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 Finite size effects

1.2.1 Finite nucleus mass

In reality, the nucleus has a finite mass and therefore also moves together with the electron. Fortunately this is a two-body problem and we can work in the center of mass frame, and the EOM of $\boldsymbol{r}_{\text{electron}} - \boldsymbol{r}_{\text{nucleus}}$ is governed by the usual Newton's second law with the mass being

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \approx m_1 - \frac{m_1^2}{m_2}, \quad m_2 \to \infty. \tag{1}$$

Thus

$$\frac{\delta E_n}{E_n} = -\frac{m_1}{m_2} = -\frac{1}{1850} \tag{2}$$

for hydrogen. This relative error is the same for all energy levels; it immediately leads to the **isotope shift**, in which adding a neutron to the nucleus changes the energy levels. This is the most important correction.

1.2.2 Going into the nucleus

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

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

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

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

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

$$V(r) = \begin{cases} -\frac{1}{r}, & r > R_{\text{n}}, \\ \frac{1}{2}\frac{r^2}{R_{\text{n}}^3} - \frac{3}{2R_{\text{n}}}, & r < R_{\text{n}}. \end{cases} \tag{5}$$

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

$$V(r) - V_0(r) = \frac{1}{r} + \frac{1}{2}\frac{r^2}{R_{\text{n}}^3} - \frac{3}{2R_{\text{n}}}. \tag{6}$$

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

1.3 Relativistic corrections

1.3.1 Spin-orbital coupling

The first order perturbation of the SOC Hamiltonian is

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

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

$$\boldsymbol{L}\cdot\boldsymbol{S} = \frac{\hbar^2}{2}(j(j+1) - l(l+1) - s(s+1)). \tag{7}$$

So the energy perturbation is just

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

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

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

to the total Hamiltonian, where

$$\left\langle \frac{1}{r^3}\right\rangle = \frac{1}{l(l+1/2)(l+1)n^3}. \tag{9}$$

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 $L_z = \sum m\,|n,l,m,m_s\rangle\langle n,l,m,m_s|$.

We can estimate the magnitude of SOC correction: we have

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

1.3.2 Relativistic kinetic energy

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

$$T = \sqrt{m^2c^4 + p^2c^2}, \tag{11}$$

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

$$T = mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots, \tag{12}$$

and the first relativistic correction is

$$H = -\frac{p^4}{8m^3c^2}. \tag{13}$$

Its expectation can be found using the following trick:

$$\begin{aligned}\langle\psi|H|\psi\rangle &\propto (\langle\psi|\,p^2)(p^2\,|\psi\rangle)\\ &= \langle\psi|\,2(E-V(r))\cdot 2(E-V(r))\,|\psi\rangle\,,\end{aligned} \tag{14}$$

and this can be further simplified using Virial's theorem

$$2\langle T\rangle = \langle \boldsymbol{r}\cdot\boldsymbol{v}V\rangle\,, \tag{15}$$

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

$$\langle T\rangle = -E_n, \quad \langle V\rangle = 2E_n. \tag{16}$$

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

$$\frac{\partial E_n(\lambda)}{\partial \lambda} = \langle \psi(\lambda) | \frac{\partial H(\lambda)}{\partial \lambda} | \psi(\lambda) \rangle \,. \tag{17}$$

Recall that there is a

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

term in the Hamiltonian, and we find

$$\frac{\partial}{\partial l} \left(-\frac{1}{(n_r + l)^2} \right)^2 = \left\langle \frac{2l+1}{r^2} \right\rangle, \tag{18}$$

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

$$E^{(1)}_{\text{rel}} = \frac{1}{2mc^2} \frac{(E^{(0)}_n)^2}{mc^2} \left(\frac{4n}{l+1/2} - 3 \right). \tag{19}$$

This term is extremely small. It can be easily seen that when $l = 0$, the term takes its maximum, but even at the maximum its magnitude is still only $\sim 1\,\text{MHz}$.

Thus the main relativistic correction to atomic energy levels is SOC. The energy level splitting caused by SOC is called the **fine structure**. But not that the relative magnitude of it compared with Coulomb interaction between electrons is not known: it's possible that the single-body SOC is more important, but the opposite case – that Coulomb interaction between electrons is stronger – is also possible.

1.3.3 The Darwin term

1.4 Electron-nucleus interaction beyond Coulomb potential

The interaction between the electron and the nucleus is of course not restricted to Coulomb interaction. The nucleus can have a spin, and then magnetic dipole interaction becomes a perturbation. We can link spin and magnetic moment by

$$\boldsymbol{\mu} = \frac{g}{2m} \boldsymbol{S}, \tag{20}$$

and we also have

$$\boldsymbol{B} = \frac{\mu_0}{4\pi r^3} (3(\boldsymbol{\mu} \cdot \hat{\boldsymbol{r}})\hat{\boldsymbol{r}} - \boldsymbol{\mu}) + \frac{2}{3} \mu_0 \boldsymbol{\mu} \delta^3(\boldsymbol{r}), \tag{21}$$

and therefore the Hamiltonian is

$$H = \frac{\mu_0 g_{\text{n}} e^2}{8\pi m_{\text{n}} m_e} \left(\frac{3(\boldsymbol{I} \cdot \hat{\boldsymbol{r}})(\boldsymbol{S} \cdot \hat{\boldsymbol{r}})}{r^3} - \boldsymbol{S} \cdot \boldsymbol{I} \right) + \frac{\mu_0 g_{\text{n}} e^2}{3\pi m_{\text{n}} m_e} \boldsymbol{I} \cdot \boldsymbol{S}. \tag{22}$$

When $l = 0$, the first-order perturbation caused by this Hamiltonian is proportion to $\langle \boldsymbol{S} \cdot \boldsymbol{I} \rangle$, because the $(\boldsymbol{I} \cdot \hat{\boldsymbol{r}})(\boldsymbol{S} \cdot \hat{\boldsymbol{r}})$ vanishes after $\int \mathrm{d}\Omega$. We define

$$\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{S}, \tag{23}$$

so that

$$2\boldsymbol{I} \cdot \boldsymbol{S} = F(F+1) - I(I+1) - S(S+1), \tag{24}$$

and we can use F to label

The energy level splitting caused by this effect is **hyperfine structure**. We have

$$\frac{E_{\text{HFS}}}{E_n} \sim 1 \times 10^{-7}, \tag{25}$$

which is still larger than the finite size nucleus effect.

1.5 Fluctuation of electromagnetic field

Lamb shift can be estimated using the following approach: we can obtain a "vacuum electric field strength" from the zero-point energy, and then apply this electric field to the atom.

After finding $\delta\boldsymbol{r}$, the perturbation of the atomic energy can be estimated by Taylor expansion of the Coulomb potential. We have

$$V(\boldsymbol{r}+\delta\boldsymbol{r}) = V(\boldsymbol{r}) + \delta\boldsymbol{r}\cdot\boldsymbol{\nabla}V + \frac{1}{2}(\delta\boldsymbol{r}\cdot\boldsymbol{\nabla})^2 V + \cdots, \tag{26}$$

and we can find its average and get

$$\Delta V = \alpha^5 mc^2 \frac{1}{6\pi}\ln\frac{2}{\pi a}. \tag{27}$$

This correction goes beyond all single-atom corrections discussed before; historically it was a strong support of quantum electrodynamics because it revealed that in a space without photons, we still can't completely ignore the presence of the electromagnetic field.

This sometimes is called a proof of the existence of the zero-point energy, although what it really proves is the quantum nature of the electromagnetic field.

2 CG coefficients and energy level splitting in external fields

We may want to know the relation between $|l,m_l\rangle\otimes|s,m_s\rangle$ and $|j,m_j\rangle$. Let's start with an example. We have

$$J_-\left|j=\frac{3}{2},m_j=\frac{3}{2}\right\rangle = \sqrt{j(j+1)-m_j(m_j-1)}\,|j,m_j-1\rangle = \sqrt{3}\left|j=\frac{3}{2},m_j=\frac{1}{2}\right\rangle. \tag{28}$$

Since the only possibility to have $j=3/2$, $m_j=3/2$ is that $l=1,m_l=1$ and $s=1/2,m_s=1/2$, we have

$$\left|j=\frac{3}{2},m_j=\frac{3}{2}\right\rangle = |l=1,m_l=1\rangle\otimes\left|s=\frac{1}{2},m_s=\frac{1}{2}\right\rangle, \tag{29}$$

and we also know that

$$J_- = S_- + L_-, \tag{30}$$

and we get

$$\begin{aligned}\sqrt{3}\left|j=\frac{3}{2},m_j=\frac{1}{2}\right\rangle &= (L_-+S_-)\,|l=1,m_l=1\rangle\otimes\left|s=\frac{1}{2},m_s=\frac{1}{2}\right\rangle\\ &= \sqrt{1(1+1)-1(1-1)}\,|l=1,m_l=0\rangle\otimes\left|s=\frac{1}{2},m_s=\frac{1}{2}\right\rangle\\ &\quad+|l=1,m_l=1\rangle\otimes\sqrt{\frac{1}{2}(\frac{1}{2}+1)-\frac{1}{2}(\frac{1}{2}-1)}\left|s=\frac{1}{2},m_s=-\frac{1}{2}\right\rangle,\end{aligned} \tag{31}$$

and we find

$$\begin{aligned}\left|j=\frac{3}{2},m_j=\frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}\Big(&\sqrt{2}\,|l=1,m_l=0\rangle\otimes\left|s=\frac{1}{2},m_s=\frac{1}{2}\right\rangle\\ &+|l=1,m_l=1\rangle\otimes\left|s=\frac{1}{2},m_s=-\frac{1}{2}\right\rangle\Big).\end{aligned} \tag{32}$$

This routine can be repeated for other states. To save space, below we use $\left|\frac{3}{2},\left|\frac{3}{2}\right\rangle\right\rangle$ to refer to $|j,m_l\rangle$, and use $|1,1\rangle\otimes\left|\frac{1}{2},-\frac{1}{2}\right\rangle$ to refer to $|l,m_l\rangle\otimes|s,m_s\rangle$.

Now we are able to evaluate the energy correction caused by external fields. For example, we have

$$\left\langle\frac{3}{2},\frac{1}{2}\right|L_z+2S_z\left|\frac{1}{2},\frac{1}{2}\right\rangle = \tag{33}$$