Variation Method- Helium

If you guess a solution to the Schrödinger Equation, how do you find out how good a guess you have made? $\hat{\mathcal{H}}\Psi_i = E_i\,\Psi_i$ can't be solved exactly:

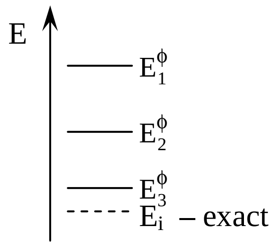
$$\frac{-\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right)\Psi_i + \frac{1}{4\pi\varepsilon_o}\left(-\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}\right)\Psi_i = E_i\Psi_i$$

but you have :

ϕ_1 guess

ϕ_2 better guess

ϕ_3 better yet $\quad E^{\phi} \geq E_i$



The Variation Theorem guarantees that the trial energy is always <u>greater than the exact energy</u>.

$\hat{\mathcal{H}}\Psi_i = E_i\,\Psi_i$

$\int \Psi_i^*\,\hat{\mathcal{H}}\Psi_i\,d\tau = \int \Psi_i^*\,E_i\,\Psi_i\,d\tau$

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solve for E_i: $\quad E_i = \dfrac{\int \Psi_i^*\,\hat{\mathcal{H}}\Psi_i\,d\tau}{\int \Psi_i^*\,\Psi_i\,d\tau}$ $\quad$ is exact

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$$E^{\phi} = \frac{\int \phi^*\hat{\mathcal{H}}\phi\,d\tau}{\int \phi^*\phi\,d\tau}$$

$E^{\phi} \geq E_i$ $\qquad$ by the variation theorem

$\phi_{gs} = \phi_{1s}(r_1)\,\phi_{1s}(r_2) = \dfrac{1}{\pi}\left(\dfrac{Z_{eff}}{a_o}\right)^3 e^{-Z_{eff}\,r_1/a_o}\,e^{-Z_{eff}\,r_2/a_o}$ $\qquad$ Z_{eff} : variation parameter

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$E^{\phi} = \dfrac{\int \phi_{gs}^*\,\hat{\mathcal{H}}\,\phi_{gs}\,d\tau}{\int \phi_{gs}^*\,\phi_{gs}\,d\tau} = \dfrac{e^2}{4\pi\varepsilon_o\,a_o}\left(Z_{eff}^2 - \dfrac{27}{8}\,Z_{eff}\right)$ $\qquad$ see Karplus and Porter 4.1.5

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minimize by changing Z_{eff}: $\quad \dfrac{dE^{\phi}}{dZ_{eff}} = 0 = \dfrac{e^2}{4\pi\varepsilon_o\,a_o}\left(2\,Z_{eff} - {}^{27}/_{8}\right)$

$Z_{eff} = {}^{27}/_{16} = 1.6875$

$E_{gs} = -\,13.6\text{ eV}(Z_{eff}^2/n_1^2 + Z_{eff}^2/n_2^2) = -77.5\text{ eV}$ $\qquad$ (exp. -79.0 eV)

$\phi_{1s}(r_1)$ and $\phi_{1s}(r_2)$ are normalized eigenfunctions of one-electron Hamiltonians with charge Z_{eff} :

$$\left(\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Z_{eff}\,e^2}{4\pi\varepsilon_o r_1}\right)\phi_{1s}(r_1) = E_1\,\phi_{1s}(r_1) \qquad \left(\frac{-\hbar^2}{2m}\nabla_2^2 - \frac{Z_{eff}\,e^2}{4\pi\varepsilon_o r_2}\right)\phi_{1s}(r_2) = E_2\,\phi_{1s}(r_2)$$

normalization: $\quad \int \phi_{1s}^*(r_1)\,\phi_{1s}(r_1)\,d\tau_1 = 1 \qquad \int \phi_{1s}^*(r_2)\,\phi_{1s}(r_2)\,d\tau_2 = 1$

and eigenvalues: $E_1 = -½\left(\dfrac{e^2}{4\pi\varepsilon_o\,a_o}\right)Z_{eff}^2 = -13.6\text{ eV }Z_{eff}^2 \qquad E_2 = -½\left(\dfrac{e^2}{4\pi\varepsilon_o\,a_o}\right)Z_{eff}^2 = -13.6\text{ eV }Z_{eff}^2$

The exact Hamiltonian uses the full nuclear charge Z = 2. We can split the Coulomb portion of the exact Hamiltonian using $Z = Z_{eff} + (Z - Z_{eff})$

$$\left(\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_o r_1}\right)\phi_{1s}(r_1) = \left(\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Z_{eff}\,e^2}{4\pi\varepsilon_o r_1}\right)\phi_{1s}(r_1) - \frac{(Z - Z_{eff})\,e^2}{4\pi\varepsilon_o r_1}\,\phi_{1s}(r_1)$$

$$\left(\frac{-\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_o r_2}\right)\phi_{1s}(r_2) = \left(\frac{-\hbar^2}{2m}\nabla_2^2 - \frac{Z_{eff}\,e^2}{4\pi\varepsilon_o r_2}\right)\phi_{1s}(r_2) - \frac{(Z - Z_{eff})\,e^2}{4\pi\varepsilon_o r_2}\,\phi_{1s}(r_2)$$

Both electrons are in the same 1s-orbital so these two previous equations give the same energies. The electrons are identical, except for spin. To calculate the expectation value of the exact Hamiltonian, $\int \phi_{1s}^*(r_1)\,\phi_{1s}^*(r_2)\,\hat{\mathcal{H}}\,\phi_{1s}(r_1)\,\phi_{1s}(r_2)\,d\tau$, we find $\hat{\mathcal{H}}\,\phi_{1s}(r_1)\,\phi_{1s}(r_2)$ using the last two equations:

$$\hat{\mathcal{H}}\,\phi_{gs} = \phi_{1s}(r_2)\left(\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_o r_1}\right)\phi_{1s}(r_1) + \phi_{1s}(r_1)\left(\frac{-\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_o r_2}\right)\phi_{1s}(r_2) + \frac{e^2}{4\pi\varepsilon_o r_{12}}\,\phi_{1s}(r_1)\phi_{1s}(r_2)$$

$$= -\left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right) Z_{eff}^2\,\phi_{1s}(r_1)\,\phi_{1s}(r_2) - 2\,\frac{(Z - Z_{eff})\,e^2}{4\pi\varepsilon_o r_1}\,\phi_{1s}(r_1)\,\phi_{1s}(r_2) + \frac{e^2}{4\pi\varepsilon_o r_{12}}\,\phi_{1s}(r_1)\phi_{1s}(r_2)$$

The variational energy for our guessed wave function is then:

$$E^\phi = \int \phi_{1s}^*(r_1)\,\phi_{1s}^*(r_2)\,\hat{\mathcal{H}}\,\phi_{1s}(r_1)\,\phi_{1s}(r_2)\,d\tau = -\left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right) Z_{eff}^2 - 2\left\langle \frac{(Z - Z_{eff})\,e^2}{4\pi\varepsilon_o r_1}\right\rangle + \left\langle \frac{e^2}{4\pi\varepsilon_o r_{12}}\right\rangle$$

The first expectation value is the difference in the Coulomb attraction of an electron with a nucleus of charge Z and a nucleus of charge Z_{eff}:

$$-\left\langle \frac{(Z - Z_{eff})\,e^2}{4\pi\varepsilon_o r_1}\right\rangle = -(Z - Z_{eff})\int \phi_{1s}^*(r_1)\,\phi_{1s}^*(r_2)\,\frac{e^2}{4\pi\varepsilon_o\, r_1}\,\phi_{1s}(r_1)\,\phi_{1s}(r_2)\,d\tau_1 d\tau_2$$

$$= -(Z - Z_{eff})\underbrace{\int \phi_{1s}^*(r_2)\,\phi_{1s}(r_2)\,d\tau_2}_{normalization}\;\underbrace{\int \phi_{1s}^*(r_1)\,\frac{e^2}{4\pi\varepsilon_o\, r_1}\,\phi_{1s}(r_1)\,d\tau_1}_{\langle V\rangle}$$

The first integral is the normalization for electron-2. The second integral is the expectation value of the potential energy for a one-electron atom with nuclear charge Z_{eff}, $\langle V\rangle$, see Problem 25.5.

$$-\left\langle \frac{(Z - Z_{eff})\,e^2}{4\pi\varepsilon_o r_1}\right\rangle = -(Z - Z_{eff})\left(\frac{Z_{eff}\,e^2}{4\pi\varepsilon_o\, a_o}\right)$$

We evaluated the expectation value of the electron-electron repulsion for our perturbation treatment of the helium atom. We only need to substitute Z_{eff} for Z:

$$\left\langle \frac{e^2}{4\pi\varepsilon_o r_{12}}\right\rangle = \int \phi_{1s}^*(r_1)\,\phi_{1s}^*(r_2)\,\frac{e^2}{4\pi\varepsilon_o r_{12}}\,\phi_{1s}(r_1)\,\phi_{1s}(r_2)\,d\tau_1 d\tau_2 = \frac{5Z_{eff}}{8}\left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right)$$

Setting Z = 2 gives the final result:

$$E^\phi = \left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right)\left(-Z_{eff}^2 - 2\,ZZ_{eff} + 2\,Z_{eff}^2 + \frac{5Z_{eff}}{8}\right)$$

$$E^\phi = \frac{e^2}{4\pi\varepsilon_o\, a_o}\left(Z_{eff}^2 - \frac{27}{8}\,Z_{eff}\right) = 27.211\text{ eV}\left(Z_{eff}^2 - \frac{27}{8}\,Z_{eff}\right)$$