Classical and Quantum Phenomenology of Diamagnetism

Origem e comportamento de momentos magnéticos

- Diamagnetismo clássico
- Diamagnetismo quântico
- Spin

Classical Treatment

Momento Angular Orbital e Momento Magnético Orbital

MODELO DE DIPOLO MAGNÉTICO ATÔMICO - $\mu_m = I \cdot A$

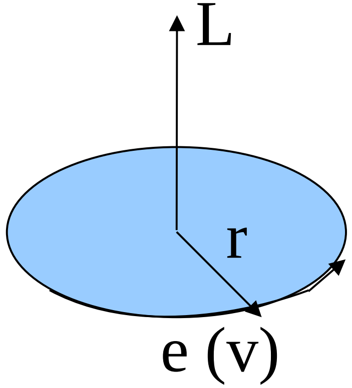
Momentos Magnéticos: são originados devido à movimentação de partículas carregadas.

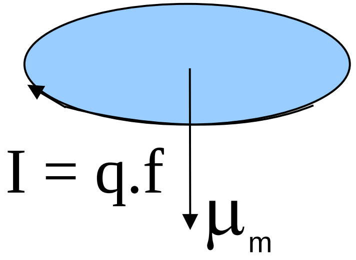
Momento angular (L) e momento (μ_m) magnético são relacionados

$$\gamma = \frac{\mu_m}{L} = \text{constante}$$

γ → Razão giromagnética

Cálculo da razão giromagnética





f é a frequência

$$\mu_m = (q.f).(\pi r_0^2)$$

$$\mathbf{L} = \boldsymbol{r} \times \boldsymbol{p} = \boldsymbol{m}(\boldsymbol{r} \times \boldsymbol{v})$$

$$|L| = m \cdot v \cdot r_0$$

μ_m

$$\omega = 2\pi f = \frac{v}{r_0} \qquad \mu_m = \frac{q.v.r_0}{2}$$

$$\gamma = \frac{\mu_m}{L} = \frac{q \cdot v \cdot r_0}{2 \cdot \underbrace{m \cdot v \cdot r_0}_{L}} = \frac{q}{2 \cdot m} = -\frac{e}{2 \cdot m} = -8{,}78 \times 10^{10}\,C/kg$$

É um número exato em materiais nos quais o magnetismo é originário do movimento orbital dos elétrons, mas em outros materiais não é. Nos outros é necessário considerar o momento magnético de spin.

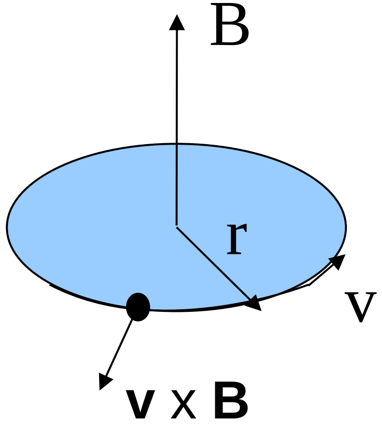
Classical Diamagnetism

Magnetic Induction B varying from 0 to B and ⊥ to the electron orbit.

The electrical current I will vary → ΔI (variation of electron velocity - Δv, at contant radius).

The magnetic flux variation dϕ/dt inside the current lace induces a B_{ind}

of same magnitude and opposite in direction to B.



Há duas forças radiais:

- a força do campo (Lorentz: **F** = q **v** x **B)** sobre o elétron F = q v B
- A reação: variação da força centrípeta ($F_c = m_e v^2 /2$) devido a variação da velocidade:

$$\Delta F_c = 2.\ m_e\ .v\ .\Delta v/r = q.v.B \rightarrow \Delta v = \frac{q\,r\,B}{2m_e}$$

O momento magnético m sofrerá uma variação devido à variação da velocidade do elétron: $\mu_m = m$

$$m = \frac{qvr}{2} \Rightarrow \Delta m = \frac{q(-\Delta v)r}{2} \Rightarrow \Delta m = -\frac{e^2 r^2}{4m_e}B$$

Diamagnetic Susceptibility

$$M = N.\Delta m = -\frac{\mu_0 N e^2 Z R^2}{6m_e} H \Rightarrow \chi = \frac{dM}{dH} \Rightarrow \chi = -\frac{\mu_0 N e^2 Z R^2}{6m_e}$$

Boa concordância com valores experimentais $\chi \approx -10^{-6}$

N é a densidade de átomos; Z é o número atômico e R o raio médio do átomo.

Z, e e m_e → independem de T

N, R^2 → dependem fracamente de T

gases raros: He, Ne, Ar

gases poliatômicos: H2, N2

sólidos iônicos: NaCl

substâncias com ligações covalentes: Si

- **Diamagnetism occurs for all substances, but in some cases, it is so weak that it can be neglected.**

- **Purely diamagnetic materials are those that have no contribution from spin to the total magnetic moment.**

- Diamagnetism is temperature independent because it results from an interaction between a magnetic field and the velocity of electronic charge. The electron velocity is a function of the energy of the electronic states and hence is essentially independent of temperature.

- Nevertheless, it is interesting to note that diamagnetism persists even though it is much weaker than *kT.*

$$|U| \approx \mu_m B = \frac{e^2 \langle r^2 \rangle B^2}{6m} \approx 10^{-28}\ \mathrm{J}$$

$$k_B T \approx 4 \times 10^{-21}\ \mathrm{J\ at\ room\ temperature\ (RT)}$$

Quantum Diamagnetism

The magnetic moment of hydrogen in the classical, Bohr model is

$$\mu_m = \frac{q.v.r_0}{2}$$

$\mu_m = 9.27 \times 10^{-24}$ A.m^2, in which $\boldsymbol{r} = a = 0.52$ Å, $q = - \boldsymbol{e} = - 1.6 \text{ x } 10^{-l9}$ C and $v = (2E/m)^{1/2}$.

At the atomic scale, position and momentum cannot be known simultaneously with arbitrary accuracy (Heisenberg's uncertainty principle)

Quantum Treatment

In quantum mechanics, the part of the Schrodinger equation that describes the angular variables of a quantum mechanical wave/particle in a central potential is given by:

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y_l^{m_l} = -l(l+1)Y_l^{m_l}$$

This equation separates into one equation for the magnitude of the angular momentum, $|L|$ and another for its *z* component *L:*

$$\boxed{L^2} Y_l^m = \boxed{\hbar^2 l(l+1)}\, Y_l^m$$

$$\boxed{L_z}\,\Phi = \boxed{\hbar m_l}\,\Phi$$

$Y_l^{m_l} = A_l^{m_l}\Phi_{m_l}$ are the spherical harmonics,

$A_l^{m_l}$ are related to the associated Legendre polynomials,

and $\Phi_{m_l} = e^{i m_l \phi}$

$\mathbf{L} = \boldsymbol{r} \times \boldsymbol{p}$ is now replaced by a discrete set of allowed values, $\hbar[l(l+1)]^{1/2}$ where l is the orbital angular momentum quantum number.

The component of L in some direction (usually set by a field) is also quantized and has the values hm, where m, takes on the integer values in the range $-l \le m_l \le l$.

Now, $|\mu_m| = \gamma\hbar[l(l+1)]^{1/2}$ and $\mu_m|_z = \gamma\hbar m_l$

These formulas indicate that the magnitude of the magnetic moment is of order of $\gamma\hbar$, which is about 10^{-23} A.m^2 (essentially what was calculated classically).

Spin

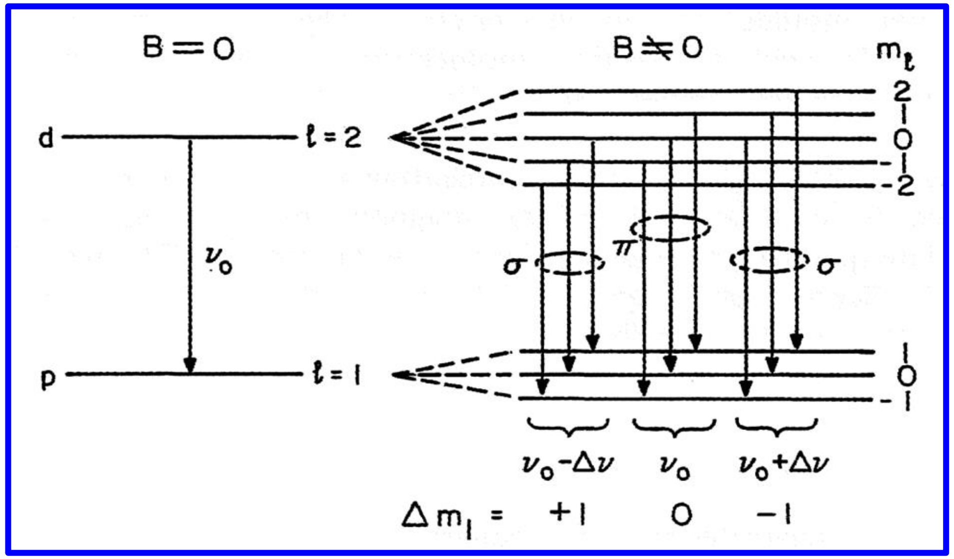
Development of quantum mechanics → as higher-resolution spectrometers were available, the optical spectral data such as the Zeeman splitting's and the more complicated aspects of those spectra became obvious.

To explain the results, this leads now to a different kind of angular momentum: **the spin**.

$$\omega = \omega_0 \text{ and } \omega_0 \pm \gamma B \text{ with } \gamma = e/2m$$

Level splitting for a *d* - p transition.

Each level splits in a B field into $2l+1$ components depending on its magnetic quantum number m_l .



Zeeman effect → explained by orbital magnetic moment precession.

But many lines showed more complex splitting → not explained by precession → “Anomalous" Zeeman effect

The anomalous Zeeman effect demanded a new quantum number to be explained, but its meaning was a matter of considerable controversy.

The new quantum number had to describe an extra electronic degree of freedom; specifically, the electron must have some dynamics in addition to translational motion (r) with angular momentum (θ, ϕ).

In *1924,* Uhlenbeck and his friend Sam Goudsmit (an expert in atomic spectra) proposed that the electron should have an intrinsic angular momentum called *spin.*

It turned out that the new angular momentum of the electron has a gyromagnetic ratio that is twice that determined for orbital motion $\mu_L/L = \gamma_L = e/2m$

$$\frac{\mu_s}{S} = \gamma_S = \frac{e}{m} = 1.76 \times 10^{11} \qquad [\mathrm{C/kg} = (\mathrm{s \cdot T})^{-1}]$$

Thus, by analogy with the angular moment, the result for an atom of spin *S* is:

$$|\mu_m| = \gamma\hbar[s(s+1)]^{1/2} \quad \text{and} \quad \mu_m|_z = \gamma\hbar m_s$$

However, Schrödinger's equation says nothing about spin.

Dirac incorporated Lorentz covariance into the wave equation (now with Dirac's name) that predicts electron spin.

It is enough to know that the previous wave function $\psi(r, \theta, \phi)$ has a new multiplicative factor $\chi(s)$.

$\chi(s)$ → occupation probability amplitude of different spin states, and: $\Psi(r,s) = \psi(r, \theta, \phi) \times \chi(s)$

The spin wavefunction $\chi(s)$ have complete analogy with solution for the angular moment:

$$\underset{\text{operator}}{\boxed{S^2}}\chi = \underset{\text{eigenvalue}}{\boxed{\hbar^2 s(s+1)}}\chi \quad \text{and} \quad \underset{\text{operator}}{\boxed{S_z}}\chi = \underset{\text{eigenvalue}}{\boxed{\hbar m_s}}\chi$$

where m_s can take on discrete values from $+s$ to $-s$, e.g., for $s = \frac{1}{2}$, $m_s = \pm\frac{1}{2}$