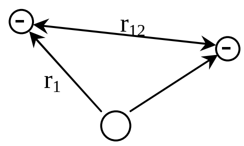
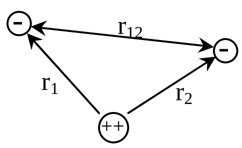
Perturbation Method-Helium



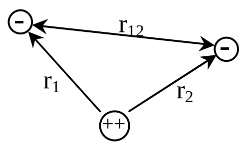
$$\hat{V}(r) = \frac{1}{4\pi\varepsilon_o}\left(-\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}\right)$$

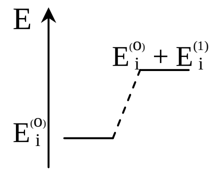
$$\frac{-\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right)\Psi + \frac{1}{4\pi\varepsilon_o}\left(-\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}\right)\Psi = E\Psi$$



$$\lambda\left(\frac{e^2}{4\pi e_o r_{12}}\right) \longrightarrow$$

$$\lambda = 0 \rightarrow 1$$





$E_i^{(0)}$ $\qquad\qquad$ $E_i^{(0)} + E_i^{(1)}$

Get first order correction to the energy:

$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(0)} + \lambda\,\hat{\mathcal{H}}'$

where $\hat{\mathcal{H}}^{(0)}\,\Psi_i^{(0)} = E_i^{(0)}\,\Psi_i^{(0)}$

$E_i \cong E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \ldots$	expand energy in a power series in λ
$E_i^{(1)} = \langle \mathcal{H}' \rangle = \int \Psi_i^{(0)*}\,\hat{\mathcal{H}}'\,\Psi_i^{(0)}\,d\tau$	expectation value of perturbation

He atom: $\quad E_{gs}^{(0)} = E_1 + E_2 = -13.6\text{ eV}(Z^2/n_1^2 + Z^2/n_2^2)$ $\qquad$ $Z = 2$

$\qquad E_{gs} \cong E_1 + E_2 + \left\langle \dfrac{e^2}{4\pi\varepsilon_o r_{12}} \right\rangle$ $\qquad$ see Karplus and Porter 4.1.4

$E_{gs}^{(0)} = -108.0$ eV

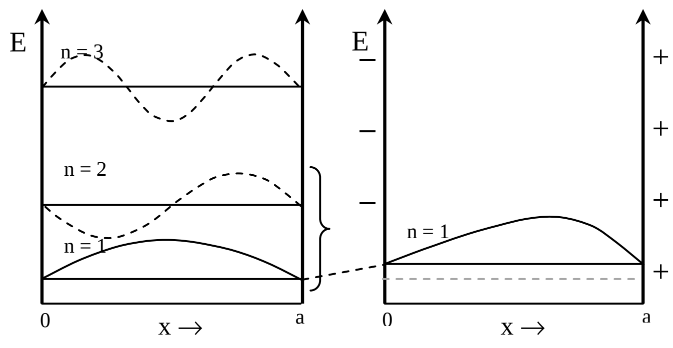
$E_{gs} \cong -74.0$ eV $\qquad$ (exp. -79.0 eV)

A correction to the wave function:

$$\Psi_i^{(1)} \cong \Psi_i^{(0)} + \lambda \sum_{k\neq i} \frac{\mathcal{H}'_{ki}}{E_i^{(0)} - E_k^{(0)}}\,\Psi_k^{(0)}$$

$$\mathcal{H}'_{ki} = \int \Psi_i^{(0)*}\,\hat{\mathcal{H}}'\,\Psi_k^{(0)}\,d\tau$$

The new wave function is a combination of all the other wave functions, but the wave functions that are closest in energy to i are most important.



$$E_i^{(1)} = \int \Psi_{1s}^*(r_1)\,\Psi_{1s}^*(r_2)\,\frac{e^2}{4\pi\varepsilon_o r_{12}}\,\Psi_{1s}(r_1)\,\Psi_{1s}(r_2)\,d\tau_1 d\tau_2 \qquad r_{12} = (r_1^2 + r_2^2 - 2\,r_1 r_2 \cos\theta)^{1/2}$$

$$E_i^{(1)} = \frac{1}{\pi^2}\left(\frac{Z}{a_o}\right)^6 \int e^{-2Zr_1/a_o}\,e^{-2Zr_2/a_o}\,\frac{e^2}{4\pi\varepsilon_o r_{12}}\,r_1^2\,r_2^2 \sin\theta\,dr_1 dr_2\,d\theta\,d\phi$$

$$\left\langle \frac{e^2}{4\pi e_o r_{12}} \right\rangle = \frac{5Z}{8}\left(\frac{e^2}{4\pi\varepsilon_o\,a_o}\right) = \frac{5Z}{8}\left(\frac{m_e\,e^4}{16\pi^2\varepsilon_o^2\,\hbar^2}\right) = \frac{5Z}{8}(27.211\text{ eV}) = 34.01\text{ eV}$$