# 3. Relativistic corrections

As we see, the spin of the electron (and proton) will play an important role : overview of angular momentums.

## A- Angular momentum $\vec{L}$ :

When describing H-atom, we introduced the angular momentum operator $\hat{L}$

$$\hat{L} = \hat{r} \times \hat{p} \quad \text{or} \quad \begin{cases} \hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \end{cases}$$

where $\hat{x}_i$ and $\hat{p}_j = -i\hbar \frac{\partial}{\partial x_j}$ are $i^{th}$ position operator & $j^{th}$ linear momentum operator

From $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$, it follows

$$\left.\begin{aligned} [\hat{L}_x, \hat{L}_y] &= i\hbar\hat{L}_z \\ [\hat{L}_y, \hat{L}_z] &= i\hbar\hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar\hat{L}_y \end{aligned}\right\} \quad \text{or} \quad [\hat{L}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{L}_k$$

Levi-Civita symbol
$= +1$ if $i,j,k$ is an even permutation of 1, 2, 3
$-1$ if odd permut.
or $0$ if indices are repeated

Usually, choose $z$-axis as quantization axis

$\Rightarrow \hat{L}_z$ : relevant operator to describe dynamics

We can combined the 2 remaining operators

$$\hat{L}_\pm \equiv \hat{L}_x \pm i \hat{L}_y \quad : \quad \text{ladder operators} \begin{cases} + & \text{raising} \\ - & \text{lowering} \end{cases}$$

Using spherical coordinates, as we did before, with

$$x = r\sin\theta\cos\varphi$$
$$y = r\sin\theta\sin\varphi$$
$$z = r\cos\theta$$

we obtain

$$\hat{L}_x = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{\operatorname{tg}\theta}\frac{\partial}{\partial\varphi}\right)$$

$$\hat{L}_y = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \frac{\sin\varphi}{\operatorname{tg}\theta}\frac{\partial}{\partial\varphi}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{\operatorname{tg}\theta}\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2}\right]$$

$$\hat{L}_\pm = \hbar e^{\pm i\varphi}\left(i\cot\theta\frac{\partial}{\partial\varphi} \pm \frac{\partial}{\partial\theta}\right)$$

Applying these operators on $\phi_{n\ell m} = \frac{1}{r}u_{n\ell}(r)Y_{\ell m}(\theta,\varphi)$

$$\Rightarrow \hat{L}^2\phi_{n\ell m} = \hbar^2\ell(\ell+1)\phi_{n\ell m}$$

$$\hat{L}_z\phi_{n\ell m} = m\hbar\,\phi_{n\ell m}$$

$$\hat{L}_\pm\phi_{n\ell m} = \hbar\sqrt{\ell(\ell+1) - m(m\pm1)}\;\phi_{n\ell m\pm1}$$

hence their name...

A general angular momentum operator $\hat{J}$ will obey the same relationship as the orbital angular momentum $\hat{L}$, i.e.

$$[\hat{J}_i, \hat{J}_j] = i\hbar\, \varepsilon_{ijk} \hat{J}_k$$

Choosing z-axis for quantization

$\Rightarrow$ $\hat{J}_z$ and $\hat{J}_\pm = \hat{J}_x \pm i \hat{J}_y$

with
$$\hat{J}^2 |k, j, m\rangle = \hbar^2 j(j+1) |k, j, m\rangle$$
$$\hat{J}_z |k, j, m\rangle = m\hbar |k, j, m\rangle$$
$$\hat{J}_\pm |k, j, m\rangle = \hbar\sqrt{j(j+1) - m(m\pm 1)}\, |k, j, m\pm 1\rangle$$

B. <u>Spin of the electron</u> $\hat{S}$

$\Rightarrow$ angular momentum that cannot be related to ordinary coordinates, ~~to~~ but follows above rules

$\hat{S}$ has no classical counterpart [known from measurement]

Again, we write state as $|s, m_s\rangle$:
$$\hat{S}^2 |s, m_s\rangle = s(s+1)\hbar^2 |s, m_s\rangle = \frac{3}{4}\hbar^2 |s, m_s\rangle$$
$$\hat{S}_z |s, m_s\rangle = m\hbar |s, m_s\rangle = \pm\frac{1}{2}\hbar |s, m_s\rangle$$

$\Rightarrow$ conclude that $s = 1/2$ and $m_s = \pm 1/2$

and $\hat{S}_\pm |s, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}\, |s, m_s \pm 1\rangle$

So, the wavefunction of an $e^-$ depends not only on its position $\vec{r}$, but also on the value of $m_s$

We introduce a useful notation (spinors):

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \equiv |1/2, 1/2\rangle \quad \text{and} \quad \chi_+^\dagger = (1 \;\; 0) \equiv \langle 1/2, 1/2|$$

$$\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \equiv |1/2, -1/2\rangle \quad \text{and} \quad \chi_-^\dagger = (0 \;\; 1) \equiv \langle 1/2, -1/2|$$

so that

$$\psi(q) = \begin{pmatrix} \psi_+(\vec{r}) \\ \psi_-(\vec{r}) \end{pmatrix} = \psi_+(\vec{r})\chi_+ + \psi_-(\vec{r})\chi_-$$

↳ stands for $\vec{r}$ and $m_s$.

This can be used to write $\hat{S}^2$ etc... in a matrix form

$$\hat{S}^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \hat{S}_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \hat{S}_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

and

$$\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-) = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{and} \quad \hat{S}_y = \frac{i}{2}(\hat{S}_+ - \hat{S}_-) = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

⇒ convenient to define a set of 2×2 matrices

$$\hat{\sigma}_x \equiv \frac{2}{\hbar}\hat{S}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y \equiv \frac{2}{\hbar}\hat{S}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \text{and} \quad \hat{\sigma}_z \equiv \frac{2}{\hbar}\hat{S}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

These are known as Pauli spin matrices.

Together with the 2X2 unit matrix $\hat{\mathbb{1}}$, they can be used to write the most general linear operator in the 2X2 Hilbert space of one electron states

$$\hat{\mathcal{O}} = \hat{\mathcal{O}}_c \hat{\mathbb{1}} + \hat{\mathcal{O}}_x \hat{\sigma}_x + \hat{\mathcal{O}}_y \hat{\sigma}_y + \hat{\mathcal{O}}_z \hat{\sigma}_z$$

where $\hat{\mathcal{O}}_j$ are spin-independent operators (e.g., $\hat{p}$, $\hat{p}^2$, $\hat{r}$ etc...)

## C- Dirac equation and relativistic corrections

We will show that the effect of relativity on one electron in the presence of an "infinitely" massive proton leads to

$$H = \underbrace{m_e c^2}_{\text{rest energy}} + \underbrace{\frac{\hat{p}^2}{2m_e} + V(r)}_{\substack{H_0 \\ \text{non-rel. energy}}} - \underbrace{\frac{\hat{p}^4}{8 m_e^3 c^2}}_{\substack{W_{mv} \\ 1^{st} \text{ correction to kinetic energy}}} + \underbrace{\frac{1}{2m_e^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\hat{L}\cdot\hat{S}}_{W_{so} \,:\, \text{spin-orbit}} + \underbrace{\frac{\hbar^2}{8m_e^2c^2}\nabla^2 V(r)}_{W_D \,:\, \text{Darwin}} + \ldots$$

~~Thus~~ The $1^{st}$ 3 terms can easily be understood by expanding the relativistic energy of a classical particle of rest mass $m_e$ and momentum $\vec{p}$ (in powers of $|\vec{p}|/m_e c$):

$$E = c\sqrt{p^2 + m_e^2c^2} \simeq m_e c^2 + \frac{\vec{p}^{\,2}}{2m_e} - \frac{\vec{p}^{\,4}}{8 m_e^3 c^2} + \ldots$$

To derive those results, let us first look at the case of a free electron.

We first notice that the Schrödinger Eq. is not a covariant equation satisfying special relativity: it has 1st derivative in time $\frac{\partial}{\partial t}$ and 2nd derivative in space $\nabla^2$.

In 1928, Dirac proposed an eq. ~~with only~~ linear in all derivatives

$$i\hbar \frac{\partial \psi}{\partial t} = \left[ c\,\hat{\alpha}\cdot\hat{p} + \hat{\beta} m_0 c^2 \right] \psi \equiv \hat{H}\psi$$

Here, "c" (speed of light) is explicit so that the parameters $\beta$ and matrix $\hat{\alpha} = (\hat{\alpha}_x, \hat{\alpha}_y, \hat{\alpha}_z)$

$$= (\hat{\alpha}_1, \hat{\alpha}_2, \hat{\alpha}_3)$$

remain dimensionless.

Squaring $\hat{H}$ and comparing with the relativistic energy $E^2 = \hat{p}^2 c^2 + m_0^2 c^4$ yields

$$\hat{H}^2 = \frac{c^2}{2} \sum_{i,j=1}^{3} (\hat{\alpha}_i \hat{\alpha}_j + \hat{\alpha}_j \hat{\alpha}_i)\hat{p}_i \hat{p}_j + m_0 c^2 \sum_{i=1}^{3} (\hat{\alpha}_i \hat{\beta} + \hat{\beta}\hat{\alpha}_i)\hat{p}_i + \hat{\beta}^2 m_0^2 c^4$$

which implies

$$\hat{\alpha}_i \hat{\alpha}_j + \hat{\alpha}_j \hat{\alpha}_i = 2\delta_{ij}$$

$$\hat{\alpha}_i \hat{\beta} + \hat{\beta}\hat{\alpha}_i = 0$$

$$\hat{\beta}^2 = 1$$