Relativistic correction

$\sqrt{1+\alpha} = 1 + \frac{1}{2}\alpha - \frac{1}{8}\alpha^2$

$\hat{H} = \hat{K} + \hat{U}$

Kinetic energy $K = \sqrt{p^2c^2 + (mc^2)^2} - mc^2$

if $p^2 \ll mc$

$K \approx \cancel{mc^2} + \frac{p^2}{2m} - \frac{1}{8}\frac{(p^2)^2}{m^3c^2} \cancel{- mc^2}$

$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} - \frac{e^2}{r}}_{\hat{H}_0} \underbrace{- \frac{1}{8}\frac{p^4}{m^3c^2}}_{\hat{V}}$

In principle, we need to follow the degenerate pert. theory recipe.

However, $[\hat{L}, \hat{p}^2] = 0 \Rightarrow [\hat{L}, \hat{p}^4] = 0$

Thus $\hat{L}$ and $\hat{p}^4$ share the same eigenfunction basis.

Thus, $\hat{V}$ is diagonal in $|n,l,m\rangle$ basis

$E^{(1)}_{|n,l,m\rangle} = - \langle n,l,m | \frac{p^4}{8m^3c^2} | n,l,m \rangle$

$\frac{p^4}{8m^3c^2} = \frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2 = \frac{1}{2mc^2}\left(\hat{H}_0 + \frac{e^2}{r}\right)^2 =$

$= \frac{1}{2mc^2}\left(\hat{H}_0^2 + \cancel{\frac{e^2}{r}}\hat{H}_0 + \hat{H}_0\frac{e^2}{r}\cancel{\Big\}} + \frac{e^4}{r^2}\right)$

$\langle nlm | \hat{H}_0^2 | nlm \rangle = (E_n^{(0)})^2$

$\langle nlm | \left\{\frac{e^2}{r}\hat{H} + \hat{H}\frac{e^2}{r}\right\} | nlm \rangle = E_n^{(0)} \langle nlm | \frac{2e^2}{r} | nlm \rangle$

$\langle nlm | \frac{2e^2}{r} | nlm \rangle = 2\langle U \rangle = -4E_n^{(0)}$ For the Coulomb potential $\langle U \rangle = 2\langle E \rangle$

$\langle nlm | \frac{e^4}{r^2} | nlm \rangle = \frac{e^4}{n^3a^2(l+\frac{1}{2})} = \frac{4n}{l+1/2}(E_n^{(0)})^2$

Adding all terms together

$$E^{(1)}_{n,\ell,m} = -\frac{1}{2mc^2}\left\{-3\left(E_n^{(0)}\right)^2 + \frac{4n}{\ell+1/2}\left(E_n^{(0)}\right)^2\right\}$$

$$E_n = \frac{e^2}{n^2 a_0} = -\frac{1}{2}mc^2\frac{\alpha^2}{n^2}$$

$$E^{(1)}_{n\ell m} = -\frac{E_n^2}{2mc^2}\left[-3 + \frac{4n}{\ell+1/2}\right] = -E_n^{(0)}\frac{\alpha^2}{n^2}\left[-\frac{3}{4} + \frac{n}{\ell+1/2}\right]$$

lifts degeneracy in ℓ (not in m!)

How large is the effect?

$$E^{(1)}_{n\ell m} \sim \frac{\left(E_n^{(0)}\right)^2}{2mc^2} \leq \frac{200(eV)^2}{2\cdot 0{,}5\,MeV} \sim \underline{2\cdot 10^{-4}\,eV}$$

$$\frac{E^{(1)}_{n\ell m}}{E_n^{(0)}} \sim \frac{E_n^{(1)}}{2mc^2} \leq \frac{13eV}{10^6 eV} \sim 10^{-5}$$

This correction becomes more pronounced for havier atoms

$$E_n^{(0)} = \frac{Z^2 e^2}{a^0}$$

$E^{(1)}_{n\ell m}$ grows as Z^4

Spin - Orbit coupling

So far we have ignored the presence of spin of the electron. => S, m_s quantum #s

Electron - spin 1/2 particle $\langle \hat{S}^2 \rangle = \hbar^2 s(s+1) = \frac{3\hbar^2}{4}$

Two possible spin orientations: $m_s = \pm 1/2$ ($|\uparrow\rangle, |\downarrow\rangle$)

Electron state $|n, \ell, m_\ell; s, m_s\rangle$

$[\vec{L}, \vec{S}] = 0$

If orbital and spin angular momenta are not coupled → all states $|\ell, m_\ell\rangle$ are double-degenerate

Relativistic effect couples these two momenta

H-atom → classical treatment

$\vec{E} = \frac{e}{r^3}\vec{r}$ in the proton's rest frame

$\vec{B} = 0$

In the electron's rest frame

$\vec{E}' \approx \vec{E}$ for $\gamma = \frac{1}{\sqrt{1 - v^2/c^2}} \approx 1 + \frac{v^2}{2c^2}$

first correction is $\sim O(v^2/c^2)$

Magnetic field

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

For a particle with non-zero magnetic moment $\vec{\mu}$: $\hat{H}_{int} = -\vec{\mu} \cdot \vec{B}'$

Magnetic moment of an electron:

- orbital angular momentum

$$\vec{\mu}_L = \frac{e}{2mc}\vec{L}$$

- adding intrinsic spin angular momentum

$$\vec{\mu}_S = g\frac{e}{2mc}\vec{S}$$

g-factor

in semi-classical theory - a phenomenological constant

electron $g_e \approx 2$ ($= 2.002317304$ from QED)

proton $g_p \simeq 5.6$

neutron $g_n \simeq -3.8$

We also often write $\vec{\mu}_e = g_e \frac{e\hbar}{2mc}\left(\frac{\vec{S}}{\hbar}\right)$

or $\vec{\mu}_e = g_e \mu_B \left(\frac{\vec{S}}{\hbar}\right)$ $\mu_B = \frac{e\hbar}{2mc}$ Bohr's magneton

$|\mu_B| = 9.274 \cdot 10^{-24}$ J/T

or $\frac{|\mu_B|}{\hbar} = 1.4$ MHz/G

For an electron in its instantaneous ref. frame

$$\hat{H}_{int} = -\vec{\mu}_e \cdot \vec{B}' = -g_e \frac{e}{2mc}\vec{S}\left(-\frac{1}{c}\right)(\vec{v}\times\vec{r})\left(\frac{e}{r^3}\right)$$

$$= \frac{e^2}{m^2c^2}\frac{1}{r^3}\vec{S}\cdot(\vec{p}\times\vec{r}) = -\frac{e^2}{m^2c^2}\frac{1}{r^3}\vec{L}\cdot\vec{S}$$

($\vec{p}\times\vec{r} = -\vec{L}$)

Spin-orbit coupling — for H-atom

$$\hat{H}_{LS} = -\frac{e^2}{m^2c^2}\frac{1}{r^3}\hat{\vec{L}}\cdot\hat{\vec{S}}$$

More precisely (from relativistic Dirac equation)

$$\hat{H}_{LS} = -\frac{e^2}{2m^2c^2}\frac{1}{r^3}\hat{\vec{L}}\cdot\hat{\vec{S}}$$

Let's estimate the value of correction

$$\langle H_{LS}\rangle = \frac{e^2}{m^2c^2}\frac{1}{a_0^3}\hbar^2 = \underbrace{\left(\frac{e^2}{a_0}\right)}_{E_R}\left(\frac{\hbar}{mca_0}\right)^2 = E_R\left(\frac{\hbar}{mc}\frac{me^2}{\hbar^2}\right)$$

$$\langle H_{LS}\rangle = E_R\left(\frac{e^2}{\hbar c}\right)^2 = \alpha^2 E_R$$

$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$ fine structure (compare to the main energy spectrum)

Same treatment is valid for more complex atoms → alkali-metals (Li, K, Na, Rb, Cs). Closed-shell electrons screen the charge of the nuclei, so the total electric potential is similar to that of a hydrogen atom. However, it is not just Coulomb potential. Corrected potential energy $V_c(r) = e\varphi(r)$

$$\vec{E} = -\frac{1}{e}\nabla V_c(r) = -\frac{1}{e}\frac{1}{r}\frac{dV_c}{dr}$$

Correspondingly the $\vec{L}\vec{S}$ interaction hamiltonian modifies as

$$\hat{H}_{LS} = \frac{1}{m^2c^2}\left(\frac{1}{r}\frac{dV_c}{dr}\right)\hat{\vec{L}}\cdot\hat{\vec{S}}$$

Order-of-magnitude estimate gives values comparable with other relativistic correction.

$\hat{H}_{LS}$ dominates for lighter nuclei, but starts to break down for heavier ones (need a different form then).

Fine structure of an H-atom

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} - \frac{e^2}{r}}_{\hat{H}_0} - \underbrace{\frac{e^2}{2m^2c^2}\frac{1}{r^3}\hat{\vec{L}}\hat{\vec{S}}}_{\text{perturbation } \hat{V}_{SO}}$$

Need to apply the degenerate perturbation theory → need to find the proper basis

Original basis: $n, \hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$

$\hat{V}_{SO}$ is clearly not diagonal

Total angular momentum $\vec{J} = \vec{L} + \vec{S}$

$$\hat{\vec{J}}^2 = (\hat{\vec{L}} + \hat{\vec{S}})^2 = \hat{\vec{L}}^2 + 2\hat{\vec{L}}\cdot\hat{\vec{S}} + \hat{\vec{S}}^2$$

Spin-orbit interaction preserves total angular momentum

New basis: $n, \hat{L}^2, \hat{S}^2, \hat{J}^2, \hat{J}_z$

$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$

$\ell \quad s \quad j \quad m_j = m$

ℓ: describes radial distr. — j, m_j: describes angular distribution

For an electron $j = \ell \pm 1/2$ → $2j+2$, $2j$ degeneracy

Wave-functions

$$|n\ell m_{(j)}\rangle = R_{n\ell}(r)\, \mathcal{Y}_\ell^{j=\ell\pm1/2,\, m_j}$$

$s = 1/2, j = \ell \pm 1/2$

Notation for the state: $n \quad {}^{(2S+1)}\ell_j$

$2\,{}^2S_{1/2} \rightarrow n=2, \ell=0, s=1/2, j=1/2$

$2\,{}^2P_{3/2} \rightarrow n=2, \ell=1, s=1/2, j=3/2$

Spin-orbit interaction is diagonal in this new basis

$$\langle n\, l\, s\, j\, m_j | \hat{V}_{SO} | n\, l\, s\, j\, m_j \rangle = -\frac{e^2}{2m^2c^2} \underbrace{\langle nl | \frac{1}{r^3} | nl \rangle}_{\text{radial functions}} \times$$

(Rem)

$$\times \underbrace{\langle l\, s\, j\, m_j | \hat{\vec{L}}\cdot\hat{\vec{S}} | l\, s\, j\, m_j \rangle}_{\text{angular functions}}$$

$$\langle l\, s\, j\, m | \hat{\vec{L}}\cdot\hat{\vec{S}} | l\, s\, j\, m \rangle = \langle l\, s\, j\, m | \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2) | l\, s\, j\, m \rangle =$$

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

For an electron: $s = 1/2$ $\quad j = l \pm 1/2$

$j = l + 1/2$: $\quad \langle \vec{L}\vec{S} \rangle = \frac{\hbar^2}{2} l$

$j = l - 1/2$: $\quad \langle \vec{L}\vec{S} \rangle = -\frac{\hbar^2}{2}(l+1)$

For an H-atom $\quad \left\langle \frac{e^2}{r^3} \right\rangle_{nl} = -\frac{2m^2c^2\alpha^2}{nl(l+1)(l+1/2)\hbar^2} E_n^{(0)}$

Spin-orbit correction to the H-atom states

$$\Delta E_{SO} = -\alpha^2 E_n^{(0)} \frac{1}{2nl(l+1)(l+1/2)} \times \begin{cases} l & j = l + 1/2 \\ -(l+1) & j = l - 1/2 \end{cases}$$

Notice that for $l = 0$

$$\Delta E_{SO} = -\alpha^2 E_n^{(0)} \cdot \frac{1}{n} \neq 0$$

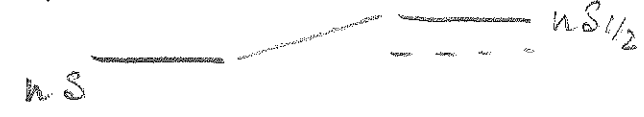
The result is counter-intuitive (shouldn't $\langle \vec{L}\vec{S} \rangle = 0$?) but it is nonetheless correct.

Examples: 1) singlet state $\ell = 0$

$nS_{1/2}$ $(\ell = 0,\ j = 1/2)$

$\Delta E_{SO} = -\alpha^2 E_n^{(0)} \cdot \frac{1}{n} > 0$ (since $E_n^{(0)} < 0$)

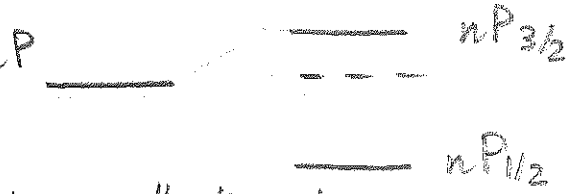
unperturbed $\hat{H}_0$ $\hat{H}_0 + H_{LS}$



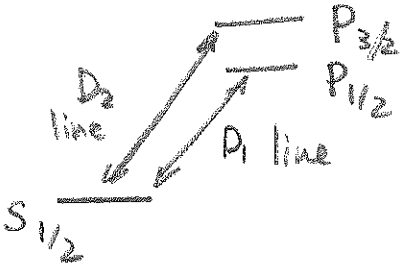
2) p-state: $nP_{1/2}$ and $nP_{3/2}$

$nP_{3/2} \Rightarrow \Delta E_{SO} = -\alpha^2 E_n^{(0)} \cdot \frac{1}{6n} > 0$

$nP_{1/2} \Rightarrow \Delta E_{SO} = \alpha^2 E_n^{(0)} \cdot \frac{1}{3n} < 0$



In alkali atoms



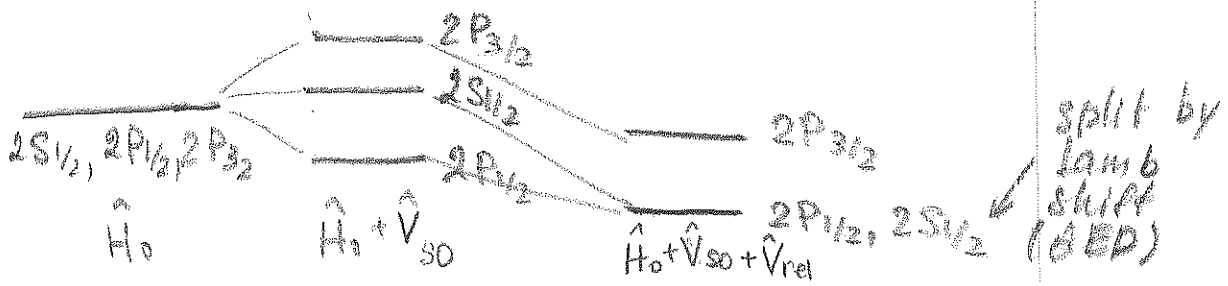
Na doublet $\Delta_D = 0.9\ nm$

Rb $\Delta_D = 15\ nm$

Cs $\Delta_D = 40\ nm$

For H-atom $\vec{L}\cdot\vec{S}$ interaction and $\frac{p^2}{8m^3c^4}$ are of the same order of magnitude

$$\Delta E^{(1)}_{SO+rel} = -\frac{1}{2} mc^2 \alpha^4 \left[\frac{1}{n^3 (j+1/2)} - \frac{3}{4n^4} \right]$$



Thus we have the states

$$\begin{array}{ll} \cdots & \\ (3^2 s_{1/2}), & (3^2 p_{1/2}, 3^2 p_{3/2}), \quad (3^2 d_{3/2}, 3^2 d_{5/2}) \\ (2^2 s_{1/2}), & (2^2 p_{1/2}, 2^2 p_{3/2}) \\ (1^2 s_{1/2}) & \end{array}$$

In the absence of perturbations, all the n, ℓ, j, and m_j states of a given n would be degenerate. However, experiment shows that states of a given n and ℓ but different j are actually separated by fine-structure splittings. For example, Figure 10.1 shows the fine structure of the $n = 2$ levels of $^4He^+$.

Fine structure is a relativistic effect that can be treated in a consistent way only by means of the Dirac relativistic wave equation, to be discussed in later chapters. However, at this stage, we can give a partial explanation of fine structure by grafting two heuristically derived perturbations of comparable significance and relativistic origin onto the nonrelativistic zero-order Schroedinger theory.

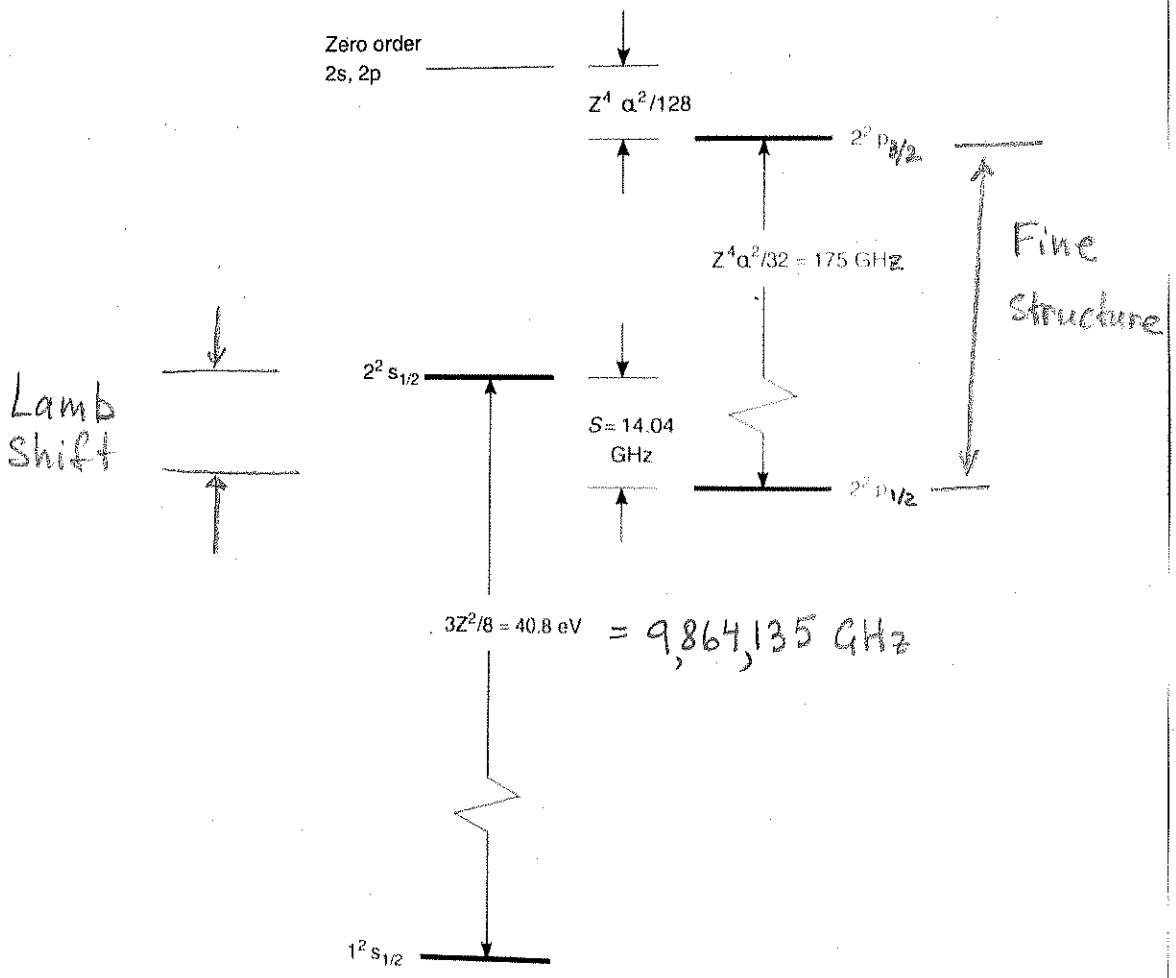


Figure 10.1 $n = 1$ and 2 energy levels of $^4He^+$ (not to scale). Note the fine-structure splitting between $2^2\,p_{3/2}$ and $2^2\,p_{1/2}$. Also, S is the Lamb shift, a quantum-electrodynamic effect that requires quantum-field theory (and specifically renormalization) for its description.