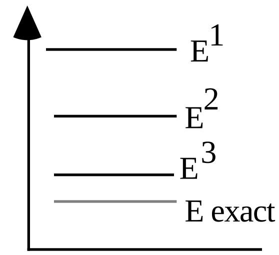
<u>Variation Method- Helium</u>

If you guess a solution to the Schrödinger Equation, how do you find out how good a guess you have made? $H\Psi = E\,\Psi$ can't be solved exactly:
but you have :

$\Psi^{(1)}$ guess

$\Psi^{(2)}$ better guess

$\Psi^{(3)}$ better yet



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

$H\Psi_i = E_i\,\Psi_i$

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

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solve for E_i: $$E_i = \frac{\int \Psi_i^{*}\, H\, \Psi_i\, d\tau}{\int \Psi_i^{*}\, \Psi_i\, d\tau}$$ is exact

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$$E_i^{(1)} = \frac{\int \Psi_i^{(1)*}\, H\, \Psi_i^{(1)}\, d\tau}{\int \Psi_i^{(1)*}\, \Psi_i^{(1)}\, d\tau}$$

$E^{(1)} \geq E$ by the variation theorem

$$\Psi_{gs}^{(1)} = \Psi_1\, \Psi_2 = \left(\frac{1}{\pi}\left(\frac{Z_{eff}}{a_o}\right)^3\right) e^{-Z_{eff}\, r_1/a_o}\; e^{-Z_{eff}\, r_2/a_o}$$

$$E^{(1)} = \frac{\int \Psi_{gs}^{(1)*}\, H\, \Psi_{gs}^{(1)}\, d\tau}{\int \Psi_{gs}^{(1)*}\, \Psi_{gs}^{(1)}\, d\tau} = \frac{e^2}{a_o}\left(Z_{eff}^2 - \frac{27}{8} Z_{eff}\right)$$

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minimize by changing Z_{eff}:

$$\frac{dE^{(1)}}{dZ_{eff}} = 0 = \frac{e^2}{a_o}\,(2\, Z_{eff} - 27/8)$$ see Karplus and Porter 4.1.5

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

$E = -77.5$ eV (exp. -79 eV)