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34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONES: 224281/2/3/4/5/6
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Atomic Spectra
Spin-Orbit Interaction and Other Relativistic Corrections

J. BAUCHE

Laboratoire Aimé Cotton
C.N.R.S. II
Campus d'Orsay, Bâtiment 505
91405 Orsay Cedex
France

Trieste
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Lectures on Atomic Spectra

II. SPIN-ORBIT INTERACTION and other relativistic corrections

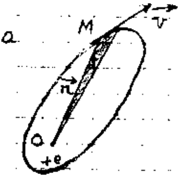
The spin-orbit interaction is important as well in Molecular Physics and Nuclear Physics as in Atomic Physics.

1. Spin-orbit interaction: semi-classical description

Inside the atomic system, each electron bears a magnetic moment associated with its spin. These magnetic moments interact with the magnetic fields created by the charge motions.

ⓐ Orbital magnetic moment.

The relation between the angular and magnetic momenta is easily found in the orbital case. Let us consider an electronic orbit in the hydrogen atom, S being the area of this elliptical orbit. The associated magnetic moment is $\vec{\mathcal{M}} = S I \vec{k}$, I being the electrical current equivalent to the electronic motion, and $\vec{k}$ a unit vector orthogonal to the orbital plane.



Now, $I = -e\nu$, where ν is the frequency of the rotation of the electron around the nucleus, and $S\nu$ is the area swept by the electronic position vector during one unit of time, also written $\frac{dS}{dt}$. But dS, the area of the blackened triangle above, is such that $\frac{dS}{dt}\vec{k} = \frac{1}{2}\vec{r}\times\frac{d\vec{r}}{dt} = \frac{1}{2m}\vec{l}$, where $\vec{l}$ is the orbital angular momentum. Therefore $\boxed{\vec{\mathcal{M}}_l = -\frac{e}{2m}\vec{l}}$ (1) is the orbital magnetic moment. $\gamma_l = \frac{-e}{2m}$ is called the orbital gyromagnetic ratio.

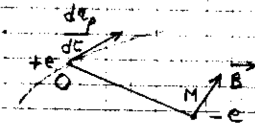
ⓑ Spin magnetic moment.

Uhlenbeck and Goudsmit, who discovered the electron spin in 1925,

also discovered empirically that its gyromagnetic ratio is $\gamma_s = -\frac{e}{m}$, i.e., twice the orbital γ_l. Therefore $\boxed{\vec{\mathcal{M}}_s = -\frac{e}{m}\vec{s}}$ (2) is the spin magnetic moment. The "abnormal" spin gyromagnetic ratio — abnormal in the sense that it cannot be explained in a classical electromagnetic model of a rotating electron, etc — is perfectly "normal" in Dirac's relativistic formalism.

ⓒ Spin-orbit interaction in the hydrogen atom.

The spin-orbit interaction is easy to visualize only if we suppose we are in the same referential as the electron (however, note that this referential is not Galilean). In this referential, the proton turns around the electron on an orbit identical with that of the electron around the proton, thus creating a magnetic field $\vec{B}$ at the location of the electron. We can compute $\vec{B}$, denoting $\vec{r}_p = \vec{MO} = -\vec{r}$ the position vector of the nucleus relative to the electron.



From Biot and Savart, $\vec{B} = \frac{\mu_0}{4\pi}(+e)\frac{d\vec{r}_p}{dt}\times\frac{-\vec{r}_p}{r_p^3}$

$= \frac{\mu_0}{4\pi}e\frac{1}{r^3}\vec{r}\times\frac{d\vec{r}}{dt} = \frac{\mu_0}{4\pi}\frac{e}{m}\frac{1}{r^3}\vec{l}$. Now, the interaction of the spin magnetic moment with $\vec{B}$ is $W = -\vec{\mathcal{M}}_s\cdot\vec{B} = \frac{\mu_0}{4\pi}\frac{e^2}{m^2}\frac{\vec{s}\cdot\vec{l}}{r^3}$

It must be allowed for the fact that this calculation has been made in a non-Galilean referential. Following a derivation made by THOMAS in 1926, we merely have to multiply our result by $\frac{1}{2}$. Using also the equation $\varepsilon_0\mu_0 c^2 = 1$, we obtain

$$\Lambda = \frac{e^2}{2m^2c^2}\frac{1}{r^3}\vec{s}\cdot\vec{l} \qquad (3)$$

for the spin-orbit operator. (note that the $\frac{1}{4\pi\varepsilon_0}$ factor has been omitted as usual.)

ⓓ Spin-orbit interaction in an alkali.

There exists another quick way to express the magnetic field $\vec{B}$ computed above, but this requires to remember the formula $\vec{B} = \frac{\vec{E} \times \vec{v}}{c^2}$ for the magnetic field "seen" by a particle moving with velocity $\vec{v}$ in a static electrostatic field $\vec{E}$. Because in the hydrogen atom $\vec{E} = -\vec{\nabla} V_{elec} = \frac{e}{r^2} \frac{\vec{r}}{r}$, we obtain again eq.(3).

The same formula $\vec{B} = \frac{\vec{E} \times \vec{v}}{c^2}$ can be applied in the more complicated case of the alkalis. An alkali system is an N-electron atom or ion where N-1 "core" electrons form a spherically-symmetric group, into which the outermost electron plunges from time to time along its orbit around the nucleus. The electrostatic potential "seen" by that "optical" electron, which is practically hydrogenic at large distances from the nucleus, increases more rapidly than $\frac{1}{r}$ when the electron enters the core (this image is developed in Lecture III for any kind of atom).

Denoting V(r) the potential energy of the outer electron in the field created by the nucleus and the electron core, we have $\vec{E} = \frac{1}{e} \vec{\nabla} V = \frac{1}{e} \frac{dV}{dr} \frac{\vec{r}}{r}$. Comparing with $\vec{E}$ obtained above for hydrogen, we see that $\frac{e}{r^2}$ is replaced by $\frac{1}{e} \frac{dV}{dr}$, so that for alkalis the spin-orbit operator reads

$$\Lambda_{alc.} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \vec{s} \cdot \vec{\ell} . \qquad (4)$$

2. Other relativistic corrections: semi-classical description

ⓐ Magnetic interactions.

There exist many other magnetic interactions than the spin-orbit inside the atom. Selecting arbitrarily two electrons with their orbital moments $\vec{\ell}_1$ and $\vec{\ell}_2$ and spins $\vec{s}_1$

and $\vec{s}_2$, we see four evident types of interactions:

$\vec{s}_1$ with $\vec{\ell}_1$ and $\vec{s}_2$ with $\vec{\ell}_2$: spin-orbit interactions
$\vec{s}_1$ with $\vec{\ell}_2$ and $\vec{s}_2$ with $\vec{\ell}_1$: spin-other-orbit interactions
$\vec{s}_1$ with $\vec{s}_2$: spin-spin interaction
$\vec{\ell}_1$ with $\vec{\ell}_2$: orbit-orbit interaction

All these interactions are of the same order of magnitude, namely, their matrix elements are of the order of magnitude of the atomic energy unit multiplied by α^2, where $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}$ is the fine-structure constant, whose numerical value is close to $\frac{1}{137}$ (to prove this, we just note that $\Lambda_{alc.}$ (eq.(4)) contains purely atomic quantities (see Lecture I, top of p. I.4) except $\frac{1}{c^2}$, which derives from $\frac{\mu_0}{4\pi}$ being used once).

Remark. Actually, the numerical calculations show that the spin-orbit and spin-other-orbit interactions largely predominate except for $Z \lesssim 5$.

ⓑ Mass correction.

It is well known that, in Relativity, mass is an increasing function of speed. Knowing that the atomic unit of energy is proportional to m, we see that the total energy of the atom is certainly lowered by the relativity phenomenon. More quantitatively, the quantity $\frac{\vec{p}^2}{2m_{rel}} = \frac{\vec{p}^2}{2m} \sqrt{1 - \frac{v^2}{c^2}}$ can be expanded to the first order in $\frac{v^2}{c^2}$, which gives the operator $-\alpha^2 \left(\frac{\vec{p}^2}{2m}\right)^2$ (in atomic units) for the so-called "relativistic mass correction".

3. Quantum-mechanical formalism.

Unfortunately, we have no time to study the relativistic formalism imagined by DIRAC in 1928. It is much

more complicated than the non-relativistic formalism.
For example, the simple non-relativistic function of the $1s, m_s = +\frac{1}{2}$ state of hydrogen is replaced by the vector
$$\begin{pmatrix} f_{1s}(r)\,|(s, \ell = 0)\, j = m = \frac{1}{2}\rangle \\ g_{1s}(r)\,|(s, \ell = 1)\, j = m = \frac{1}{2}\rangle \end{pmatrix}$$
where $f_{1s}(r)$ and $g_{1s}(r)$ are solutions of two coupled differential equations. Accordingly, the non-relativistic operators are replaced by 2×2 matrices.

Remark: this formalism is sometimes presented with four-component vectors and 4×4 matrices, i.e. when the spin functions themselves are written as two-component spinors.

Reference: the book by Bethe and Salpeter, *Quantum Mechanics of one- and two-electron systems*, Springer-Verlag, Berlin (1957).

It has been shown that, to order α^2 (or, equivalently, $\frac{v^2}{c^2}$) of the expansion of the relativistic matrix elements, the relativistic corrections to the non-relativistic energy values of the atomic levels can be reproduced by *effective operators* acting in the non-relativistic scheme (Blume and Watson, Proc. Roy. Soc. A 271, 565 (1963); Armstrong, J. Math. Phys. 7, 1891 (1966)). These operators turn to be identical with those described in 2. above, plus some contact interactions like the Darwin term and the spin-spin contact term.