Relativistic corrections to the SE

only for small energies $\epsilon = E - mc^2$ is small

2. DE

$$\Rightarrow \psi_B = \frac{c}{E - V(r) + mc^2}\,\hat{\vec{\sigma}}\cdot\hat{\vec{p}}\,\psi_A$$

into 1. DE

$$\Rightarrow \hat{\vec{\sigma}}\cdot\hat{\vec{p}}\,\frac{c^2}{mc^2 + E - V}\,\hat{\vec{\sigma}}\cdot\hat{\vec{p}}\,\psi_A = (E - V - mc^2)\,\psi_A$$

$\Rightarrow$ diff. eqn. for "large" components ψ_A

enter $\epsilon = E - mc^2$

$$\frac{1}{2m}\,\hat{\vec{\sigma}}\cdot\hat{\vec{p}}\,\underbrace{\left[1 + \frac{\epsilon - V}{2mc^2}\right]^{-1}}_{\text{for } \frac{\epsilon}{mc^2},\ \frac{V}{mc^2} \ll 1 \quad \simeq 1 - \frac{\epsilon - V}{2mc^2}}\,\hat{\vec{\sigma}}\,\hat{\vec{p}}\,\psi_A = (\epsilon - V)\,\psi_A$$

l.h.s. $\frac{1}{2m}\,\hat{\vec{\sigma}}\,\hat{\vec{p}}\left(1 - \frac{\epsilon - V}{2mc^2}\right)\hat{\vec{\sigma}}\,\hat{\vec{p}}\,\psi_A$ mom. op. $\hat{\vec{p}} = \frac{\hbar}{i}\vec{\nabla}$ + product rule

$$= \left[\left(1 - \frac{\epsilon - V}{2mc^2}\right)\frac{(\hat{\vec{\sigma}}\cdot\hat{\vec{p}})(\hat{\vec{\sigma}}\cdot\hat{\vec{p}})}{2m} + \frac{\hbar}{i}\,\frac{(\hat{\vec{\sigma}}\cdot\hat{\vec{\nabla}}V)(\hat{\vec{\sigma}}\cdot\hat{\vec{p}})}{4m^2c^2}\right]\psi_A$$

use $(\hat{\vec{\sigma}}\cdot\hat{\vec{A}})(\hat{\vec{\sigma}}\,\hat{\vec{B}}) = \vec{A}\vec{B} + i\vec{\sigma}\,(\vec{A}\times\vec{B})$

and radially symmetric potential $V = V(r) \rightarrow \vec{\nabla}V = \frac{\vec{r}}{r}\frac{dV}{dr}$

$$= \left[\left(1 - \frac{\epsilon - V}{2mc^2}\right)\frac{\hat{\vec{p}}^{\,2}}{2m} + \frac{\hbar}{i}\,\frac{1}{4m^2c^2}\,\frac{1}{r}\,\frac{dV}{dr}\,(\hat{\vec{r}}\times\hat{\vec{p}}) + \frac{\hbar}{4m^2c^2}\,\frac{1}{r}\,\frac{dV}{dr}\,\hat{\vec{\sigma}}\cdot(\hat{\vec{r}}\times\hat{\vec{p}})\right]\psi_A$$

$$= \Big[\Big(1 - \frac{\quad}{2mc^2}\Big) \frac{\quad}{2m} \quad \frac{\quad}{i} \; \frac{\quad}{4m^2c^2} \, \frac{\quad}{r} \, \frac{\quad}{dr} \quad \cdots \quad \frac{\quad}{4m^2c^2} \, \frac{\quad}{r} \, \frac{\quad}{dr} \quad \cdots \Big] \psi_A$$

2nd term vanishes because $\hat{\vec{p}} \times \hat{\vec{p}} = 0$

$\hbar \hat{\vec{\sigma}} \cdot (\hat{\vec{r}} \times \hat{\vec{p}})$

$= 2 \cdot \hat{\vec{L}} \cdot \hat{\vec{S}}$

orbital angular momentum

<u>Spin</u> $\hat{\vec{S}} = \frac{1}{2} \hbar \hat{\vec{\sigma}}$

approx: $\epsilon - V \approx \frac{\hat{\vec{p}}^2}{2m}$

→ "Darwin-Term" hermitian average of middle term (which is non-hermitian because ψ_B)

$$\hat{H}_D = \frac{1}{8m^2c^2} \Big[\frac{\hbar}{i} \frac{1}{r} \frac{dV}{dr} (\vec{r} \cdot \vec{p}) - \frac{\hbar}{i} (\hat{\vec{p}} \cdot \vec{r}) \frac{1}{r} \frac{dV}{dr} \Big]$$

$$= \ldots$$

$$= \frac{\hbar^2}{8m^2c^2} \Big(\frac{2}{r} \frac{dV}{dr} + \frac{d^2V}{dr^2} \Big)$$

$$= \frac{\hbar^2}{8m^2c^2} \Delta V(r)$$

$$\Longrightarrow \Big(\frac{\hat{\vec{p}}^2}{2m} \underbrace{- \frac{\hat{\vec{p}}^2 \hat{\vec{p}}^2}{8m^3c^2}}_{\text{correction to kin. energy, 4th order in momentum}} + V(r) + \hat{H}_{LS} + \hat{H}_D \Big) \psi_A = \epsilon \psi_A$$

$$\hat{H}_{LS} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \hat{\vec{L}} \cdot \hat{\vec{S}}$$

$\hat{=}$ Schrödinger Equation with correction terms

Energy eigenvalue changes due to relativistic corr.

Woodgate
Elementary Atomic Structure
§ 4.2.

e.g. correction to kin. energy

$$-\frac{1}{8}\frac{p^4}{m^3c^2} = -\frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2 = -\frac{1}{2mc^2}\left(E_{kin}\right)^2$$

$$= -\frac{1}{2mc^2}\left(E_n - V(r)\right)^2$$

$\Rightarrow$ level shift

$$\Delta E_n^1 = -\frac{1}{2mc^2}\left\langle\left(E_n - V(r)\right)^2\right\rangle$$

$$= -\frac{1}{2mc^2}\left\{E_n^2 - 2E_n\left\langle-\frac{Ze^2}{4\pi\varepsilon_0 r}\right\rangle + \left\langle\frac{Z^2e^4}{(4\pi\varepsilon_0)^2 r^2}\right\rangle\right\}$$

use $\left\langle\frac{1}{r}\right\rangle = \frac{1}{n^2}\frac{Z}{a_0}$

$$\left\langle\frac{1}{r^2}\right\rangle = \frac{1}{(l+\frac{1}{2})n^3}\left(\frac{Z}{a_0}\right)^2$$

$$E_n = \frac{1}{4\pi\varepsilon_0}\frac{Z^2e^2}{2a_0}\frac{1}{n^2}$$

$$\Rightarrow \Delta E_n^1 = -\frac{\alpha^2 Z^2}{n^2}E_n\left(\frac{3}{4} - \frac{n}{l+\frac{1}{2}}\right)$$

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depends on n, l

is smaller by $\alpha^2 Z^2 \sim \frac{v^2}{c^2}$ than E_n

Spin - Orbit - Interaction

Magnetic field from motion of electron (inside Coulomb potential)

$$\vec{B} = -\frac{1}{c^2} \vec{v} \times \vec{E}$$

$$\vec{E} = \frac{1}{e} \frac{\partial V}{\partial r} \frac{\vec{r}}{r}$$

$$\Rightarrow \vec{B} = \frac{1}{mc^2} \left(\frac{1}{er} \frac{\partial V}{\partial r} \right) \underbrace{\vec{r} \times m\vec{v}}_{=\hbar \vec{l}}$$

(we're looking only at states $l \neq 0$)

interacting with magnetic moment (e^--spin)

$$\vec{\mu} = -g_s \mu_B \vec{s}$$

$$g_s \simeq 2$$

$$\mu_B = \frac{e\hbar}{2m}$$

$$\Rightarrow H_{spin-orbit} = -\vec{\mu} \cdot \vec{B}$$

$$= g_s \mu_B \vec{s} \cdot \frac{\hbar}{mc^2} \left(\frac{1}{er} \frac{\partial V}{\partial r} \right) \vec{l}$$

"almost" correct (factor of 2) classical picture

missing "Thomas precession"

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$$H_{S-O} = -\frac{\hbar^2}{2m^2c^2} \frac{Ze^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r^3} \right\rangle \underline{\langle \vec{s} \cdot \vec{\ell} \rangle}$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_0^3 n^3 \ell(\ell+\frac{1}{2})(\ell+1)}$$

$$\vec{j} = \vec{s} + \vec{\ell}$$

$$\vec{j}^2 = \ell^2 + 2\vec{\ell}\vec{s} + s^2$$

$$\rightarrow \langle \vec{s}\,\vec{\ell} \rangle = \frac{1}{2} \langle \vec{j}^2 - \vec{\ell}^2 - \vec{s}^2 \rangle$$

$$= \frac{\hbar}{2} \left(j(j+1) - \ell(\ell+1) - s(s+1) \right)$$

$$\Delta E_n^u = -\frac{\alpha^2 Z^2}{n^2} E_n \frac{n \cdot \frac{1}{2} \left[j(j+1) - \ell(\ell+1) - s(s+1) \right]}{\ell(\ell+\frac{1}{2})(\ell+1)}$$