Diamagnetism and paramagnetism
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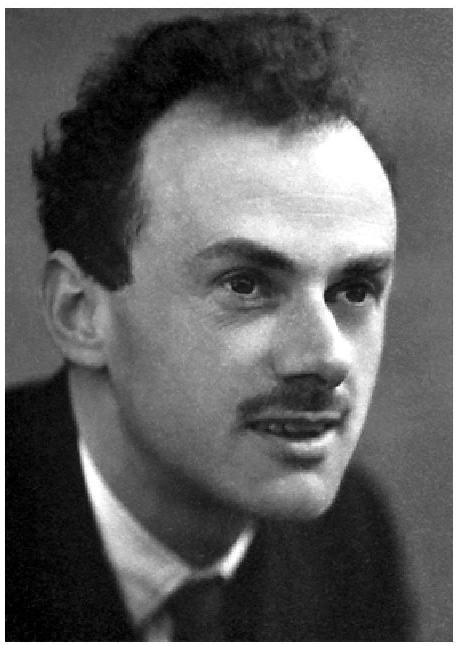
Paul Adrien Maurice Dirac, OM, FRS (8 August 1902 – 20 October 1984) was an English theoretical physicist who made fundamental contributions to the early development of both quantum mechanics and quantum electrodynamics. He held the Lucasian Chair of Mathematics at the University of Cambridge, was a member of the Center for Theoretical Studies, University of Miami, and spent the last decade of his life at Florida State University. Among other discoveries, he formulated the Dirac equation, which describes the behaviour of fermions, and predicted the existence of antimatter. Dirac shared the Nobel Prize in Physics for 1933 with Erwin Schrödinger, "for the discovery of new productive forms of atomic theory."



http://en.wikipedia.org/wiki/Paul_Dirac

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1. Lagrangian of particles with mass *m** and charge *q** in the presence of magnetic field

The Lagrangian L for the motion of a particle in the presence of magnetic field and electric field is given by

$$L = \frac{1}{2} m\boldsymbol{v}^2 - q(\varphi - \frac{1}{c}\boldsymbol{v}\cdot\boldsymbol{A}),$$

where m and q are the mass and charge of the particle. $\boldsymbol{A}$ is a vector potential and ϕ is a scalar potential. The canonical momentum is defined as

$$\boldsymbol{p} = \frac{\partial L}{\partial \boldsymbol{v}} = m\boldsymbol{v} + \frac{q}{c}\boldsymbol{A}.$$

The mechanical momentum (the measurable quantity) is given by

$$\boldsymbol{\pi} = m\boldsymbol{v} = \boldsymbol{p} - \frac{q}{c}\boldsymbol{A}.$$

The Hamiltonian H is given by

$$H = \boldsymbol{p}\cdot\boldsymbol{v} - L = (m\boldsymbol{v} + \frac{q}{c}\boldsymbol{A})\cdot\boldsymbol{v} - L = \frac{1}{2}m\boldsymbol{v}^2 + q\varphi = \frac{1}{2m^*}(\boldsymbol{p} - \frac{q}{c}\boldsymbol{A})^2 + q\varphi.$$

The Hamiltonian formalism uses $\boldsymbol{A}$ and ϕ, and not $\boldsymbol{E}$ and $\boldsymbol{B}$, directly. The result is that the description of the particle depends on the gauge chosen.

2. Hamiltonian of an electron in the presence of an external magnetic field

Here we use the notation; $q = -e$ (charge of electron); m (mass of electron). We also assume that $\phi = 0$. The Hamiltonian of the electron is given by

$$\begin{aligned} H &= \frac{1}{2m}(\boldsymbol{p} - \frac{q}{c}\boldsymbol{A})^2 \\ &= \frac{1}{2m}(\boldsymbol{p} + \frac{e}{c}\boldsymbol{A})\cdot(\boldsymbol{p} + \frac{e}{c}\boldsymbol{A}) \\ &= \frac{1}{2m}[\boldsymbol{p}^2 + \frac{e}{c}(\boldsymbol{p}\cdot\boldsymbol{A} + \boldsymbol{A}\cdot\boldsymbol{p})] + \frac{e^2}{2mc^2}\boldsymbol{A}^2 = H_0 + H' \end{aligned}$$

with

$$H_0 = \frac{1}{2m}\boldsymbol{p}^2,$$

and

$$H' = \frac{e}{2mc}(\boldsymbol{p}\cdot\boldsymbol{A} + \boldsymbol{A}\cdot\boldsymbol{p})] + \frac{e^2}{2mc^2}\boldsymbol{A}^2.$$

We note that

$$H'\psi(\boldsymbol{r}) = \frac{e}{2mc}(\boldsymbol{p}\cdot\boldsymbol{A} + \boldsymbol{A}\cdot\boldsymbol{p})\psi(\boldsymbol{r}) + \frac{e^2}{2mc^2}\boldsymbol{A}^2\psi(\boldsymbol{r}).$$

Using the formula (vector analysis),

$$\nabla\cdot[\boldsymbol{A}\psi(\boldsymbol{r})] = \boldsymbol{A}\cdot\nabla\psi(\boldsymbol{r}) + \psi(\boldsymbol{r})\nabla\cdot\boldsymbol{A},$$

we get

$$H'\psi(\boldsymbol{r}) = \frac{e\hbar}{2mci}[\psi(\boldsymbol{r})\nabla\cdot\boldsymbol{A} + 2\boldsymbol{A}\cdot\nabla\psi(\boldsymbol{r})] + \frac{e^2}{2mc^2}\boldsymbol{A}^2\psi(\boldsymbol{r}).$$

We use the vector potential,

$$\boldsymbol{A} = \frac{1}{2}\boldsymbol{B}\times\boldsymbol{r} = \frac{1}{2}\begin{vmatrix} \boldsymbol{e}_x & \boldsymbol{e}_y & \boldsymbol{e}_z \\ 0 & 0 & B \\ x & y & z \end{vmatrix} = \frac{1}{2}(-By, Bx, 0),$$

and

$$\nabla\cdot\boldsymbol{A} = 0$$

where a constant magnetic field $\boldsymbol{B}$ is applied along the z axis.

((**Note**))
When $\boldsymbol{B}$ is the uniform field,

$$\boldsymbol{A} = \frac{1}{2}\boldsymbol{B}\times\boldsymbol{r},$$

from

$$\boldsymbol{B} = \nabla\times\boldsymbol{A}.$$

((**Mathematica**))

```
Clear["Global`*"]; Needs["VectorAnalysis`"];
SetCoordinates[Cartesian[x, y, z]];
B = {Bx, By, Bz}; r = {x, y, z};
eq1 = Curl[1/2 Cross[B, r]]
{Bx, By, Bz}
```

Then we get

$$H'\psi(\mathbf{r}) = [-i\frac{e\hbar B}{2mc}(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}) + \frac{e^2B^2}{8mc^2}(x^2+y^2)]\psi(\mathbf{r})$$
$$= [-i\mu_B\frac{iL_z}{\hbar}B + \frac{e^2B^2}{8mc^2}(x^2+y^2)]\psi(\mathbf{r})$$
$$= [\mu_B\frac{L_z}{\hbar}B + \frac{e^2B^2}{8mc^2}(x^2+y^2)]\psi(\mathbf{r})$$

The Bohr magneton is defined as

$$\mu_B = \frac{e\hbar}{2mc} = 9.27400915 \text{ x } 10^{-21} \text{ erg/G} = 9.27400915 \text{ x } 10^{-23} \text{ emu}$$

or

$$\mu_B = 9.27400915 \text{ x } 10^{-24} \text{ J/T} \qquad \text{(SI units)}$$

where emu = erg/Gauss = erg/Oe. 1T = 10^4 Oe.

The orbital angular momentum $\boldsymbol{L}$ is defined as

$$\boldsymbol{L} = \boldsymbol{r}\times\boldsymbol{p} = \frac{\hbar}{i}\boldsymbol{r}\times\nabla = \frac{\hbar}{i}\begin{vmatrix} \boldsymbol{e}_x & \boldsymbol{e}_y & \boldsymbol{e}_z \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}.$$

in the quantum mechanics. The z component of the angular momentum is

$$L_z = \frac{\hbar}{i}(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}).$$

which is in the unit of $\hbar$ .The orbital magnetic moment $\boldsymbol{\mu}_L$ is

$$\boldsymbol{\mu}_L = -\frac{\mu_B}{\hbar}\boldsymbol{L}.$$

which is in the units of emu. Then the Hamiltonian can be written as

$$H = H_0 + H' = \frac{\boldsymbol{p}^2}{2m} - \boldsymbol{\mu}_L \cdot \boldsymbol{B} + \frac{e^2 B^2}{8mc^2}(x^2 + y^2).$$

The second term is the Zeeman energy. From the third term we get the magnetization from core as

$$M_{core} = -\frac{e^2 B}{4mc^2}(x^2 + y^2)$$

3. Calculation using Mathematica

The above calculation can be carried out by using the Mathematica.

Diamagnetism of electron (qunatum mechanics)

```
Clear["Global`*"]; Needs["VectorAnalysis`"];
SetCoordinates[Cartesian[x, y, z]]; R = {x, y, z}; B = {0, 0, B1};
A1[x_, y_, z_] := {Ax[x, y, z], Ay[x, y, z], Az[x, y, z]};

L1 :=
 (e1 ℏ/(2 m1 c ⅈ) ((Div[# A1[x, y, z]]) + A1[x, y, z].Grad[#]) +
    e1^2/(2 m1 c^2) A1[x, y, z].A1 [x, y, z] #) &

eq1 = L1[ψ[x, y, z]] // Simplify
```

$$\frac{1}{2\,c^2\,m1}\,e1\,\Big(e1\,\big(Ax[x,y,z]^2+Ay[x,y,z]^2+Az[x,y,z]^2\big)\,\psi[x,y,z]-i\,c\,\hbar\,\Big(\psi[x,y,z]\,\big(Az^{(0,0,1)}[x,y,z]+Ay^{(0,1,0)}[x,y,z]+Ax^{(1,0,0)}[x,y,z]\big)+2\,\big(Az[x,y,z]\,\psi^{(0,0,1)}[x,y,z]+Ay[x,y,z]\,\psi^{(0,1,0)}[x,y,z]+Ax[x,y,z]\,\psi^{(1,0,0)}[x,y,z]\big)\Big)\Big)$$

```
rule1 = {Ax → (-1/2 B1 #2 &), Ay → (1/2 B1 #1 &), Az → (0 #3 &)};

eq11 = eq1 /. rule1 // Simplify
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$$\frac{B1\,e1\,\big(B1\,e1\,(x^2+y^2)\,\psi[x,y,z]-4\,i\,c\,\hbar\,\big(x\,\psi^{(0,1,0)}[x,y,z]-y\,\psi^{(1,0,0)}[x,y,z]\big)\big)}{8\,c^2\,m1}$$

4. Relativistic theory of electron (Dirac equation)

According to Dirac, the relativistic Hamiltonian of electron is given by

$$H = c\boldsymbol{\alpha}\cdot\boldsymbol{p} + \boldsymbol{\beta} mc^2$$

in the absence of external fields, where

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \qquad \boldsymbol{\beta} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The Schrödinger equation is given by

$$i\hbar\frac{\partial}{\partial t}\psi = H\psi .$$

with

$$\psi = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}.$$

Thus the wavefunction must be a four-component object. Two of the components correspond to positive-energy solutions and the other two correspond to negative-energy solutions. Holes in the negative-energy spectrum corresponds to positron and require energies of the order of mc^2 for their production

5. Exapansion in powers of 1/*c* (Pauli approximation)

The effect of an external magnetic field is described by the vector potential ***A*** and the electric potential ϕ. The Hamiltonian can be rewritten as

$$H = c\boldsymbol{\alpha}\cdot(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})+\boldsymbol{\beta}mc^2-e\phi\,,$$

by making the usual replacements, where the charge of electron is -*e* (*e*>) and *m* is the mass of electron,

$$\boldsymbol{B} = \nabla\times\boldsymbol{A}\,,\qquad \boldsymbol{E} = -\nabla\phi-\frac{1}{c}\frac{\partial\boldsymbol{A}}{\partial t}\,.$$

Since the energies encountered in magnetic phenomena are much smaller than mc^2, it is convenient to decouple the positive and negative-energy solutions.

$$i\hbar\frac{\partial}{\partial t}\psi = \{c\boldsymbol{\alpha}\cdot(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})+\boldsymbol{\beta}mc^2-e\phi\}\psi$$

The relativistic energy of the electron includes also its rest energy mc^2. Here we put

$$\psi = \psi'\exp(-i\frac{mc^2t}{\hbar})$$

Then

$$(i\hbar\frac{\partial}{\partial t}+mc^2)\psi' = \{c\boldsymbol{\alpha}\cdot(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})+\boldsymbol{\beta}mc^2-e\varphi\}\psi'\,.$$

Substituting $\psi' = \begin{pmatrix}\chi_A\\ \chi_B\end{pmatrix}$, we obtain the equations

$$(i\hbar\frac{\partial}{\partial t}+mc^2+e\phi)\begin{pmatrix}\chi_A\\ \chi_B\end{pmatrix} = \begin{pmatrix} mc^2 & c\boldsymbol{\sigma}\cdot(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A}) \\ c\boldsymbol{\sigma}\cdot(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A}) & -mc^2 \end{pmatrix}\begin{pmatrix}\chi_A\\ \chi_B\end{pmatrix}$$

or

$$(i\hbar\frac{\partial}{\partial t}+mc^2+e\phi)\chi_A = c\boldsymbol{\sigma}\cdot(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})\chi_B + mc^2\chi_A ,$$

$$(i\hbar\frac{\partial}{\partial t}+mc^2+e\phi)\chi_B = c\boldsymbol{\sigma}\cdot(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})\chi_A - mc^2\chi_B ,$$

or

$$(i\hbar\frac{\partial}{\partial t}+e\phi)\chi_A = c\boldsymbol{\sigma}\cdot(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})\chi_B ,$$

$$(i\hbar\frac{\partial}{\partial t}+2mc^2+e\phi)\chi_B = c\boldsymbol{\sigma}\cdot(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})\chi_A .$$

In the first approximation, only the term $2mc^2\chi_B$ is retained on the left side of the second equation, which leads to

$$\chi_B = \frac{1}{2mc}\boldsymbol{\sigma}\cdot(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})\chi_A .$$

Then we get

$$(i\hbar\frac{\partial}{\partial t}+e\phi)\chi_A = \frac{1}{2m}[\boldsymbol{\sigma}\cdot(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})]^2\chi_A .$$

We use the formula

$$(\boldsymbol{\sigma}\cdot\boldsymbol{a})(\boldsymbol{\sigma}\cdot\boldsymbol{b}) = \boldsymbol{a}\cdot\boldsymbol{b} + i\boldsymbol{\sigma}\cdot(\boldsymbol{a}\times\boldsymbol{b}) ,$$

where ***a*** and ***b*** are arbitrary vectors. In the present case,

$$\begin{aligned}[(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})\times(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})]\chi_A &= -i\frac{e\hbar}{c}(\boldsymbol{A}\times\nabla+\nabla\times\boldsymbol{A})\chi_A \\ &= -i\frac{e\hbar}{c}(\nabla\times\boldsymbol{A})\chi_A = -i\frac{e\hbar}{c}\boldsymbol{B}\chi_A\end{aligned}$$

((**Note**))

$$(\boldsymbol{A}\times\nabla+\nabla\times\boldsymbol{A})\chi_A = \boldsymbol{A}\times\nabla\chi_A+\nabla\times(\chi_A\boldsymbol{A})$$
$$= \boldsymbol{A}\times\nabla\chi_A+\nabla\chi_A\times\boldsymbol{A}+\chi_A\nabla\times\boldsymbol{A}$$
$$= (\nabla\times\boldsymbol{A})\chi_A$$

Then we have

$$i\hbar\frac{\partial}{\partial t}\chi_A = [\frac{1}{2m}(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})^2 - e\phi + \frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\boldsymbol{B}]\chi_A.$$

This is exactly the non-relativistic equation, the Pauli equation (with respect to $1/c$), obeyed by a charged spin ½ particle in an electromagnetic field. We notice that the magnetic moment associated with the spin of the particle is predicted to be $\mu_B = \frac{e\hbar}{2mc}$ (Bohr magneton). We do not have to put it in; it is there. *This is one of the great triumphs of the Dirac equation.*

6. Exapnsion in powers of $1/c^2$

The resulting Hamiltonian associated with the positive-energy solutions (up to $1/c^2$) has the form

$$H = \frac{1}{2m}(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A})^2 - e\phi + \frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\boldsymbol{B}$$
$$+i\frac{e\hbar^2}{8m^2c^2}\boldsymbol{\sigma}\cdot\nabla\times\boldsymbol{E} + \frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\boldsymbol{E}\times\boldsymbol{p}) + \frac{e\hbar^2}{8m^2c^2}\nabla\cdot\boldsymbol{E} - \frac{p^4}{8m^3c^2}$$

where $-e$ is the charge of electron ($e>0$). The last four terms are the required corrections of order $1/c^2$. The elegant method for the derivation of the above Hamiltonian, is presented by Landau-Lifshitz, vol.4 of Course of Theoretical Physics Second edition, Quantum Electrodynamics.

(i) The Zeeman energy due to the spin magnetic moment (the order of $1/c$)

The spin magnetic moment is given by

$$\boldsymbol{\mu}_s = -\frac{2\mu_B}{\hbar}\boldsymbol{S} = -\frac{2\mu_B}{\hbar}\frac{\boldsymbol{\sigma}}{2}\hbar = -\mu_B\boldsymbol{\sigma}$$

where μ_B is the Bohr magneton defined by

$$\mu_B = \frac{e\hbar}{2mc}.$$

The Zeeman energy due to the spin magnetic moment is

$$-\boldsymbol{\mu}_s \cdot \boldsymbol{B} = \mu_B \boldsymbol{\sigma} \cdot \boldsymbol{B} = \frac{e\hbar}{2mc} \boldsymbol{\sigma} \cdot \boldsymbol{B} .$$

(ii) Spin-orbit interaction (the order of $1/c^2$)

$$\boldsymbol{E} = -\frac{1}{c}\frac{\partial \boldsymbol{A}}{\partial t} - \nabla \phi , \qquad \boldsymbol{B} = \nabla \times \boldsymbol{A}$$

In a stationary vector potential,

$$\boldsymbol{E} = -\nabla \phi , \qquad \nabla \times \boldsymbol{E} = 0$$

Then we have

$$H' = \frac{e\hbar}{4m^2c^2} \boldsymbol{\sigma} \cdot (\boldsymbol{E} \times \boldsymbol{p}) + \frac{e\hbar^2}{8m^2c^2} \nabla \cdot \boldsymbol{E} - \frac{p^4}{8m^3c^2}$$

If the electric potential ϕ is spherically symmetric,

$$\phi = V(r)$$

we get

$$\boldsymbol{E} = -\nabla V(r) = -\frac{1}{r}\frac{\partial V}{\partial r} \boldsymbol{r}$$

Then

$$\begin{aligned}
\frac{e\hbar}{4m^2c^2} \boldsymbol{\sigma} \cdot (\boldsymbol{E} \times \boldsymbol{p}) &= \frac{e\hbar}{4m^2c^2} \boldsymbol{\sigma} \cdot [(-\frac{1}{r}\frac{\partial V}{\partial r} \boldsymbol{r}) \times \boldsymbol{p}] \\
&= -\frac{e\hbar}{4m^2c^2} \frac{1}{r}\frac{\partial V}{\partial r} \boldsymbol{\sigma} \cdot (\boldsymbol{r} \times \boldsymbol{p}) \\
&= -\frac{e\hbar}{4m^2c^2} \frac{1}{r}\frac{\partial V}{\partial r} \boldsymbol{\sigma} \cdot \boldsymbol{L} \\
&= -\frac{e\hbar^2}{4m^2c^2} \frac{1}{r}\frac{\partial V}{\partial r} \boldsymbol{\sigma} \cdot \frac{\boldsymbol{L}}{\hbar}
\end{aligned}$$

This is what would be expected for an electron spin interacting with the field produced by its orbital motion, except that it is reduced by a factor of *1/2 due to relativistic kinematics, also known as the Thomas precession.*

(iii) The Darwin term

$$\frac{e\hbar^2}{8m^2c^2}\nabla\cdot\boldsymbol{E}$$

which represents a correction to the Coulomb interaction due to fluctuations (zitterbewegung) in the electron position arising from the presence of the negative component in the wavefunction.

(iv) The term $\frac{p^4}{8m^3c^2}$

which is very small, and along with the Darwin term, it may be neglected here.

Then we have the Hamiltonian as

$$H=\frac{1}{2m}\boldsymbol{p}^2+\frac{\mu_B}{\hbar}(\boldsymbol{L}+2\boldsymbol{S})\cdot\boldsymbol{B}-e\phi-\frac{e}{2m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}(\boldsymbol{L}\cdot\boldsymbol{S})+\frac{e^2B^2}{8mc^2}(x^2+y^2)$$

J is the total angular momentum, and is de4fined as

$$\boldsymbol{J}=\boldsymbol{L}+\boldsymbol{S}$$

where ***L*** is the orbital; angular momentum and ***S*** is the spin angular momentum. The total magnetic moment is

$$\boldsymbol{\mu}=\boldsymbol{\mu}_L+\boldsymbol{\mu}_S=-\frac{\mu_B}{\hbar}(\boldsymbol{L}+2\boldsymbol{S})$$

7. Spin magnetic moment

$$\boldsymbol{\mu}_s=-\frac{g_s\mu_B S}{\hbar}$$

Note that g-value is equal to 2 from the Dirac equation. The real g-value is slightly deviated from 2.0;

g = 2.0023193043622.

This deviation can be well explained from the quantum electrodynamics, standard model.

$$H_{SO}=-\frac{e\hbar^2}{4m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\cdot\frac{\boldsymbol{L}}{\hbar}\cdot\frac{g\boldsymbol{S}}{\hbar}$$
$$=-\frac{ge^2}{4m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\cdot(\boldsymbol{L}\cdot\boldsymbol{S})$$
$$=-\frac{g\mu_B{}^2}{\hbar^2}\frac{1}{r}\frac{\partial V}{\partial r}\cdot(\boldsymbol{L}\cdot\boldsymbol{S})$$

When the electric potential $V(r)$ is given from the Coulomb potential as

$$(-e)V(r)=-\frac{Ze^2}{r} \qquad \text{(attractive potential)}$$

or

$$V(r)=\frac{Ze}{r}$$

we get

$$\frac{1}{r}\frac{\partial V(r)}{\partial r}=-\frac{Ze}{r^3}.$$

Then we have the spin-orbit interaction

$$H_{SO}=\frac{g\mu_B{}^2Ze}{\hbar^2}\left\langle\frac{1}{r^3}\right\rangle_{AV}(\boldsymbol{L}\cdot\boldsymbol{S})=\varsigma(\boldsymbol{L}\cdot\boldsymbol{S})$$

((**Note**))

$$H_{SO}=\frac{1}{2}Ze\left(\frac{e\hbar}{mc}\right)^2\left\langle\frac{1}{r^3}\right\rangle_{AV}\frac{(\boldsymbol{L}\cdot\boldsymbol{S})}{\hbar^2}.$$

The factor ½ is called the Thomas correction.

8. Spin-orbit coupling for many electrons

For the system with many electrons, the spin-orbit coupling is given by

$$H_{SO}=\varsigma(n,l)\sum_i(\boldsymbol{L}_i\cdot\boldsymbol{S}_i)=\lambda(n:L,S)\boldsymbol{L}\cdot\boldsymbol{S},$$

where ***L*** and ***S*** are total angular and spin angular momentum

$$\boldsymbol{L} = \sum_i \boldsymbol{L}_i , \qquad \boldsymbol{S} = \sum_i \boldsymbol{S}_i$$

and the units of $\boldsymbol{L}_i$ and $\boldsymbol{S}_i$ is dimensionless, and n is the number of electrons.

$$\varsigma(n,l)\sum_i (m_i^s \cdot m_i^l) = \lambda(n:L,S)M_L M_S$$

(a) In the ground state of an incompletely filled shell (Hund's rule), all the electrons are parallel to each other, if the electron number n is smaller than 2*l*+1 ($l = 2$ for 3d electrons).

$$\varsigma(n,l)\frac{1}{2}L = \lambda(n:L,S)L\frac{n}{2}$$

or

$$\frac{\varsigma(n,l)}{n} = \lambda(n:L,S)$$

(b) If n is larger than 2*l*+1, the sum of $\boldsymbol{L}_i$ over the electrons having spin parallel to $\boldsymbol{S}$ vanishes and we are left with the contribution from the electrons with antiparallel spin.

$$\varsigma(n,l)(-\frac{1}{2})L = \lambda(n:L,S)L\frac{2(2l+1)-n}{2}$$

or

$$\lambda(n:L,S) = -\frac{\varsigma(n,l)}{2(2l+1)-n}$$

Note that the coefficient λ is positive for less than half-filling, and negative for the more than half-filled case. Note that the value of l increases with increasing the value of Z.

REFERENCES

G. Baym, *Lectures on Quantum Mechanics* (W.A. Benjamin, New York, 1969).
R.M. White, *Quantum Theory of Magnetism* (Springer-Verlag, Berlin, 2007).
V.B. Berestetskii, E.M. Lifshitz, and L.P. Pitaevskii, *Quantum Electrodynamics* (Pergamon Press, Oxford, 1980).
L.I. Schiff, *Quantum Mechanics*