Theory of atom

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1 Hydrogen

The energy unit Hartree is defined as twice of E_1. That's to say, one Hartree is equal to 27.6 eV, and if the Hartree unit is used, then the energy levels of the hydrogen atom are $1/2n^2$.

1.1 Stability

The hydrogen atom is bound together by Coulomb potential $1/r$. From Virial theorem, we will find not all attractive potentials lead to stable bound states. Specifically, $1/r^2$ or $1/r^3$ doesn't give us bound states in 3D. This can be shown by explicitly calculating $T + V$: if it's greater than zero for the whole spectrum, then of course we don't have stable bound states.

1.2 Spin-orbital coupling

The first order perturbation of the SOC Hamiltonian is

$$E^{(1)} = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2 c} \left\langle \frac{\boldsymbol{L} \cdot \boldsymbol{S}}{r^3} \right\rangle .$$

Note that $\boldsymbol{L} \cdot \boldsymbol{S}$ extracts information about m and m_s (which are good quantum numbers) in the wave function: we have

$$\boldsymbol{L} \cdot \boldsymbol{S} = \frac{\hbar^2}{2} (j(j+1) - l(l+1) - s(s+1)). \tag{1}$$

So the energy perturbation is just

$$E^{(1)} = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2 c} \left\langle \frac{1}{r^3} \right\rangle \cdot \frac{\hbar^2}{2} (j(j+1) - l(l+1) - s(s+1)).$$

Now we just add $E^{(1)}$ to $T + V$, and we find the influence of SOC can be seen as adding

$$H = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2 c} \left\langle \frac{1}{r^3} \right\rangle \boldsymbol{L} \cdot \boldsymbol{S}, \tag{2}$$

to the total Hamiltonian, where

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

Formally, this means we have averaged over $1/r^3$ only; but note that strictly speaking $\boldsymbol{L}$ is no longer the old $\boldsymbol{L}$ obtained from $V + T$, because after perturbation of SOC, the eigenstates themselves are changed, and so is $L_z = \sum m \left|n, l, m, m_s\right\rangle\!\left\langle n, l, m, m_s\right|$.

We can estimate the magnitude of SOC correction: we have

$$\frac{\delta E_n}{E_n} = \frac{E_n}{mc^2} = \frac{10^{-5} Z^2}{n^2}. \tag{4}$$

1.3 Going into the nucleus

When r is *smaller* than the radius of the nucleus, it can be verified by Gauss's theorem that

$$V(r) = \frac{1}{2}\frac{r^2}{R_\mathrm{n}^3} - \frac{3}{2R_\mathrm{n}}. \tag{5}$$

To see why, just calculate the force using this potential and check the force obtained by

$$4\pi r^2 \cdot F(r) = \int_0^r \frac{Ze}{\frac{4}{3}\pi R_\mathrm{n}^3} \cdot 4\pi r'^2 \, \mathrm{d}r' \,. \tag{6}$$

The constant term is there to guarantee continuity at $r = R_\mathrm{n}$. So

$$V(r) = \begin{cases} -\frac{1}{r}, & r > R_\mathrm{n}, \\ \frac{1}{2}\frac{r^2}{R_\mathrm{n}^3} - \frac{3}{2R_\mathrm{n}}, & r < R_\mathrm{n}. \end{cases} \tag{7}$$

So, we find the existence of a finite-size nucleus means we have a perturbation Hamiltonian

$$V(r) - V_0(r) = \frac{1}{r} + \frac{1}{2}\frac{r^2}{R_\mathrm{n}^3} - \frac{3}{2R_\mathrm{n}}. \tag{8}$$

The first-order energy correction can therefore be determined. The magnitude is $1.6 \times 10^{-10} E_\mathrm{H}$. It's small, but is already observable using existing spectrography techniques.

1.4 Relativistic kinetic energy

Another relativistic effect, apart from SOC, is the kinetic energy of an electron is actually

$$T = \sqrt{m^2c^4 + p^2c^2}, \tag{9}$$

and not just $p^2/2m$. So now we have a perturbation term in the kinetic energy. The Taylor expansion gives

$$T = mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots \,, \tag{10}$$

and the first relativistic correction is

$$H = -\frac{p^4}{8m^3c^2}. \tag{11}$$

Its expectation can be found using the following trick:

$$\begin{aligned} \langle\psi|H|\psi\rangle &\propto (\, \langle\psi|\, p^2)(p^2 \,|\psi\rangle) \\ &= \langle\psi|\, 2(E - V(r)) \cdot 2(E - V(r)) \,|\psi\rangle \,, \end{aligned} \tag{12}$$

and this can be further simplified using Virial's theorem

$$2\,\langle T\rangle = \langle \boldsymbol{r} \cdot \boldsymbol{v} V\rangle \,, \tag{13}$$

which, in the Coulomb case, means for *all* eigenstates (and not just the ground state), we have

$$\langle T\rangle = -E_n, \quad \langle V\rangle = 2E_n. \tag{14}$$

The $\left\langle V^2\right\rangle$ term can be evaluated using Feynman-Hellmun theorem

$$\frac{\partial E_n(\lambda)}{\partial\lambda} = \langle\psi(\lambda)|\frac{\partial H(\lambda)}{\partial\lambda}|\psi(\lambda)\rangle \,. \tag{15}$$

Recall that there is a

$$\frac{l(l+1)}{2r^2}$$

term in the Hamiltonian, and we find

$$\frac{\partial}{\partial l}\left(-\frac{1}{(n_r + l)^2}\right)^2 = \left\langle\frac{2l+1}{r^2}\right\rangle, \tag{16}$$

and $\left\langle 1/r^2\right\rangle$ can then be found by taking the derivative of $E_n = E_{n_r+l}$.