He atom, ground state

$$\hat{H} = -\frac{1}{2}\Delta_1 - \frac{Z}{r_1} - \frac{1}{2}\Delta_2 - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (Z=2) \qquad \Rightarrow \quad \hat{H}\psi_0 = E_0 \psi_0$$

Method A: perturbation

$$\hat{H} = \hat{H}^{(0)} + \frac{1}{r_{12}} \leftarrow \text{perturbation} \qquad \hat{H}^{(0)} = -\frac{1}{2}\Delta_1 - \frac{Z}{r_1} - \frac{1}{2}\Delta_2 - \frac{Z}{r_2}$$

without $\frac{1}{r_{12}}$ $\quad \hat{H}^{(0)}\psi_0^{(0)} = E_0^{(0)}\psi_0^{(0)}$

$$\Rightarrow \psi_0^{(0)}(1,2) = \varphi(r_1)\cdot\varphi(r_2)\cdot\underbrace{\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)}_{\text{spin singlet}}$$

where $\varphi(r) = \underset{\text{H-like}}{1s_Z}(r) = \sqrt{\frac{Z^3}{\pi}}\, e^{-Zr}$

and

$$E_0^{(0)} = 2\cdot\Big(\underset{\text{pot}}{-Z^2} + \underset{\text{kin}}{\frac{Z^2}{2}}\Big) = 2\cdot\Big(-\frac{Z^2}{2}\Big) = -Z^2 = -4 \text{ a.u.} \approx -108.8\,\text{eV}$$

1st order correction: $\Delta E_0^{(1)} = \langle \psi_0^{(0)} | \frac{1}{r_{12}} | \psi_0^{(0)} \rangle = J \leftarrow$ Coulomb-integral

$$\Rightarrow \underline{E_0^{(1)} = -Z^2 + J} \qquad \underline{J = ?}$$

$$J = \int d^3r_1 \int d^3r_2\, \varphi^*(r_1)\varphi^*(r_2)\frac{1}{r_{12}}\varphi(r_1)\varphi(r_2) =$$

$$= \int d^3r_1\, d^3r_2\, \underbrace{|\varphi(r_1)|^2}_{\rho(r_1)} \cdot \frac{1}{r_{12}} \cdot \underbrace{|\varphi(r_2)|^2}_{\rho(r_2)} \qquad \Leftarrow \text{Cb-interaction between two spherical symmetric charge distribution}$$

$$\rho(r) = \frac{Z^3}{\pi}e^{-2Zr}$$

Trick for calculation of J:

$$J = \int d^3r_1\, d^3r_2 \ldots = \int_{|r_2|<|r_1|} d^3r_1\, d^3r_2 \ldots + \int_{|r_1|<|r_2|} d^3r_2\, d^3r_1 \ldots = 2\cdot\int d^3r_1\, \rho(r_1) \int_{|r_2|<|r_1|} d^3r_2 \frac{\rho(r_2)}{|\underset{\text{fixed}}{r_1} - r_2|} \leftarrow$$

potential of a spherical charge distribution in an external point r_1

$$\Rightarrow \frac{1}{r_1}\cdot\int_{|r_2|<r_1} d^3r_2\, \rho(r_2) \equiv \frac{1}{r_1}\cdot\int_0^{r_1} dr_2\, 4\pi r_2^2\, \rho(r_2)$$

$$\Rightarrow J = 2\cdot\int d^3r_1\, \rho(r_1)\cdot\frac{1}{r_1}\int_{|r_2|<|r_1|} d^3r_2\, \rho(r_2) = 2\cdot\int_0^\infty dr_1\, 4\pi r_1^2 \rho(r_1)\cdot\frac{1}{r_1}\cdot\int_0^{r_1} dr_2\, 4\pi r_2^2 \rho(r_2) = \frac{Z^6}{\cancel{\pi^2}}\cdot 32\cancel{\pi^2}\int_0^\infty dr_1\, r_1^2 e^{-2Zr_1}\cdot\frac{1}{r_1}\cdot\int_0^{r_1} dr_2\, \underbrace{r_2^2 e^{-2Zr_2}}_{r^2 e^{-\alpha r} = \frac{\partial^2}{\partial\alpha^2}e^{-\alpha r}}$$

$$\Big(\rho(r) = \frac{Z^3}{\pi}e^{-2Zr}\Big) \qquad (\alpha = 2Z)$$

$$\int_0^{r_1} dr\, r^2 e^{-\alpha r} = \frac{\partial^2}{\partial\alpha^2}\int_0^{r_1} dr\, e^{-\alpha r} = \frac{\partial^2}{\partial\alpha^2}\Big[-\frac{1}{\alpha}\big(e^{-\alpha r_1} - 1\big)\Big] = \frac{1}{8Z^3}\cdot 2\Big\{1 - e^{-2Zr_1}\big[1 + 2Zr_1 + 2Z^2r_1^2\big]\Big\}$$

$$\Rightarrow J = 32Z^6\int_0^\infty dr_1\, r_1^2\cdot e^{-2Zr_1}\cdot\frac{1}{r_1}\cdot\frac{1}{4Z^3}\Big\{1 - e^{-2Zr_1}\big[1 + 2Zr_1 + 2Z^2r_1^2\big]\Big\} \underset{!\, x = Z\cdot r}{=} Z\cdot 8\cdot\int_0^\infty dx\cdot x\cdot e^{-2x}\cdot\Big\{1 - e^{-2x}\big[1 + 2x + 2x^2\big]\Big\} = \ldots = \underline{\frac{5}{8}Z}$$

$$J = \frac{5}{8}Z$$

$$E_0^{(1)} = -Z^2 + \frac{5}{8}Z = -4 + \frac{5}{4} = -\frac{11}{4} = -2.75 \text{ au} \approx -74.8\,\text{eV}$$

experiment: $-79.005\,\text{eV}$

Very bad: 4 eV is missing! ($\approx 5\%$ missing)

Reason: $\frac{\Delta E_0^{(1)}}{E_0^{(0)}} = \frac{J}{2E_{1s,Z}} = \frac{5}{16} \leftarrow$ not small!

Performance of perturbational method: poor

$\Rightarrow$ <u>CHANGE TO VARIATIONAL METHOD</u>