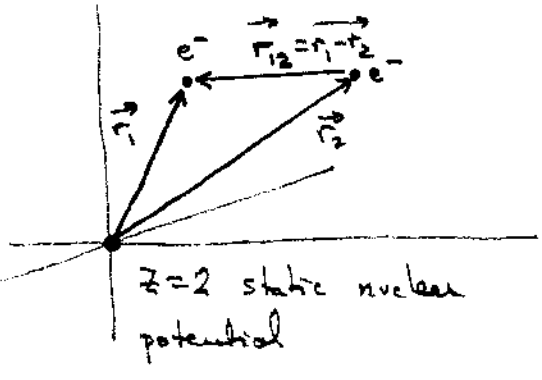
e.g. of a perturbation theory problem — Helium ground state energy

1^{st} order correction of $e^- - e^-$ interaction to He ground state energy



$$H = \underbrace{-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2\alpha\hbar c}{r_1} - \frac{2\alpha\hbar c}{r_2}}_{H_0} + \underbrace{\frac{\alpha\hbar c}{r_{12}}}_{H_I}$$

H_0 ground state, neglecting $e^- - e^-$ interaction, is

$$\Psi_0(\vec{r}_1, \vec{r}_2) = \psi_0^{1s}(r_1)\,Y_{00}(\hat{\Omega}_1)\,\psi_0^{1s}(r_2)\,Y_{00}(\hat{\Omega}_2) \equiv |\Phi_0\rangle, \ H_0 \text{ eigenstate}$$

$$E_0^{Z,\text{ hydrogenic, } 1e^-} = -\frac{mc^2\alpha^2}{2N^2}Z^2 = -2mc^2\alpha^2 \quad \text{for He per } e^-, \quad N=1$$

2 electrons, $E_0 = -4mc^2\alpha^2$

$$\boxed{E_0 = -Z^2 mc^2\alpha^2 \quad \text{arbitrary } Z}$$

Lowest order correction to the system energy is

$$E_0(1) = \langle\Phi_0|H_I|\Phi_0\rangle = \alpha\hbar c\langle\phi_0|\frac{1}{r_{12}}|\phi_0\rangle \qquad \boxed{= -2Z^2\cdot R_y}$$

$$= \alpha\hbar c\iint d\vec{r}_1\, d\vec{r}_2\ \Psi_0^*(\vec{r}_1,\vec{r}_2)\frac{1}{r_{12}}\Psi_0(\vec{r}_1,\vec{r}_2)$$

$$= \alpha\hbar c\iint \frac{d\vec{r}_1}{4\pi}\frac{d\vec{r}_2}{4\pi}\,|\psi_0^{1s}(r_1)|^2\,|\psi_0^{1s}(r_2)|^2\,\frac{1}{r_{12}}$$

Hydrogenic wavefunctions are e.g.)

$$\psi_0^{1s}(r_1) = \underbrace{2\left(\frac{Z}{a_0}\right)^{3/2}}_{\eta_{1s}} e^{-Zr/a_0}, \text{ so} \qquad a_0 = \frac{\hbar}{\alpha mc}$$

$$E_0(1) = \alpha \hbar c\, \eta_{1s}^4 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2\, e^{-\frac{2Z}{a_0}(r_1+r_2)} \frac{1}{r_{12}}$$

Use trick $\displaystyle \frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} \underbrace{P_l(\cos\theta_{12})}_{\text{integrates to zero unless } l=0}$

$$E_0(1) = \alpha\hbar c\,\eta_{1s}^4 \int_0^\infty r_1^2 e^{-\frac{2Z}{a_0}r_1} dr_1 \left\{ \underbrace{\frac{1}{r_1}\int_0^{r_1} r_2^2 e^{-\frac{2Z}{a_0}r_2} dr_2}_{} + \underbrace{\int_{r_1}^\infty r_2 e^{-\frac{2Z}{a_0}r_2} dr_2}_{} \right\}$$

call $\frac{2Z}{a_0} \equiv p$

$$\underbrace{\frac{2}{p^3}\frac{(1-e^{-pr_1})}{r_1} - \left(\frac{2}{p^2}+\frac{r_1}{p}\right)e^{-pr_1} + \left(\frac{1}{p^2}+\frac{r_1}{p}\right)e^{-pr_1}}_{\frac{2}{p^3}\frac{(1-e^{-pr_1})}{r_1} - \frac{1}{p^2}e^{-pr_1}}$$

$$\underbrace{\frac{2}{p^3}\underbrace{\int_0^\infty r_1(1-e^{-pr_1})e^{-pr_1}dr_1}_{\frac{3}{4p^2}}}_{\frac{3}{2}p^{-5}} \underbrace{- \frac{1}{p^2}\underbrace{\int_0^\infty r_1^2 e^{-2pr_1}dr_1}_{\frac{1}{4p^3}}}_{-\frac{1}{4}p^{-5}}$$

$$\frac{5}{4}(Z/a_0)^{-5}\cdot 2^{-5}$$

$$E_0(1) = \alpha\hbar c \cdot \overbrace{16\cdot(Z/a_0)^6}^{(\eta_{1s})^4} \cdot \frac{5}{4}(Z/a_0)^{-5}\cdot 2^{-5} = \frac{5}{4}Z\cdot \underbrace{\frac{1}{2}mc^2\alpha^2}_{Ry}$$

$= \alpha\hbar c\cdot 16\cdot \frac{5}{4}(Z/a_0)\frac{1}{32},\ Z/a_0 = Z\alpha mc/\hbar$

So

$$E(\text{Helium-like ground state}) = Ry\cdot\Big[\underbrace{-2Z^2}_{E(0)} + \underbrace{\frac{5}{4}Z}_{E_0(1)} + \dots\Big]$$

	E_{exp}	$-2Z^2 Ry$	$\leftarrow + \frac{5}{4}Z\,Ry$
He	78.62 eV	108.24 eV	74.42 eV
C^{++++}	876.2 eV	974.16 eV	872.69 eV

From Pauling & Wilson