

Theory of atom

Jinyuan Wu

March 28, 2023

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

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

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 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

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

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

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

and we also know that

$$J_- = S_- + L_-, \quad (30)$$

and we get

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

and we find

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

This routine can be repeated for other states. To save space, below we use $|\frac{3}{2}, \frac{3}{2}\rangle$ to refer to $|j, m_j\rangle$, and use $|1, 1\rangle \otimes |\frac{1}{2}, -\frac{1}{2}\rangle$ 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 from first principles. For example, we have

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

The fact that the non-diagonal matrix elements don't vanish means the external fields mix different $|j, m_j\rangle$ states. This then means that generally, the energy change caused by external magnetic fields is not linear. When the external magnetic field is weak, only first order perturbation is important and we can use the effective Lande g factor approach, and $\Delta E \propto B$; but when the external magnetic field is stronger, this no longer works.