

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 $\mathbf{r}_{\text{electron}} - \mathbf{r}_{\text{nucleus}}$ is governed by the usual Newton's second law with the mass being

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \approx m_1 - \frac{m_1^2}{m_2}, \quad m_2 \rightarrow \infty. \quad (1)$$

Thus

$$\frac{\delta E_n}{E_n} = -\frac{m_1}{m_2} = -\frac{1}{1850} \quad (2)$$

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

$$V(r) = \frac{1}{2} \frac{r^2}{R_n^3} - \frac{3}{2R_n}. \quad (3)$$

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

$$4\pi r^2 \cdot F(r) = \int_0^r \frac{Ze}{\frac{4}{3}\pi R_n^3} \cdot 4\pi r'^2 dr'. \quad (4)$$

The constant term is there to guarantee continuity at $r = R_n$. So

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

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

$$V(r) - V_0(r) = \frac{1}{r} + \frac{1}{2} \frac{r^2}{R_n^3} - \frac{3}{2R_n}. \quad (6)$$

The first-order energy correction can therefore be determined. The magnitude is $1.6 \times 10^{-10} E_H$. 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

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

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

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

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

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

to the total Hamiltonian, where

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

Formally, this means we have averaged over $1/r^3$ only; but note that strictly speaking \mathbf{L} is no longer the old \mathbf{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

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

1.3.2 Relativistic kinetic energy

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

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

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

$$T = mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots, \quad (12)$$

and the first relativistic correction is

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

Its expectation can be found using the following trick:

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

and this can be further simplified using Virial's theorem

$$2 \langle T \rangle = \langle \mathbf{r} \cdot \nabla V \rangle, \quad (15)$$

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

$$\langle T \rangle = -E_n, \quad \langle V \rangle = 2E_n. \quad (16)$$

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

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

Recall that there is a

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

term in the Hamiltonian, and we find

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

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

$$E_{\text{rel}}^{(1)} = \frac{1}{2mc^2} \frac{(E_n^{(0)})^2}{mc^2} \left(\frac{4n}{l+1/2} - 3 \right). \quad (19)$$

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 ~ 1 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

$$\boldsymbol{\mu} = \frac{g}{2m} \mathbf{S}, \quad (20)$$

and we also have

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

and therefore the Hamiltonian is

$$H = \frac{\mu_0 g_n e^2}{8\pi m_n m_e} \left(\frac{3(\mathbf{I} \cdot \hat{\mathbf{r}})(\mathbf{S} \cdot \hat{\mathbf{r}})}{r^3} - \mathbf{S} \cdot \mathbf{I} \right) + \frac{\mu_0 g_n e^2}{3\pi m_n m_e} \mathbf{I} \cdot \mathbf{S}. \quad (22)$$

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

$$\mathbf{F} = \mathbf{I} + \mathbf{S}, \quad (23)$$

so that

$$\mathbf{I} \cdot \mathbf{S} = F(F+1) - I(I+1) - S(S+1), \quad (24)$$

and we can use F to label

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

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

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

$$V(\mathbf{r} + \delta\mathbf{r}) = V(\mathbf{r}) + \delta\mathbf{r} \cdot \nabla V + \frac{1}{2}(\delta\mathbf{r} \cdot \nabla)^2 V + \dots, \quad (26)$$

and we can find its average and get

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

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 Energy level splitting in external fields

$$E_n = \frac{-13.6 \text{ eV}}{n^2} + \mu_B(2m_s + m_l). \quad (28)$$