Hartree-Foch equation in atomic physics

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Douglas Hartree (27 March 1897 – 12 February 1958) was an English mathematician and physicist most famous for the development of numerical analysis and its application to the Hartree-Fock equation of atomic physics.

Douglas Hartree was born in Cambridge, England. His father, William, was a lecturer in engineering at the University of Cambridge. He wanted his son to be mathematician. Hartree attended St John's College in Cambridge but the first Wold War interrupted his studies. After the end of World War I, Hartree returned to Cambridge and graduated his education in 1922.

In 1921, a visit by Niels Bohr to Cambridge inspired Hartree to apply his numerical skills to Bohr’s theory of the atom, for which he obtained his PhD in 1926 – his advisor was Ernest Rutherford. I remind you that Bohr's model of the hydrogen atom is based on the nonclassical assumption that an electron travels in specific shells, or orbits, around the nucleus. This model of hydrogen was suggested to the physical society in 1913.

With the publication of Schrödinger’s equation in 1926, Hartree was able to apply his knowledge of differential equations and numerical analysis to the new quantum theory. He derived the Hartree equations for the distribution of electrons in an atom and proposed the self-consistent field method for their solution.

The self-consisted field method of Hartree

$$Li\left(1s^2, 2s; {}^2S_0\right)$$

$$\left\{\left(-\frac{\hbar^2}{2m}\Delta_1 - \frac{3e^2}{r_1}\right) + \left(-\frac{\hbar^2}{2m}\Delta_2 - \frac{3e^2}{r_2}\right) + \left(-\frac{\hbar^2}{2m}\Delta_3 - \frac{3e^2}{r_3}\right) + \left(\frac{e^2}{\left|\vec{r}_1 - \vec{r}_2\right|} + \frac{e^2}{\left|\vec{r}_1 - \vec{r}_3\right|} + \frac{e^2}{\left|\vec{r}_2 - \vec{r}_3\right|}\right)\Psi\left(\vec{r}_1, \vec{r}_2, \vec{r}_3\right)\right\} = E\Psi\left(\vec{r}_1, \vec{r}_2, \vec{r}_3\right).$$

$$\Psi\left(\vec{r}_1, \vec{r}_2, \vec{r}_3\right) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\psi_3(\vec{r}_3)$$

D. R. Hartree, *Proc. Camb. Phil. Soc.* **24,** 89 (1928); **24,** 111 (1928)

$$\hat{H}(\vec{r}_i) = -\frac{\hbar^2}{2m}\Delta_i - \frac{3e^2}{r_i}$$

$$U = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_3|} + \frac{e^2}{|\vec{r}_2 - \vec{r}_3|}$$

$$\begin{aligned}
&\psi_2(\vec{r}_2)\psi_3(\vec{r}_3)\hat{H}\left(\vec{r}_1\right)\psi_1(\vec{r}_1) + \psi_1(\vec{r}_1)\psi_3(\vec{r}_3)\hat{H}\left(\vec{r}_2\right)\psi_2(\vec{r}_2) \\
&+\psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\hat{H}\left(\vec{r}_3\right)\psi_3(\vec{r}_3) + U\psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\psi_3(\vec{r}_3) \\
&= E\psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\psi_3(\vec{r}_3).
\end{aligned}$$

$$\psi_2^*(\vec{r}_2)\psi_3^*(\vec{r}_3); \quad \psi_1^*(\vec{r}_1)\psi_3^*(\vec{r}_3); \quad \psi_1^*(\vec{r}_1)\psi_2^*(\vec{r}_2);$$

$$\left[-\frac{\hbar^2}{2m}\Delta_1-\frac{3e^2}{r_1}+e^2\int\frac{\left|\psi_2(\vec{r}_2)\right|^2}{\left|\vec{r}_1-\vec{r}_2\right|}d\vec{r}_2+e^2\int\frac{\left|\psi_3(\vec{r}_3)\right|^2}{\left|\vec{r}_1-\vec{r}_3\right|}d\vec{r}_3-E_1\right]\psi_1(\vec{r}_1)=0$$

$$\left[-\frac{\hbar^2}{2m}\Delta_2-\frac{3e^2}{r_2}+e^2\int\frac{\left|\psi_1(\vec{r}_1)\right|^2}{\left|\vec{r}_2-\vec{r}_1\right|}d\vec{r}_1+e^2\int\frac{\left|\psi_3(\vec{r}_3)\right|^2}{\left|\vec{r}_2-\vec{r}_3\right|}d\vec{r}_3-E_2\right]\psi_2(\vec{r}_2)=0$$

$$\left[-\frac{\hbar^2}{2m}\Delta_3-\frac{3e^2}{r_3}+e^2\int\frac{\left|\psi_1(\vec{r}_1)\right|^2}{\left|\vec{r}_3-\vec{r}_1\right|}d\vec{r}_1+e^2\int\frac{\left|\psi_2(\vec{r}_2)\right|^2}{\left|\vec{r}_3-\vec{r}_2\right|}d\vec{r}_2-E_3\right]\psi_3(\vec{r}_3)=0$$

$$E=E_1+E_2+E_3$$

$$\left[-\frac{\hbar^2}{2m}\Delta_1-\frac{3e^2}{r_1}+V_1(\vec{r}_1)-E_1\right]\psi_1(\vec{r}_1)=0$$

$$\left[-\frac{\hbar^2}{2m}\Delta_2-\frac{3e^2}{r_2}+V_2(\vec{r}_2)-E_2\right]\psi_2(\vec{r}_2)=0$$

$$\left[-\frac{\hbar^2}{2m}\Delta_3-\frac{3e^2}{r_3}+V_3(\vec{r}_3)-E_3\right]\psi_3(\vec{r}_3)=0$$

$$V_1(\vec{r}_1)=e^2\left[\int\frac{|\psi_2(\vec{r}_2)|^2}{|\vec{r}_1-\vec{r}_2|}d\vec{r}_2+\int\frac{|\psi_3(\vec{r}_3)|^2}{|\vec{r}_1-\vec{r}_3|}d\vec{r}_3\right]$$

$$V_2(\vec{r}_2)=e^2\left[\int\frac{|\psi_1(\vec{r}_1)|^2}{|\vec{r}_2-\vec{r}_1|}d\vec{r}_1+\int\frac{|\psi_3(\vec{r}_3)|^2}{|\vec{r}_2-\vec{r}_3|}d\vec{r}_3\right]$$

$$V_3(\vec{r}_3)=e^2\left[\int\frac{|\psi_1(\vec{r}_1)|^2}{|\vec{r}_3-\vec{r}_1|}d\vec{r}_1+\int\frac{|\psi_2(\vec{r}_2)|^2}{|\vec{r}_3-\vec{r}_2|}d\vec{r}_2\right]$$

$$\hat{H}(\vec{r}_i) = -\frac{\hbar^2}{2m}\Delta_i - \frac{3e^2}{r_i}$$

$$\left(-\frac{\hbar^2}{2m}\Delta_1 - \frac{3e^2}{r_1}\right)\psi_1^{(0)}(\vec{r}_1) = E_1^{(0)}\psi_1^{(0)}(\vec{r}_1)$$

$$\left(-\frac{\hbar^2}{2m}\Delta_2 - \frac{3e^2}{r_2}\right)\psi_2^{(0)}(\vec{r}_2) = E_2^{(0)}\psi_2^{(0)}(\vec{r}_2)$$

$$\left(-\frac{\hbar^2}{2m}\Delta_3 - \frac{3e^2}{r_3}\right)\psi_3^{(0)}(\vec{r}_3) = E_3^{(0)}\psi_3^{(0)}(\vec{r}_3)$$

$$V_1^{(1)}(\vec{r}_1) = e^2\left[\int \frac{\left|\psi_2^{(0)}(\vec{r}_2)\right|^2}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 + \int \frac{\left|\psi_3^{(0)}(\vec{r}_3)\right|^2}{|\vec{r}_1 - \vec{r}_3|} d\vec{r}_3\right]$$

$$V_2^{(1)}(\vec{r}_2) = e^2\left[\int \frac{\left|\psi_1^{(0)}(\vec{r}_1)\right|^2}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 + \int \frac{\left|\psi_3^{(0)}(\vec{r}_3)\right|^2}{|\vec{r}_2 - \vec{r}_3|} d\vec{r}_3\right]$$

$$V_3^{(1)}(\vec{r}_3) = e^2\left[\int \frac{\left|\psi_1^{(0)}(\vec{r}_1)\right|^2}{|\vec{r}_3 - \vec{r}_1|} d\vec{r}_1 + \int \frac{\left|\psi_2^{(0)}(\vec{r}_2)\right|^2}{|\vec{r}_3 - \vec{r}_2|} d\vec{r}_2\right]$$

$$\left[-\frac{\hbar^2}{2m}\Delta_1-\frac{3e^2}{r_1}+V_1^{(1)}(\vec{r}_1)-E_1^{(1)}\right]\psi_1^{(1)}(\vec{r}_1)=0$$

$$\left[-\frac{\hbar^2}{2m}\Delta_2-\frac{3e^2}{r_2}+V_2^{(1)}(\vec{r}_2)-E_2^{(1)}\right]\psi_2^{(1)}(\vec{r}_2)=0$$

$$\left[-\frac{\hbar^2}{2m}\Delta_3-\frac{3e^2}{r_3}+V_3^{(1)}(\vec{r}_3)-E_3^{(1)}\right]\psi_3^{(1)}(\vec{r}_3)=0$$

$$V_1^{(2)}(\vec{r}_1)=e^2\left[\int\frac{\left|\psi_2^{(1)}(\vec{r}_2)\right|^2}{|\vec{r}_1-\vec{r}_2|}d\vec{r}_2+\int\frac{\left|\psi_3^{(1)}(\vec{r}_3)\right|^2}{|\vec{r}_1-\vec{r}_3|}d\vec{r}_3\right]$$

$$V_2^{(2)}(\vec{r}_2)=e^2\left[\int\frac{\left|\psi_1^{(1)}(\vec{r}_1)\right|^2}{|\vec{r}_2-\vec{r}_1|}d\vec{r}_1+\int\frac{\left|\psi_3^{(1)}(\vec{r}_3)\right|^2}{|\vec{r}_2-\vec{r}_3|}d\vec{r}_3\right]$$

$$V_3^{(2)}(\vec{r}_3)=e^2\left[\int\frac{\left|\psi_1^{(1)}(\vec{r}_1)\right|^2}{|\vec{r}_3-\vec{r}_1|}d\vec{r}_1+\int\frac{\left|\psi_2^{(1)}(\vec{r}_2)\right|^2}{|\vec{r}_3-\vec{r}_2|}d\vec{r}_2\right]$$

$$V_1^{(n)}(\vec{r}_1) = e^2 \left[\int \frac{\left| \psi_2^{(n)}(\vec{r}_2) \right|^2}{\left| \vec{r}_1 - \vec{r}_2 \right|} d\vec{r}_2 + \int \frac{\left| \psi_3^{(n)}(\vec{r}_3) \right|^2}{\left| \vec{r}_1 - \vec{r}_3 \right|} d\vec{r}_3 \right]$$

$$V_2^{(n)}(\vec{r}_2) = e^2 \left[\int \frac{\left| \psi_1^{(n)}(\vec{r}_1) \right|^2}{\left| \vec{r}_2 - \vec{r}_1 \right|} d\vec{r}_1 + \int \frac{\left| \psi_3^{(n)}(\vec{r}_3) \right|^2}{\left| \vec{r}_2 - \vec{r}_3 \right|} d\vec{r}_3 \right]$$

$$V_3^{(n)}(\vec{r}_3) = e^2 \left[\int \frac{\left| \psi_1^{(n)}(\vec{r}_1) \right|^2}{\left| \vec{r}_3 - \vec{r}_1 \right|} d\vec{r}_1 + \int \frac{\left| \psi_2^{(n)}(\vec{r}_2) \right|^2}{\left| \vec{r}_3 - \vec{r}_1 \right|} d\vec{r}_2 \right]$$

$$\left[-\frac{\hbar^2}{2m}\Delta_1-\frac{3e^2}{r_1}+V_1^{(n)}(\vec{r}_1)-E_1^{(n)}\right]\psi_1^{(n)}(\vec{r}_1)=0$$

$$\left[-\frac{\hbar^2}{2m}\Delta_2-\frac{3e^2}{r_2}+V_2^{(n)}(\vec{r}_2)-E_2^{(n)}\right]\psi_2^{(n)}(\vec{r}_2)=0$$

$$\left[-\frac{\hbar^2}{2m}\Delta_3-\frac{3e^2}{r_1}+V_3^{(n)}(\vec{r}_3)-E_3^{(n)}\right]\psi_3^{(n)}(\vec{r}_3)=0$$

$$E_1^{(n)} = H_{11}^{(n)} + \int \psi_1^{(n)*}(\vec{r}_1) V_1^{(n)}(\vec{r}_1) \psi_1(\vec{r}_1) d\vec{r}_1$$

$$E_2^{(n)} = H_{22}^{(n)} + \int \psi_2^{(n)*}(\vec{r}_2) V_2^{(n)}(\vec{r}_2) \psi_2(\vec{r}_2) d\vec{r}_2$$

$$E_3^{(n)} = H_{33}^{(n)} + \int \psi_3^{(n)*}(\vec{r}_3) V_3^{(n)}(\vec{r}_3) \psi_3(\vec{r}_3) d\vec{r}_3$$

$$H_{ii}^{(n)} = \int \psi_i^{(n)*}(\vec{r}_i) \left(-\frac{\hbar^2}{2m} \Delta_i - \frac{3e^2}{r_i} \right) \psi_i^{(n)}(\vec{r}_i) d\vec{r}_i$$

$$E^{(n)} = E_1^{(n)} + E_2^{(n)} + E_3^{(n)}$$

$$V_{11}^{(n)} = \int \psi_1^{(n)*}(\vec{r}_1) V_1^{(n)}(\vec{r}_1) \psi_1^{(n)}(\vec{r}_1)$$

$$= e^2 \left[\int \frac{\left|\psi_1^{(n)}(\vec{r}_1)\right|^2 \left|\psi_2^{(n)}(\vec{r}_2)\right|^2}{\left|\vec{r}_1 - \vec{r}_2\right|} d\vec{r}_1 d\vec{r}_2 + \frac{\left|\psi_1^{(n)}(\vec{r}_1)\right|^2 \left|\psi_3^{(n)}(\vec{r}_3)\right|^2}{\left|\vec{r}_1 - \vec{r}_3\right|} d\vec{r}_1 d\vec{r}_3 \right]$$

$$V_{22}^{(n)} = \int \psi_2^{(n)*}(\vec{r}_2) V_2^{(n)}(\vec{r}_2) \psi_2^{(n)}(\vec{r}_2)$$

$$= e^2 \left[\int \frac{\left|\psi_1^{(n)}(\vec{r}_1)\right|^2 \left|\psi_2^{(n)}(\vec{r}_2)\right|^2}{\left|\vec{r}_2 - \vec{r}_1\right|} d\vec{r}_1 d\vec{r}_2 + \frac{\left|\psi_2^{(n)}(\vec{r}_2)\right|^2 \left|\psi_3^{(n)}(\vec{r}_3)\right|^2}{\left|\vec{r}_2 - \vec{r}_3\right|} d\vec{r}_1 d\vec{r}_3 \right]$$

$$V_{33}^{(n)} = \int \psi_3^{(n)*}(\vec{r}_3) V_3^{(n)}(\vec{r}_3) \psi_3^{(n)}(\vec{r}_3) d\vec{r}_3$$

$$= e^2 \left[\int \frac{\left|\psi_1^{(n)}(\vec{r}_1)\right|^2 \left|\psi_3^{(n)}(\vec{r}_3)\right|^2}{\left|\vec{r}_3 - \vec{r}_1\right|} d\vec{r}_1 d\vec{r}_3 + \frac{\left|\psi_2^{(n)}(\vec{r}_2)\right|^2 \left|\psi_3^{(n)}(\vec{r}_3)\right|^2}{\left|\vec{r}_3 - \vec{r}_2\right|} d\vec{r}_2 d\vec{r}_3 \right]$$

$$E^{(n)} = H_{11}^{(n)} + H_{22}^{(n)} + H_{33}^{(n)} + V_{11}^{(n)} + V_{22}^{(n)} + V_{33}^{(n)}$$

$$= H_{11}^{(n)} + H_{22}^{(n)} + H_{33}^{(n)} + 2e^2 \int \frac{\left|\psi_1^{(n)}(\vec{r}_1)\right|^2 \left|\psi_2^{(n)}(\vec{r}_2)\right|^2}{\left|\vec{r}_1 - \vec{r}_2\right|} d\vec{r}_1 d\vec{r}_2$$

$$+2e^2 \int \frac{\left|\psi_1^{(n)}(\vec{r}_1)\right|^2 \left|\psi_3^{(n)}(\vec{r}_3)\right|^2}{\left|\vec{r}_1 - \vec{r}_3\right|} d\vec{r}_1 d\vec{r}_3 + 2e^2 \int \frac{\left|\psi_2^{(n)}(\vec{r}_2)\right|^2 \left|\psi_3^{(n)}(\vec{r}_3)\right|^2}{\left|\vec{r}_2 - \vec{r}_3\right|} d\vec{r}_2 d\vec{r}_3$$

$$E^{(n)}=E_1^{(n)}+E_2^{(n)}+E_3^{(n)}-e^2\left[\int\frac{\left|\psi_1^{(n)}(\vec r_1)\right|^2\left|\psi_2^{(n)}(\vec r_2)\right|^2}{\left|\vec r_1-\vec r_2\right|}d\vec r_1 d\vec r_2+\int\frac{\left|\psi_1^{(n)}(\vec r_1)\right|^2\left|\psi_3^{(n)}(\vec r_3)\right|^2}{\left|\vec r_1-\vec r_3\right|}d\vec r_1 d\vec r_3\right.$$

$$+\int\frac{\left|\psi_2^{(n)}(\vec r_2)\right|^2\left|\psi_3^{(n)}(\vec r_3)\right|^2}{\left|\vec r_2-\vec r_3\right|}d\vec r_2 d\vec r_3$$

$$E=H_{11}+H_{22}+H_{33}+e^2\left[\int\frac{\left|\psi_1(\vec r_1)\right|^2\left|\psi_2(\vec r_2)\right|^2}{\left|\vec r_1-\vec r_2\right|}d\vec r_1 d\vec r_2+\int\frac{\left|\psi_1(\vec r_1)\right|^2\left|\psi_3(\vec r_3)\right|^2}{\left|\vec r_1-\vec r_3\right|}d\vec r_1 d\vec r_3\right.$$
$$\left.+\int\frac{\left|\psi_2(\vec r_2)\right|^2\left|\psi_3(\vec r_3)\right|^2}{\left|\vec r_2-\vec r_3\right|}d\vec r_2 d\vec r_3\right]$$

$$\Psi\left(\vec r_1,\vec r_2,\vec r_3\right)=\psi_1(\vec r_1)\psi_2(\vec r_2)\psi_3(\vec r_3)$$

Many-electron atom

$$\left[\sum_{i=1}^{N}\hat{H}(\vec{r}_i)+\frac{1}{2}\sum_{j=1}^{N}{}' \frac{e^2}{\left|\vec{r}_i-\vec{r}_j\right|}-E\right]\Psi(\vec{r}_1,\vec{r}_2,\ldots\vec{r}_N)=0$$

$$\hat{H}(\vec{r}_i)=-\frac{\hbar^2}{2m}\Delta_i-\frac{Ze^2}{r_i}$$

$$\Psi(\vec{r}_1,\vec{r}_2,\ldots\vec{r}_N)=\psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\ldots\psi_N(\vec{r}_N)$$

$$\left[-\frac{\hbar^2}{2m}\Delta_i-\frac{Ze^2}{r_i}+e^2\sum_{j\neq i}^{N}\int\frac{\left|\psi_j(\vec{r}_j)\right|^2}{\left|\vec{r}_i-\vec{r}_j\right|}d\vec{r}_j-E_i\right]\psi_i(\vec{r}_i)=0$$

$$i=1,2,3,\ldots N$$

$$E = \sum_{i=1}^{N} H_{ii} + e^2 \sum_{j>i}^{N} \int \frac{\left|\psi_i(\vec{r}_i)\right|^2 \left|\psi_j(\vec{r}_j)\right|^2}{\left|\vec{r}_i - \vec{r}_j\right|} d\vec{r}_i d\vec{r}_j$$

$$H_{ii} = \int \psi_{ii}(\vec{r}_i) \left(-\frac{\hbar^2}{2m} \Delta_i - \frac{Ze^2}{r_i} \right) \psi_i(\vec{r}_i) d\vec{r}_i$$

$$V_j(\vec{r}_i) = e^2 \int \frac{\left|\psi_j(\vec{r}_j)\right|^2}{\left|\vec{r}_i - \vec{r}_j\right|} d\vec{r}_j$$

$$\frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} = 4\pi \sum_{l,m} \frac{1}{(2l+1)} \left\{ \begin{matrix} \dfrac{r_i^l}{r_j^{l+1}} \\ \dfrac{r_j^l}{r_i^{l+1}} \end{matrix} \right\} Y_{lm}^*(\vartheta_i, \varphi_i) Y_{lm}(\vartheta_j, \varphi_j)$$

$$\psi_j(\vec{r}_j) = R_{l_j}(r_j) Y_{l_j m_j}(\vartheta_j, \varphi_j)$$

$$V_i(\vec{r}_i) = e^2 \int \frac{\left|\psi(\vec{r}_j)\right|^2}{\left|\vec{r}_i - \vec{r}_j\right|} d\vec{r}_j = 4\pi e^2 \sum_{l,m} \frac{B_{l,m}}{(2l+1)} A_l(r_i) Y_{lm}^*(\vartheta_i, \varphi_i)$$

$$A_l(r_i) = \frac{1}{r_i^{l+1}} \int_0^{r_i} R_{l_j}^2(r_j) r_j^{l+2} dr_j + r_i^l \int_{r_i}^{\infty} R_{l_j}^2(r_j) r_j^{-l+1} dr_j$$

$$B_l = \int Y_{l_j m_j}^*(\vartheta_j, \varphi_j) Y_{l_j m_j}(\vartheta_j, \varphi_j) Y_{lm}(\vartheta_j, \varphi_j) d\Omega_j$$

$$\left[-\frac{\hbar^2}{2m}\Delta_i-\frac{Ze^2}{r_i}+V_i\left(r_i\right)-E_i\right]\psi_i(\vec{r}_i)=0$$

$$\frac{d^2R_{l_i}}{dr^2}+\frac{2}{r_i}\frac{dR_{l_i}}{dr_i}+\frac{2m}{\hbar^2}\left[E_i+\frac{Ze^2}{r_i}-V_i\left(r_i\right)-\frac{\hbar^2 l(l+1)}{2mr_i^2}\right]R_{l_i}=0$$

$$R_{l_i}(r)=\frac{\chi_{l_i}(r_i)}{r_i} \qquad \chi_{l_i}(0)=0$$

$$\frac{d^2\chi_{l_i}}{dr^2}+\frac{2m}{\hbar^2}\left[E_i+\frac{Ze^2}{r_i}-V_i\left(r_i\right)-\frac{\hbar^2 l(l+1)}{2mr_i^2}\right]\chi_{l_i}=0$$

$$i=1,2,3,\ldots N$$

H o m e w o r k

1. Write a system of Hartri equations for the Helium atom being in the ground state

2. Find the first iterative solution of this system

3. Write a system of Hartri-Foch equations for the Helium atom being in the ground state

Vladimir Fock (1898 - 1974) was a Russian physicist who worked in quantum mechanics and quantum electrodynamics

Schrödinger published his two fundamental papers on quantum theory in the spring of 1926 and Fock immediately started to develop the ideas and by the end of the year two of his own important papers on the Schrödinger equation had been published.

The paper devoted to the calculation of wavefunctions and energy terms of atoms was published in 1930.

Hartree-Fock equation

$$\Psi(\xi_1,\xi_1,\ldots\xi_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(\xi_1), & \psi_1(\xi_2), & \psi_1(\xi_3),\ldots & \psi_1(\xi_N)\\ \psi_2(\xi_1), & \psi_2(\xi_2), & \psi_2(\xi_3),\ldots & \psi_2(\xi_N)\\ \cdots & \cdots & \cdots & \cdots\\ \psi_N(\xi_1), & \psi_N(\xi_2), & \psi_N(\xi_3),\ldots & \psi_N(\xi_N)\end{vmatrix}$$

$$\xi\equiv(x,y,z,s_z)$$

$$\psi(\xi)=\varphi(\vec{r})\chi(s_z)$$

V. A. Fok, *Zs. f. Phys.* **61**,126 (1930); **62**, 795 (1930);

$$He(1s,2s;\,^1S)$$

$$\Psi(\xi_1,\xi_2)=\frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_1(\vec r_1)\alpha(1) & \varphi_1(\vec r_2)\alpha(2)\\ \varphi_2(\vec r_1)\beta(1) & \varphi_2(\vec r_2)\beta(2)\end{vmatrix}-\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_1(\vec r_1)\beta(1) & \varphi_1(\vec r_2)\beta(2)\\ \varphi_2(\vec r_1)\alpha(1) & \varphi_2(\vec r_2)\alpha(2)\end{vmatrix}\right]$$

$$=\frac{1}{\sqrt{2}}\left[\varphi_1(\vec r_1)\varphi_2(\vec r_2)+\varphi_1(\vec r_2)\varphi_2(\vec r_1)\right]\frac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}}.$$

$$He(1s,2s;\,^3S)$$

$$\Psi_1(\xi_1,\xi_2)=\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_1(\vec r_1)\alpha(1) & \varphi_1(\vec r_2)\alpha(2)\\ \varphi_2(\vec r_1)\alpha(1) & \varphi_2(\vec r_2)\alpha(2)\end{vmatrix}$$

$$=\frac{1}{\sqrt{2}}\left[\varphi_1(\vec r_1)\varphi_2(\vec r_2)-\varphi_1(\vec r_2)\varphi_2(\vec r_1)\right]\alpha(1)\alpha(2)$$

$$\Psi_2(\xi_1,\xi_2)=\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_1(\vec r_1)\beta(1) & \varphi_1(\vec r_2)\beta(2)\\ \varphi_2(\vec r_1)\beta(1) & \varphi_2(\vec r_2)\beta(2)\end{vmatrix}$$

$$=\frac{1}{\sqrt{2}}\left[\varphi_1(\vec r_1)\varphi_2(\vec r_2)-\varphi_1(\vec r_2)\varphi_2(\vec r_1)\right]\beta(1)\beta(2)$$

$$\Psi_3(\xi_1,\xi_2)=\frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_1(\vec r_1)\alpha(1) & \varphi_1(\vec r_2)\alpha(2)\\ \varphi_2(\vec r_1)\beta(1) & \varphi_2(\vec r_2)\beta(2)\end{vmatrix}+\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_1(\vec r_1)\beta(1) & \varphi_1(\vec r_2)\beta(2)\\ \varphi_2(\vec r_1)\alpha(1) & \varphi_2(\vec r_2)\alpha(2)\end{vmatrix}\right]$$

$$=\frac{1}{\sqrt{2}}\left[\varphi_1(\vec r_1)\varphi_2(\vec r_2)-\varphi_1(\vec r_2)\varphi_2(\vec r_1)\right]\frac{\alpha(1)\beta(2)+\alpha(2)\beta(1)}{\sqrt{2}}.$$

$$He(1s, nl;\, ^{1,3}S)$$

$$\left\{\left(-\frac{\hbar^2}{2m}\Delta_1 - \frac{2e^2}{r_1}\right) + \left(-\frac{\hbar^2}{2m}\Delta_2 - \frac{2e^2}{r_2}\right) + \frac{e^2}{\left|\vec{r}_1 - \vec{r}_2\right|}\right\}\Psi\left(\vec{r}_1, \vec{r}_2\right) = E\Psi\left(\vec{r}_1, \vec{r}_2\right)$$

$$\left(\hat{H}(\vec{r}_1) + \hat{H}(\vec{r}_2) + V\right)\Psi\left(\vec{r}_1, \vec{r}_2\right) = E\Psi\left(\vec{r}_1, \vec{r}_2\right)$$

$$\Phi^{(\pm)} = \frac{1}{\sqrt{2}}\left[\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) \pm \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\right]$$

$$\varphi_2(\vec{r}_2)\hat{H}(\vec{r}_1)\varphi_1(\vec{r}_1)+\varphi_1(\vec{r}_1)\hat{H}(\vec{r}_2)\varphi_2(\vec{r}_2)+V\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)-E\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)$$
$$\pm\varphi_1(\vec{r}_2)\hat{H}(\vec{r}_1)\varphi_2(\vec{r}_1)\pm\varphi_2(\vec{r}_1)\hat{H}(\vec{r}_2)\varphi_1(\vec{r}_2)\pm V\varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)\mp E\varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)=0$$

$$\left[-\frac{\hbar^2}{2m}\Delta_1-\frac{2e^2}{r_1}+H_{22}-e^2\int\frac{\left|\varphi_2(\vec{r}_2)\right|^2}{\left|\vec{r}_1-\vec{r}_2\right|}d\vec{r}_2-E\right]\varphi_1(\vec{r})$$
$$\pm\left[\int\varphi_2^*(\vec{r}_2)\hat{H}(\vec{r}_2)\varphi_1(\vec{r}_2)d\vec{r}_2+\int\varphi_2^*(\vec{r}_2)\frac{e^2}{\left|\vec{r}_1-\vec{r}_2\right|}\varphi_1(\vec{r}_2)d\vec{r}_2\right]\varphi_2(\vec{r}_1)=0$$

$$\left[-\frac{\hbar^2}{2m}\Delta_2-\frac{2e^2}{r_2}+H_{11}-e^2\int\frac{\left|\varphi_1(\vec{r}_1)\right|^2}{\left|\vec{r}_1-\vec{r}_2\right|}d\vec{r}_1-E\right]\varphi_2(\vec{r}_2)$$
$$\pm\left[\int\varphi_1^*(\vec{r}_1)\hat{H}(\vec{r}_1)\varphi_2(\vec{r}_1)d\vec{r}_1+\int\varphi_1^*(\vec{r}_1)\frac{e^2}{\left|\vec{r}_1-\vec{r}_2\right|}\varphi_2(\vec{r}_1)d\vec{r}_1\right]\varphi_1(\vec{r}_1)=0$$

$$E^{(\pm)} = \int \Phi^{(\pm)^*}(\vec{r}_1, \vec{r}_2)\left[\hat{H}(\vec{r}_1) + \hat{H}(\vec{r}_2) + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\right]\Phi^{(\pm)}(\vec{r}_1, \vec{r}_2)d\vec{r}_1 d\vec{r}_2$$

$$= H_{11} + H_{22} + e^2 \int \frac{|\varphi_1(\vec{r}_1)|^2 |\varphi_2(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2$$

$$\pm e^2 \int \frac{\varphi_1^*(\vec{r}_1)\varphi_2(\vec{r}_1)\varphi_2^*(\vec{r}_2)\varphi_1(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2$$

პარაჰელიუმი

$$E = -1.886\, e^2 / a_0$$

$$E_{\exp} = -2.14598\, e^2 / a_0$$

ორთოჰელიუმი

$$E = -1.905\, e^2 / a_0$$

$$E_{exp} = -2.17524\, e^2 / a_0$$

$$H_e\left(1s^2,{}^1S_0\right)$$

$$\psi_i^0(\vec{r}_i) = R_{10}^0(r_i)Y_{00}^0(\vartheta_i,\varphi_i) \qquad i=1,2$$

$$R_{10}^0(r_i) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Z}{a_0}r_i} \qquad Y_{00}^0 = \frac{1}{\sqrt{4\pi}}$$

$$Z=2 \qquad a_0 = \frac{\hbar^2}{me^2} = 0.529\cdot 10^{-8}\ \text{სმ}$$

$$V_i^1(r_i) = e^2\left[\frac{1}{r_i} - e^{-\frac{4}{a_0}r_i}\left(\frac{1}{r_i}+\frac{2}{a_0}\right)\right]$$

$$\frac{d^2R_0^1}{dr_i^2} + \frac{2}{r_i}\frac{dR_0^1}{dr_i} + \frac{2m}{\hbar^2}\left[E_i + \frac{e^2}{r_i} + e^{-\frac{4}{a_0}r_i}\left(\frac{e^2}{r_i}+\frac{2e^2}{a_0}\right)\right]R_0^1 = 0$$

$$r_i > 1$$

$$R_{10}^{1}(r_i) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Z}{a_0} r_i} \qquad Z = 1$$

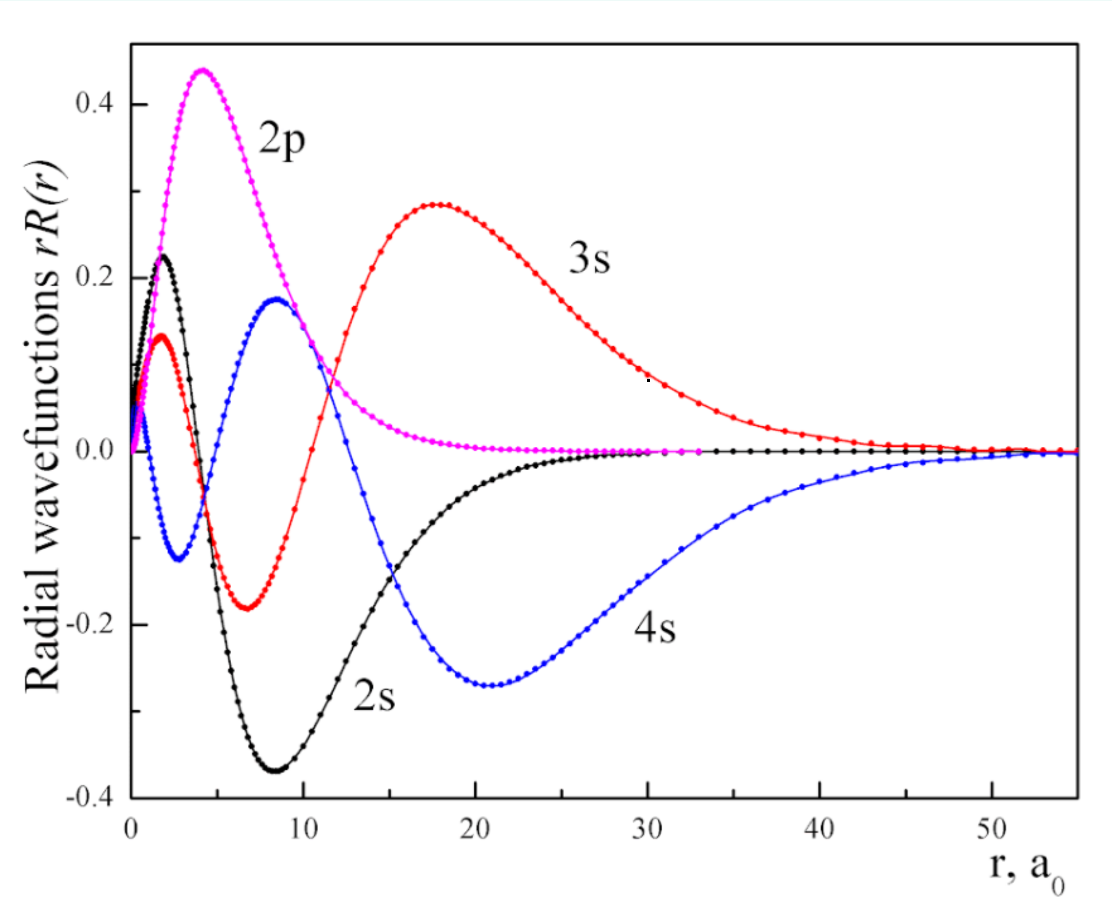
$$r_i < 1$$

$$e^{-\frac{4}{a_0} r_i}\left(\frac{e^2}{r_i} + \frac{2e^2}{a_0}\right) \cong \frac{e^2}{r_i} - \frac{2e^2}{a_0} + O\left(r_i^2\right)$$

$$\frac{d^2 R_0^1}{dr_i^2} + \frac{2}{r_i}\frac{dR_0^1}{dr_i} + \frac{2m}{\hbar^2}\left[E_i^{'} + \frac{2e^2}{r_i} + O\left(r_i^2\right)\right] R_0^1 = 0$$

$$R_{10}^{1}(r_i) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Z}{a_0} r_i}$$

$$Z = 2$$



The normalized wavefunctions of an excited electron of helium obtained in the Hartree-Fock approximation; $a_0 = \hbar^2 / m_e e^2 = 0.529\times10^{-8}$

$$L_i\left(1s^2, 2s; {}^1S_0\right)$$

$$\Psi = C_1\begin{vmatrix} \varphi_1(\vec{r}_1)\alpha(1) & \varphi_1(\vec{r}_2)\alpha(2) & \varphi_1(\vec{r}_2)\alpha(2) \\ \varphi_1(\vec{r}_1)\beta(1) & \varphi_1(\vec{r}_2)\beta(2) & \varphi_1(\vec{r}_2)\beta(2) \\ \varphi_2(\vec{r}_1)\alpha(1) & \varphi_2(\vec{r}_2)\alpha(2) & \varphi_2(\vec{r}_2)\alpha(2) \end{vmatrix} + C_2\begin{vmatrix} \varphi_1(\vec{r}_1)\beta(1) & \varphi_1(\vec{r}_2)\beta(2) & \varphi_1(\vec{r}_2)\beta(2) \\ \varphi_1(\vec{r}_1)\alpha(1) & \varphi_1(\vec{r}_2)\alpha(2) & \varphi_1(\vec{r}_2)\alpha(2) \\ \varphi_2(\vec{r}_1)\alpha(1) & \varphi_2(\vec{r}_2)\alpha(2) & \varphi_2(\vec{r}_2)\alpha(2) \end{vmatrix}$$

$$= \left(C_1 - C_2\right)\begin{vmatrix} \varphi_1(\vec{r}_1)\alpha(1) & \varphi_1(\vec{r}_2)\alpha(2) & \varphi_1(\vec{r}_2)\alpha(2) \\ \varphi_1(\vec{r}_1)\beta(1) & \varphi_1(\vec{r}_2)\beta(2) & \varphi_1(\vec{r}_2)\beta(2) \\ \varphi_2(\vec{r}_1)\alpha(1) & \varphi_2(\vec{r}_2)\alpha(2) & \varphi_2(\vec{r}_2)\alpha(2) \end{vmatrix}.$$

$$C_1 = \pm C_2$$

$$\Psi = \frac{1}{\sqrt{6}}\Bigg[\varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)\varphi_1(\vec{r}_3)\cdot\alpha(1)\frac{\alpha(2)\beta(3)-\alpha(3)\beta(2)}{\sqrt{2}}$$

$$-\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)\varphi_1(\vec{r}_3)\cdot\alpha(2)\frac{\alpha(1)\beta(3)-\alpha(3)\beta(1)}{\sqrt{2}}$$

$$+\varphi_1(\vec{r}_1)\varphi_1(\vec{r}_2)\varphi_2(\vec{r}_3)\cdot\alpha(3)\frac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}}\Bigg].$$

$$\left(\hat{H}_{tot} - E\right)\left[\varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)\varphi_1(\vec{r}_3) - \frac{1}{2}\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)\varphi_1(\vec{r}_3) - \frac{1}{2}\varphi_1(\vec{r}_1)\varphi_1(\vec{r}_2)\varphi_2(\vec{r}_3)\right] = 0$$

$$\left(\hat{H}_{tot} - E\right)\left[\frac{1}{2}\varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)\varphi_1(\vec{r}_3) - \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)\varphi_1(\vec{r}_3) + \frac{1}{2}\varphi_1(\vec{r}_1)\varphi_1(\vec{r}_2)\varphi_2(\vec{r}_3)\right] = 0$$

$$\left(\hat{H}_{tot} - E\right)\left[\frac{1}{2}\varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)\varphi_1(\vec{r}_3) + \frac{1}{2}\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)\varphi_1(\vec{r}_3) - \varphi_1(\vec{r}_1)\varphi_1(\vec{r}_2)\varphi_2(\vec{r}_3)\right] = 0$$

$$\hat{H}_{tot} = \hat{H}(\vec{r}_1) + \hat{H}(\vec{r}_2) + \hat{H}(\vec{r}_3) + V$$

$$\hat{H}(\vec{r}_i) = -\frac{\hbar^2}{2m}\Delta_i - \frac{3e^2}{r_i}$$

$$U = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_3|} + \frac{e^2}{|\vec{r}_2 - \vec{r}_3|}$$

$$\left[-\frac{\hbar^2}{2m}\Delta-\frac{3e^2}{r}-\left(E-H_{11}-H_{22}\right)+\left\langle\varphi_2\varphi_1\middle|U\middle|\varphi_2\varphi_1\right\rangle-\frac{1}{2}\left\langle\varphi_2\varphi_1\middle|U\middle|\varphi_1\varphi_2\right\rangle\right]\varphi_1(\vec{r})$$

$$-\frac{1}{2}\left[H_{21}+\left\langle\varphi_2\varphi_1\middle|U\middle|\varphi_1\varphi_1\right\rangle\right]\varphi_2(\vec{r})=0$$

,

$$\left[-\frac{\hbar^2}{2m}\Delta-\frac{3e^2}{r}-\left(E-H_{11}-H_{22}\right)+\left\langle\varphi_1\varphi_2\middle|V\middle|\varphi_1\varphi_2\right\rangle-\frac{1}{2}\left\langle\varphi_1\varphi_2\middle|U\middle|\varphi_2\varphi_1\right\rangle\right]\varphi_1(\vec{r})$$

$$-\frac{1}{2}\left[H_{21}+\left\langle\varphi_1\varphi_2\middle|U\middle|\varphi_1\varphi_1\right\rangle\right]\varphi_2(\vec{r})=0$$

$$\left[-\frac{\hbar^2}{2m}\Delta-\frac{3e^2}{r}-\left(E-2H_{11}\right)-\left\langle\varphi_1\varphi_1\middle|U\middle|\varphi_1\varphi_1\right\rangle\right]\varphi_2(\vec{r})-\left[H_{12}+\left\langle\varphi_1\varphi_1\middle|U\middle|\varphi_1\varphi_2\right\rangle\right]\varphi_1(\vec{r})=0$$

$$\left\langle\varphi_2\varphi_1\middle|U\middle|\varphi_2\varphi_1\right\rangle=e^2\left[\int\frac{|\varphi_2(\vec{r}_1)|^2|\varphi_1(\vec{r}_2)|^2}{|\vec{r}_1-\vec{r}_2|}d\vec{r}_1d\vec{r}_2+\int\frac{|\varphi_2(\vec{r}_1)|^2}{|\vec{r}_1-\vec{r}_3|}d\vec{r}_1+\int\frac{|\varphi_1(\vec{r}_2)|^2}{|\vec{r}_2-\vec{r}_3|}d\vec{r}_2\right]$$

$$\left\langle\varphi_2\varphi_1\middle|U\middle|\varphi_1\varphi_2\right\rangle=e^2\int\frac{\varphi_2^*(\vec{r}_1)\varphi_1(\vec{r}_1)\varphi_1^*(\vec{r}_2)\varphi_2(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}d\vec{r}_1d\vec{r}_2$$

$$\left\langle\varphi_2\varphi_1\middle|U\middle|\varphi_1\varphi_1\right\rangle=e^2\left[\int\frac{\varphi_2^*(\vec{r}_1)\varphi_1(\vec{r}_1)|\varphi_1(\vec{r}_2)|^2}{|\vec{r}_1-\vec{r}_2|}d\vec{r}_1d\vec{r}_2+\int\frac{\varphi_2^*(\vec{r}_1)\varphi_1(\vec{r}_1)}{|\vec{r}_1-\vec{r}_3|}d\vec{r}_1\right]$$

$$\left\langle\varphi_1\varphi_1\middle|U\middle|\varphi_1\varphi_1\right\rangle=e^2\left[\int\frac{|\varphi_1(\vec{r}_1)|^2|\varphi_1(\vec{r}_2)|^2}{|\vec{r}_1-\vec{r}_2|}d\vec{r}_1d\vec{r}_2+\int\frac{|\varphi_1(\vec{r}_1)|^2}{|\vec{r}_1-\vec{r}_3|}d\vec{r}_1+\int\frac{|\varphi_1(\vec{r}_2)|^2}{|\vec{r}_2-\vec{r}_3|}d\vec{r}_2\right]$$

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Thank you for the attention
and good luck!