13.7 lamb splitting

in the above we said that $2p_{1/2}$ and $2s_{1/2}$ had the same energy - but actually there IS a (very small - of order α^5 ie factor 137 smaller than the fine structure) energy difference between $2s_{1/2}$ and $2p_{1/2}$ which comes from the Lamb shift (an interaction between the electron and the vacuum). it gives a difference between states of the same n, j but different l.

13.8 hyperfine splitting

but there is also hyperfine splitting which gives an energy shift of $E^1_{n,hyperfine} \propto \alpha^4.m_e/m_p$ ie a factor 10 smaller even than the Lamb shift.

The proton itself has spin, $\underline{S}_p$, giving a magnetic dipole $\underline{\mu}_p = \frac{g_p e}{2m_p}\underline{S}_p$ where $g_p = 5.59$. In classical electrodynamics, a dipole sets up a magnetic field

$$\underline{B_p} = \frac{\mu_0}{4\pi r^3}[3(\underline{\mu_p}.\underline{\hat{r}})\underline{\hat{r}} - \underline{\mu_p}] + \frac{2\mu_0}{3}\underline{\mu_p}\delta^3(\underline{r})$$

The electron also has a magnetic dipole $\underline{\mu}_e = -\frac{g_e e}{2m_e}\underline{S}_e$, but $g_e \sim 2$ so $\underline{\mu}_e = -\frac{e}{m_e}\underline{S}_e$ so there is an additional contribution to the potential $H' = -\underline{\mu}_e.\underline{B_p}$ from the interaction of this with the magnetic field induced from the proton spin.

if we can use our original wavefunctions, we'd get $E^1_{nlm} =< \psi_{nlm}|H'\psi_{nlm} >$ and for states with $l = 0$ so $m_l = 0$ the radial dot product goes to zero due to spherical symmetry. so $E^1 \propto \underline{S}_e.\underline{S}_p$ In the same way that we used total angular momentum $\underline{J} = \underline{L} + \underline{S}_e$ we can use total spin $\underline{F} = \underline{S}_e + \underline{S}_p$ to get the energy shift and this is 5.877×10^{-6} eV which corresponds to 21cm, perhaps the most famous line ever....

14 More on Formalism

14.1 Time evolution of expectation values

$$\frac{d<Q>}{dt} = \frac{d}{dt} <\psi|Q\psi> = <\frac{\partial\psi}{\partial t}|Q\psi> + <\psi|\frac{\partial Q}{\partial t}\psi> + <\psi|Q\frac{\partial\psi}{\partial t}>$$

But $H\psi = i\hbar\partial\psi/\partial t$ so $\partial\psi/\partial t = -i/\hbar H$ and $\partial\psi^*/\partial t = i/\hbar H$.

$$= <-\frac{i}{\hbar}H|Q\psi> + <\psi|\frac{\partial Q}{\partial t}\psi> + <\psi|Q\frac{-i}{\hbar}H\psi>$$

$$= \frac{i}{\hbar} <H\psi|Q\psi> + <\psi|\frac{\partial Q}{\partial t}\psi> - \frac{i}{\hbar} <\psi|QH\psi>$$

$$= \frac{i}{\hbar}(<H\psi|Q\psi> - <\psi|QH\psi>) + <\psi|\frac{\partial Q}{\partial t}\psi>$$

H is hermitian so $<H\psi|f> = <\psi|Hf>$ so

$$= \frac{i}{\hbar}(<\psi|HQ\psi> - <\psi|QH\psi>) + <\psi|\frac{\partial Q}{\partial t}\psi>$$

$$= \frac{i}{\hbar} <[H,Q]> + \left\langle\frac{\partial Q}{\partial t}\right\rangle$$

14.2 Ehrenfest theorem (1st)

let $Q = x$ then

$$\frac{d<x>}{dt} = \frac{i}{\hbar} <[H,x]> + \left\langle\frac{\partial Q}{\partial t}\right\rangle$$

We saw that $[H,x] = -\frac{i\hbar}{m}p$, and we know that the operator (coordinate!) x has no dependence on coordinate t so $\partial x/\partial t = 0$.

$$\frac{d<x>}{dt} = \frac{i}{\hbar} <-i\hbar\frac{p}{m}>$$

$$= \frac{<p>}{m}$$

and we have indeed the link to classical physics we talked about earlier.

similarly we could prove the second one $d<p>/dt = F = -<dV/dx>$

14.3 Virial theorem

let $Q = xp$

$$\frac{d < xp >}{dt} = \frac{i}{\hbar} < [H, xp] > + \Big\langle \frac{\partial(xp)}{\partial t} \Big\rangle$$

again, we earlier showed that $[H, p] = i\hbar dV/dx$ so $[H, xp] = [H, x]p + x[H, p] = -(i\hbar/m)p.p + x.i\hbar dV/dx$.

$$= \frac{i}{\hbar} \Big\langle -(i\hbar/m)p.p + x.i\hbar dV/dx \Big\rangle + 0$$

$$=< p^2/m - xdV/dx >$$

but in steady state $d/dx < xp >= 0$ so $0 =< p^2/m - xdV/dx >$ or $< p^2/2m >=< T >= 1/2 < xdV/dx >$

so stationary states (energy eigenfunctions) should have $< T >= 1/2xdV/dx$. for the harmonic oscillartor $V = 1/2m\omega^2x^2$ so $dV/dx = m\omega^2 x$ and $< T >= 1/2 < xm\omega^2 x >= 1/2 < m\omega^2 x^2 >=< V >$

in general calculating $< T >$ is hard as its a second order differential operator, whereas calculating $< V >$ is easier.