$$E(\alpha) = -\alpha^2 - 2(Z-\alpha)4\alpha^3\int_0^\infty dr r e^{-2\alpha r}$$

$$+16\alpha^6\int_0^\infty dr_1 r_1^2 e^{-2\alpha r_1}\left[\frac{1}{r_1}\int_0^{r_1} dr_2 r_2^2 e^{-2\alpha r_2} + \int_{r_1}^\infty dr_2 r_2 e^{-2\alpha r_2}\right]. \tag{3}$$

Performing the integrations

$$E(\alpha) = -\alpha^2 - 2(Z-\alpha)\alpha + \frac{5}{8}\alpha = \alpha^2 - 2Z\alpha + \frac{5}{8}\alpha. \tag{4}$$

We obtain the energy minimum if

$$\frac{\partial E}{\partial \alpha} = 0, \tag{5}$$

meaning

$$2\alpha - 2Z + \frac{5}{8} = 0, \tag{6}$$

$$\alpha = Z - \frac{5}{16} = 1,6875. \tag{7}$$

The energy of the ground state will be

$$E_{0v} = -\left(Z - \frac{5}{16}\right)^2 = -2,8477 \text{ hartree} = -77,456 \text{ eV} \tag{8}$$

While the experimental value is

$$E_{0k} = -2,904 \text{ hartree} = -79,00 \text{ eV}, \tag{9}$$

The variational method using more parameters

Hylleras

$$s = \quad r_1 + r_2; \quad 0 \le s \le \infty \tag{10}$$

$$t = \quad r_1 - r_2; \quad -\infty \le \infty \tag{11}$$

$$u = \quad r_{12}; \quad 0 \le u \le \infty. \tag{12}$$

Trial function

$$\phi_{s,t,u} = e^{-\alpha s} \sum_{i,j,k=0}^{n} c_{i,2j,k} s^i t^{2j} u^k. \tag{13}$$

$c_{i,2j,k}$, α - parameters

Frankowski and Pekeris - 1024 parameters

$$E_0 = -2,90372437703 \text{ hartree.} \tag{14}$$

– exact value

1.3. The excited states of He

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

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

Typical trial functions

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

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

The energy function

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

Variational conditions

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

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

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

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

with $m = 0, \pm 1$.

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

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

$2^1 P$ – $\alpha = 2,00$ and $\beta = 0,97$,
$2^3 P$ – $\alpha = 1,99$ and $\beta = 1,09$.

In case of the $2^1 S$ state we have to impose orthogonality to the ground state. We take the trial function

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

and orthogonalize it

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

1.4. The Hartree method

General method for multielectron atoms

IEA – instead the real Hamiltonian

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

we take a sum of one-electron Hamiltonians

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

$V(\mathbf{r_i})$ – screaning potential created by the other electrons.
If we write the Schrödinger equation in this approximation

$$H_{\text{IE}}\phi(\mathbf{r_1}, \mathbf{r_2}, ..., \mathbf{r_N}) = E_{\text{IE}}\phi(\mathbf{r_1}, \mathbf{r_2}, ..., \mathbf{r_N}), \tag{27}$$

the equation can be separated into N one-electron equations

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

with

$$\phi(\mathbf{r_1}, \mathbf{r_2}, ..., \mathbf{r_N}) = u_{a_1}(\mathbf{r_1})u_{a_2}(\mathbf{r_2})\cdots u_{a_N}(\mathbf{r_N}). \tag{29}$$

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

$$
\begin{aligned}
E[\phi] \;&=\; \langle \phi | H | \phi \rangle \\
&=\; \langle u_{a_1}(\mathbf{r_1})u_{a_2}(\mathbf{r_2})\cdots u_{a_N}(\mathbf{r_N})| \left[\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{i<j}\frac{1}{r_{ij}}\right] \\
&\qquad\qquad\qquad \times |u_{a_1}(\mathbf{r_1})u_{a_2}(\mathbf{r_2})\cdots u_{a_N}(\mathbf{r_N})\rangle. \quad (30)
\end{aligned}
$$

The wavefunctions are normalized

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

We can write

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

Where

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

one-electron integral, and

$$J_{a_i a_j} = \langle u_{a_i}(\mathbf{r_i})u_{a_j}(\mathbf{r_j})|\frac{1}{r_{ij}}|u_{a_i}(\mathbf{r_i})u_{a_j}(\mathbf{r_j})\rangle. \tag{34}$$

Coulomb-integral.

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

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

Using the Lagrange multiplier method

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

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

$$
\begin{aligned}
\sum_{i} \Bigg[\langle \delta u_{a_i}| &\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) |u_{a_i}\rangle \\
&+ \sum_{j>i} \langle \delta u_{a_i} u_{a_j}|\frac{1}{r_{ij}}|u_{a_i} u_{a_j}\rangle + \sum_{j>i} \langle u_{a_i}\delta u_{a_j}|\frac{1}{r_{ij}}|u_{a_i} u_{a_j}\rangle \\
&\hspace{6cm} -E_{a_i}\langle \delta u_{a_i}|u_{a_i}\rangle \Bigg] = 0.
\end{aligned} \tag{37}
$$

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

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

4

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

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

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.