10.4.2 Quantum Theory of Diamagnetism

In a magnetic field, the generalized momentum $\overrightarrow{P}$ of a particle carrying a charge e is

$$P = m\dot{\vec{r}} + e\overrightarrow{A} = m\vec{v} + e\overrightarrow{A} \qquad v = \frac{1}{m}(P - e\vec{A}) \tag{10.11}$$

where $\overrightarrow{A}$ is the *vector potential* defined through Eq. (10.17).

The force $\vec{F}$ acting on the charge e moving with a velocity $\vec{v}$ in an electric and magnetic field is known as *Lorentz force* and is given by

$$\vec{F} = e\left[\vec{E} + \left(\vec{v} \times \vec{H}\right)\right] \tag{10.12}$$

where E and H are electric and magnetic field strengths respectively.

The electric and magnetic fields satisfy Maxwell's equations given by

$$\vec{\nabla} \cdot \vec{D} = \rho \tag{10.13}$$

$$\vec{\nabla} \cdot \vec{B} = 0 \tag{10.14}$$

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{10.15}$$

$$\vec{\nabla} \times \vec{B} = \mu_0 \vec{J} \tag{10.16}$$

From Eq. (10.14) it follows that $\vec{B}$ can be expressed as the curl of a vector, i.e.

$$H \rightarrow \underline{\underline{\vec{B}}} = \vec{\nabla} \times \vec{A} \quad \text{, since its divergence is} = 0 \tag{10.17}$$

where $\vec{A}$ is the *vector potential.* of field H

Thus, Eq. (10.15) takes the form

$$\vec{\nabla} \times \vec{E} = -\frac{\partial}{\partial t}\left(\vec{\nabla} \times \vec{A}\right)$$

$\Rightarrow$

$$\vec{\nabla} \times \left(\vec{E} + \frac{\partial \vec{A}}{\partial t}\right) = 0 \tag{10.18}$$

Hence, we may set

$$\vec{E} + \frac{\partial \vec{A}}{\partial t} = -\vec{\nabla}\phi \quad \left[\nabla \times (\nabla\phi) = 0\right] \tag{10.19}$$

where ϕ is known as *scalar potential* of field H.

We, therefore, get

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t} \tag{10.20}$$

hence eq of motion

In terms of vector and scalar potentials, the Lorentz force, given by Eq. (10.12), becomes

$$\vec{F} = m\frac{d\vec{v}}{dt} = e\left[-\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t} + \left(\vec{v} \times \vec{\nabla} \times \vec{A}\right)\right] \rightarrow \tag{10.21}$$

Now,

$$\left(\vec{v} \times \vec{\nabla} \times \vec{A}\right)_x = v_y\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right) - v_z\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right) \tag{10.22}$$

Since
$$\frac{\partial}{\partial x}\left(\vec{v} \cdot \vec{A}\right) = \frac{\partial}{\partial x}\left(v_x A_x + v_y A_y + v_z A_z\right) \tag{10.23}$$

Scanned with CamScanner

and
$$\frac{dA_x}{dt} = \frac{\partial A_x}{\partial t} + v_x \frac{\partial A_x}{\partial x} + v_y \frac{\partial A_x}{\partial y} + v_z \frac{\partial A_x}{\partial z} \tag{10.24}$$

$$\Rightarrow \quad \frac{dA_x}{dt} - \frac{\partial A_x}{\partial t} = v_x \frac{\partial A_x}{\partial x} + v_y \frac{\partial A_x}{\partial y} + v_z \frac{\partial A_x}{\partial z} \tag{10.25}$$

Subtracting Eq. (10.25) from Eq. (10.23), we get

$$\frac{\partial}{\partial x}\left(\vec{v} \cdot \vec{A}\right) - \frac{dA_x}{dt} + \frac{\partial A_x}{\partial t} = v_y \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right) - v_z \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right) \tag{10.26}$$

Comparing Eq. (10.22) with Eq. (10.26) we find that

$$\left(\vec{v} \times \vec{\nabla} \times \vec{A}\right)_x = \frac{\partial}{\partial x}\left(\vec{v} \cdot \vec{A}\right) - \cancel{\frac{dA_x}{dt}} + \cancel{\frac{\partial A_x}{\partial t}} \tag{10.27}$$

Using Eq. (10.27) the components of Lorentz force, given by Eq. (10.21), along the three coordinate axes may be written as

$$\rightarrow \quad F_x = m\frac{dv_x}{dt} = -e\frac{\partial \phi}{\partial x} - e\frac{dA_x}{dt} + e\frac{\partial}{\partial x}\left(\vec{v} \cdot \vec{A}\right) \quad ? \checkmark \tag{10.28}$$

$$F_y = m\frac{dv_y}{dt} = -e\frac{\partial \phi}{\partial y} - e\frac{dA_y}{dt} + e\frac{\partial}{\partial y}\left(\vec{v} \cdot \vec{A}\right) \tag{10.29}$$

$$F_z = m\frac{dv_z}{dt} = -e\frac{\partial \phi}{\partial z} - e\frac{dA_z}{dt} + e\frac{\partial}{\partial z}\left(\vec{v} \cdot \vec{A}\right) \tag{10.30}$$

The above three equations may be conveniently put in the following compact vector equation:

$$\frac{d}{dt}\left(m\vec{v} + e\vec{A}\right) = \vec{\nabla}\left[-e\phi + e\left(\vec{v} \cdot \vec{A}\right)\right] \quad ? \checkmark \tag{10.31}$$

We now put the above equation in the Lagrangian form

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) = \frac{\partial L}{\partial q_j} \tag{10.32}$$

where L is the Lagrangian and $q_1 = x$, $q_2 = y$ and $q_3 = z$.

Clearly, if we assume the Lagrangian to be of the form

$$L = \frac{1}{2}m\vec{v} \cdot \vec{v} - e\phi + e\left(\vec{A} \cdot \vec{v}\right) \tag{10.33}$$

$L = T - V$

$p.A = pA\cos\theta$

$\vec{A} \cdot \vec{V} = \vec{v} \cdot \vec{A}$

$p.A = A.p$

$p.A = A.p$

$\therefore \cos\theta = \cos(-\theta)$

and substitute it in Eq. (10.32), we get Eq. (10.31).

The Hamiltonian is given by

$$\mathcal{H} = \vec{p} \cdot \vec{v} - L$$

$$\Rightarrow \quad \mathcal{H} = p \cdot \left[\frac{1}{m}\left(\vec{p} - e\vec{A}\right)\right] - \frac{1}{2}m\left[\frac{1}{m}\left(\vec{p} - e\vec{A}\right)\right]^2 + e\phi - \frac{e\vec{A}}{m} \cdot \left(\vec{p} - e\vec{A}\right)$$

eA?

$$\Rightarrow \quad H = \frac{1}{2m}\left(\vec{p} - e\vec{A}\right)^2 + e\phi \quad ?? \tag{10.34}$$

where we have used

$$\vec{v} = \frac{1}{m}\left(\vec{p} - e\vec{A}\right)$$

from Eq. (10.11).

The stationary state Schrödinger equation describing the motion of a non-relativistic material particle is given by

$$\mathcal{H}\psi = E\psi \tag{10.35}$$

Using Eq. (10.34) and making the substitution $\vec{p} \to -i\hbar\vec{\nabla}$, the Schrödinger equation takes the form

$$\frac{1}{2m}\left(-i\hbar\vec{\nabla} - e\vec{A}\right)^2\psi + e\phi\psi = E\psi$$

$2\vec{\nabla}\vec{A}\psi$?

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\nabla^2\psi + \frac{\cancel{2}\,ie\hbar}{\cancel{2}m}\left[\underbrace{\left(\vec{\nabla}\cdot\vec{A}\right)\psi + \vec{A}\cdot\vec{\nabla}\psi}_{\text{vector addition}}\right] + \frac{e^2}{2m}A^2\psi + e\phi\psi = E\psi \tag{10.36}$$

where we have used the vector identity

$$\vec{\nabla}\cdot\left(\vec{A}\psi\right) = \left(\vec{\nabla}\cdot\vec{A}\right)\psi + \vec{A}\cdot\vec{\nabla}\psi$$

From Eq. (10.36) we see that the effect of the magnetic field is to add to the Hamiltonian the terms

$$\mathcal{H}' = \frac{ie\hbar}{m}\left(\vec{\nabla}\cdot\vec{A} + \vec{A}\cdot\vec{\nabla}\right) + \frac{e^2}{2m}A^2 \tag{10.37}$$

For an electron these terms may be treated as small perturbation. If the magnetic field $\vec{B}$ is uniform, we may choose $\vec{A}$ as

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

$\Rightarrow$ as

$$\vec{A} = \frac{1}{2}\begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ B_x & B_y & B_z \\ x & y & z \end{vmatrix} \tag{10.38}$$

If the field vector $\vec{B}$ is in the z-direction then we have

$$B_x = B_y = 0; B_z = B$$

and Eq. (10.38) may be written as

$$\vec{A} = \frac{1}{2}\begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ 0 & 0 & B \\ x & y & z \end{vmatrix}$$

This gives the component of $\vec{A}$ along the three coordinate axes as

$$A_x = -\frac{1}{2}By; \quad A_y = \frac{1}{2}Bx; \quad A_z = 0$$

$B \times y$, $B \times x$

Scanned with CamScanner

Hence,
$$\vec{\nabla}\cdot\vec{A} = \left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)\cdot\left(\hat{i}A_x+\hat{j}A_y+\hat{k}A_z\right)$$

$$\Rightarrow \quad \vec{\nabla}\cdot\vec{A} = \left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)\cdot\left(-\hat{i}\cdot\frac{1}{2}By+\hat{j}\cdot\frac{1}{2}Bx+0\right)$$

$i \cdot j = j \cdot k = 0$

$$\Rightarrow \quad \vec{\nabla}\cdot\vec{A} = 0 \tag{10.39}$$

$\frac{\partial By}{\partial x} = \frac{\partial Bx}{\partial y} = 0$

Again,
$$\vec{A}\cdot\vec{\nabla} = \left(\hat{i}A_x+\hat{j}A_y+\hat{k}A_z\right)\cdot\left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)$$

$$\Rightarrow \quad \vec{A}\cdot\vec{\nabla} = \left(-\hat{i}\cdot\frac{1}{2}By+\hat{j}\cdot\frac{1}{2}Bx+0\right)\cdot\left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)$$

$$\Rightarrow \quad \vec{A}\cdot\vec{\nabla} = -\frac{1}{2}By\frac{\partial}{\partial x}+\frac{1}{2}Bx\frac{\partial}{\partial y}$$

$$\Rightarrow \quad \vec{A}\cdot\vec{\nabla} = \frac{B}{2}\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right) \tag{10.40}$$

and
$$A^2 = A_x^2 + A_y^2 + A_z^2 = \frac{1}{4}B^2y^2 + \frac{1}{4}B^2x^2$$

$$\Rightarrow \quad A^2 = \frac{1}{4}B^2(x^2+y^2) \tag{10.41}$$

Using Eqs. (10.39) to (10.41), Eq. (10.37) takes the form

$$\mathcal{H}' = \frac{ie\hbar}{m}\cdot\frac{B}{2}\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)+\frac{e^2}{2m}\cdot\frac{1}{4}B^2\left(x^2+y^2\right) \tag{10.42}$$

The first term on the right-hand side of Eq. (10.42) is proportional to the orbital angular momentum component L_z. In mono-nuclear systems, this term gives rise to paramagnetism. The second term gives for a spherically symmetric system a contribution

$$E' = \frac{e^2B^2}{12m}\cdot\overline{r^2}, \text{ as } x^2+y^2 = \frac{2}{3}\overline{r^2}$$

by first order perturbation energy. The associated magnetic moment is diamagnetic:

$$\mu = -\frac{\partial E'}{\partial B} = -\frac{e^2B}{6m}\cdot\overline{r^2}$$

Hence, the atomic susceptibility χ_{At} is given by

$$\chi_{\text{At}} = \frac{\mu}{H} = -\left(\frac{\mu_0e^2}{6m}\right)\overline{r^2}, \text{ as } B = \mu_0H \tag{10.43}$$

and is in agreement with the classical result.

10.4.3 Discussion

On the basis of quantum orbital theory, the mean value of r^2 for an orbit about an effective nuclear charge Z is given by

$$\overline{r^2} = a_0^2 \cdot \frac{n^2}{Z^2}\left(\frac{5}{2}n^2 - \frac{3}{2}k^2\right) \tag{10.44}$$

where $a_0 (= 0.528 \times 10^{-10}$ m) is the radius of the innermost orbit in hydrogen atom, n is the radial quantum number and k, the azimuthal quantum number.

This gives for the contribution of the orbit to the gram atomic diamagnetic susceptibility

$$\chi_A = -2.83 \times 10^{10}\overline{r^2}$$

$$\Rightarrow \quad \chi_A = -0.785 \times 10^{-6}\left[\frac{n^2}{Z^2}\left(\frac{5}{2}n^2 - \frac{3}{2}k^2\right)\right] \tag{10.45}$$

If the effective nuclear charge is calculated from this expression for helium with two electrons from its observed susceptibility ($\chi_A = -1.9 \times 10^{-6}$), it comes out to be 0.93 which is too small.

To make the expression for susceptibility more accurate, van Vleck and Pauling modified the above expression as

$$\chi_A = -0.785 \times 10^{-6}\left[\frac{n^2}{Z^2}\left(\frac{5}{2}n^2 - \frac{3l(l+1)-1}{2}\right)\right] \tag{10.46}$$

where l, the orbital quantum number, is equal to $(k-1)$.

Pauling's calculations necessarily involve a number of approximations. For spherically symmetric atoms, Hartree has devised a method with which the charge distribution satisfying the Schrödinger equation may be worked out more precisely. He has given tables and curves for a number of ions and atoms showing the charge per unit radial distance in a spherical shell of unit thickness.

If $\dfrac{dN}{dr}$ be the charge in electron unit per unit radial distance, then the number of electrons in the ions is equal to $\displaystyle\int_0^\infty \left(\frac{dN}{dr}\right) dr$.

For the diamagnetic susceptibility, he obtained

$$\chi_A = -2.83 \times 10^{10}\int_0^\infty \left(\frac{dN}{dr}\right) dr \tag{10.47}$$

This integral can be evaluated graphically (Figure 10.2). Using atomic units for distances, the susceptibility is given by

$$\chi_A = -0.785 \times 10^{-6} \times \text{ area under the shaded portion of the curve}$$

For helium this gives

$$\chi_A = -1.89 \times 10^{-6}$$

a value which agrees remarkably closely with the observed one (-1.9×10^{-6}).

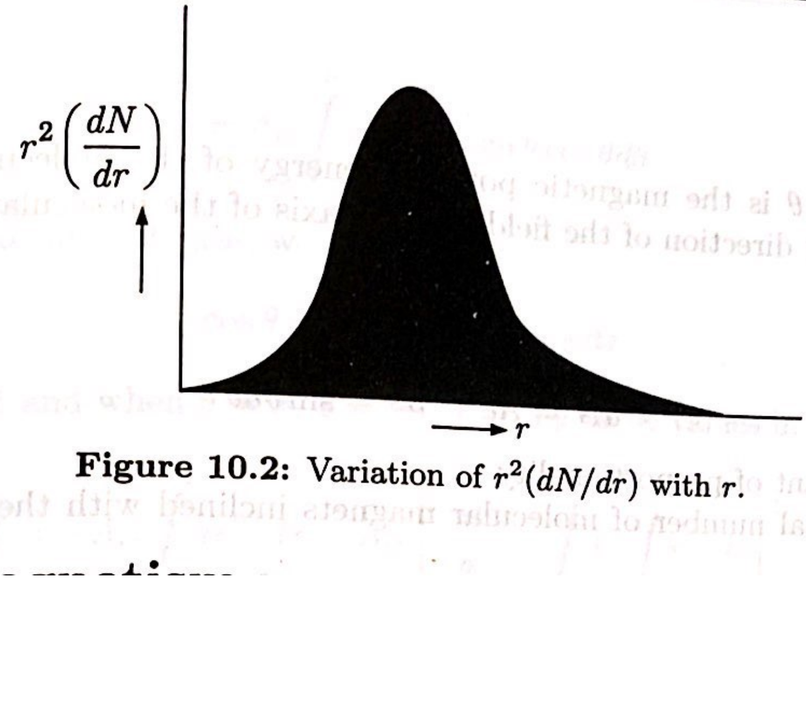

Figure 10.2: Variation of $r^2(dN/dr)$ with r.