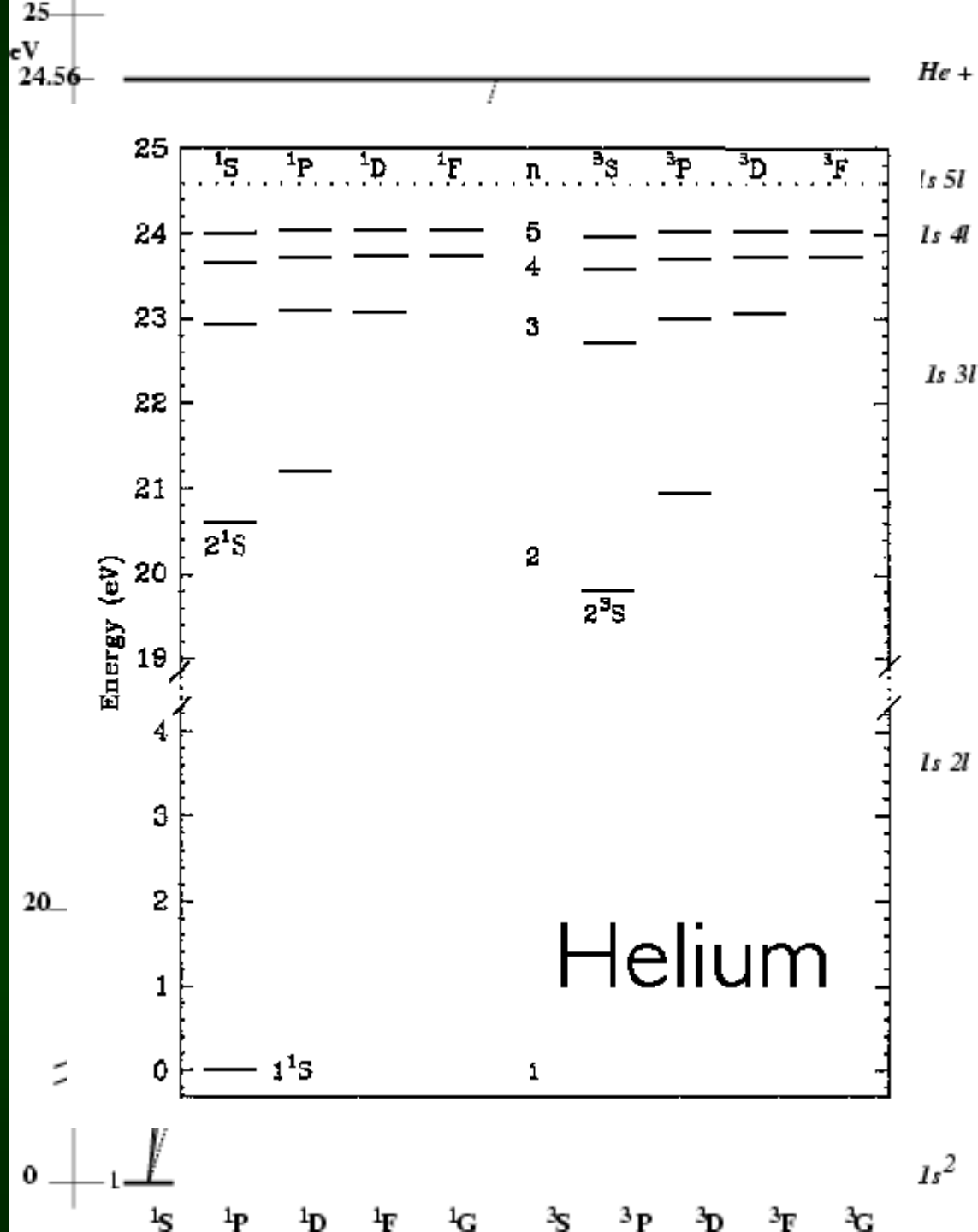


The Helium atom



Variational method

Useful for the determination of energies and wavefunctions of different atomic states.

H – the time-independent Hamiltonian of the system

E_n – eigenenergies

Ψ_n - eigenfunctions

Schrödinger-equation

$$H\Psi_n = E_n\Psi_n \quad (1)$$

ϕ - wavefunction with finite norm

$E[\phi]$ functional

$$E[\phi] = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}. \quad (2)$$

If $\phi = \Psi_n$ than $E[\phi] \equiv E_n$ eigenstates. We prove, that if

$$\phi = \Psi_n + \delta\phi, \quad (3)$$

than

$$\delta E = 0. \quad (4)$$

We make the variation on (2)

$$\begin{aligned} \delta E[\phi] &= \frac{\int \delta\phi^* H\phi d\tau + \int \phi^* H\delta\phi d\tau}{\int \phi^* \phi d\tau} \\ &\quad - \frac{(\int \delta\phi^* \phi d\tau + \int \phi^* \delta\phi d\tau) \int \phi^* H\phi d\tau}{(\int \phi^* \phi d\tau)^2}, \end{aligned} \quad (5)$$

where we have used $\delta(H\phi) = H\delta\phi$. Using (2) and making $\delta E = 0$ one obtains

$$\int \delta\phi^* (H - E)\phi d\tau + \int \phi^* (H - E)\delta\phi d\tau = 0. \quad (6)$$

Making $\delta\phi \rightarrow i\delta\phi$ we get

$$-i \int \delta\phi^* (H - E)\phi d\tau + i \int \phi^* (H - E)\delta\phi d\tau = 0. \quad (7)$$

Using the above two equations, we can write

$$\int \delta\phi^* (H - E)\phi d\tau = 0 \quad (8)$$

$$\int \phi^* (H - E)\delta\phi d\tau = 0. \quad (9)$$

This should be true for any $\delta\phi$, so the equations are equivalent to the Schrodinger-equation

$$(H - E)\phi = 0. \quad (10)$$

Another important property of the (2) functional is, that gives a superior limit for the ground-state energy E_0 of the system.

We expand ϕ in terms of the Ψ_n eigenfunctions of the Hamiltonian H .

$$\phi = \sum_n a_n \Psi_n. \quad (11)$$

Introducing this expansion to (2)

$$E[\phi] = \frac{\sum_n a_n^* a_n \langle \Psi_n | H | \Psi_n \rangle}{\sum_n a_n^* a_n \langle \Psi_n | \Psi_n \rangle} = \frac{\sum_n |a_n|^2 E_n}{\sum_n |a_n|^2}, \quad (12)$$

where we have used $H\Psi_n = E_n\Psi_n$. Subtracting the ground-state energy E_0 , we get

$$E[\phi] - E_0 = \frac{\sum_n |a_n|^2 (E_n - E_0)}{\sum_n |a_n|^2}. \quad (13)$$

Using $E_n \geq E_0$, the right side of the equation is nonnegative, so

$$E_0 \leq E[\phi]. \quad (14)$$

In practice we perform the variation only for a class of functions. E.g.:
Rayleigh–Ritz method

In this case the trial function $\phi = \phi(\alpha_i, \tau)$ depends on some parameters, so

$$E = E(\alpha_i); \quad \overline{i = 1, n}, \quad (15)$$

If we make the variation on the class of of the trial functions, the $\delta E = 0$ condition is equivalent to

$$\frac{\partial E}{\partial \alpha_i} = 0; \quad \overline{i = 1, n} \quad (16)$$

We can use this method also for the excited states by imposing the orthogonality of ϕ to all states with lower energy

$$\langle \phi | \Psi_n \rangle = 0; \quad \overline{n = 0, i - 1}, \quad (17)$$

Simple variational method for the ground state of Helium

We apply the independent electron approximation – product wavefunction

$$\phi(r_1, r_2) = \psi_{1s}(r_1)\psi_{1s}(r_2), \quad (18)$$

Each 1s wavefunction is a hydrogenlike function with 1 parameter – the effective charge α

$$\psi_{1s}(r) = \left(\frac{\alpha^3}{\pi}\right)^{\frac{1}{2}} e^{-\alpha r}. \quad (19)$$

The energy functional:

$$E[\phi] = \langle \phi | H | \phi \rangle. \quad (20)$$

The Hamiltonian:

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \quad (21)$$

where $Z = 2$ is the atomic number

The matrix element can be calculated as

$$\begin{aligned}
 \langle \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) | H | \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) \rangle &= -\frac{\alpha^2}{2} - \frac{\alpha^2}{2} \\
 &- (Z - \alpha) \int_0^\infty r_1^2 dr_1 \frac{1}{r_1} R_{1s}^2(r_1) - (Z - \alpha) \int_0^\infty r_2^2 dr_2 \frac{1}{r_2} R_{1s}^2(r_2) \\
 &+ \int_0^\infty dr_1 r_1^2 R_{1s}^2(r_1) \int_0^\infty dr_2 r_2^2 \frac{1}{r_2} R_{1s}^2(r_2), \tag{1}
 \end{aligned}$$

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

$$\begin{aligned}
 E(\alpha) &= -\alpha^2 - 2(Z - \alpha)4\alpha^3 \int_0^\infty dr r e^{-2\alpha r} \\
 &+ 16\alpha^6 \int_0^\infty dr_1 r_1^2 e^{-2\alpha r_1} \left[\frac{1}{r_1} \int_0^{r_1} dr_2 r_2^2 e^{-2\alpha r_2} + \int_{r_1}^\infty dr_2 r_2 e^{-2\alpha r_2} \right]. \tag{3}
 \end{aligned}$$

Performing the integrations

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

We obtain the energy minimum if

$$\frac{\partial E}{\partial \alpha} = 0, \quad (5)$$

meaning

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

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

The energy of the ground state will be

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

While the experimental value is

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

The variational method using more parameters

Hylleras

$$s = r_1 + r_2; \quad 0 \leq s \leq \infty \quad (10)$$

$$t = r_1 - r_2; \quad -\infty \leq t \leq \infty \quad (11)$$

$$u = r_{12}; \quad 0 \leq u \leq \infty. \quad (12)$$

Trial function

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

$c_{i,2j,k}$, α - parameters

Frankowski and Pekeris - 1024 parameters

$$E_0 = -2,90372437703 \text{ hartree.} \quad (14)$$

- exact value