25

Magnetic Field Perturbations

So far, we have looked at a number of perturbation problems involving an external electric field, $\vec{\mathcal{E}}$. We would like to look at similar problems involving external magnetic fields.

A The Quantum Mechanics of a Free, Charged Particle in a Magnetic Field

Classically, the Hamiltonian of a charged particle, of charge e and mass m, in a magnetic field, $\vec{B}$, derivable from a vector potential, $\vec{A}$, via $\vec{B} = \text{curl}\vec{A}$, is given by

$$H = \frac{1}{2m}(\vec{p} - \frac{e}{c}\vec{A}) \cdot (\vec{p} - \frac{e}{c}\vec{A}). \tag{1}$$

In a uniform field, $\vec{B}_0$, e.g., with $\vec{A} = \frac{1}{2}[\vec{B}_0 \times \vec{r}]$, the classical equations of motion in Hamiltonian formalism lead to

$$m\frac{d^2\vec{r}}{dt^2} = \frac{e}{c}[\vec{v} \times \vec{B}_0]. \tag{2}$$

The Schrödinger equation follows from eq. (1) via $\vec{p} \to \frac{\hbar}{i}\vec{\nabla}$. At first glance, this equation seems to be dependent on the choice of gauge of the vector potential. [With the choice of the so-called symmetric gauge for an electron in a uniform magnetic field in the z-direction, see eq. (15) below.] If $\vec{A}$ gives rise to a magnetic induction $\vec{B}$, a vector potential $\vec{A}'$ with $\vec{A}' = \vec{A} + \vec{\nabla}f$, where f is any function $f(x, y, z)$, will give rise to the *same* field $\vec{B}$. To keep the Schrödinger equation

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form invariant to this gauge transformation, we must gauge not only $\vec{A}$, but the Schrödinger wave function as well. The quantum-mechanical form of eq. (1) is form invariant under the gauge transformation (see problem 3),

$$\begin{aligned} \vec{A} &\to \vec{A}' = \vec{A} + \vec{\nabla} f(x, y, z), \\ \psi &\to \psi' = \psi e^{\frac{ie}{\hbar c} f(x,y,z)}. \end{aligned} \tag{3}$$

B Aharanov–Bohm Effect

The above gauge transformation was exploited by Bohm and Aharanov in a famous paper (Phys. Rev. **115** (1959) 485) to show that the quantum-mechanical wave function describing the motion of electrons can be influenced by the presence of magnetic fields, even if the electron trajectories are such that the electrons do not experience the Lorentz force $\frac{e}{c}[\vec{v} \times \vec{B}]$, if the trajectories are limited to regions in which $\vec{B} = 0$. They proposed the following experiment: An electron beam from an electron source is split into two identical beams, subsequently reflected from identical reflectors to end in a detector, as shown in Fig. 25.1. If the electrons in beam 1 are described by the wave function ψ_1 and the electrons in beam 2 are described by the wave function ψ_2, the number of electrons arriving at the common detector will be proportional to $|\psi_1 + \psi_2|^2$. Bohm and Aharanov proposed to place a tightly wound, infinitely long solenoid of small radius, a, behind the screen. A magnetic field $\vec{B}_0$ exists *inside* the solenoid, parallel to the solenoid axis, but the field outside the solenoid is precisely zero. The electrons therefore traverse only regions of space where the $\vec{B}$ field is precisely zero. (Of course, this infinitely long, tightly wound solenoid is a "theorist's" solenoid, but it can be approximated very well in the actual experiment.) Because the electrons are always in regions of zero field, choose a gauge in which the vector potential $\vec{A}'$ is also zero outside the solenoid; i.e., choose a gauge for which

$$\begin{aligned} \vec{A}' = 0 &= \vec{A} + \vec{\nabla} f(x, y, z) \\ \psi' &= \psi e^{\frac{ie}{\hbar c} f(x,y,z)}. \end{aligned} \tag{4}$$

Therefore, taking a line integral of $\vec{A}'$ around the exterior contour shown in Fig. 25.1,

$$\begin{aligned} 0 &= \oint \vec{A} \cdot d\vec{l} + \oint \vec{\nabla} f \cdot d\vec{l} \\ &= \int_0^a r dr \int_0^{2\pi} d\phi [\vec{\nabla} \times \vec{A}] \cdot \vec{n} + \int_0^{2\pi} \frac{\partial f(r, \theta, \phi)}{r \partial \phi} r d\phi \\ &= B_0 \pi a^2 + \Big(f(r, \theta, \phi = 2\pi) - f(r, \theta, \phi = 0) \Big), \end{aligned} \tag{5}$$

where we have converted the first line integral to a surface integral via Stokes's theorem. The unit vector $\vec{n}$ is parallel to the solenoid axis. The above therefore leads to

$$B_0 \pi a^2 = -\Big(f(2\pi) - f(0) \Big). \tag{6}$$

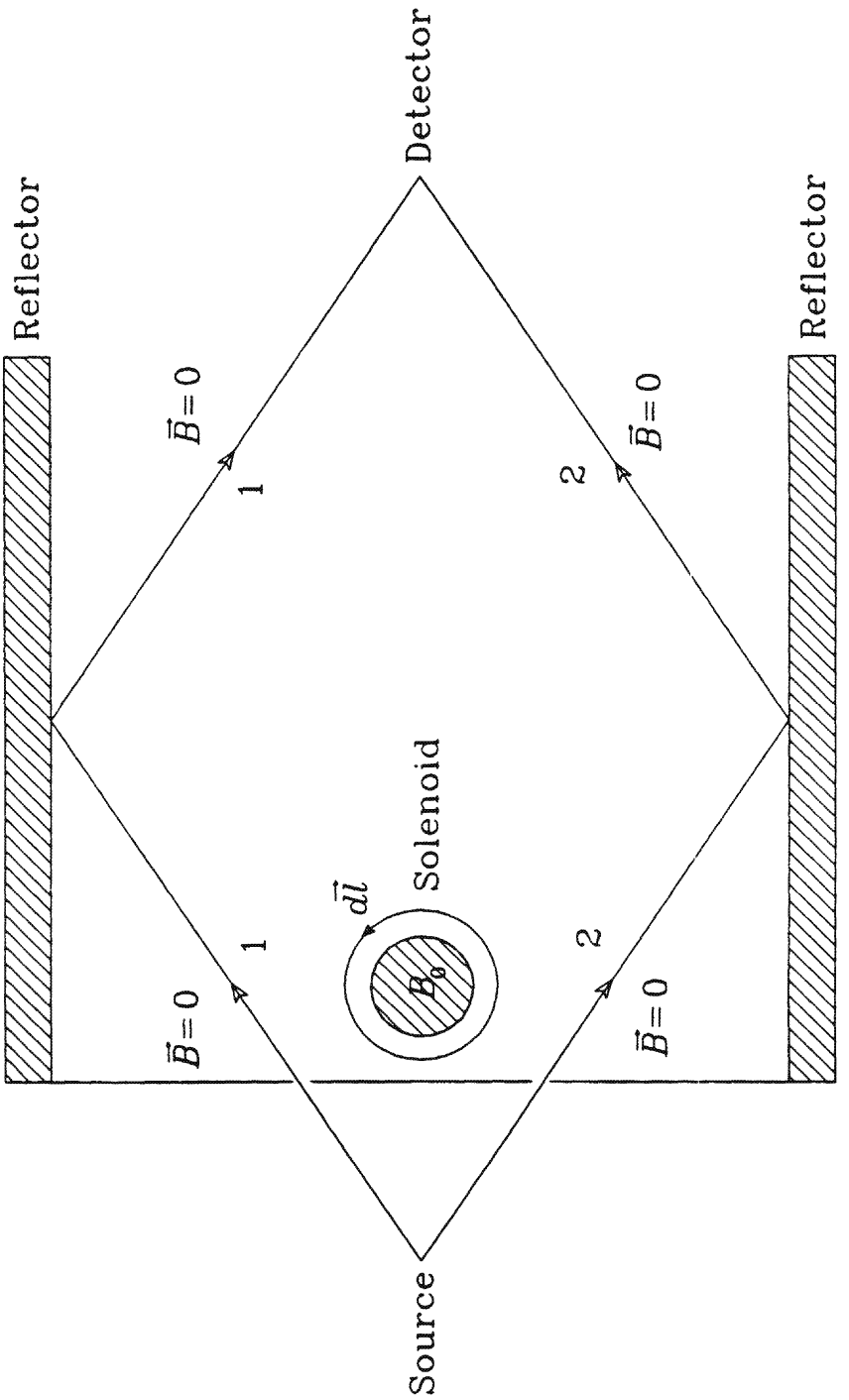


FIGURE 25.1. The Aharanov–Bohm effect

We have chosen a cylindrical coordinate system centered in the solenoid. The electrons traveling along trajectory 1 are, therefore, specified by

$$\psi_1 = \psi_1' e^{-\frac{ie}{\hbar c} f(\phi=0)}, \tag{7}$$

so, at the detector, D,

$$\psi_1 = \psi_D(\text{no field}) e^{-\frac{ie}{\hbar c} f(0)}. \tag{8}$$

Similarly, electrons traveling along trajectory 2 will, at the detector, D, be specified by the wave function

$$\psi_2 = \psi_D(\text{no field}) e^{-\frac{ie}{\hbar c} f(2\pi)}. \tag{9}$$

At the detector, therefore, the total wave function will be given by

$$\begin{aligned} \psi_1 + \psi_2 &= \psi_D(\text{no field}) e^{-\frac{ie}{\hbar c} f(0)} \left[1 + e^{-\frac{ie}{\hbar c}(f(2\pi) - f(0))}\right] \\ &= \psi_D(\text{no field}) e^{-\frac{ie}{\hbar c} f(0)} \left[1 + e^{+\frac{ie}{\hbar c} B_0 \pi a^2}\right]. \end{aligned} \tag{10}$$

The number of particles reaching the detector will then be proportional to

$$\begin{aligned} |\psi_D|^2 &= 2|\psi_D(\text{no field})|^2 \left[1 + \cos\left(\frac{eB_0\pi a^2}{\hbar c}\right)\right] \\ &= 4|\psi_D(\text{no field})|^2 \cos^2\left(\frac{eB_0\pi a^2}{2\hbar c}\right). \end{aligned} \tag{11}$$

That is, the number of particles arriving at the detector depends on the magnetic field strength in the solenoid, even though $\vec{B} = 0$ in the region of the particle trajectories. The experiment has been done, both with long solenoids and with highly magnetized "magnetic whiskers." Other experiments using the basic Bohm–Aharanov idea have also been successfully done. [For a review of experiments and ideas, see M. Peshkin and A. Tonomura, Lecture Notes in Physics **340**, Springer-Verlag (1989).]

C Zeeman and Paschen–Back Effects in Atoms

We shall start by studying the perturbations of magnetic fields, both external and internal, on the energies of one-electron atoms. We shall start, however, with alkali atoms, Li, Na, K, Cs, or Rb. In these one-valence-electron atoms, the n^2-fold degeneracy of hydrogen is removed. Levels with different l have considerably different zeroth-order energies, each with a $(2l+1)$-fold degeneracy. The hydrogenic potential, $V = -\frac{e^2}{r}$, is replaced by

$$V(r) = -\frac{Z_{\text{eff.}}(r)e^2}{r}. \tag{12}$$

The $Z_{\text{eff.}}(r)$ removes the degeneracy of levels with the same n but different l. In Na, e.g., with ground-state configuration $(1s^2 2s^2 2p^6 3s)$, the $n = 3, l = 0, l = 1$,

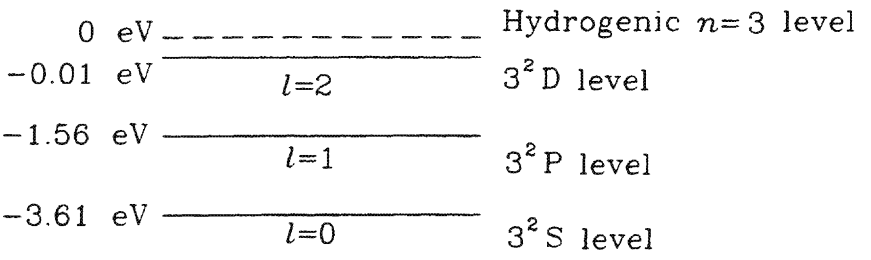


FIGURE 25.2. The Na-valence electron spectrum.

and $l = 2$ valence electron levels ($3^2S, 3^2P, 3^2D$) are split in zeroth order, as shown in Fig. 25.2. The s ($l = 0$) and p ($l = 1$) orbits are penetrating orbits. They penetrate the spherically symmetric innershell electron cloud and see effectively a $Z > 1$; hence, they lie at lower energy, with the s orbit having a considerably larger $Z_{\text{eff.}}$ than the p orbit. The d ($l = 2$) electron spends most of its time outside the innershell electron cloud and thus sees an effective charge very nearly equal to $(11 - 10) = 1$. This level has been shifted to lower energy by only $-.01$ eV, relative to a purely hydrogenic value with $Z = 1$.

In a uniform, external magnetic field, $\vec{B}_0$, with $\vec{A} = \frac{1}{2}[\vec{B}_0 \times \vec{r}]$ (where we have chosen a specific gauge, the so-called symmetric gauge), the Hamiltonian (ignoring for the moment the spin of the electron) has the form

$$H = \frac{1}{2m}(\vec{p} - \frac{e}{c}\vec{A}) \cdot (\vec{p} - \frac{e}{c}\vec{A}) + V(r). \tag{13}$$

Choosing $\vec{B}_0$ along the z-direction, so

$$A_x = -\frac{1}{2}B_0 y, \qquad A_y = +\frac{1}{2}B_0 x. \tag{14}$$

$$\begin{aligned} H &= \frac{p_x^2 + p_y^2 + p_z^2}{2m} - \frac{eB_0}{2mc}(xp_y - yp_x) + \frac{m}{2}\left(\frac{eB_0}{2mc}\right)^2 (x^2 + y^2) + V(r) \\ &= \frac{p_x^2 + p_y^2}{2m} + \frac{m}{2}\omega_L^2(x^2 + y^2) + \hbar\omega_L L_z + \frac{p_z^2}{2m} + V(x, y, z), \end{aligned} \tag{15}$$

where we have used the Larmor frequency

$$\omega_L = \frac{|e|B_0}{2mc}, \qquad \text{with} \quad \hbar\omega_L = 5.8 \times 10^{-5}\frac{B_0}{\text{tesla}}\text{-}eV,$$

and we have converted to a dimensionless, orbital angular momentum operator, L_z. (Remember the electron charge is negative.) For a free particle, with $V(x, y, z) = 0$, L_z and p_z commute with the Hamiltonian of eq. (15) and can be replaced by their eigenvalues, m_l, and $\hbar k_z$. The problem of a free particle in a uniform magnetic field therefore reduces to a 2-D harmonic oscillator problem (see problem 42). For an atomic problem with a central $V(r)$, it will of course be useful to convert to spherical coordinates and dimensionless atomic units, with a physical $\vec{r} = (x, y, z)$,

with $|\vec{r}| = a_0 r$, so

$$H = H^{(0)} + \hbar\omega_L L_z + \frac{1}{2}\frac{(\hbar\omega_L)^2}{(me^4/\hbar^2)} r^2 \sin^2\theta. \tag{16}$$

$(\hbar\omega_L)/(\frac{me^4}{\hbar^2}) \approx 10^{-6}$ for a magnetic field of 1 tesla = 10^4 gauss, so the term proportional to $\hbar\omega_L$, the so-called paramagnetic term can be treated as $H^{(1)}$, whereas the term proportional to $(\hbar\omega_L)^2$, the diamagnetic term, can be treated as $H^{(2)}$. The paramagnetic term can be put in the form

$$H^{(1)} = -(\vec{\mu}^{(\text{magn.})}_{\text{orbital}} \cdot \vec{B}) \ , \qquad \text{with} \quad \vec{\mu}^{(\text{magn.})}_{\text{orbital}} = \frac{e\hbar}{2mc}\vec{L} \ . \tag{17}$$

In 1924, when Uhlenbeck and Goudsmit postulated the existence of electron spin, with an associated spin magnetic moment, they added empirically a spin magnetic moment interaction to this paramagnetic term, but they found (empirically by fitting the predicted Zeeman spectra to the experimentally observed data) the gyromagnetic ratio for the spin magnetic moment requires an additional factor $g_s = 2$ relative to that predicted for the orbital magnetic moment, so

$$\vec{\mu}^{(\text{magn.})}_{\text{spin}} = \frac{e\hbar}{2mc} g_s \vec{S}. \tag{18}$$

Although introduced empirically in 1924, the factor $g_s = 2$ comes out automatically from the Dirac relativistic quantum theory of the electron. Thus,

$$H^{(1)} = -(\vec{\mu}^{(\text{magn.})}_{\text{orbital}} \cdot \vec{B}_0) - (\vec{\mu}^{(\text{magn.})}_{\text{spin}} \cdot \vec{B}_0) = \hbar\omega_L(L_z + 2S_z). \tag{19}$$

This perturbation has extremely simple matrix elements in the $|nlm_l m_s\rangle$ basis, where we have added the eigenvalue m_s of the operator S_z to complete the basis, leading to the first-order magnetic field correction to the energy

$$E^{(1)}_{nlm_l m_s} = \hbar\omega_L(m_l + 2m_s). \tag{20}$$

This formula would be correct in the limit in which the external field $\vec{B}_0$ is large compared with the internal atomic magnetic fields and their effects on the spin magnetic moment. We shall look at these effects next.

D Spin-Orbit Coupling and Thomas Precession

Because of the motion of the valence electron, the electron sees an effective internal magnetic field that can interact with the spin magnetic moment of the electron. To first order in $\frac{v}{c}$, the magnetic field at the electron is

$$\vec{B} = \frac{1}{c}[\vec{\mathcal{E}} \times \vec{v}] = -\frac{1}{c}[\vec{\nabla}\Phi^{(\text{el.})} \times \frac{\vec{p}}{m}] = +\frac{1}{|e|mc}\frac{dV}{dr}\frac{1}{r}[\vec{r} \times \vec{p}], \tag{21}$$

where we have converted the electric scalar potential to the potential function $V(r)$ and have used the fact that the electron charge is negative. We could of course also

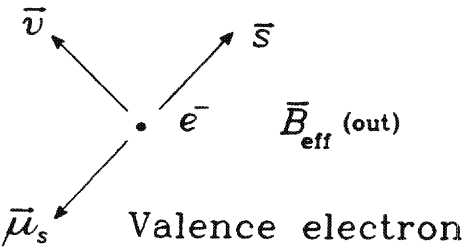
think of an observer "sitting on the electron" seeing the nuclear and innerelectron charge moving with a velocity $-\vec{v}$ relative to the electron, therefore setting up a current giving rise to the magnetic field at the site of the electron (see Fig. 25.3). When the electron's spin magnetic moment interacts with this internal magnetic field, we get a new contribution to the perturbed Hamiltonian of the one-electron atom

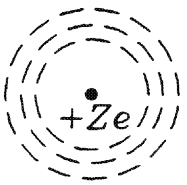
$$H^{(1)}_{\text{spin-orbit}} = -\vec{\mu}_s \cdot \vec{B} = +\frac{|e|\hbar g_s}{2mc}\frac{1}{r}\frac{dV}{dr}\frac{\hbar}{|e|mc}(\vec{S}\cdot\vec{L}) = \frac{\hbar^2}{m^2c^2}\left(\frac{1}{r}\frac{dV}{dr}\right)(\vec{S}\cdot\vec{L}), \quad (22)$$

where $\vec{L}$ and $\vec{S}$ are dimensionless. Besides this magnetic spin-orbit term, a second purely relativistic correction term exists, the Thomas precession term, which has exactly the same form, but has an additional numerical factor of $-\frac{1}{2}$,

$$H^{(1)}_{\text{Thomas}} = -\frac{1}{2}H^{(1)}_{\text{spin-orbit}}. \quad (23)$$

This purely relativistic term follows because two successive Lorentz transformations along different successive directions in the orbit are equivalent to a single Lorentz transformation plus a rotation in 3-D space. This rotation causes a precession of the intrinsic spin vector of the electron, the so-called Thomas precession,





Inner shell of electron cloud

FIGURE 25.3. Model of an alkali atom.

which cancels half of the magnetic spin orbit term. Thus,

$$H^{(1)}_{\text{spin-orbit}} + H^{(1)}_{\text{Thomas}} = \frac{\hbar^2}{2m^2c^2}\left(\frac{1}{r}\frac{dV}{dr}\right)(\vec{S}\cdot\vec{L}) = \frac{\hbar^2}{2m^2c^2}\left(\frac{\bar{Z}_{\text{eff.}}e^2}{r^3}\right)(\vec{S}\cdot\vec{L}), \quad (24)$$

where $\bar{Z}_{\text{eff.}}(r) = Z_{\text{eff.}}(r) - r\frac{dZ_{\text{eff.}}}{dr}$ in an alkali atom; but $\bar{Z}_{\text{eff.}}$ can be replaced by 1 in hydrogen. Converting the physical r in this equation to a dimensionless r via $r_{\text{phys.}} = a_0 r$, we have

$$H^{(1)} = \frac{1}{2}\frac{\left(\frac{me^4}{\hbar^2}\right)^2}{mc^2}\left(\frac{\bar{Z}_{\text{eff.}}}{r^3}\right)(\vec{S}\cdot\vec{L}) = \frac{1}{2}mc^2\alpha^4\left(\frac{\bar{Z}_{\text{eff.}}}{r^3}\right)(\vec{S}\cdot\vec{L}), \quad (25)$$

where r, $\vec{S}$, and $\vec{L}$ are now all dimensionless and α is the fine structure constant. This term is of order

$$\frac{1}{mc^2}\left(\frac{me^4}{\hbar^2}\right)^2 = mc^2\left(\frac{e^2}{\hbar c}\right)^4 = mc^2\alpha^4 \approx 0.5MeV(\frac{1}{137})^4 \approx 10^{-3}eV. \quad (26)$$

To this order of magnitude, we must also consider the first-order relativistic mass correction. From

$$W = \sqrt{m_0^2c^4 + p^2c^2} = m_0c^2 + \frac{p^2}{2m_0} - \frac{p^4}{8m_0^3c^2} + \cdots, \quad (27)$$

we get the relativistic mass correction to the kinetic energy term

$$W - m_0c^2 = \frac{p^2}{2m_0} - \frac{1}{2m_0c^2}\left(\frac{p^2}{2m_0}\right)^2 + \cdots = \frac{p^2}{2m_0} - \frac{(E^{(0)} - V(r))^2}{2m_0c^2} + \cdots. \quad (28)$$

To get the hydrogen energies correct to order $mc^2\alpha^4$, we must include this relativistic mass correction term along with the combined spin-orbit and Thomas term of eq. (25). This relativistic mass correction term, however, has been converted to a function of r only in the last form of eq. (28). In an alkali atom, therefore, it can be simply absorbed into the $Z_{\text{eff.}}(r)/r$ term. This term merely establishes the zeroth-order energies of the separated $l = 0$, $l = 1$, $l = 2$,... terms. These terms are essentially taken from experiment and not calculated very precisely. We shall calculate accurately the splitting of such a $2(2l+1)$-fold degenerate term into fine structure and Zeeman components, but take the zeroth-order positions of the different l levels from experiment. For the alkali atoms, therefore, this perturbation term can be absorbed into the zeroth-order terms.