Understanding dia- and para-magnetism

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Materials interact with magnetic fields via electric currents and their magnetization $\mathbf{M}$ as described by Maxwell's equations. The macroscopic magnetization is based on the average density of local magnetic moments $\mathbf{m}$. In classical electromagnetism, a magnetic moment is realized by a current I flowing in a wire enclosing the area A with orientation $\mathbf{n}_A$. This is depicted in Fig. 1, where the current is flowing anti-clockwise around $\mathbf{n}_A$ pointing upwards. This provides the magnetic moment

$$\mathbf{m} = IA\mathbf{n}_A\,. \tag{1}$$

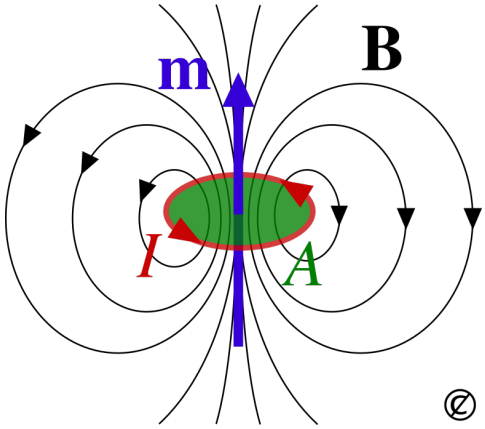

Figure 1: A magnetic dipole $\mathbf{m}$ realized by a current I floating around an area A.

A corresponding picture on atomic level is an electron circling around the nucleus. The presence of a magnetic field $\mathbf{B}$ affects the microscopic magnetic moments and therefore also the macroscopic magnetization $\mathbf{M}$ as given by the density of local magnetic moments. For many materials one observes a linear relation

$$\mathbf{M} = \frac{\chi}{\mu_0}\mathbf{B}\,, \tag{2}$$

with the dimensionless magnetic susceptibility χ. [This implies $\mathbf{B} = \mu_r\mu_0\mathbf{H}$ with $\mu_r = 1/(1-\chi)$, which is often applied in electromagnetism for media, see, e.g. Sec. 5.8 of [1].] Actually both signs of χ are observed and materials with $\chi > 0$ are called *paramagnetic* and materials with $\chi < 0$ are called *diamagnetic*. (In addition, ferromagnetic substances exist, where $\mathbf{M}$ remains finite for vanishing $\mathbf{B}$, which is not addressed here.) The sign and value of χ can be traced back to the microscopic interaction of electrons with the magnetic field. (Magnetic moments of nuclei are three orders of magnitude lower.) This raises the question, how such strikingly different behavior like paramagnetism and diamagnetism can occur. These notes shall provide a simple picture for these phenomena in Sec. 1 which is substantiated by more detailed calculations and proofs in the subsequent sections.

1 A heuristic approach

1.1 A classical model

In a classical model we can attribute a magnetic dipole, such as shown in Fig. 1, to an electron in an orbit (around one or several nuclei) with angular frequency ω. The average current is

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given by one electron charge $-e$ per period $2\pi/\omega$ and Eq. (2) provides

$$\mathbf{m} = -e\frac{\omega}{2\pi}A\mathbf{n}_A\,. \tag{3}$$

Without magnetic field, Newton's equation of motion is symmetric upon the reversal of velocities. Thus, any orbit can be run clockwise or anti-clockwise with the same frequency and energy but opposite magnetic moment. In thermal equilibrium, the occupation of all orbits is given by the Boltzmann distribution and depends only on its energy. This implies, that the clockwise and anti-clockwise motion is equally likely, and results in a zero magnetization $\mathbf{M}$ for $\mathbf{B} = 0$, as observed both for dia- and para-magnetic materials.

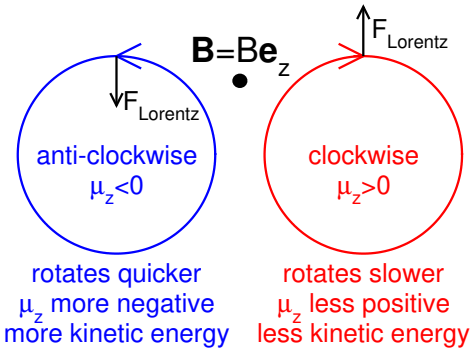

Figure 2: Change of magnetic moments μ_z for electrons circling in an anti-clockwise and clockwise orbit around the magnetic field pointing out of the area.

In a magnetic field, the orbits are modified due to the Lorentz force $\mathbf{F}_{\rm Lorentz} = -e\mathbf{v}\times\mathbf{B}$. Let us assume, that the magnetic field points in z direction, i.e. $\mathbf{B} = B\mathbf{e}_z$. Then the orbits running clockwise around $\mathbf{e}_z$ will experience an additional outward force, while the orbits running anti-clockwise experience an additional inward force as shown in Fig. 2. This force can be compensated by changing the velocity (and rotation frequency), so that the modified centrifugal force compensates the Lorentz force. Thus anti-clockwise orbits move faster while clockwise orbits move slower. This change in motion affects both the magnetic moment and kinetic energy of the orbits as addressed in Fig. 2. (These qualitative arguments given here are manifested for a two-dimensional harmonic oscillator in Sec. 4.1.)

Based on this picture, reasons for both diamagnetism and paramagnetism can be given:

(i) As the magnetic moment is decreasing in the direction of the magnetic field for both types of orbits, we expect the magnetization to drop with the magnetic field. As shown in the example in Sec. 4.1, the drop is proportional to the magnetic field. This provides a negative susceptibility $\chi < 0$ in Eq. (2), which constitutes **diamagnetism**.

(ii) The energy of the clockwise orbit is lower in a magnetic field and thus this orbit is more likely to be taken by an electron, associated with a magnetic moment in the direction of the magnetic field. This provides a positive susceptibility $\chi > 0$, which constitutes **paramagnetism**. According to statistical physics the ratio of probabilities for the electron to be in both types of orbits is $P_{\text{anti-clockwise}}/P_{\text{clockwise}} = e^{-\Delta E/k_BT}$, where ΔE is the energy difference between both orbits. This provides

$$\frac{P_{\text{clockwise}} - P_{\text{anti-clockwise}}}{P_{\text{clockwise}} + P_{\text{anti-clockwise}}} = \frac{1-e^{-\Delta E/k_BT}}{1+e^{-\Delta E/k_BT}} \approx \frac{\Delta E}{2k_BT} \tag{4}$$

as ΔE is typically much smaller than k_BT. This excess occupation of the clockwise orbits is directly proportional to the magnetization. As exemplified in Sec. 4.1, $\Delta E \propto B$, which provides $\mathbf{M} \propto \mathbf{B}/T$ and the susceptibility $\chi \propto 1/T$ as experimentally found by Pierre Curie for several paramagnetic materials at the end of the 19th century.

While these considerations within classical physics, as developed in [2], can serve as a motivation for dia- and para-magnetism and are presented in many textbooks, they do not hold. It can be shown that both effects exactly cancel each other in classical mechanics, where a continuum of orbits is possible. This was pointed out, independently from each other, by Niels Bohr (PhD thesis, Kopenhagen, 1911) and Johanna von Leeuwen (PhD thesis, Leiden, 1919). In these

notes this is demonstrated for a harmonic potential in Sec. 4.1 and generally in Sec. 5. *Thus classical physics can neither explain para- nor dia-magnetism.*

1.2 Relevance of quantum physics

The solution relies on quantum physics. Here the existence of discrete energy levels, which are occupied following the Pauli principle allows to separate both issues addressed above. In addition, the electron spin has a magnetic moment. If a level is occupied with two electrons with opposite spin direction, the corresponding magnetic moments add up to zero. If a level is occupied with a single electron, the energy is lower, if its magnetic moment is oriented in the direction of the magnetic field (similar to the orbits in Fig. 2). Thus, unpaired spins provide an important paramagnetic contribution following the reasoning (ii) in Sec. 1.1.

The main aspect is that the quantum levels are grouped in shells of equal energy. In the ground state, the electrons subsequently occupy the shells with increasing energy until the number of electrons balances the charge of the nuclei, as the Pauli principle forbids double occupation with the same spin. The last shell being filled is referred to as *valence shell*, where all shells with lower energy are entirely filled and all shells with higher energy are empty.[2]

These shells can be related to symmetries and always contain the quantum correspondence of both the clockwise and anti-clockwise orbit addressed above. For example, the p-shell in an atom contains both the levels with $m_l = 1$ and $m_l = -1$ exhibiting opposite rotations around the z-axis. Thus, in a completely filled shell, the magnetic moments of the levels compensate each other in the absence of a magnetic field. In the presence of a magnetic field, the changes in magnetic moments due to the Lorentz force provides a diamagnetic contribution for all orbits similar to the classical case in Fig. 2. Furthermore, the magnetic moments due to spin cancel as each level in a full shell is occupied by a pair of electrons. On the other hand, for a partially filled shell in a magnetic field, those levels and spin-directions get mainly occupied, where the magnetic moment is oriented in the direction of the magnetic field, similar to the classical case in Fig. 2. This provides a paramagnetic contribution. These qualitative statements are demonstrated for a detailed calculation for a 2-dimensional harmonic oscillator in Sec. 4.2.

1.3 Magnetic behavior of different materials

As the paramagnetic contribution of a partially filled shell is stronger than the diamagnetic contribution from filled shells, we find the following general rule: Systems are diamagnetic, if the valence shell is entirely filled. Prominent examples are noble gases, many molecules without radicals (e.g., water), semiconductors, and insulators. Typical values are $-10^{-4} \lesssim \chi < 0$. On the other hand, systems are paramagnetic if the valence shell is partially filled. Examples are single alkali atoms and NO molecules (both with an odd number of electrons), or crystals containing rare earth elements (where the f-shell is partially filled). Also molecular oxygen O_2 is paramagnetic due to a half-filled shell of anti-binding degenerate π-orbitals. Typical values are $0 < \chi \lesssim 10^{-3}$ at room temperature. Finally, it is worth to mention, that metals have the Fermi energy within a continuous band, where paramagnetism (rather constant in temperature, thus not following the Curie law) is much weaker and can be superseded by diamagnetism.

[2]While in the simplified picture of independent electrons only one valence shell exists, there may be several partially filled outermost shells with similar energies, such as the 4s and 3d shells in chromium. In such cases, the term valence shell relates to both of them.

2 Magnetic moments in classical electrodynamics

The magnetic moment $\mathbf{m}$ of a system localized around a point $\mathbf{r}_0$ with a current density $\mathbf{j}(\mathbf{r})$ satisfying $\nabla \cdot \mathbf{j} = 0$ is defined by

$$\mathbf{m} = \frac{1}{2} \int \mathrm{d}^3 r \, (\mathbf{r} - \mathbf{r}_0) \times \mathbf{j}(\mathbf{r}) \tag{5}$$

A prototype is a current I around a closed wire of area A and orientation $\mathbf{n}_A$, which provides $\mathbf{m} = IA\mathbf{n}_A$ as shown in Fig. 1. Note that $\mathbf{m}$ actually does not depend on $\mathbf{r}_0$ due to the left relation in Eq. (30) presented in Appendix A. If an external magnetic field is approximately constant over the size of the current distribution, the interaction energy is

$$U_{\mathrm{dipole}} = -\mathbf{m} \cdot \mathbf{B} \tag{6}$$

These relations are motivated in Appendix A which essentially follows standard textbooks such as [1, 3].

2.1 Magnetization

We consider a material which has a set of magnetic moments $\mathbf{m}_\mathbf{R}$ due to individual current distributions $\mathbf{j}_\mathbf{R}(\mathbf{r})$ in the vicinity of $\mathbf{R}$ (such as the location of individual molecules or the Bravais vectors of a crystal), satisfying individually $\nabla \cdot \mathbf{j}_\mathbf{R} = 0$. Physically, this refers to bound electrons localized around $\mathbf{R}$ with a density $n_\mathbf{R}(\mathbf{r})$. In addition, there may be free carries $n_{\mathrm{free}}(\mathbf{r})$, related to free currents and free charges in the four field version of Maxwell's equations. Then, the magnetization is given by [1, 3]

$$\mathbf{M} = \frac{1}{V} \sum_{\mathbf{R} \in V} \mathbf{m}_\mathbf{R} = n_{\mathrm{moments}} \langle \mathbf{m} \rangle$$

where V is a volume, covering a range over which the magnetic field is approximately constant, and n_{moments} is the spatial density of the moments (e.g., the density of molecules) and $\langle \mathbf{m} \rangle$ denotes the average moment for the ensemble $\{\mathbf{m}_\mathbf{R}\}$. From the definition of the magnetic susceptibility (2) we find for isotropic materials

$$\chi = n_{\mathrm{moments}} \frac{\mu_0 \langle m_z \rangle}{B_z} \tag{7}$$

2.2 Magnetization by induction

The induction law and Poisson's equation,

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad \text{and} \quad \epsilon_0 \nabla \cdot \mathbf{E} = \rho \,,$$

provide for a spatially constant, time-varying magnetic field $\mathbf{B}(t)$ and vanishing charges, $\rho = 0$, the electric field

$$\mathbf{E}(\mathbf{r}, t) = \frac{1}{2} \mathbf{r} \times \dot{\mathbf{B}}(t)$$

Now let us consider the magnetic moment at $\mathbf{R}$. The acceleration of individual electrons $m_e \dot{\mathbf{v}} = -e\mathbf{E}$, provides the temporal change in current density $\mathbf{j}_\mathbf{R} = -e n_\mathbf{R} \langle \mathbf{v} \rangle$ and

$$\frac{\partial}{\partial t} \mathbf{j}_\mathbf{R}(\mathbf{r}, t) = \frac{e^2 n_\mathbf{R}(\mathbf{r}, t)}{2 m_e} \mathbf{r} \times \dot{\mathbf{B}}(t)$$

and the change of the magnetic moment (5)

$$\dot{\mathbf{m}}_{\mathbf{R}} = \frac{e^2}{4m_e} \int \mathrm{d}^3 r \, n_{\mathbf{R}}(\mathbf{r})(\mathbf{r}-\mathbf{R}) \times \Big[\mathbf{r} \times \dot{\mathbf{B}}(t)\Big] \, .$$

As mentioned above, the center $\mathbf{r}_0$ in Eq. (5) can be chosen arbitrarily and here we choose the location $\mathbf{R}$ of the moment considered. Furthermore, we explicitly specify the location $\mathbf{R}$ to be the center of gravity of its electron distribution $n_{\mathbf{R}}(\mathbf{r})$ such that

$$\int \mathrm{d}^3 r \, n_{\mathbf{R}}(\mathbf{r})(\mathbf{r}-\mathbf{R}) = 0 \, .$$

Then we find

$$\dot{\mathbf{m}}_{\mathbf{R}} = \frac{e^2}{4m_e} \int \mathrm{d}^3 r \, n_{\mathbf{R}}(\mathbf{r})(\mathbf{r}-\mathbf{R}) \times \Big[(\mathbf{r}-\mathbf{R}) \times \dot{\mathbf{B}}(t)\Big] = \frac{e^2}{4m_e} \int \mathrm{d}^3 r' \, n_{\mathrm{local}}(\mathbf{r}')\mathbf{r}' \times \Big[\mathbf{r}' \times \dot{\mathbf{B}}(t)\Big]$$

assuming equal molecules/lattice sites with $n_{\mathbf{R}}(\mathbf{r}'+\mathbf{R}) = n_{\mathrm{local}}(\mathbf{r}')$. (An extension to different species is straightforward.) With $\mathbf{B}(t) = B(t)\mathbf{e}_z$, this provides the z-component of the magnetic moment (which is identical for all sites $\mathbf{R}$)

$$\dot{m}_z = -\frac{e^2}{4m_e} \int \mathrm{d}^3 r' \, n_{\mathrm{local}}(\mathbf{r}')(x'^2 + y'^2)\dot{B}(t) \, . \tag{8}$$

Thus, a change in magnetic field in time provides a diamagnetic response of the electrons. For circular orbits with constant radius one can easily show, that this quantitatively agrees with the change of magnetic moments addressed in Fig. 2 balancing the Lorentz force (as exemplified in Sec. 4.1). This indicates some generality of this diamagnetic term, as already discussed by Langevin [2]. Using Eq. (7), this results in the diamagnetic susceptibility

$$\chi_{\mathrm{dia}} = -n_{\mathrm{moments}} \frac{e^2\mu_0}{4m_e} \int \mathrm{d}^3 r' \, n_{\mathrm{local}}(\mathbf{r}')(x'^2 + y'^2) \tag{9}$$

which we will re-derive in Sec. 3 via Eq. (15). For a typical atomic density $n_{\mathrm{moments}} \approx 5\times 10^{28}/\mathrm{m}^3$ in a solid and 6 outer electrons with $\langle x^2+y^2\rangle \approx 1\text{Å}^2$, we find $\chi_{\mathrm{dia}} \approx -3\times 10^{-5}$. This is a rather typical value for diamagnetic substances. However, within a classical picture, this initial change of magnetic moments due to the changing magnetic field (8) should be restored by thermalization after a certain time.

3 Quantum mechanical treatment

In order to formulate the Hamiltonian of a charged particle in an electromagnetic field, we need the scalar potential $\phi(\mathbf{r},t)$ and the vector potential $\mathbf{A}(\mathbf{r},t)$, which are related to the electric field $\mathbf{E}(\mathbf{r},t)$ and the magnetic field $\mathbf{B}(\mathbf{r},t)$ according to

$$\mathbf{E}(\mathbf{r},t) = -\nabla\phi(\mathbf{r},t) - \frac{\partial \mathbf{A}(\mathbf{r},t)}{\partial t} \quad \text{and} \quad \mathbf{B}(\mathbf{r},t) = \nabla \times \mathbf{A}(\mathbf{r},t) \, . \tag{10}$$

Then the Hamilton operator for a particle with mass m and charge q reads[3]

$$\hat{H} = \frac{(\hat{\mathbf{p}} - q\mathbf{A}(\hat{\mathbf{r}},t))^2}{2m} + q\phi(\hat{\mathbf{r}},t) \tag{11}$$

[3]See a textbook of quantum mechanics such as [4] or the notes [5] for a quick orientation.

where the operators $\hat{\mathbf{p}}$ and $\hat{\mathbf{r}}$ satisfy the canonical commutation relations

$$[\hat{p}_j, \hat{r}_k] = \frac{\hbar}{\mathrm{i}}\delta_{ij} \qquad [\hat{p}_j, \hat{p}_k] = 0 \qquad [\hat{r}_j, \hat{r}_k] = 0 \quad \text{for } j,k \in x,y,z \tag{12}$$

In spatial representation with wave functions $\Psi(\mathbf{r},t)$, the momentum operator $\hat{\mathbf{p}}$ becomes $\frac{\hbar}{\mathrm{i}}\nabla$ as usual. Note that the average velocity is given by

$$\langle \mathbf{v} \rangle = \frac{\langle \hat{\mathbf{p}}^{\text{kinetic}} \rangle}{m} \quad \text{with the kinetic momentum} \quad \hat{\mathbf{p}}^{\text{kinetic}} = \hat{\mathbf{p}} - q\mathbf{A}(\hat{\mathbf{r}},t) \tag{13}$$

For stationary systems with a homogeneous magnetic field $\mathbf{B} = B\mathbf{e}_z$, we may choose the vector potential $\mathbf{A}(\mathbf{r},t) = \frac{1}{2}\mathbf{B}\times\mathbf{r}$. Then we obtain for electrons with $q=-e$ after some algebra

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + \frac{e}{2m}B\hat{L}_z + \frac{e^2B^2}{8m}(\hat{x}^2+\hat{y}^2) + V(\hat{\mathbf{r}}) \tag{14}$$

where $V(\mathbf{r}) = -e\phi(\hat{\mathbf{r}})$ is the electrostatic potential resulting from the nuclei or ionic cores.

The magnetic moment (5) of a quantum state $|\Psi\rangle$, located around $\mathbf{R} = \langle\Psi|\mathbf{r}|\Psi\rangle$ is given by

$$\mathbf{m}_{\mathbf{R}} = \frac{q}{2}\langle\Psi|(\hat{\mathbf{r}}-\mathbf{R})\times\hat{\mathbf{v}}|\Psi\rangle = \frac{q}{2m}\langle\Psi|(\hat{\mathbf{r}}-\mathbf{R})\times\hat{\mathbf{p}} - q(\hat{\mathbf{r}}-\mathbf{R})\times\mathbf{A}(\hat{\mathbf{r}},t)|\Psi\rangle$$

where Eq. (13) was used. Now $\langle\Psi|(\hat{\mathbf{r}}-\mathbf{R})\times\mathbf{A}(\mathbf{R},t)|\Psi\rangle = \langle\Psi|(\hat{\mathbf{r}}-\mathbf{R})|\Psi\rangle\times\mathbf{A}(\mathbf{R},t) = 0$, due to the definition of $\mathbf{R}$. Thus we may replace $\mathbf{A}(\hat{\mathbf{r}},t)$ by $[\mathbf{A}(\hat{\mathbf{r}},t) - \mathbf{A}(\mathbf{R},t)]$ on the right-hand side. For $\mathbf{A}(\mathbf{r},t) = \frac{1}{2}\mathbf{B}\times\mathbf{r}$ we then find

$$\mathbf{m}_{\mathbf{R}} = \frac{q}{2m}\langle\Psi|\hat{\mathbf{r}}'\times\hat{\mathbf{p}} - \frac{q}{2}\hat{\mathbf{r}}'\times(\mathbf{B}\times\hat{\mathbf{r}}')|\Psi\rangle$$

with $\hat{\mathbf{r}}' = \hat{\mathbf{r}} - \mathbf{R}$. For electrons in a homogeneous magnetic field $\mathbf{B} = B\mathbf{e}_z$, this provides the z-component of the magnetic moment (we use μ instead of m_z in order not to confuse with mass or quantum numbers)

$$\mu_{\mathbf{R}} = \frac{-e}{2m_e}\langle\Psi|\hat{L}'_z|\Psi\rangle - \left\langle\Psi\left|\frac{e^2B}{4m_e}(\hat{x}'^2+\hat{y}'^2)\right|\Psi\right\rangle . \tag{15}$$

The second term on the right-hand side provides a diamagnetic contribution and summing over all occupied states, we find χ_{dia} from Eq. (9).

3.1 Shells and Kramers degeneracy

Without magnetic field the Hamiltonian

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m_e} + V(\hat{\mathbf{r}})$$

has eigenstates $|\Psi_{n\ell}\rangle$ with energies E_n, where the index ℓ counts states with the same energy. These states form the *shell* with energy E_n. Typical examples are the $2l+1$-degenerate shells in a spherical symmetric atom ($l=0,1,2,3$ for s,p,d,f shells, respectively), where ℓ becomes the magnetic quantum number m_l with possible values $-l, -l+1, \ldots, l$ (here without spin). According to the Pauli principle, each quantum state can accommodate a single electron (or two with spin degeneracy). Thus, in the ground state, the occupation of states follows the Aufbau principle, where the states are subsequently filled with electrons, until all electrons required by

charge balance with the cores are accommodated as already sketched in Sec. 1.2. The valence shell is the last shell affected and may either be partially or completed filled, while all shells with lower energy are completely filled and all shells with higher energy are empty. Typically, the energy spacing between the shells is much larger than k_BT, and thermal fluctuations provide an equal average population of the states in the valence shell, but does not effect the populations in the other shells.

In spatial representation

$$\hat{H}_0^{\rm SR} = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\mathbf{r})$$

is real and thus for any eigenfunction $\Psi_{n\ell}(\mathbf{r})$, satisfying $\hat{H}_0^{\rm SR}\Psi_{n\ell}(\mathbf{r}) = E_n\Psi_{n\ell}(\mathbf{r})$, there exists another function $\Psi_{n\bar{\ell}}(\mathbf{r}) = \Psi^*_{n\ell}(\mathbf{r})$, satisfying

$$\hat{H}_0^{\rm SR}\Psi_{n\bar{\ell}}(\mathbf{r}) = \hat{H}_0^{\rm SR*}\Psi^*_{n\ell}(\mathbf{r}) = E^*_n\Psi^*_{n\ell}(\mathbf{r}) = E_n\Psi_{n\bar{\ell}}(\mathbf{r})\,.$$

Thus $\Psi_{n\bar{\ell}}(\mathbf{r})$ is an eigenstate of the same shell. Unless $\Psi_{n\ell}(\mathbf{r})$ is real, we have $\bar{\ell}\neq\ell$. These pairs $\ell,\bar{\ell}$ are called *Kramers degenerate* and examples are the states with $\pm m_l$ in an atom with spherical symmetry or the Bloch states with $\pm\mathbf{k}$ in a crystal. As $\hat{L}_z^{\rm SR} = \frac{\hbar}{\rm i}\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$ is purely imaginary, while its expectation value is real, we find

$$\langle\Psi_{n\ell}|\hat{L}_z|\Psi_{n\ell}\rangle = -\langle\Psi_{n\bar{\ell}}|\hat{L}_z|\Psi_{n\bar{\ell}}\rangle$$

Thus the contributions from the first term in Eq. (15) cancel each other when summing over the states of a completely filled shell. As the second term in Eq. (15) provides a magnetic moment oriented opposite to the magnetic field, we find:

Completely filled shells provide the diamagnetic contribution $\chi_{\rm dia}$ from Eq. (9).

If the valence shell is partially occupied, the states with $\langle\Psi_{n\ell}|\hat{L}_z|\Psi_{n\ell}\rangle<0$ have lower energy for $B>0$, due to Eq. (14) and are more likely to be occupied than their counterparts $|\Psi_{n\bar{\ell}}\rangle$. This results in a positive contribution to the magnetic moment from the first term in Eq. (15). Quantitatively, we have $\langle\Psi_{n\ell}|\hat{L}_z|\Psi_{n\ell}\rangle\sim-\hbar$ (e.g., $m_l\hbar$ for the atomic shells). Thus the

$$\text{Bohr magneton } \mu_B = \frac{e\hbar}{2m_e}\approx 58\frac{\mu\text{eV}}{\text{T}} \tag{16}$$

is a good number for the absolute value of the magnetic moment. The energy differences between the ℓ and $\bar{\ell}$ state is then $\Delta E = 2B\mu_B$ and with Eq. (4) we find

$$\langle\mu\rangle \approx \mu_B\frac{B\mu_B}{k_BT}$$

resulting in [4]

$$\chi_{\rm para}\approx n_{\rm moments}\mu_0\frac{\mu_B^2}{k_BT} \tag{17}$$

For room temperature $k_BT = 25$ meV and a typical atomic density $n_{\rm moments}\approx 5\times10^{28}/\text{m}^3$ in a solid, we find $\chi_{\rm para}\approx10^{-3}$, which is much larger than $\chi_{\rm dia}$. Thus:

Partially filled shells provide a dominating paramagnetic contribution (17) to the magnetic susceptibility.

[4] This holds for two degenerate states with magnetic moments $\pm\mu_B$. For the common atomic shells, an additional factor $l(l+1)/3$ appears. Including spin, the corresponding factor is $g^2j(j+1)/3$, where j describes the total angular momentum and g is the Landé factor of the shell. See Ref. [6].

3.2 Spin

On the level of the Pauli equation, spin can be added in Eqs. (14,15), by replacing $\hat{L}_z \to (\hat{L}_z + g_e \hat{s}_z)$, where $\hat{s}_z$ is the z-component of the spin operator and $g_e \approx 2.0023$ the g-factor of the electron. In spinor representation, the spin operator becomes $\hat{\mathbf{s}} \to \frac{\hbar}{2}\boldsymbol{\sigma}$

$$\text{with the Pauli matrices } \boldsymbol{\sigma} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \mathbf{e}_x + \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \mathbf{e}_y + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \mathbf{e}_z$$

At this level, the spatial and spin part are decoupled, and we get the same shells as before, but with two states in spinor representation

$$\begin{pmatrix} \Psi_{n\ell}(\mathbf{r}) \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ \Psi_{n\ell}(\mathbf{r}) \end{pmatrix}$$

The z-component of the magnetic moment due to the electron spin is $g\mu_B/2 \approx \mu_B$, so that both spin directions have the moment $\mp\mu_B$. Thus, Eq. (17) is exact for the case of an unpaired spin in an s-level.

Spin-orbit coupling complicates the picture as the Hamiltonian in spinor representation [4]

$$\hat{H}_0^{\mathrm{SR}} = \left[-\frac{\hbar^2}{2m_e}\Delta + V(\mathbf{r}) \right] \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + V_{\mathrm{SO}}(\mathbf{r}) \left[\mathbf{r} \times \frac{\hbar}{\mathrm{i}} \nabla \right] \cdot \frac{\hbar}{2} \boldsymbol{\sigma}$$

is not real any longer. Then the Kramers-degeneracy involves the switch of spin components:

$$|\Psi_{n\bar{\ell}}\rangle^{\mathrm{SR}} = \begin{pmatrix} \Psi^{\uparrow}_{n\bar{\ell}}(\mathbf{r}) \\ \Psi^{\downarrow}_{n\bar{\ell}}(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} \Psi^{\downarrow *}_{n\ell}(\mathbf{r}) \\ -\Psi^{\uparrow *}_{n\ell}(\mathbf{r}) \end{pmatrix}$$

Inserting into the Hamiltonian, shows that $\hat{H}_0|\Psi_{n\bar{\ell}}\rangle = E_n|\Psi_{n\bar{\ell}}\rangle$ if $\hat{H}_0|\Psi_{n\ell}\rangle = E_n|\Psi_{n\ell}\rangle$, so that both states are in the same shell. Furthermore

$$\langle \Psi_{n\bar{\ell}}|\hat{L}_z + g\hat{s}_z|\Psi_{n\bar{\ell}}\rangle = -\langle \Psi_{n\ell}|\hat{L}_z + g\hat{s}_z|\Psi_{n\ell}\rangle$$

so that each shell consists of pairs of states with opposite magnetic moment and we can repeat the arguments given in 3.1.

4 Example: Harmonic oscillator in two dimensions

In order to illustrate the heuristic concept in Sec. 1, we consider an electron with mass m in a 2-dimensional harmonic oscillator with spring constant $m\omega_0^2$ in a perpendicular magnetic field $\mathbf{B} = B\mathbf{e}_z$. With respect to the three-dimensional case, we assume that the z-dependence decouples and we have a system with rotation symmetry around $\mathbf{e}_z$.

4.1 Classical solution

We consider an electron in an isotropic harmonic force $\mathbf{F}(\mathbf{r}) = -m\omega_0^2(x\mathbf{e}_x + y\mathbf{e}_y)$ corresponding to the potential $V(\mathbf{r}) = m\omega_0^2(x^2+y^2)/2$. Then the solutions can be written as

$$x(t) = r_+ \cos(\omega_+ t + \varphi_+) + r_- \cos(\omega_- t + \varphi_-) \tag{18}$$

$$y(t) = r_+ \sin(\omega_+ t + \varphi_+) - r_- \sin(\omega_- t + \varphi_-) \tag{19}$$

where the motion in the x, y plane is here given as a superposition of anti-clockwise (+) and clockwise (−) circulating orbits. Without magnetic field, we have $\omega_\pm = \omega_0$. In the presence of a magnetic field $\mathbf{B} = B\mathbf{e}_z$, we have the Lorentz fore

$$\mathbf{F}_{\rm Lorentz} = -eB\mathbf{v} \times \mathbf{e}_z$$

For the anti-clockwise/clockwise modes r_+/r_- it points inwards/outwards, respectively, as sketched in Fig. 2. Balancing centripetal force and the total force along the radial direction, we get new frequencies. (Note that the velocity is $r_\pm\omega_\pm$ in tangential direction.)

$$m\omega_\pm^2 r_\pm \mp eB\omega_\pm r_\pm - m\omega_0^2 r_\pm = 0 \Rightarrow \omega_\pm = \sqrt{\omega_0^2 + \left(\frac{eB}{2m}\right)^2} \pm \frac{eB}{2m}$$

for anti-clockwise and clockwise orbits in Eqs. (18,19), respectively.

The magnetic moment in z-direction (referred to by μ in the following) evaluated by Eq. (3) with $A = \pi r^2$ reads

$$\mu_\pm(r_\pm) = \mp\frac{e}{2}\omega_\pm r_\pm^2 = \mp\frac{e}{2}\sqrt{\omega_0^2 + \left(\frac{eB}{2m}\right)^2} r_\pm^2 - \frac{e^2B}{4m} r_\pm^2 \tag{20}$$

The energy is given by the sum of kinetic and potential energy

$$E_\pm(x_\pm) = \frac{m}{2}(\omega_\pm r_\pm)^2 + \frac{m}{2}(\omega_0 r_\pm)^2 = m(\omega_0 r_\pm)^2 \pm \frac{eB\omega_\pm}{2} r_\pm^2 = m(\omega_0 r_\pm)^2 - \mu_\pm(r_\pm)B \tag{21}$$

where the last term is just $U_{\rm dipole}$ from Eq. (6). Comparing anti-clockwise and clockwise rotating orbits with identical radius $r_+ = r_-$, provides directly the results sketched in Fig. 2. Quantitatively, all magnetic moments are reduced by $\frac{e^2B}{4m}\langle x^2 + y^2\rangle$, which provides the diamagnetic term (9).

Now we consider clockwise and anti-clockwise orbits with the same energy $E_0 = m(\omega_0 x_0)^2$ of the oscillator without magnetic field. We find the radii

$$r_\pm^2(E_0) = \frac{x_0^2\omega_0^2}{\omega_0^2 \pm \frac{eB}{2m}\omega_\pm} = \frac{x_0^2\omega_0^2}{\omega_\pm\sqrt{\omega_0^2 + \left(\frac{eB}{2m}\right)^2}}$$

The corresponding magnetic moments

$$\mu_\pm(E_0) = \mp\frac{e}{2}\frac{x_0^2\omega_0^2}{\sqrt{\omega_0^2 + \left(\frac{eB}{2m}\right)^2}}$$

are just opposite to each other. In thermal equilibrium, the clockwise and anti-clockwise orbits at the same energy have equal occupation probabilities and thus their magnetic moments cancel. We conclude, that in thermal equilibrium there is no net magnetic moment in the presence of a magnetic field.

4.2 Quantum solution

Setting $V(\mathbf{r}) = m\omega_0^2(\hat{x}^2 + \hat{y}^2)/2$, Eq. (14) provides

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + \frac{e}{2m}B\hat{L}_z + \frac{e^2}{8m}B^2(\hat{x}^2 + \hat{y}^2) + \frac{m\omega_0^2}{2}(\hat{x}^2 + \hat{y}^2) = \hat{H}_{\rm osc}^B + \frac{e}{2m}B\hat{L}_z \tag{22}$$

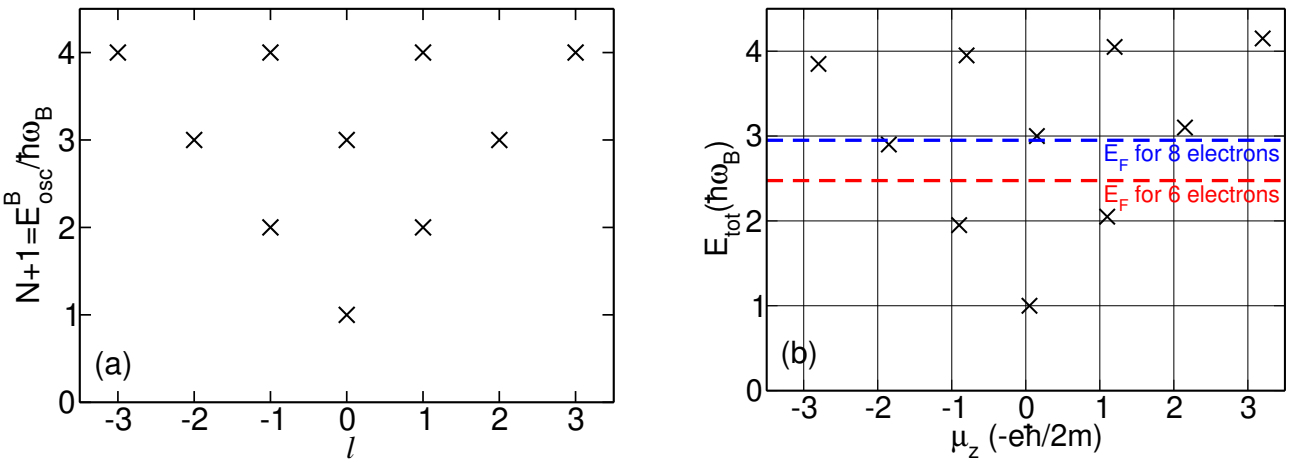

Figure 3: (a) Energy eigenvalues for the 2-dimensional harmonic oscillator $\hat{H}^B_{\rm osc}$ resolved by the quantum numbers ℓ, corresponding to the eigenvalues $\ell\hbar$ of $\hat{L}_z$. (b) Energy eigenvalues for the full Hamiltonian of the harmonic oscillator in a magnetic field, sorted by the magnetic moment of the eigenstates. Here $eB/(2m\omega_B) = 0.05$, is chosen for illustrative purpose, which corresponds to unrealistically large magnetic fields for atomic systems.

Here $\hat{H}^B_{\rm osc}$ is the Hamilton operator of the Harmonic oscillator with angular frequency $\omega_B = \sqrt{\omega_0^2 + (eB/2m)^2}$. Being the sum of two one-dimensional oscillators (in x and y direction) with energies $E_n = \hbar\omega_B(n + 1/2)$, the eigen-energies of $\hat{H}^B_{\rm osc}$ are simply the energy levels $E_N = \hbar\omega_B(N + 1)$ where $N = 0, 1, 2, \ldots$. For each level N there are $N + 1$ degenerate states corresponding to the different possibilities to distribute $N = n_x + n_y$ onto both oscillators.

A straightforward calculation, shows that $\hat{L}_z = \hat{p}_x\hat{y} - \hat{p}_y\hat{x}$ commutes with $\hat{H}^B_{\rm osc}$ and we have a complete set of common eigenstates to $\hat{H}^B_{\rm osc}$ and $\hat{L}_z$, which constitute also the eigenstates of $\hat{H}$. In spatial representation with polar coordinates r, φ we find $\hat{L}_z^{\rm SR} = \frac{\hbar}{\rm i}\frac{\partial}{\partial\varphi}$ with eigenstates $\mathrm{e}^{\mathrm{i}\ell\varphi}$ and eigenvalues $\ell\hbar$, in analogy to the three dimensional case.[5] Then one finds the

Proposition: The eigenstates of the two-dimensional harmonic oscillator $\hat{H}^B_{\rm osc}$ with energy $E_N = \hbar\omega_B(N + 1)$ can be classified as the $(N + 1)$ states $|N, \ell\rangle$ with $\ell = -N, 2 - N, \ldots N$, where $\hat{L}_z|N, \ell\rangle = \ell\hbar|N, \ell\rangle$.

which is proven in appendix B and displayed in Fig. 3(a). By construction, these states $|N, \ell\rangle$ are the eigenstates of the full Hamiltonian (22) with energies

$$E(N, \ell) = \hbar\omega_B(N + 1) + \frac{e\hbar}{2m}B\ell \tag{23}$$

Thus the degenerate level N splits into anti-clockwise ($\ell > 0$) and clockwise ($\ell < 0$) rotating levels with increased/decreased energy.

The z-component of the magnetic moment from Eq. (15) reads

$$\mu = -\frac{e\hbar}{2m}\ell - \frac{e^2B}{4m}\langle N, \ell|(\hat{x}^2 + \hat{y}^2)|N, \ell\rangle \tag{24}$$

Thus anti-clockwise ($\ell > 0$) and clockwise ($\ell < 0$) rotating levels have negative and positive magnetic moment, which are both reduced in the presence of a magnetic field in full agreement

[5] Note that $\hat{H}_{\rm osc}$ does not commute with $\hat{L}_x$ and $\hat{L}_y$. Thus we do not find the multiplets $m = -l, -l+1, \ldots l$ as characteristic for systems which are rotational invariant in all three spatial directions.

with the classical scenario in Fig. 2. Note that the last term, describing an overall reduction of the magnetic moment with increasing B fully agrees with the classical result (20).[6]

In order to judge the magnitudes of the different contributions, we can rewrite Eq. (24) as

$$\mu = -\frac{e\hbar}{2m}\left(\ell + \frac{\pi\langle N,\ell|(\hat{x}^2+\hat{y}^2)|N,\ell\rangle B}{2\pi\hbar/e}\right)$$

where the nominator of the second term is the magnetic flux through the area covered by the bound state and the denominator is twice the magnetic flux quantum $h/2e = 2068\mathrm{Tnm}^2$. Thus, for $\ell \neq 0$, the second term is several orders of magnitudes smaller than the first assuming atomic dimensions and conventional magnetic fields up to a few Tesla.

For a system with several electrons (such as an atom) the Pauli principle only allows one electron per level and spin direction. For six electrons the lowest energy is achieved by occupying the lowest three levels below the Fermi energy, as shown in Fig. 3(b). As each level is occupied by one electron with spin up and one electron with spin down, the magnetic moments due to spin cancel. The sum of the orbital magnetic moments is negative and thus the system is diamagnetic. In contrast for systems with 8 electrons, we find a positive sum of magnetic moments and expect paramagnetism. Note that in this case all three levels with $N = 2$ are actually partially occupied, as the energy spacing $e\hbar B/m \approx 0.1\mathrm{meV} \times B/\mathrm{T}$ is small compared to the thermal energy $k_BT \approx 25$ meV at room temperature for magnetic field up to a few Tesla. However, the Boltzmann factor provides typically a sufficient overweight for the state with $\ell = -2$ with lowest energy. Furthermore, the magnetic moments of the electron spin provide a parametric contribution if the spins are not all paired. This illustrates the more phenomenological statements made in Sec. 1.

5 Hamiltonian kinetics and zero classical magnetization

The classical Hamilton function for particles with mass m and charge q in an electromagnetic field with potentials $\mathbf{A}(\mathbf{r},t)$ and $\phi(\mathbf{r},t)$ reads[7]

$$\mathcal{H}(\mathbf{p},\mathbf{r},t) = \frac{1}{2m}\big[\mathbf{p} - q\mathbf{A}(\mathbf{r},t)\big]^2 + q\phi(\mathbf{r},t) \tag{25}$$

which is the classical correspondence of Eq. (11). The canonical momentum

$$\mathbf{p} = m\mathbf{v} + q\mathbf{A} \tag{26}$$

differs from the conventional kinetic momentum $\mathbf{p}^{\mathrm{kin}} = m\mathbf{v}$.

For classical particles with charge q and velocity $\mathbf{v}$, we find the statistical average of the magnetic moment (5)

$$\langle\mathbf{m}\rangle = \left\langle \frac{q}{2}\mathbf{r}\times\mathbf{v}\right\rangle = \left\langle \frac{q}{2m}\mathbf{r}\times(\mathbf{p}-q\mathbf{A}(\mathbf{r}))\right\rangle \tag{27}$$

[6]For the harmonic oscillator we have $m\omega_B^2\langle N,\ell|(\hat{x}^2+\hat{y}^2)|N,\ell\rangle/2 = E_N/2$, as the total energy is equally distributed to the kinetic and potential energy. Thus

$$\mu(N,\ell) = -\frac{e\hbar}{2m}\left[\ell + \frac{eB}{2m\omega_B}(N+1)\right]. \quad \text{Together with } E(N,\ell) = \hbar\omega_B\left[N+1+\frac{eB}{2m\omega_B}\ell\right]$$

this allows to perform the limit to free electrons $\omega_0 \to 0$, where $\frac{eB}{2m\omega_B} \to 1$ provides the Landau levels.

[7]See a textbook of analytic mechanics such as [7] or the notes [5] for a quick orientation.

where we applied Eq. (26). In thermal equilibrium, the Boltzmann distribution provides

$$\langle \mathbf{m} \rangle = \frac{\int \mathrm{d}^3 r \int \mathrm{d}^3 p \, \frac{q}{2m} \mathbf{r} \times (\mathbf{p} - q\mathbf{A}(\mathbf{r})) \mathrm{e}^{-\mathcal{H}(\mathbf{p},\mathbf{r})/k_B T}}{\int \mathrm{d}^3 r \int \mathrm{d}^3 p \, \mathrm{e}^{-\mathcal{H}(\mathbf{p},\mathbf{r})/k_B T}} \tag{28}$$

(Note that here we use the proposition that the possible states of the particle are evenly distributed in the phase space of canonical variables q and p_q.) Using the Hamilton function (25), we can now make the substitution $\mathbf{p} \to \mathbf{p}^{\mathrm{kin}} = \mathbf{p} - q\mathbf{A}(\mathbf{r})$ and obtain

$$\langle \mathbf{m} \rangle = \frac{\int \mathrm{d}^3 r \int \mathrm{d}^3 p^{\mathrm{kin}} \, \frac{q}{2m} \mathbf{r} \times (\mathbf{p}^{\mathrm{kin}}) \mathrm{e}^{-\mathcal{H}(\mathbf{p}^{\mathrm{kin}} + q\mathbf{A},\mathbf{r})/k_B T}}{\int \mathrm{d}^3 r \int \mathrm{d}^3 p^{\mathrm{kin}} \, \mathrm{e}^{-\mathcal{H}(\mathbf{p}^{\mathrm{kin}} + q\mathbf{A},\mathbf{r})/k_B T}} \tag{29}$$

which does not depend on $\mathbf{A}$ due to the structure of $\mathcal{H}$ in Eq. (25). Thus, we conclude that the average magnetic moment does not depend on $\mathbf{B} = \nabla \times \mathbf{A}$ for classical particles. (The extension to many-particles systems is straightforward.) In particular we would neither expect dia- nor paramagnetism on the basic of classical physics, as first pointed out by Niels Bohr (PhD thesis, Kopenhagen, 1911) and, independently, Johanna von Leeuwen (PhD thesis, Leiden, 1919).

A Justification of Eqs. (5,6)

A.1 Magnetic field of a current distribution

In magnetostatics, the magnetic fields can be evaluated via the vector potential $\mathbf{A}(\mathbf{r})$ as

$$\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r}) \quad \text{with } \mathbf{A}(\mathbf{r}) = \frac{\mu_0}{4\pi} \int \mathrm{d}^3 r' \frac{\mathbf{j}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Assuming that $\mathbf{j}(\mathbf{r}')$ is localized to a small region around $\mathbf{r}_0$, we use the Taylor expansion with respect to the deviation $(\mathbf{r}' - \mathbf{r}_0)$:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} \approx \frac{1}{|\mathbf{r} - \mathbf{r}_0|} + \frac{\mathbf{r} - \mathbf{r}_0}{|\mathbf{r} - \mathbf{r}_0|^3} \cdot (\mathbf{r}' - \mathbf{r}_0)$$

For a current distribution $\mathbf{j}(\mathbf{r})$, which is restricted to a finite region in space and satisfies $\nabla \cdot \mathbf{j} = 0$, we have the identities

$$\int \mathrm{d}^3 r \, j_k = 0 \quad \text{and} \quad \int \mathrm{d}^3 r \, j_k r_l = \sum_i \epsilon_{kil} \frac{1}{2} \int \mathrm{d}^3 r \, \mathbf{e}_i \cdot (\mathbf{r} \times \mathbf{j}(\mathbf{r})) \tag{30}$$

as shown in Sec 5.6 of [1] and Sec 11.1 in [3]. Thus the first term in the Taylor expansion for $\mathbf{A}(\mathbf{r})$ vanishes and the second term provides

$$\mathbf{A}(\mathbf{r}) \approx \frac{\mu_0}{4\pi} \frac{\mathbf{m} \times (\mathbf{r} - \mathbf{r}_0)}{|\mathbf{r} - \mathbf{r}_0|^3}$$

with $\mathbf{m}$ given by (5) and the dipole field

$$\mathbf{B}(\mathbf{r}) \approx \frac{\mu_0}{4\pi} \frac{3(\mathbf{r} - \mathbf{r}_0)[\mathbf{m} \cdot (\mathbf{r} - \mathbf{r}_0)] - \mathbf{m}|\mathbf{r} - \mathbf{r}_0|^2}{|\mathbf{r} - \mathbf{r}_0|^5}$$

as sketched in Fig. 1. Thus the magnetic moment provides the leading contribution to the far field of a finite current distribution. (The higher terms from the Taylor expansion provide fields which are vanishing quicker than $1/|\mathbf{r} - \mathbf{r}_0|^3$.) Note that this expression only makes sense outside the current distribution. In order to be consistent, a term $2\mu_0 \mathbf{m} \delta(\mathbf{r} - \mathbf{r}_0)/3$ should be added for point-like dipoles in order to satisfy basic properties of the magnetic field, see Sec. 5.6 of [1] .

A.2 Forces and torques on magnetic moments

In a constant external magnetic field, we find with Eq. (30) the torque

$$\boldsymbol{\tau} = \int \mathrm{d}^3 r\, (\mathbf{r}-\mathbf{r}_0) \times (\mathbf{j}(\mathbf{r}) \times \mathbf{B}) = \mathbf{m} \times \mathbf{B}$$

where we used $\mathbf{r}\cdot\mathbf{j} = \frac{1}{2}\nabla\cdot(r^2\mathbf{j})$, which holds for $\nabla\cdot\mathbf{j}=0$. Against this torque, the work $mB\sin\theta \mathrm{d}\theta$ is done on the system by changing the polar angle θ of the dipole quasi-statically. Thus we obtain the potential energy $U_{\mathrm{dipole}} = -mB\cos\theta$ which is just (6).

For an inhomogeneous magnetic field, we find the total force

$$\mathbf{F} = \int \mathrm{d}^3 r\, \mathbf{j}(\mathbf{r}) \times \mathbf{B}(\mathbf{r}_0) + \mathbf{j}(\mathbf{r}) \times [(\mathbf{r}-\mathbf{r}_0)\cdot\nabla)]\mathbf{B}(\mathbf{r}_0) = \sum_k m_k \nabla B_k$$

as shown in Section 12.4.1 of [3]. If $\mathbf{m}$ is constant, this can be written as $\mathbf{F} = \nabla(\mathbf{m}\cdot\mathbf{B}) = -\nabla U_{\mathrm{dipole}}$, so that Eq. (6) also makes sense in inhomogeneous fields.

If the homogeneous magnetic field changes in time, it induces an electric field $\mathbf{E} = \frac{1}{2}(\mathbf{r}-\mathbf{r}_0)\times\dot{\mathbf{B}}$ (satisfying $\nabla\times\mathbf{E} = -\dot{\mathbf{B}}$). This provides the power to the current distribution

$$P = \int \mathrm{d}^3 r\, \mathbf{j}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r}) = -\mathbf{m}\cdot\dot{\mathbf{B}} = \frac{\partial U_{\mathrm{dipole}}}{\partial t}$$

A model for changing the dipole moment is a annular loop (perpendicular to $\mathbf{B}$), where we change the radius. The work, externally supplied, to overcome the Lorentz force is $\mathrm{d}W = -IB2\pi r\mathrm{d}r = -IB\mathrm{d}A = -B\mathrm{d}m = \mathrm{d}U_{\mathrm{dipole}}$.[8]

All these issues provide that the energy U_{dipole}, as given in Eq. (6), is stored in a dipole, which is subjected to space- and time-dependent magnetic fields and where the internal wires may also move with a constant current.

B Determining the possible ℓ-values of the states $|N,\ell\rangle$

Here we want to proof the proposition on page 10. Using the standard definitions

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x\,, \quad \hat{a}_x = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \mathrm{i}\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}_x\,, \quad \text{and} \quad \hat{a}_y = \sqrt{\frac{m\omega}{2\hbar}}\hat{y} + \mathrm{i}\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}_y$$

for angular momentum and lowering operators, we can directly identify

$$\hat{L}_z = \mathrm{i}\hbar(a_y^\dagger a_x - a_x^\dagger a_y) \tag{31}$$

and calculate the commutator relations

$$[\hat{L}_z, a_x^\dagger] = \mathrm{i}\hbar a_y^\dagger \quad \text{and} \quad [\hat{L}_z, a_y^\dagger] = -\mathrm{i}\hbar a_x^\dagger \tag{32}$$

With these tools at hand we proof the proposition by induction in N:

For $N=0$ the ground state of the harmonic oscillator satisfies $a_x|0,0\rangle = 0$ and $a_y|0,0\rangle = 0$. Thus we find from Eq. (31) $\hat{L}_z|0,0\rangle = 0$ and this state is indeed an eigenstate of $\hat{L}_z$ with eigenvalues $\ell = 0$.

[8] It would be nice to treat the case of changing current. Here I do not understand how to evaluate this as the self-inductance of a ring is diverging for infinitesimal wires (Problem 5.32 of [1]).

Assume the proposition is valid for a given $N \geq 0$. Then we consider the state

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(a_x^\dagger - \mathrm{i}a_y^\dagger)|N,\ell\rangle$$

and find

$$\hat{H}|\Psi\rangle = \hbar\omega(a_x^\dagger a_x + a_y^\dagger a_y + 1)\frac{1}{\sqrt{2}}(a_x^\dagger - \mathrm{i}a_y^\dagger)|N,\ell\rangle = \ldots = (N+2)\hbar\omega|\Psi\rangle$$
$$\hat{L}_z|\Psi\rangle = \hat{L}_z\frac{1}{\sqrt{2}}(a_x^\dagger - \mathrm{i}a_y^\dagger)|N,\ell\rangle = \ldots = (\ell-1)\hbar|\Psi\rangle$$

where the commutation rules for the lowering/raising operators and Eq. 32 are applied in the explicit calculation. Thus the state $|\Psi\rangle$ can be classified as $|N+1,\ell-1\rangle$. Similarly the state $|\Psi\rangle = \frac{1}{\sqrt{2}}(a_x^\dagger + \mathrm{i}a_y^\dagger)|N,\ell\rangle$ can be classified as $|N+1,\ell+1\rangle$. Considering the definition of ℓ this procedure constructs states $|N+1,m_{N+1}\rangle$ with $m_{N+1} = -(N+1), -(N+1)+2, \ldots (N+1)$. As the dimension of the subspace of the operator $\hat{H}$ with eigenvalue $(N+1)\hbar\omega$ is just $N+1$, only $N+1$ states can be linearly independent, i.e. those with different m. Thus the states $\frac{1}{\sqrt{2}}(a_x^\dagger - \mathrm{i}a_y^\dagger)|N,\ell\rangle$ and $\frac{1}{\sqrt{2}}(a_x^\dagger + \mathrm{i}a_y^\dagger)|N,\ell-2\rangle$ may only differ by a phase factor.
Thus the proposition is shown for $N+1$ and the proof by induction is closed.

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