If we neglect the $1/r_{12}$ term in the hamiltonian $\hat{H}$ of the helium atom, it becomes a sum of two hamiltonians, $\hat{H} = \hat{H}_1 + \hat{H}_2$, where $\hat{H}_1$ depends only on the coordinates of electron 1 and $\hat{H}_2$ depends only on the coordinates of electron 2. As a consequence of that, the wavefunction $\psi(x_1, y_1, z_1, x_2, y_2, z_2) \equiv \psi(1,2)$ can be put in the form of a *product*.

$$\psi(1,2) = \psi_1(1)\psi_2(2)$$

Further, the total energy of the He atom becomes the *sum* of two single-electron energies.

$E = E_1 + E_2$

This is shown on the next two pages.

$$\hat{H}\psi(1,2) = [\hat{H}_1 + \hat{H}_2]\,\psi(1,2) = E\psi(1,2)$$

$$\psi(1,2) \stackrel{?}{=} \psi_1(1)\psi_2(2)$$

Can the 2-electron wavefunction be put in the form of a product of two 1-electron functions (ie, orbitals) when $\hat{H} = (\hat{H}_1 + \hat{H}_2)$? The simplest way to answer this question is to just try and see if it leads to a contradiction.

$$\begin{aligned}\hat{H}\psi(1,2) &= [\hat{H}_1 + \hat{H}_2]\,\psi_1(1)\psi_2(2) \\ &= \hat{H}_1\psi_1(1)\psi_2(2) + \hat{H}_2\psi_1(1)\psi_2(2)\end{aligned}$$

$$\hat{H}\psi_1(1)\psi_2(2) = \psi_2(2)\hat{H}_1\psi_1(1) + \psi_1(1)\hat{H}_2\psi_2(2)$$

$$E\psi_1(1)\psi_2(2) = \psi_2(2)\hat{H}_1\psi_1(1) + \psi_1(1)\hat{H}_2\psi_2(2)$$

$$E = \frac{\hat{H}_1\psi_1(1)}{\psi_1(1)} + \frac{\hat{H}_2\psi_2(2)}{\psi_2(2)}$$

$\psi_1(1)$ and $\psi_2(2)$ depend on different variables: they vary independently of each other. So the only way the rhs of the equation can be constant is if *each term, taken separately, is constant.* Call these two constants E_1 and E_2, then:

$$E = E_1 + E_2$$

$$\hat{H}_1 \psi_1(1) = E_1 \psi_1(1)$$

$$\hat{H}_2 \psi_2(2) = E_2 \psi_2(2)$$

There were no assumptions in the derivation leading up to here, and nothing wrong with the last three equations. This shows that the initial assumption that the wavefunction is a product $\psi_1(1)\,\psi_2(2)$ is correct, provided of course that $\hat{H} = \hat{H}_1 + \hat{H}_2$ (that was the starting point).

Note that the two one-electron equations obtained in the end are exactly like the hydrogenlike problem: the solutions are in Equation 10.17 and Table 10.1.