electrodynamics (QED). One finds that the $2s_{1/2}$ level is raised wrt the $2p_{1/2}$ level by the "Lamb shift"

$$\begin{array}{l} 2s_{1/2} \;\text{———} \\ \qquad\qquad \updownarrow \;\sim 4.4\times 10^{-6}\,\text{eV} \;(\sim 1057\ \text{MHz}) \\ 2p_{1/2} \;\text{———} \end{array}$$

6.5. The Hydrogen Atom In Electric and Magnetic Fields

In addition to the fine structure relativistic corrections to the Coulomb Hydrogen spectrum, we can also consider the effects of external, constant uniform electric and magnetic fields on the spectrum. The electric field $\vec{E}$ and magnetic field $\vec{B}$ are given in terms of the scalar ϕ and vector $\vec{A}$ potentials

$$\vec{B} = \vec{\nabla}\times\vec{A}$$

get rid of c p. 954 to p. 965

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial}{c\partial t}\vec{A}\ .$$

Recall that the physical values of the electric & magnetic fields $\vec{B}, \vec{E}$ are given by an equivalence class of potentials ϕ and $\vec{A}$. That is given $\phi, \vec{A}$ we have a unique $\vec{E}$ & $\vec{B}$ given above, but given $\vec{E}$ and $\vec{B}$ we do not determine $\phi, \vec{A}$ uniquely only up to a <u>gauge</u> <u>transformation</u>.

If $\vec{A}' \equiv \vec{A} + \vec{\nabla}\Lambda$ and $\phi' \equiv \phi - \frac{\partial}{\partial t}\Lambda$

where $\Lambda = \Lambda(\vec{r}, t)$ is an arbitrary function,

then
$$
\begin{aligned}
\vec{E}' &= -\vec{\nabla}\phi' - \frac{\partial}{\partial t}\vec{A}' \\
&= -\vec{\nabla}\phi + \vec{\nabla}\frac{\partial}{\partial t}\Lambda - \frac{\partial}{\partial t}\vec{A} - \frac{\partial}{\partial t}\vec{\nabla}\Lambda \\
&= \vec{E} - \left[\frac{\partial}{\partial t}, \vec{\nabla}\right]\Lambda \\
&= \vec{E} \qquad \text{for smooth enough } \Lambda,
\end{aligned}
$$

and likewise

$$
\begin{aligned}
\vec{B}' &= \vec{\nabla} \times \vec{A}' \\
&= \vec{\nabla} \times \vec{A} + \vec{\nabla} \times \vec{\nabla}\Lambda \\
&= \vec{\nabla} \times \vec{A} = \vec{B}.
\end{aligned}
$$

$\vec{E}$ & $\vec{B}$ are invariant under gauge transformations.

Then when a charged particle interacts with an electric and magnetic field it must do it in a manner that is also gauge invariant, that is that depends only on the gauge equivalence class of potentials $\phi, \vec{A}$, not the particular choice within an equivalence class.

Since the potential energy of a charged q particle in the scalar potential ϕ is simply $q\phi$ a gauge transformation of $\phi \to \phi' = \phi - \frac{1}{c}\frac{\partial}{\partial t}\Lambda$ will change the Hamiltonian $H \to H - \frac{q}{c}\frac{\partial}{\partial t}\Lambda$. Then

for Schrödinger's equation to be unchanged we must make a gauge transformation of the wavefunction by a phase that depends on time and space

$$\psi'(\vec{r},t) \equiv e^{+\frac{iq}{\hbar c}\Lambda(\vec{r},t)}\,\psi(\vec{r},t)$$

Then $$i\hbar\frac{\partial}{\partial t}\psi' = -\frac{q}{c}\frac{\partial}{\partial t}\Lambda\,\psi' + e^{+\frac{iq}{\hbar c}\Lambda}\,i\hbar\frac{\partial}{\partial t}\psi$$

will give rise to a $-\frac{q}{c}\frac{\partial}{\partial t}\Lambda$ term exactly cancelling the $-\frac{q}{c}\frac{\partial}{\partial t}\Lambda$ term from the Hamiltonian. But now the wavefunction ψ' depends on a Λ-phase then since the momentum in the $\{|\vec{r}\rangle\}$ basis is just the gradient we have that

$$\vec{p}\,\psi' = -i\hbar\vec{\nabla}\psi'$$

$$= +\frac{q}{c}\vec{\nabla}\Lambda\,\psi' + e^{+\frac{iq\Lambda}{c\hbar}}(-i\hbar\vec{\nabla}\psi).$$

Hence we pick up an extra term that depends on the gauge Λ. Then if ψ interacts with $\vec{A}$ in such a way that whenever we have a momentum factor we also have a $-q\vec{A}$ factor; under a gauge transformation this will result in

$$(\vec{p}-\frac{q}{c}\vec{A})\psi \longrightarrow (\vec{p}-\frac{q}{c}\vec{A}')\psi'$$

$$= (-i\hbar\vec{\nabla}-\frac{q}{c}\vec{A}-\frac{q}{c}\vec{\nabla}\Lambda)e^{+\frac{iq}{c\hbar}\Lambda}\psi$$

$$= (\cancel{-\frac{q}{c}\vec{\nabla}\Lambda}+\cancel{\frac{q}{c}\vec{\nabla}\Lambda})\psi'$$

$$+e^{+\frac{iq}{c\hbar}\Lambda}(-i\hbar\vec{\nabla}-\frac{q}{c}\vec{A})\psi$$

$$= e^{+\frac{iq}{c\hbar}\Lambda}(\vec{p}-\frac{q}{c}\vec{A})\psi$$

The unwanted gauge phase Λ cancels! Thus we have the means of determining the form of interaction of a charged particle with electric and magnetic fields in a gauge invariant manner.

<u>The gauge Principle</u>: If a charged q particle evolves in time according to the Hamiltonian $H(\vec{p},\vec{R})$ in the absence of electric and magnetic fields, then in their presence the charged particle evolves in time according to the Hamiltonian

$$H_{E\text{-}M} = H(\vec{P}-\frac{q}{c}\vec{A},\vec{R}) + q\,\phi(\vec{R},t) .$$

The replacement of $\vec{p} \to \vec{p}-\frac{q}{c}\vec{A}$ is called the principle of minimal substitution.

To summarize then. The simultaneous transformation of the state $|\psi\rangle \to |\psi'\rangle$ and the electromagnetic potentials $\phi \to \phi'$; $\vec{A} \to \vec{A}'$ by a gauge transformation

$$\phi' = \phi - \frac{\partial}{c\partial t}\Lambda$$

$$\vec{A}' = \vec{A} + \vec{\nabla}\Lambda$$

$$|\psi'\rangle = e^{+\frac{iq}{c\hbar}\Lambda}|\psi\rangle$$

leaves the Schrödinger equation unchanged (i.e. the dynamics is given for the above equivalence class)

$$i\hbar\frac{\partial}{\partial t}|\psi'\rangle = H_{E\text{-}m}\left(\vec{P} - \frac{q}{c}\vec{A}', q\phi', \vec{R}\right)|\psi'\rangle$$

$$\Leftrightarrow i\hbar\frac{\partial}{\partial t}|\psi\rangle = H_{e\text{-}m}\left(\vec{P} - \frac{q}{c}\vec{A}, q\phi, \vec{R}\right)|\psi\rangle.$$

Since $|\psi'\rangle = U(\Lambda)|\psi\rangle$ is a unitary transformation,
(ok) ~~all matrix elements are left invariant,~~
so all physical observables are the same.

Thus for a free particle with charge which is described by the Hamiltonian

$$H_0 = \frac{1}{2m}\vec{P}^2$$

we have that the Hamiltonian describing the particle's interaction with the external electromagnetic fields is simply

$$H_{em} = \frac{1}{2m}\left(\vec{P} - \frac{q}{c}\vec{A}\right)^2 + q\phi$$

$$= \frac{1}{2m}\vec{P}^2 - \frac{q}{2mc}\left(\vec{P}\cdot\vec{A} + \vec{A}\cdot\vec{P}\right) + \frac{q^2}{2mc^2}\vec{A}^2$$

$$+ q\phi$$

as we already know.

For constant, uniform external electric and magnetic fields we can choose a gauge so that

$$\vec{A} = \frac{1}{2}\vec{B}\times\vec{R}$$

$$\phi = -\vec{E}\cdot\vec{R} \, .$$

Thus we can check that $\vec{E} = -\vec{\nabla}\phi - \cancelto{0}{\frac{\partial}{\partial t}\vec{A}}$
$= +\vec{\nabla}(\vec{E}\cdot\vec{R}) = \vec{E}$ ✓

$$\vec{B} = \vec{\nabla}\times\vec{A} \Rightarrow B_i = \epsilon_{ijk}\frac{\partial}{\partial x_j}A_k$$

$$= \epsilon_{ijk}\frac{\partial}{\partial x_j}\left(\frac{1}{2}\epsilon_{klm}B_l x_m\right)$$

$$= \frac{1}{2}\underbrace{\epsilon_{ijk}\epsilon_{klm}}_{=(\delta_{il}\delta_{jm}-\delta_{im}\delta_{jl})} B_l \underbrace{\frac{\partial}{\partial x_j}x_m}_{=\delta_{jm}}$$

$$= \tfrac{1}{2}(\delta_{i\ell}\delta_{jm} - \delta_{im}\delta_{j\ell})B_\ell \delta_{jm}$$

$$= \tfrac{1}{2}(\delta_{i\ell}\delta_{jj} - \delta_{ij}\delta_{j\ell})B_\ell = \tfrac{1}{2}(3B_i - B_i)$$

$$= B_i \checkmark .$$

Thus

$$H_{em} = \frac{1}{2m}\vec{P}^2 - \frac{q}{2m}\left[\vec{P}\cdot\tfrac{1}{2}(\vec{B}\times\vec{R}) + \tfrac{1}{2}(\vec{B}\times\vec{R})\cdot\vec{P}\right]$$

$$+ \frac{q^2}{2m}\,\frac{1}{4}(\vec{B}\times\vec{R})^2 - q\vec{E}\cdot\vec{R}$$

As usual

$$\vec{P}\cdot\tfrac{1}{2}(\vec{B}\times\vec{R}) + \tfrac{1}{2}(\vec{B}\times\vec{R})\cdot\vec{P}$$

$$= \tfrac{1}{2}P_i\,\epsilon_{ijk}B_jX_k + \tfrac{1}{2}\epsilon_{ijk}B_jX_kP_i$$

$$= \tfrac{1}{2}\epsilon_{ijk}B_j\left[X_kP_i + \underbrace{[P_i,X_k]}_{=-i\hbar\delta_{ik}} + X_kP_i\right]$$

$$= \epsilon_{ijk}B_jX_kP_i - \frac{i\hbar}{2}\underbrace{\epsilon_{iji}}_{0}B_j$$

$$= \vec{B}\cdot(\vec{R}\times\vec{P})$$

$$= \vec{B}\cdot\vec{L} = \vec{L}\cdot\vec{B} .$$

And $\vec{A}^2 = \frac{1}{4}(\vec{B}\times\vec{R})^2$

$$= \frac{1}{4}\epsilon_{ijk}\epsilon_{ilm} B_j X_k B_l X_m$$

$$= \frac{1}{4}(\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}) B_j B_l X_k X_m$$

$$= \frac{1}{4}\left(\vec{B}^2\vec{R}^2 - (\vec{B}\cdot\vec{R})^2\right) .$$

Thus

$$\boxed{H_{em} = \frac{1}{2m}\vec{P}^2 - \frac{q}{2m}\vec{B}\cdot\vec{L} + \frac{q^2}{8m}[\vec{B}^2\vec{R}^2 - (\vec{B}\cdot\vec{R})^2] - q\vec{E}\cdot\vec{R}.}$$

If in addition the particle has spin it will have a magnetic moment, and hence an interaction with the magnetic field

$$H_{mag} = -\vec{M}\cdot\vec{B}$$

with $\vec{M} = g\frac{q}{2m}\vec{S}$

anomalous magnetic moment

So $\boxed{H_{mag} = -g \frac{q}{2m} \vec{B} \circ \vec{S}}$

For a spin $\frac{1}{2}$ electron we have that

$g \approx 2$; $q = -e$ so this becomes

$$H_{mag} = \frac{e}{m} \vec{B} \circ \vec{S}$$

$$= 2 \mu_B \frac{1}{\hbar} \vec{B} \circ \vec{S}$$

where the Bohr magneton $\mu_B \equiv \frac{e\hbar}{2m}$.

For a Hydrogen atom subjected to external constant uniform electric and magnetic fields we proceed similarly. Recall the Hamiltonian in the absence of the external fields

$H = H_0 + H_{fs}$ with

$$H_0 = \frac{1}{2m} \vec{P}^2 - \frac{e^2}{R}$$

$H_{fs} = H_{kin} + H_{so} + H_D$ where

$$H_{Kin} = -\frac{1}{8m^3c^2}\vec{P}^4 = mc^2\alpha^4\left(\frac{-a_0^4}{8\hbar^4}\vec{P}^4\right)$$

$$H_{SO} = +\frac{e^2}{2m^2c^2}\frac{1}{R^3}\vec{L}\cdot\vec{S} = mc^2\alpha^4\left(\frac{a_0^3}{2\hbar^2}\frac{1}{R^3}\vec{L}\cdot\vec{S}\right)$$

$$H_D = \frac{\pi e^2\hbar^2}{4\pi\epsilon_0\, 2m^2c^2}\delta^3(\vec{R}) = mc^2\alpha^4\left(\frac{\pi}{2}a_0^3\delta^3(\vec{R})\right).$$

Thus in the presence of additional external electric and magnetic fields the Hydrogen Hamiltonian is

$$H_{ext} = \frac{1}{2m}(\vec{P}+e\vec{A})^2 - \frac{1}{8m^3c^2}(\vec{P}+e\vec{A})^4$$

$$- \frac{1}{2m^2c^2}\frac{1}{R^3}\vec{L}\cdot\vec{S} + \frac{\pi e^2\hbar^2}{4\pi\epsilon_0\, 2m^2c^2}\delta^3(\vec{R})$$

$\frac{e^2}{4\pi\epsilon_0}$

$$+ 2\mu_B\frac{1}{\hbar}\vec{B}\cdot\vec{S} - \frac{e^2}{4\pi\epsilon_0 R} + e\vec{E}\cdot\vec{R}$$

$$= H_0 + H_{fs} + \mu_B\frac{1}{\hbar}\vec{B}\cdot(\vec{L}+2\vec{S})$$

$$+ \frac{e^2}{8m}\left[\vec{B}^2\vec{R}^2 - (\vec{B}\cdot\vec{R})^2\right] + e\vec{E}\cdot\vec{R}$$

$$- \frac{1}{8m^3c^2}\left[(\vec{P}+e\vec{A})^4 - \vec{P}^4\right]$$

having used Hem from before.

Note that this is just the Hamiltonian we would find if we 1) couple the orbital and spin magnetic moments to the $\vec{B}$-field and 2) we make a non-relativistic expansion of the relativistic kinetic energy formula

$$T = \sqrt{(\vec{p}+e\vec{A})^2c^2 + m^2c^4} - mc^2$$

$$\simeq \frac{1}{2m}(\vec{P}+e\vec{A})^2 - \frac{1}{8m^3c^2}(\vec{P}+e\vec{A})^4$$

3) include electrostatic energy $q\phi$ in addition to the spin-orbit and Darwin fine structure terms of before.

In general the external field energy is quite small compared to mc^2 and so we will only keep terms through the order of $\left(\frac{\text{kinetic energy}}{mc^2}\right)^2$ and ignore terms the order of $\left(\frac{\text{kinetic energy} \times \text{field energy}}{m^2c^4}\right)$. Thus we drop the $\frac{[(\vec{P}+e\vec{A})^4 - \vec{P}^4]}{m^3c^2}$ term.

In addition the $\vec{B}^2$ and $(\vec{B}\circ\vec{R})^2$ terms are dropped. Thus we have

The Hamiltonian describing the Hydrogen atom in external electric and magnetic fields

$$H_{ext} = H_0 + H_{fs} + \mu_B \frac{1}{\hbar} \vec{B} \cdot (\vec{L} + 2\vec{S}) + e\vec{E} \cdot \vec{R}$$

6.5.1. Constant, Uniform External Magnetic Field $\vec{B}$: The Zeeman Effect

The above Hamiltonian becomes

$$H = \frac{1}{2m}\vec{P}^2 - \frac{e^2}{R} + H_{kin} + H_{SO} + H_D + \mu_B \frac{1}{\hbar} \vec{B} \cdot (\vec{L} + 2\vec{S})$$

Choosing $\vec{B}$ to be in the z-direction

$\vec{B} = B\hat{z}$; we have