The importance of the spectroscopy of atoms and ions for the understanding of the whole physics of matter cannot be overestimated. The study of atoms starts off naturally from the exact dynamics of a single electron in the central field of one positively charged nucleus (Sect. 2.1) because, beside the intrinsic interest of this system, the notation and concepts developed here are at the basis of the language of all atomic physics. This language is then used to introduce (Sect. 2.2) the spectroscopy of many-electron atoms, clusters of 2 to about $10^2$ electrons repelling each other, but trapped together in the attractive central field of a single nucleus.

### 2.1 One-Electron Atom/Ions

The one-electron atom is one of the few quantum problems whose Schrödinger equation (1.7) is solved exactly. Here, comparison of theory and experiment allows physicists to evaluate the limits of validity and predictive power of the quantum mechanical model Eqs. (1.1)–(1.6). When relativistic effects are included (Sect. 2.1.7), this model is found in almost perfect agreement with extremely accurate experimental data, all the tiny discrepancies being satisfactorily accounted for by a perturbative treatment of residual interactions (Sect. 2.1.8).

The solution of the Schrödinger equation (1.7), or rather its time-independent counterpart (B.30), for the one-electron atom is a basic exercise in quantum mechanics (QM). Both the $V_{ee}$ and $V_{nn}$ terms in Eq. (1.1) vanish, and only the nuclear and electronic kinetic energies plus the Coulomb attraction $V_{ne}$ are relevant. Many textbooks [5, 15, 16] provide detailed solutions of the one-electron atom problem. Here we recall the general strategy and main results.

- **Separation of the center-of-mass motion.** In analogy to the solution of the classical Kepler-Newton two-body “planetary” problem, the position operator of the nucleus $\mathbf{R}$, of mass $M$, and that of the electron $\mathbf{r}_e$ are replaced by the combinations

$$
\mathbf{R}_{\text{cm}} = \frac{M\mathbf{R} + m_e\mathbf{r}_e}{M + m_e} \quad \text{and} \quad \mathbf{r} = \mathbf{r}_e - \mathbf{R}.
$$

(2.1)
In these new coordinates, the Hamiltonian separates into a purely kinetic term for the free translational motion of the atomic center of mass $R_{\text{cm}}$

$$H_{\text{cm}} = -\frac{\hbar^2}{2(M + m_e)} \nabla^2 R_{\text{cm}},$$  \hspace{1cm} (2.2)

plus a Coulombic Hamiltonian for the relative coordinate $r$

$$H_{\text{Coul}} = -\frac{\hbar^2}{2\mu} \nabla^2 r - \frac{Ze^2}{|r|},$$  \hspace{1cm} (2.3)

where

$$\mu = \frac{Mm_e}{M + m_e}$$  \hspace{1cm} (2.4)

is the reduced mass of this 2-particle system. The free global $R_{\text{cm}}$ translational motion is described trivially in terms of plane waves. The internal atomic dynamics is that of a single particle of mass $\mu$ in the same Coulombic central field as the original nucleus-electron attraction.

**Separation in spherical coordinates.** To exploit the spherical symmetry of the potential, the Schrödinger equation is conveniently rewritten in polar coordinates $r, \theta, \varphi$. By factorizing the total wavefunction $\psi(r, \theta, \varphi) = R(r) \Theta(\theta) \Phi(\varphi)$, the variables separate, and the original three-dimensional (3D) equation splits into three independent second-order equations for the $r, \theta,$ and $\varphi$ motions:

$$-\frac{d^2 \Phi}{d\varphi^2} = \eta \Phi,$$  \hspace{1cm} (2.5)

$$-\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{\eta}{\sin^2 \theta} \Theta = \lambda \Theta,$$  \hspace{1cm} (2.6)

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ U(r) + \frac{\hbar^2 \lambda}{2\mu} \right] R = ER.$$  \hspace{1cm} (2.7)

Here we put a general function $U(r)$ in place of the potential energy $-Ze^2/r$, to emphasize that this same technique can be applied to any central potential (e.g. in Sect. 3.3).

**Solution** of the separate eigenvalue problems: the differential equations are solved under the appropriate boundary conditions for $R(r), \Theta(\theta)$ and $\Phi(\varphi)$. The eigenvalues $\eta, \lambda,$ and $E$ can assume only certain values, compatible with the boundary conditions\(^1\):

$$\eta = \eta m_l = m_l^2,$$ \hspace{1cm} (2.8)

$$\lambda = \lambda l = l(l + 1), \quad l = |m_l|, |m_l| + 1, |m_l| + 2, \ldots$$  \hspace{1cm} (2.9)

\(^1\) The “quantization” of the angular motion originates from the boundary conditions $\Phi(\varphi + 2\pi) = \Phi(\varphi)$, and finite $\Theta(0)$ and $\Theta(\pi)$ for the solutions of Eqs. (2.5) and (2.6): these conditions are granted only for integer values of the quantum numbers $m_l$ and $l \geq |m_l|$ [16]. Likewise, the discrete energies originate from the requirement of a regular behavior of $R(0)$ and $R(\infty)$ solving Eq. (2.7).
\[ E = \varepsilon_n = -\frac{\mu Z^2 e^4}{2 \hbar^2 n^2} = -\frac{\mu}{m_e} \frac{E_{\text{Ha}} Z^2}{n^2}, \quad n = l + 1, l + 2, l + 3, \ldots \quad (2.10) \]

The integer numbers \( m_l \) (magnetic quantum number), \( l \) (azimuthal q.n.), and \( n \) (principal q.n.) parameterize the eigenvalues and the corresponding eigenfunctions:

\[ \Phi_{m_l}(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im_l \varphi} \quad (2.11) \]

\[ \Theta_{lm_l}(\theta) = (-1)^{m_l/2} \sqrt{\frac{2l + 1}{2(l + |m_l|)!} P_{l}^{m_l}(\cos \theta)} \quad (2.12) \]

\[ R_{nl}(r) = \frac{k^{3/2}}{2\sqrt{n(n + l)!}} (kr)^l L_{n+l}^{2l+1}(kr) e^{-kr/2} \quad (2.13) \]

where \( k \) is a shorthand for \( 2Z/(an) \), \( a \) is a mass-corrected Bohr atomic length unit \( a = a_0 m_e/\mu = \hbar^2/(\mu e^2) \). For nonnegative integers \( l \) and \( m \), the associated Legendre functions \( P_{l}^{m}(x) \) are defined by

\[ P_{l}^{m}(x) = (1 - x^2)^{m/2} \frac{d^m}{dx^m} P_l(x), \quad P_l(x) = \frac{1}{2l!} \frac{d^l}{dx^l} (x^2 - 1)^l. \quad (2.14) \]

The associated Laguerre polynomials \( L_{p}^{q}(\rho) \) are polynomials of degree \( p - q \), defined by

\[ L_{p}^{q}(\rho) = \frac{d^q}{d\rho^q} L_{p}(\rho), \quad L_{p}(\rho) = e^\rho \frac{d^p}{d\rho^p} (\rho^p e^{-\rho}). \quad (2.15) \]

Since each individual wavefunction of Eqs. (2.11)–(2.13) is properly normalized by its own square-root factor, so is the total atomic wavefunction

\[ \psi_{nlm_l}(r, \theta, \varphi) = R_{nl}(r) \Theta_{lm_l}(\theta) \Phi_{m_l}(\varphi) \quad (2.16) \]

representing the atomic state \(|n, l, m_l\rangle\). Explicitly, the orthogonality relation reads:

\[ \langle n, l, m_l | n', l', m'_l \rangle = \int r^2 dr \sin \theta d\theta d\varphi \psi_{nlm_l}^*(r, \theta, \varphi) \psi_{n'l'm'_l}^*(r, \theta, \varphi) = \delta_{nn'} \delta_{ll'} \delta_{m_lm'_l}. \quad (2.17) \]

In addition to all these bound states, a continuum of unbound states of arbitrary positive energy represents the ionic states, where the electron moves far away from the nucleus.
2.1.1 The Energy Spectrum

The energy eigenvalues (2.10) of the nonrelativistic one-electron atom depend on the principal quantum number \( n \) only, and exhibit the characteristic structure sketched in Fig. 2.1. In particular, the lowest-energy state is \(|n, l, m_l\rangle = |1, 0, 0\rangle\). For hydrogen \((Z = 1)\), its energy \( \varepsilon_1 = -0.5 \EHa \mu/m_e = -13.5983 \text{ eV} \). Due to the reduced-mass correction \( \mu/m_e = 0.999456 \), this energy is slightly less negative than \(-0.5 \EHa = -13.6057 \text{ eV} \).

Above this ground state we find a sequence of energy levels. The lowest excited \((n = 2)\) level is 4-fold degenerate: it consists of \(|2, 0, 0\rangle, |2, 1, -1\rangle, |2, 1, 0\rangle, \) and \(|2, 1, 1\rangle\). Its energy is \( \varepsilon_2 = -\frac{1}{2}(Z/2)^2 \EHa \frac{\mu}{m_e} = -\frac{1}{8} Z^2 \EHa \frac{\mu}{m_e} \). In hydrogen this level is \( \varepsilon_2 - \varepsilon_1 = \frac{3}{8} Z \EHa \frac{\mu}{m_e} = 10.1987 \text{ eV} \) above the ground state. Successive \( \varepsilon_3, \varepsilon_4 \ldots \) levels exhibit an increasing degeneracy, because of the multiple values \( l = 0, \ldots, n - 1 \) compatible with larger \( n \), and the values \( m_l = 0, \pm 1, \ldots, \pm l \) compatible with larger \( l \). The \( m_l \)-degeneracy \((2l + 1 \text{ states})\) is a general feature of central potentials, representing the possibility for the orbital angular momentum to point in any direction in 3D space without affecting the energy of the atom. In contrast, the extra \( l \)-degeneracy \((n \text{ values of } l, \text{ for a total of } n^2 \text{ states})\) is peculiar of the Coulombic potential energy \( U(r) \propto -r^{-1} \); none of this “accidental” degeneracy occurs for a different radial dependence of \( U(r) \), e.g. as encountered below in Sect. 2.2.4 for many-electron atoms, and in Sect. 3.3.1 for diatomic molecules.

Transitions between any two energy levels are observed, Fig. 2.2. Historically, the close agreement of the H-atom Schrödinger spectrum of Eq. (2.10) with accurate spectroscopic observations marked an early triumph of QM. The transitions group naturally in series of transitions \( n_i \to n_f \), characterized by the same lower-energy level (usually the final level \( n_f \) in emission experiments, see Fig. 2.2). Each series of transitions of hydrogen is observed in a characteristic spectral region and is named after the scientist who carried out its earliest investigations: the transitions...

![Fig. 2.1](image_url)
The observed emission line spectrum of atomic hydrogen, with a a broad full IR-UV range spectrum, b a closeup of the Balmer plus the overlapping infrared series, and c a further closeup of the Balmer series, with its 4 visible lines, plus a few low-energy UV lines.

whose lower level is \( n = 1 \) form the Lyman series (10.2–13.6 eV, UV); those whose lower level is \( n = 2 \) constitute the Balmer series (1.89–3.40 eV, visible-UV); those whose lower level is \( n = 3 \) form the Paschen series (0.66–1.51 eV, IR); those whose lower level is \( n = 4 \) form the Brackett series (0.31–0.85 eV, IR). Note in particular, that the Lyman and Balmer series do not overlap with any other series, since the energy distance between their lower level (\( n = 1 \) or 2) and the next one (\( n + 1 \)) exceeds the whole range of bound-state energies from level \( n + 1 \) to the ionization threshold.

The weak dependence of the spectrum on the nuclear mass \( M \) [through the ratio \( \mu/m_e = (1 + m_e/M)^{-1} \)] produces a duplication (relative energy separation \( \approx 0.03 \% \) —see Fig. 2.3) of the spectral lines of a mixture of different isotopes such as regular hydrogen \(^1\text{H}\) and twice as heavy deuterium \(^2\text{H}\) (or D). Finally, note that the \( Z^2 \) dependence of the eigenvalues Eq. (2.10) makes one half of the lines of one half of the series of the \( \text{He}^+ \) ion (one third of those of \( \text{Li}^{2+}, \ldots \)) almost coincident (except for the reduced-mass correction, and relativistic effects) with the lines of hydrogen, as illustrated in Fig. 2.4.
Fig. 2.3 A high-resolution line spectrum of the Balmer H$_\alpha$ emission of an isotope mixture. $^1$H emits the longer-wavelength structure near 1.8887 eV; deuterium $^2$H emits the shorter-wavelength lines near 1.8892 eV. The finer doublet structure is due to relativistic effects analyzed in Sect. 2.1.7

2.1.2 The Angular Wavefunction

The angular solutions (2.11) and (2.12) combine to form the spherical harmonics $Y_{lm_l}(\theta, \varphi) = \Theta_{lm_l}(\theta) \Phi_{ml}(\varphi)$, which are the normalized eigenfunctions$^2$ of the angular motion of a freely rotating quantum-mechanical particle. $Y_{lm_l}$ contains complete information about an important observable: the orbital angular momentum. In detail, $\hbar^2 \times \{\text{the angular part of } -\nabla^2 \text{ occurring at the left side of Eq. (2.6)}\}$ represents the squared orbital angular momentum $|\mathbf{L}|^2$ of the rotating two-body system. $\hbar^2 \lambda = \hbar^2 l(l+1)$ are the eigenvalues of $|\mathbf{L}|^2$. Likewise, $\hbar m_l$ are the eigenvalues of the angular-momentum component $L_z$ represented by $-i \hbar \frac{\partial}{\partial \varphi}$, thus clarifying the physical meaning of Eq. (2.5). Only statistical information about the $L_x$ and $L_y$ components is available, since these other components do not commute with $L_z$.

Note however that the choice of the $\hat{z}$ direction in 3D space (related to the choice of the polar coordinate system) is arbitrary: due to spherical symmetry, any alternative choice would lead to the same observable results.

The spherical harmonics carry complete information about the angular distribution of $\mathbf{r}$. In a state $|l, m_l\rangle$ with squared angular momentum fixed by $l$ and $z$-projection by $m_l$, the probability that the vector $\mathbf{r}$ joining the nucleus to the electron is directed as $(\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$ equals $|\langle \theta, \varphi | l, m_l \rangle|^2 \sin \theta \, d\theta \, d\varphi \equiv |Y_{lm_l}(\theta, \varphi)|^2 \sin \theta \, d\theta \, d\varphi$. Equation (2.11) indicates that the $\varphi$ dependence of $|Y_{lm_l}|^2$ is always trivial: $|Y_{lm_l}|^2$ are constant functions on all circles at fixed $\theta$. Figure 2.5 illustrates the $\theta$ dependence as polar plots of $|Y_{lm_l}|^2$ for several values of $l$ and $m_l$.

Several textbooks and web sites report alternative visualizations of the $Y_{lm_l}$ functions. It is apparent that $l - |m_l|$ counts the number of zeros (nodes) of $|Y_{lm_l}|^2$ as the polar angle $\theta$ spans the 0 to $\pi$ range. A large number of nodes indicates a large angular-momentum component perpendicular to $\hat{z}$.

Observations: (i) The visible (Fig. 2.5) increase of $|Y_{l0}(0, \varphi)|^2$ with $l$ does not contradict normalization (2.17), because of the $\sin \theta$ integration factor. (ii) If the $r^l$ factor taken from the radial wavefunction (2.13) is grouped together with $Y_{lm_l}(\theta, \varphi)$,

$^2$ We stick to the standard convention for the phases of $Y_{lm_l}(\theta, \varphi)$. 

one can express $r^l Y_{lm}(\theta, \varphi)$ in Cartesian components $(r_x, r_y, r_z)$, obtaining a homogeneous polynomial of degree $l$. For example,

$$r Y_{10}(\theta, \varphi) = \sqrt{\frac{3}{4\pi}} r_z, \quad r Y_{1 \pm 1}(\theta, \varphi) = \sqrt{\frac{3}{8\pi}} (\mp r_x - i r_y).$$

(iii) Observation (ii) implies that the parity of $Y_{lm}(\theta, \varphi)$ (i.e. its character for $r \rightarrow -r$) is the same as that of $l$, i.e. $(-1)^l$. (iv) $m_l = 0$ spherical harmonics are real
functions. (v) Occasionally $m_l \neq 0$ spherical harmonics are combined to construct real wavefunctions, e.g.

$$\psi_{px} = \frac{Y_{1-1} - Y_{11}}{\sqrt{2}}, \quad \psi_{py} = i \frac{Y_{11} + Y_{1-1}}{\sqrt{2}}.$$ (2.19)

(vi) It is easy and useful to retain the expression for the simplest spherical harmonic function (a polynomial of degree 0, i.e. a constant): $Y_{00}(\theta, \varphi) = (4\pi)^{-1/2}$.

**Important notation**: Spectroscopists have adopted a letter code for the value of the orbital angular momentum. This standard notation is: s, p, d, f, g, h…, for $l = 0, 1, 2, 3, 4, 5…$ respectively.

### 2.1.3 The Radial Wavefunction

The radial wavefunction $R_{nl}(r)$, Eq. (2.13), is structured as the product of (i) a normalization factor, (ii) a power $r^l$ (mentioned above in relation to $Y_{lm_l}$), (iii) a polynomial of degree $n - l - 1$ in $r$ (with a nonzero $r^0$ term), and (iv) the exponential of $-Zr/(2an)$. The power term is responsible for the $R_{nl}(r) \propto r^l$ behavior at small $r$. The Laguerre polynomial $L_{n+l}^{2l+1}(\rho)$ vanishes at as many different $\rho > 0$ points as its degree $(n - l - 1)$: each of these zeroes produces a radial node, i.e. a spherical shell of radius $r$ where $R_{nl}(r)$, and thus the overall wavefunction, vanishes and changes sign. The exponential decay dominates at large $r$, where $R_{nl}(r) \sim r^{n-1} \exp(-Zr/na)$. Figure 2.6 illustrates these features for the square moduli of the lowest-$n$ radial eigenfunctions.

The radial probability distribution $P(r) = r^2 |R(r)|^2$ drawn in Fig. 2.7 and the $|R(r)|^2$ of Fig. 2.6 contain different information about the electron state. $P(r) \, dr$ yields the probability that the nucleus-electron distance is within $dr$ of $r$, regardless
Fig. 2.6 \( Z = 1 \) hydrogenic s p and d squared radial eigenfunctions \( |R_{nl}(r)|^2 \). \textit{Solid}, \( n = 1 \); \textit{dashed}, \( n = 2 \); \cdots, \( n = 3 \); \cdots, \( n = 4 \); \cdots, \( n = 5 \). Due to squaring, the \((n - l - 1)\) radial nodes, where \( R_{nl}(r) \) vanishes and changes sign, appear as tangencies to the horizontal axis of the linear plots (left), and as downward kinks in the plots in log_{10} scale (right).
of the direction where \( \mathbf{r} \) points. The \( r^2 \) weighting factor is precisely the spherical-coordinates Jacobian, proportional to the surface of the sphere of radius \( r \), or rather the volume of the spherical shell “between \( r \) and \( r + dr \)”. In Fig. 2.7, note that for increasing \( n \), \( P(r) \) peaks at larger and larger distance from the origin.

The probability that the electron is found at a specific position \( \mathbf{r} \) relative to the nucleus is not \( P(r) \), but is given by

\[
P_{3D}(\mathbf{r}) d^3\mathbf{r} = |\psi(\mathbf{r})|^2 d^3\mathbf{r} = |\psi_{nlm}(r, \theta, \phi)|^2 d^3\mathbf{r} = |R_{nl}(r)|^2 |Y_{lm}(\theta, \phi)|^2 d^3\mathbf{r}, \tag{2.20}
\]

where the polar coordinates are those representing that point \( \mathbf{r} \). Equation (2.20) indicates that \( |\psi(r, \theta, \phi)|^2 \) gives the actual 3D probability distribution in space. This means, e.g., that the probability density profile along a line through the nucleus (specified by fixing \( \theta \) and \( \phi \)) is simply \( |R(r)|^2 \), multiplied by the constant \( |Y_{lm}(\theta, \phi)|^2 \). Note that all \( s \) eigenfunctions have nonzero \( R_{n0}(0) = 2[Z/(an)]^{3/2} \). Moreover, \( r = 0 \) is a cusp-type absolute maximum of \( |R_{n0}(r)|^2 \), see Fig. 2.6. It is no surprise that the most likely point in space for \( s \) electrons coincides with the nucleus, \( \mathbf{r} = 0 \), the spot with the most attractive potential energy \( U(\mathbf{r}) \). This fact is hidden by the vanishing of \( P(r \to 0) \) which is entirely due to the \( r^2 \) weight in \( P(r) \). For \( l > 0 \), even the probability density \( |R_{nl}(r)|^2 \) vanishes at the origin, where the centrifugal repulsion \( \propto \lambda/r^2 = l(l+1)/r^2 \) “effective potential” term in Eq. (2.7) diverges. The vanishing of \( |R_{nl}(r)|^2 \) reflects the impossibility of a point particle carrying nonzero angular momentum to reach the origin of a central potential. The wave-mechanical reason is the following: for \( l > 0 \), \( \mathbf{r} = 0 \) is a common point of one or several nodes of the angular wavefunction, therefore if \( \psi \) did not vanish there, it would be multiple-valued.

For increasing nuclear charge \( Z \), \( |R_{nl}(r)|^2 \) and thus \( P(r) \) move in closer and closer to the origin: the mean electron–nucleus separation decreases as \( \propto Z^{-1} \), and this fact combined with \( V_{ne} \propto Z/r \) explains the \( \propto Z^2 \) dependence of the eigenenergies (2.10). The simplest radial wavefunction, that of the ground state, exemplifies well this \( Z \) dependence:

\[3\] The scaling laws are \( R_{nZ}(r) = Z^{3/2} R_{n1}(rZ) \) and \( P_{Z}(r) = Z P_1(rZ) \).
\[ R_{10}(r) = \sqrt{\frac{k^3}{2}} e^{-kr/2} = 2 \left( \frac{Z}{a} \right)^{3/2} \exp\left(-\frac{Zr}{a}\right). \] (2.21)

Accordingly, the ground state of He\(^+\) has the same overall shape but half the size of that of H.

**Notation**: the hydrogenic kets/eigenfunctions \(|n, l, m_l\rangle\) of Eq. (2.16) are often shorthanded as \(n[l]\), where \(n\) is the principal quantum number and \([l]\) is the relevant letter s, p, d, \ldots for that value of \(l\). For example, 4p refers to any of \(\psi_{41 -1}, \psi_{41 0}, \psi_{41 1}\). This notation is incomplete and ambiguous: (i) information about \(m_l\) is lacking, and (ii) the same 4p symbol implies different radial dependence \(R_{41}(r)\) for a nucleus of different charge and mass.

### 2.1.4 Orbital Angular Momentum and Magnetic Dipole Moment

The angular momentum of an orbiting charged particle such as an electron is associated to a magnetic dipole moment. This is illustrated (Fig. 2.8) for a classical point particle of mass \(m\) and charge \(q\) rotating along a circular orbit of radius \(r\) at speed \(v\). Its angular momentum \(L = r \times p = mrv\hat{n}\), where \(\hat{n}\) is the unit vector perpendicular to its trajectory. As the rotation period is \(\tau = 2\pi r/v\), the current along the loop \(I = q/\tau = qv/(2\pi r)\). The magnetic moment of a ring current equals the product of the current times the loop area:

\[ \mu = I \pi r^2 \hat{n} = \frac{qv}{2\pi r} \pi r^2 \hat{n} = \frac{q}{2} v r \hat{n} = \frac{q}{2m} L. \] (2.22)

One can show that this equality holds for arbitrary shape of the periodic orbit.

---

**Fig. 2.8** The relation between the mechanical angular momentum \(L\) and the magnetic moment \(\mu\) generated by an electron of charge \(-q_e\) orbiting circularly. The curved lines represent the magnetic induction field \(B\) produced by the circulating current.
Relation (2.22) holds also in QM, as an operatorial relation. For an electron of charge \( q = -q_e \), where the angular momentum is quantized in units of \( \hbar \), it is convenient to write Eq. (2.22) as

\[
\mu = -\frac{q_e}{2m_e} L = -\frac{\hbar q_e}{2m_e} \frac{L}{\hbar} = -g_l \mu_B \frac{L}{\hbar},
\]  

(2.23)

where the Bohr magneton \( \mu_B = \hbar q_e / (2m_e) = 9.27401 \times 10^{-24} \text{ JT}^{-1} \) (alias A m\(^2\)) is the natural scale of atomic magnetic moments. \( g_l = 1 \) is the orbital g-factor, introduced for uniformity of notation with those situations, discussed below, with nontrivial proportionality factors \( g \neq 1 \) between \( \mu_B L / \hbar \) and \( \mu \). g-factors arise because, while angular momenta are universal (i.e. simple multiples of \( \hbar \)), magnetic moments are usually non-universal multiples of \( \mu_B \).

The atomic angular momenta can be detected by letting the associated magnetic moments interact with a magnetic field. If the field \( B \) is uniform, it induces a precession of \( \mu \) around the direction of \( B \) with a frequency (the Larmor frequency) \( \omega = q_e B / (2m_e) \), routinely detected in microwave resonance experiments. If the field is nonuniform instead, a net force acts on the atom, as we discuss in the next section.

### 2.1.5 The Stern-Gerlach Experiment

The interaction energy of a magnetic moment with a magnetic field is

\[
H_{\text{magn}} = -\mu \cdot B.
\]  

(2.24)

Unless some external mechanism alters the angle between \( \mu \) and \( B \), this energy is conserved in time. A force arises on the magnetic dipole when the field \( B \) is nonconstant in space:

\[
F = -\nabla (-\mu \cdot B) = \nabla (\mu \cdot B).
\]  

(2.25)

In particular, in a magnetic field with a dominant \( B_z \) component, the \( z \) force component \( F_z \) is proportional to the derivative of \( B_z \) along the same direction:

\[
F_z \simeq \mu_z \nabla_z B_z = \mu_z \frac{\partial B_z}{\partial z}.
\]  

(2.26)

The “microscopical” origin of this force is pictured in Fig. 2.9. The observation that a nonuniform magnetic field produces a force proportional to a magnetic-moment component is at the basis of the Stern-Gerlach experiment.

As illustrated in Fig. 2.10, a collimated beam of neutral atoms at thermal speeds is emitted from an oven into a vacuum chamber where it traverses a region of
2.1 One-Electron Atom/Ions

Fig. 2.9 The origin of the force that a nonuniform magnetic field produces on a magnetic moment. 

(a) If the magnetic dipole is seen as a circulating current, the net force originates from a force component consistently pointing in the direction of increasing $B$. 

(b) If the dipole is viewed as a pair of magnetic monopoles, a net force arises from the unbalance between the forces on the individual monopoles.

inhomogeneous magnetic field, where $F_z$ deflects individual atoms proportionally to their magnetic moment $z$ component, and is finally collected by a suitable detector. Basically, the Stern-Gerlach apparatus is an instrument for measuring the component of atomic magnetic moments in the field-gradient direction. This makes it one of the key tools in QM, as detailed in the initial sections of Ref. [17]. The original (1922) experiment was carried out using Ag atoms, but a similar pattern of deflections is observed using atomic H.

The main outcome of the Stern-Gerlach experiment is that the $z$ component of $\mu$ is not distributed continuously as one would expect for a classical vector pointing randomly in space, but rather peaked at discrete values. Figure 2.10c shows the clustering of the deflected atoms in two lumps.

According to QM, the $\hat{z}$-component $L_z$ of angular momentum (and thus $\mu_z$ of magnetic moment) should indeed exhibit discrete eigenvalues. However, (i) the number of eigenvalues of $L_z$ should be odd [$2l + 1$, with integer $l$—see Eq. (2.9)] and (ii) the ground state of hydrogen has $l = 0$, thus H should show no magnetic moment at all, and one undeflected lump should be observed, rather than splitting into two. This is a first hint that some extra degree of freedom must play a role in the one-electron atom.

2.1.6 Electron Spin

The outcome of the Stern-Gerlach experiment, the multiplet fine structure of the spectral lines (the fine doublets of Fig. 2.3), and the Zeeman splitting of the spectral lines (see Sect. 2.1.10) are three pieces of evidence pointing at the existence of an extra degree of freedom of the electron, beside its position in space. W. Pauli introduced
In the Stern-Gerlach experiment, a collimated beam of atoms emitted from an oven transverses a region of inhomogeneous magnetic field created by a magnet with asymmetric core expansions: the atoms are finally detected at a collector plate. In an inhomogeneous magnetic field, a magnet experiences a net force which depends on its orientation. The deflection pattern recorded on the detecting plate in a Stern-Gerlach measurement of the $z$ component of the magnetic dipole moment of Ag atoms (the outcome would be the same for H atoms). Contrary to the classical prediction of an even distribution of randomly oriented magnetic moments, two discrete components are observed, due to the quantization of an angular-momentum component.

A nonclassical internal degree of freedom, later named spin, with properties similar to orbital angular momentum. Even though this picture is imprecise, the electron spin may be viewed as the intrinsic angular momentum of the rotation of the electron around itself. When spin is measured along a given direction, say $\hat{z}$, one detects eigenvalues of $S_z$, $\hbar m_s$, where the quantum number $m_s$ takes $(2s + 1)$ values $m_s = -s, \ldots, s$, like the orbital $L_z$ takes values $m_l = -l, \ldots, l$. Since a Stern-Gerlach deflector splits an H beam into two lumps, $2 = 2s + 1$ components are postulated, requiring that the intrinsic angular momentum of the electron must be $s = 1/2$. This in turn is associated to a squared spin angular-momentum operator $|S|^2$ whose eigenvalue is $1/2(1/2 + 1)\hbar^2 = 3/4\hbar^2$.

A complete wavefunction, necessary to specify all degrees of freedom of the electron, is slightly more complicated than $R(r) Y_l m_l(\theta, \phi)$: an extra spin dependence
must be inserted. Assuming, as apparent from the nonrelativistic Hamiltonian (1.1), that spin and orbital motions do not interact, the full eigenfunction of a one-electron atom with spin pointing up (↑, i.e. \( m_s = \frac{1}{2} \)) or down (↓, i.e. \( m_s = -\frac{1}{2} \)) along a fixed orientation is written

\[
\psi_{n l m_l m_s}(r, \theta, \varphi, \sigma) = R_{nl}(r) Y_{lm_l}(\theta, \varphi) \chi_{m_s}(\sigma).
\]  

(2.27)

Here \( \sigma \) is the variable for the spin degree of freedom, which spans values \( \pm \frac{1}{2} \), i.e. checking if the electron spin points up or down in the \( \hat{z} \) direction. The quantum number \( m_s = \pm \frac{1}{2} \) indicates which way the spin of this specific state is actually pointing relative to the reference direction. These basis spin functions are therefore simply \( \chi_{m_s}(\sigma) = \langle \sigma | m_s \rangle = \delta_{m_s \sigma} \).

Less trivial spin wavefunctions arise when the spin points in some direction other than \( \hat{z} \) (non-\( S_z \) eigenstates). A Stern-Gerlach apparatus can be employed to purify a spin polarized beam of atoms with spins pointing in some oblique direction. This beam can then be analyzed by a second apparatus to measure the spin component \( \sigma \) along the reference \( \hat{z} \) direction. For the oblique-spin state, the (now nontrivial) spin wavefunction \( \chi(\sigma) \) bears the standard significance of a wavefunction in QM: \( |\chi(\uparrow)|^2 \) is the probability that, when \( S_z \) is measured, \( +1/2 \hbar \) is found, while \( |\chi(\downarrow)|^2 \) is the probability to obtain \(-1/2 \hbar \). When a \( \hat{z} \)-Stern-Gerlach measurement is carried out, the spin \( z \) component is found pointing either up or down, therefore the total probability \( \sum_\sigma |\chi(\sigma)|^2 = |\chi(\uparrow)|^2 + |\chi(\downarrow)|^2 = 1 \).

A remarkable novelty regarding spin is that the separation of the \( \uparrow \) and \( \downarrow \) sub-beams in a Stern-Gerlach apparatus is compatible with a g-factor for spin \( g_s \approx 2 \), quite distinct from the orbital \( g_l = 1 \). The precise value \( g_s = 2.00232 \) generating the electron intrinsic magnetic moment \( g_s \mu_B \) is measured extremely accurately by electron spin resonance (ESR) experiments, where the electron spin interacts with a uniform magnetic field which splits the \( \uparrow \) and \( \downarrow \) states.

At the present basic level of understanding, electron spin is just an extra quantum number which, in the absence of magnetic fields only provides an extra degeneracy to all states of the one-electron atom: the total degeneracy of the \( n \)th level is \( 2n^2 \), rather than \( n^2 \). Spin will however affect the atomic energy levels when the magnetic effects of relativistic origin are considered, in Sect. 2.1.7.

### 2.1.7 Fine Structure

The smallness of the observed fine splittings (a fraction of meV, see Fig. 2.3) in the spectrum of H hints at some small correction, such as due to relativistic effects, neglected in the original Hamiltonian (1.1). We come to investigate these corrections in detail.
2.1.7.1 Spin-Orbit Coupling

Consider first the action of the magnetic field experienced by the electron spin due to its own orbital motion. This is a subtle relativistic effect, due to the Lorentz transformation of the nuclear electric field into the frame of reference of the electron. Call $v$ the electron velocity in the nuclear rest frame. In the electron frame of reference, the nucleus is seen to move with velocity $-v$, and thus carries a “current element” $-Zq_e v$. According to the Biot-Savart law of electromagnetism, at the point where the electron sits (reached from the nucleus by vector $r$), this moving charge generates a magnetic field

$$ B(r) = -\frac{1}{4\pi\varepsilon_0 c^2} \frac{r \times (-Zq_e v)}{|r|^3} = \frac{E(r) \times v}{c^2}. \quad (2.28) $$

Equation (2.28) identifies this magnetic field as a relativistic effect \(\text{of order } (v/c)^2\), and expresses it in terms of the electric field generated by the nucleus at the electron location

$$ E(r) = \frac{Zq_e}{4\pi\varepsilon_0} \frac{r}{|r|^3}. \quad (2.29) $$

In Eq. (2.28) we recognize the orbital angular-momentum operator:

$$ B(r) = \frac{Zq_e}{4\pi\varepsilon_0 c^2} \frac{r \times v}{|r|^3} = \frac{Zq_e}{4\pi\varepsilon_0 c^2 m_e} \frac{L}{|r|^3}. \quad (2.30) $$

This magnetic field $B(r)$ acts on the electron at each point in space. By analogy with Eq. (2.24), the interaction energy of the electron-spin magnetic moment $\mu_s$ with $B$ should equal $-\mu_s \cdot B(r)$. However, this energy must actually be reduced by a factor $1/2$ (first recognized by L.H. Thomas) due to the electron frame of reference being accelerated [1]. The correct magnetic interaction energy operator is therefore:

$$ H_{s-o} = -\frac{1}{2} \mu_s \cdot B(r) = \frac{1}{2} \frac{g_s \mu_B}{\hbar} S \cdot \left( \frac{Zq_e}{4\pi\varepsilon_0 c^2 m_e} \frac{L}{|r|^3} \right) = \frac{Ze^2}{2 m_e^2 c^2} \frac{1}{r^3} S \cdot L. \quad (2.31) $$

This operator, named spin-orbit interaction, exhibits nonzero diagonal and off-diagonal elements $\langle n, l, m_l, m_s | H_{s-o} | n', l, m'_l, m'_s \rangle$ connecting states with equal or different $n, m_l, m_s$. States with $n \neq n'$ have vastly different nonrelativistic energies (2.10): the tiny $n$-off-diagonal spin-orbit couplings perturb these energies negligibly, and can practically be neglected, see Appendix B.5.2 and B.9. For given $l$ and considering only the $n$-diagonal matrix elements of $H_{s-o}$, we rewrite Eq. (2.31) as

$$ H_{s-o} \simeq \frac{Ze^2}{2 m_e^2 c^2} \sum_{n,l} |n, l\rangle \langle n, l| r^{-3} |n, l\rangle \langle n, l| S \cdot L. \quad (2.32) $$
The radial integral can be evaluated for \( l \geq 0 \) hydrogenic wavefunctions \( R_{nl} \), obtaining

\[
\langle n, l | r^{-3} | n, l \rangle = \int_0^\infty r^{-3} [R_{nl}(r)]^2 r^2 dr = \left( \frac{Z}{a} \right)^3 \frac{2}{n^3 l(l+1)(2l+1)}. \tag{2.33}
\]

The spin-orbit Hamiltonian is thus conveniently rewritten as

\[
H_{s-o} = \sum_{n,l} \xi_{nl} |n, l\rangle \langle n, l| \frac{S \cdot L}{\hbar^2}, \tag{2.34}
\]

where the projectors \( |n, l\rangle \langle n, l| \) select a radial wavefunction, and the spin-orbit energy is

\[
\xi_{nl} = \frac{Ze^2 \hbar^2}{2 m_e^2 c^2} \left( \frac{Z}{a} \right)^3 \frac{2}{n^3 l(l+1)(2l+1)} = Z^4 \alpha^2 E_{\text{Ha}} \left( \frac{\mu}{m_e} \right)^3 \frac{1}{n^3 l(l+1)(2l+1)}. \tag{2.35}
\]

The last equality uses the expression for the mass-rescaled atomic length scale \( a = a_0 m_e/\mu \), the definition (1.9) of the Hartree energy, and the expression \( \alpha^2 = E_{\text{Ha}}/(m_e c^2) \) for the fine-structure constant. In this form, it is apparent that the typical spin-orbit energy scale \( \xi_{nl} \)

- is positive, and therefore \( H_{s-o} \) favors antiparallel alignment of \( L \) and \( S \);
- is a leading \( \alpha^2 \sim (v/c)^2 \) relativistic correction;
- is \( \alpha^2 \approx 5.3 \times 10^{-5} \) times smaller than the typical orbital energies;
- grows as \( Z^4 \), reflecting the increase in nuclear field intensity \( \propto Z \) and the reduction \( \propto Z^{-1} \) of the average electron–nucleus distance so that \( \langle n, l | r^{-3} | n, l \rangle \propto Z^3 \);
- decreases as \( n^{-3} \), reflecting the increase \( \propto n \) of the average electron–nucleus distance, and the \( r^{-3} \) dependence of the interaction energy (2.31);
- decreases roughly as \( l^{-3} \) (but \( S \cdot L \propto l \)), due to the \( r^l \) suppression of the radial wavefunction close to the origin, the region where spin-orbit interaction (2.31) dominates.

The energy scale of \( \xi_{nl} \) amounts to \( \alpha^2 E_{\text{Ha}} (\mu/m_e)^3 = 2.318 \times 10^{-22} \text{ J} = 1.447 \text{ meV} \) for hydrogen. Note however that the lowest-energy state for which spin-orbit applies, \( 2p \), has \( n^3 l(l+1)(2l+1) = 48 \), thus \( \xi_{2p} = 0.0301 \text{ meV} \) only. For all higher levels \( \xi_{nl} \) is even smaller.

Consider now the remaining operatorial part in Eq. (2.34): \( S \cdot L \). In the basis \( |l, s, m_l, m_s\rangle \) where spin and orbital motion are uncoupled, the operator \( S \cdot L \) has plenty of nonzero off-diagonal matrix elements. In computing the relativistic corrected eigenvalues and eigenstates with the methods of Appendix B.5, one needs to diagonalize \( S \cdot L \), within each (initially degenerate) space at fixed \( l \) and \( s \). Introducing the coupling of spin and orbital angular momenta with the methods of
Appendix B.8.1, the \(|l, s, j, m_j\rangle\) coupled basis introduced in Eq. (B.73) shows its advantage: \(S \cdot L\) is diagonal in this coupled basis. To prove this result, take the square of \((L + S) = J\) and invert it as follows:

\[
S \cdot L = \frac{|J|^2 - |S|^2 - |L|^2}{2}.
\]

(2.36)

All operators at the right hand side are of course diagonal in the \(|l, s, j, m_j\rangle\) basis: the expression for the general matrix element is therefore

\[
\langle l, s, j, m_j | S \cdot L \frac{\hbar^2}{2} | l, s, j', m_j' \rangle = \frac{j(j + 1) - s(s + 1) - l(l + 1)}{2} \delta_{jj'} \delta_{m_j m_j'}.
\]

(2.37)

In summary: in the coupled basis \(|l, s, j, m_j\rangle\), the spin-orbit interaction is diagonal and its eigenvalues are given by Eq. (2.37), multiplied by the energy \(\xi_{nl}\).

**Notation:** states of the coupled basis are commonly indicated as \(2s + \frac{1}{2} [l] j\), where \([l]\) is the relevant capital letter S, P, D,... for that value of \(l = 0, 1, 2, \ldots\) Information about \(n\) is encoded elsewhere, e.g. in the \(n[l]\) notation, and information about \(m_j\) is usually omitted. For example, \(3d \ 2D_{3/2}\) stands for any of the four \(|n = 3, l = 2, j = \frac{3}{2}, m_j\rangle\) kets.

As an example of spin-orbit split states, for one p level of a one-electron atom, the two different eigenvalues of the \(S \cdot L / \hbar^2\) operator

\[
\langle 1, \frac{1}{2}, j, m_j | S \cdot L \frac{\hbar^2}{2} | 1, \frac{1}{2}, j, m_j \rangle = \begin{cases} -1 & \text{for } j = \frac{1}{2} \\ +1 & \text{for } j = \frac{3}{2} \end{cases}
\]

Accordingly, spin-orbit splits any p level (\(3 \times 2 = 6\) orbital \times spin states) of 1-electron atoms into a doublet \(2P_{1/2}\) plus a quartet \(2P_{3/2}\), separated by an energy \(3/2 \xi_{n1}\). For the 2p level of hydrogen this splitting amounts to 45.2 \(\mu\text{eV}\).

2.1.7.2 The Relativistic Kinetic Correction

A second relativistic correction of the same order \((v/c)^2\) as spin-orbit must be included. This energy contribution accounts for the leading correction to the kinetic energy expression \(p^2/(2\mu)\):

\[
T_r = \sqrt{\mu^2 c^4 + p^2 c^2} - \mu c^2 = \mu c^2 \left( 1 + \frac{1}{2} \frac{p^2}{\mu^2 c^2} - \frac{1}{8} \frac{p^4}{\mu^4 c^4} + \cdots - 1 \right)
\]

\[
= \frac{p^2}{2\mu} - \frac{p^4}{8\mu^3 c^2} + \cdots
\]

(2.38)

Like for \(H_{s-o}\), to treat the weak perturbation \(- p^4/(8\mu^3 c^2)\) at first order, we just need the \(n\)-diagonal matrix elements of this operator. Although \(p^4\) looks like a formidable differential operator, the trick \(p^4 = (p^2)^2 = [2\mu (H_{\text{Coul}} - V_{\text{ne}})]^2\) allows us to rewrite
the diagonal matrix elements of $p^4$ in terms of simple radial integrals of $r^{-1}$ and $r^{-2}$. The final result is

$$\langle n, l | -\frac{p^4}{8\mu^3 c^2} | n, l \rangle = -\frac{Z^4 \alpha^2}{n^3} E_{Ha} \left( \frac{\mu}{m_e} \right)^3 \left( \frac{1}{2l + 1} - \frac{3}{8n} \right),$$

(2.39)

where we omit either $m_l$, $m_s$ or $j$, $m_j$, which are irrelevant for such radial integrals.

By combining the spin-orbit and kinetic correction

$$H_{rel} = H_{s-o} - \frac{p^4}{8\mu^3 c^2},$$

(2.40)

we obtain the diagonal matrix elements of the total relativistic correction to order $\alpha^2$:

$$\langle n, l, j | H_{rel} | n, l, j \rangle = -\frac{Z^4 \alpha^2}{n^3} E_{Ha} \left( \frac{\mu}{m_e} \right)^3 \times \left[ \frac{j(j + 1) - s(s + 1) - l(l + 1)}{2l(l + 1)(2l + 1)} - \frac{1}{2l + 1} + \frac{3}{8n} \right],$$

(2.41)

where the last simplification is based on spin being $s = 1/2$, thus $l = j \pm 1/2$. A separate derivation shows that this Eq. (2.41) (but not all previous steps) holds for $s$ states too.

Expression (2.41) can be combined with the nonrelativistic eigenvalues (2.10) to obtain the following expression for the energy eigenvalues, correct to order $\alpha^2$:

$$\langle n, l, j | H_{tot} + H_{rel} | n, l, j \rangle = -\frac{E_{Ha}}{2} \frac{\mu}{m_e} \frac{Z^2}{n^2} \left[ 1 + \left( Z\alpha \frac{\mu}{m_e} \right)^2 \frac{1}{n} \left( \frac{2}{2j + 1} - \frac{3}{4n} \right) \right].$$

(2.42)

This remarkable relation yields a quantitative prediction for the spectrum that can be directly compared to experiment: all $n$-levels should be split, for the different values of $j$, but not for different values of $l$ giving the same $j$, e.g., $^2S_{1/2}$ and $^2P_{1/2}$ for the same $n$. This extra $l$-degeneracy is retained even in the solutions of Dirac’s equation, which is exact to all orders in $\alpha$, not just $\alpha^2$ as Eq. (2.42).

### 2.1.7.3 The Lamb Shift

As the $l$-degeneracy is rather surprising, the occurrence of a splitting between levels with same $j$ and different $l$ was investigated closely, both theoretically and experimentally. Indeed, quantum fluctuations of the electromagnetic field and the finite nuclear size eventually lift this degeneracy, introducing tiny splittings named Lamb
shift. Figure 2.11b reports the expected spectral fine structure of the Balmer H$_\alpha$ line, including both the relativistic correction and the Lamb shift.

Due mainly to Doppler broadening (see Sect. 1.2), the spectral lines are not sharp enough to resolve these tiny energy differences. To circumvent Doppler broadening and acquire the high-resolution spectrum of Fig. 2.11a, the authors of Ref. [18] devised a trick based on double resonance. An intense tunable monochromatic light beam is split into a strong interruptible “pump” beam plus a second weak “probe” beam, Fig. 2.11c. When the light frequency matches a resonant transition, absorption takes place and the probe beam is attenuated, as in a regular absorption spectroscopy experiment. This absorption is strongly reduced if the pump beam happens to “saturate” the transition in the sample, as discussed quantitatively in Sect. 4.4. The spectrum of Fig. 2.11a records the probe-beam absorption difference between time intervals when the pump beam is on and when it is off. All atoms with a sizable translational velocity component in the beam direction are Doppler shifted in
opposite directions relative to the two beams, which are almost antiparallel: these atoms do not contribute to the difference signal. As a result, a subset of atoms is selected by the matching pump/probe frequency, namely those with practically null instantaneous translational velocity component, thus negligible Doppler shift: this selection prevents Doppler broadening.

### 2.1.8 Nuclear Spin and Hyperfine Structure

Like electrons, several nuclei carry an intrinsic spin \( I \). For example, the proton has spin \( I = \frac{1}{2} \). Unsurprisingly, the nuclear magnetic moment \( \mu_N \) is proportional to its angular momentum:

\[
\mu_N = g_n \mu_n \frac{I}{\hbar}.
\]

Like for the electron, the nuclear magneton \( \mu_n \) is defined by

\[
\mu_n = \frac{q_e \hbar}{2M_n} = \mu_B \frac{m_e}{M_n} \cdot \frac{I \cdot S}{\hbar^2}.
\]

and the nuclear g-factor \( g_n \) is a number of order unity whose value depends on the inner nuclear structure. For example, \( g_n = 5.58569 \) for the proton.

The nuclear spin generates a magnetic field that is extremely weak compared to typical electronic fields, because it is suppressed by the ratio \( m_e/M_n \). Through this field, the nuclear and electron magnetic moments interact. Due to the \( r^l \) term in Eq. (2.13), this interaction is very weak for \( l > 0 \) orbitals, where the electron hardly ever moves close to the nucleus: for simplicity we neglect it here. For \( s \) orbitals, the only nonzero electronic magnetic moment is associated to the electron spin \( S \).

Like for spin-orbit, the interaction Hamiltonian is proportional to the simplest scalar combination of the two involved vector quantities:

\[
\mathcal{H}_{SI} = -C \mu_N \cdot \mu_e = C g_n g_s \mu_B \frac{m_e}{M_n} \frac{I \cdot S}{\hbar^2}.
\]

The coupling factor \( C \) is the relevant radial matrix element, which equals

\[
C = \frac{2}{3} \frac{1}{4\pi \epsilon_0 c^2} R_{n0}(0)^2.
\]

Using \( R_{n0}(0) = 2[Z/(an)]^{1/2} \), the characteristic coupling energy

\[
\xi_N = C g_n g_s \mu_B \frac{m_e}{M_n} = \frac{2}{3} g_n g_s \frac{Z^3}{n^3 m_e c^2} E_{\text{Ha}} \frac{m_e}{M_n} = \frac{4}{3} g_n \frac{Z^3}{n^3} \alpha^2 \frac{m_e}{M_n} E_{\text{Ha}} = g_n \frac{Z^3}{n^3} \frac{1.06 \, \mu eV}{M_n/\text{a.m.u.}}.
\]
where we replaced $\alpha^2$ for $E_{1\text{H}}/(m_e c^2)$, and expressed the nuclear mass $M_n$ in atomic mass units (a.m.u.). For the ground state of $^1\text{H}$, Eq. (2.44) yields $\xi_N = 5.88$ $\mu$eV.

The electron and nuclear spins couple to a grand total angular momentum $\mathbf{F} = \mathbf{I} + \mathbf{S}$, with the rules described in Appendix B.8.1. In analogy with Eq. (2.36), we obtain

$$\mathbf{I} \cdot \mathbf{S} = \frac{|\mathbf{F}|^2 - |\mathbf{I}|^2 - |\mathbf{S}|^2}{2},$$

so that the expectation value of $\mathbf{I} \cdot \mathbf{S}/\hbar^2$ equals $[f(f + 1) - i(i + 1) - s(s + 1)]/2$ in the coupled basis, the one where $|\mathbf{F}|^2$ and $|F_z|$, rather than $I_z$ and $S_z$, are diagonal. As $s = 1/2$, two coupled states $f = i \pm 1/2$ occur, with an energy separation of $\xi_N (i + 1/2)$.

For $^1\text{H}$, the proton has spin $i = 1/2$, so that $\mathbf{I} \cdot \mathbf{S}/\hbar^2 = -3/4$ and $1/4$ for $f = 0$ and 1, respectively. The separation between these two hyperfine-split states equals therefore $\xi_N \simeq 5.88$ $\mu$eV: it corresponds to a wavelength $2\pi \hbar c \xi_N^{-1} \simeq 21$ cm, and a frequency of $\xi_N (2\pi \hbar)^{-1} \simeq 1.42$ GHz. This transition, in the radio-frequency range at $1420405751.8$ Hz, was discovered in 1951 in astrophysical spectra, has been adopted as a frequency standard, and is now used to map the distribution of interstellar atomic $^1\text{H}$.

### 2.1.9 Electronic Transitions, Selection Rules

Not all conceivable transitions are equally easy to observe. Experimentally, certain transitions proceed at a fast rate, while others occur immensely more slowly. This fact can be explained by a quantum-mechanical analysis of the interaction of the atom with the electromagnetic field. The probability per unit time that a quantum object (e.g. an atom) decays radiatively from an initial state $|i\rangle$ to a final state $|f\rangle$ is given by

$$\gamma_{if} = \frac{1}{3\pi\varepsilon_0 \hbar^4 c^5} \frac{e_0^3}{\hbar} |\langle f|d|i\rangle|^2,$$

where $e_{if} = h\omega_{if} = E_i - E_f$, and $d$ is the operator describing coupling to the radiation field. In the approximation that the radiating object is much smaller than the radiation wavelength (see Fig.1.2), this operator is the electric-dipole operator $d = -q_e \mathbf{r}$. All transitions for which the matrix element $\langle f|d|i\rangle$ vanishes are "forbidden" in the electric-dipole approximation: this means that they occur at very low rates, associated to higher multipoles in the field expansion.

The matrix elements of the dipole operator of the one-electron wavefunction are:

$$\langle n_f, l_f, m_{l_f} | d | n_i, l_i, m_{l_i} \rangle = \int \psi^*_n_{l_f, m_{l_f}}(\mathbf{r}) d \psi_{n_i, l_i, m_{l_i}}(\mathbf{r}) d^3r.$$

(2.46)
This integration is carried out conveniently in polar coordinates: express the dipole operator $\mathbf{d}$ as $-q_e r (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$, and observe that

\[
\begin{align*}
 r_x &= r \sqrt{\frac{2\pi}{3}} \left[ Y_{1-1}(\theta, \varphi) - Y_{11}(\theta, \varphi) \right] \\
 r_y &= r i \sqrt{\frac{2\pi}{3}} \left[ Y_{1-1}(\theta, \varphi) + Y_{11}(\theta, \varphi) \right] \\
 r_z &= r \sqrt{\frac{4\pi}{3}} Y_{10}(\theta, \varphi)
\end{align*}
\]

[the inverse of Eq. (2.18)], so that the squared dipole matrix element is proportional to

\[
|\langle f | r | i \rangle|^2 = |\langle f | r_x | i \rangle|^2 + |\langle f | r_y | i \rangle|^2 + |\langle f | r_z | i \rangle|^2
\]

with factored radial and angular matrix elements. Explicitly, in terms of the wavefunctions

\[
|\langle n_f, l_f, m_f | d | n_i, l_i, m_i \rangle|^2 = q_e^2 \int_0^\infty \! \int d \theta \int_0^{2\pi} \sin \theta d \varphi \left| \int_0^\infty \! R_{n_f l_f}(r) r R_{n_i l_i}(r) r^2 dr \right|^2 \\
\times \frac{4\pi}{3} \sum_m \left| \int_0^{2\pi} \sin \theta d \theta \int_0^\pi \sin \theta d \theta \int_0^{2\pi} d \varphi Y_{l_f m_f}^*(\theta, \varphi) Y_{l_i m_i}(\theta, \varphi) \right|^2.
\]

No radial integral vanishes, because the function $r R_{n_i l_i}(r)$ has nonzero expansion coefficients on all radial basis wavefunctions of Eq. (2.13). The radial integral can be computed analytically between any initial $(n_i, l_i)$ and final $(n_f, l_f)$: it decreases rapidly when $n_i$ and $n_f$ differ by large amounts, because $R_{n_i l_i}(r)$ and $R_{n_f l_f}(r)$ take nonnegligible values in remote region, so that the product $R_{n_i l_i}(r) R_{n_f l_f}(r)$ is small everywhere.

Much stricter results are found for the angular part: the integration in the second row of Eq. (2.47) represents the angular overlap of a state with angular momentum $l = l_f$ with the product $Y_{1 m} Y_{l_i m_i}$. By applying the rule (B.72) of angular-momentum coupling, this product of objects carrying angular momenta $l = 1$ and
$l = l_i$ can be decomposed into the following allowed values\(^4\) of the total coupled angular momentum:

$$l_f = |l_i - 1|, l_i, l_i + 1. \quad (2.48)$$

Final states characterized by angular momentum $l_f$ not satisfying Eq. (2.48) are guaranteed to make the angular integral vanish. Moreover, the angular integral vanishes also when $l_f = l_i$. The reason is that the parity of $Y_{1m}$, like that of $r$, is $(-1)^1 = -1$, while the parity of $Y^*_{l_i m_f} Y_{l_i m_i}$ is $(-1)^{2l_i} = 1$. As a result, the parity of the integrated product function $Y^*_{l_i m_f} Y_{l_i m_i}$ is odd, and therefore its integration over the entire solid angle vanishes.

In summary, in the dipole approximation, nonzero matrix element can occur only for transitions involving states with $l$ changing by exactly unity. The allowed transitions have therefore

$$\Delta l = l_f - l_i = \pm 1. \quad (2.49)$$

This equality is the electric-dipole selection rule regarding $l$.

The fact that the dipole operator is associated to an orbital $l = 1$ implies also that its component $m = -1, 0, 1$. Accordingly, the only value of $m_f$ for which the angular integral is nonzero, is obtained by adding $m$ to $m_{l_i}$. From this observation we formulate the $m_l$-selection rule:

$$\Delta m_l = m_{l_f} - m_{l_i} = 0, \pm 1. \quad (2.50)$$

Until this point, spin was ignored because the dipole operator is purely spatial: it does nothing to spin. Indeed in the uncoupled basis $|n, l, m_l, m_s\rangle$, see Appendix B.8.1, $d$ only affects the spatial degrees of freedom, while for spin it acts as the identity. As a result, we have

$$\Delta s = s_f - s_i = 0 \quad (2.51)$$

$$\Delta m_s = m_{s_f} - m_{s_i} = 0. \quad (2.52)$$

The first spin selection rule (2.51) is trivial for a one-electron atom, as $s \equiv \frac{1}{2}$ anyway, but it will become relevant for many-electron atoms.

By analyzing the composition of the coupled states $|n, l, j, m_j\rangle$ in terms of the $|n, l, m_l, m_s\rangle$ uncoupled basis, see Eq. (B.73), one can obtain the following selection rules for the coupled states:

\(^4\) In general it can be shown that the angular integral within the absolute value in Eq. (2.47) is proportional to the Clebsch-Gordan coefficient $C_{l_f m_f}^{l_i m_i 1 m}$, see Eq. (B.73).
\[ \Delta j = j_f - j_i = 0, \pm 1 \quad \text{(not 0 \rightarrow 0)} \quad (2.53) \]

\[ \Delta m_j = m_{j_f} - m_{j_i} = 0, \pm 1. \quad (2.54) \]

After determining what transitions are allowed in the dipole approximation, we should use Eq. (2.45) to estimate typical rates of radiative atomic transitions. By noting that \( \epsilon_{if} \approx Z^2 E_{Ha} \) and observing that the order of magnitude of \( |\langle f | d | i \rangle| \approx q_e a_0 / Z \), we can estimate

\[
\gamma_{if} = \frac{\epsilon_{if}^3 |\langle f | d | i \rangle|^2}{3\pi \varepsilon_0 \hbar^4 c^3} \approx \frac{Z^4}{\varepsilon_0 \hbar^3 c^3} E_{Ha}^2 \omega_{if} q_e^2 a_0^2 \frac{Z^2}{2} \approx \frac{e^2 Z^2}{(\hbar c)^3} e^4 \omega_{if} = Z^2 \left( \frac{e^2}{\hbar c} \right)^3 \omega_{if},
\]

where we have used \( E_{Ha} a_0 = e^2 \) and \( \alpha = e^2 / (\hbar c) \). As \( \alpha^3 \approx 10^{-7} \) and in one-electron atoms \( \omega_{if} = \epsilon_{if} / \hbar \approx Z^2 10^{16} \) Hz, we expect typical radiative transition rates of the order \( \gamma_{if} \approx Z^4 10^9 \) s\(^{-1} \), i.e. decay times \( \gamma_{if}^{-1} \approx Z^{-4} \) ns. The strong \( (\epsilon_{if}^3) \) dependence of \( \gamma_{if} \) makes this rate faster for more energetic transitions, and slower for low-energy transitions. Much slower transition occur for dipole-forbidden transitions, associated to weaker higher-order couplings to the electromagnetic field (magnetic dipole, electric quadrupole…).

In a gaseous sample, other nonradiative transitions can also occur due to collisions with other atoms and/or with the vessel walls. Nonradiative mechanisms can dominate the decay of long-lived metastable states, i.e. those lacking fast dipole-allowed decay transitions.

### 2.1.10 Spectra in a Magnetic Field

We conclude this Section with a brief analysis of atomic spectra in the condition where a maximum of information can be extracted from them, namely when the atomic sample is immersed in a uniform magnetic field. In these conditions, the atom, depending on the component of its magnetic moment along the field direction, acquires a little extra energy which can then be detected by spectroscopy.

In the presence of both orbital and spin angular momenta, the total atomic magnetic moment is the vector sum

\[
\mu = \mu_f + \mu_s = -\mu_B \frac{g_f L + g_s S}{\hbar} \approx -\mu_B \frac{L + 2S}{\hbar}. \quad (2.56)
\]
By studying the matrix elements of the \( \mu \) operator, one can evaluate the magnetic properties of an atom, where both spin and orbital magnetic moments come into play. Following Eqs. (2.24) and (2.56), the coupling with the external magnetic field can be expressed as:

\[
H_{\text{magn}} = -B \cdot \mu = \mu_B \mathbf{B} \cdot \frac{\mathbf{L} + 2\mathbf{S}}{\hbar} = \mu_B B_z \frac{L_z + 2S_z}{\hbar}.
\]

This operator is diagonal in the uncoupled \(|l, s, m_l, m_s\rangle\) basis. Remember however (Sect. 2.1.7) that \(H_{s-o}\) is not diagonal in that basis, but rather in the coupled basis \(|l, s, j, m_j\rangle\). In fact, \(H_{s-o}\) and \(H_{\text{magn}}\) cannot be diagonalized simultaneously, as they do not commute. To obtain the eigenenergies and eigenkets one must diagonalize the total operator \(H_{\text{magn}} + H_{s-o}\), within each \((2l+1) \cdot (2s+1)\)-dimensional subspace at fixed \(n, l, s\). This diagonalization is not especially complicated, but it is perhaps more instructive to understand in detail the two limiting cases where either characteristic energy scale \(\mu_B |B|\) or \(\xi\) dominates.

The simplest limit (\(\mu_B |B| \gg \xi\)), of magnetic field energy \(\mu_B |B|\) much larger than the spin-orbit energy \(\xi\), occurs for sufficiently large field intensity. The “sufficiently large” threshold depends on the considered atom and level: for hydrogen 2p, the strong-field limit is reached for \(|B| \gg 0.5\) T, while for He\(^+\) 2p it takes a magnetic field as large as \(|B| \gg 8\) T, due to the \(Z^4\)-dependence of the spin-orbit energy, Eq. (2.35). In this limit of very strong field, the coupled basis is not especially good, as full rotational invariance of the atom is badly broken. The uncoupled basis \(|l, s, m_l, m_s\rangle\) works fine instead: spin and orbital moments align relative to the field with separate energy contributions depending on their different \(g\)-factors. In this basis, the dominating interaction \(H_{\text{magn}}\) is diagonal: if we neglect the smaller \(H_{s-o}\), the magnetic energy levels are simply

\[
E_{\text{magn}}(m_l, m_s) \simeq \langle m_l, m_s | H_{\text{magn}} | m_l, m_s \rangle = \mu_B B_z (m_l + 2m_s)
\]

(Paschen-Back limit). \(H_{s-o}\) corrections may be added perturbatively.

In the (more common) opposite weak-field limit (\(|B| \ll \xi/\mu_B\)), spherical symmetry is perturbed only weakly. The states \(|l, s, j, m_j\rangle\) in the coupled basis are exact eigenstates of \(H_{s-o}\) and approximate eigenstates of \(H_{\text{magn}} + H_{s-o}\). Following the results of Appendix B.8.2, to first order in \(\mu_B |B|/\xi\), the energy contribution of \(H_{\text{magn}}\) is given by Eq. (B.75):

\[
E_{\text{magn}}(m_j) \simeq \langle j, m_j | H_{\text{magn}} | j, m_j \rangle = \langle j, m_j | -\mu_z B_z | j, m_j \rangle = g_j \mu_B B_z m_j
\]

(Zeeman limit), where \(g_j\) is the Landé \(g\)-factor, Eq. (B.78).
Fig. 2.12 Spin-orbit and magnetic splitting of a $^2P$ multiplet. With the shorthand $b = \mu_B B/\xi$, the expression for the $m_j = \pm \frac{3}{2}$ energies (solid lines) is simply $(\frac{1}{2} \pm 2b) \xi$. The energies of the four other levels are
$$\frac{1}{4}(-1 \pm 2b + d)\xi$$
dot-dashed lines) and
$$\frac{1}{4}(-1 \pm 2b - d)\xi$$
dashed lines), where
$$d = \sqrt{9 + 4b(1 + b)}$$

In the intermediate-field regime $\mu_B |B| \simeq \xi$ neither basis is appropriate and neither of expressions (2.58) and (2.59) is accurate. Figure 2.12 displays the exact pattern of splittings of the six $^2P$ states under the action of a magnetic field, changing from the Zeeman (weak field) to the Paschen-Back (strong-field) limit. The initial slopes of the energy curves at $B \to 0$, divided by the relevant $m_j$, measure the values of the Landé $g_j$.

The experimentally observed spectra confirm the theory outlined here. For H, provided that a sufficiently strong magnetic field is applied, the Paschen-Bach is relatively straightforward to observe as a triplication of all lines. If very high spectral resolution can be achieved, also the weak-field Zeeman splitting of the H lines shown in the conceptual scheme of Fig. 2.13 can be detected. Such Zeeman effect is called “anomalous” since the lines are spaced irregularly. In fact, in atomic physics, such irregular splittings are rather the rule than an anomaly: only selected spin-orbit-free $S = 0$ lines in many-electron atoms happen to show “regular” Zeeman splittings (see Fig. 2.30 in Sect. 2.2.8.4).

2.2 Many-Electron Atoms

2.2.1 Identical Particles

The concept of indistinguishable particles is central to all the physics of matter where two or more electrons are involved. Note that in classical mechanics each particle is labeled by its own position and momentum: one could in principle track individual trajectories along the motion, and thus tell identical particles $i$ and $j$ apart at any time.
In QM, indistinguishable particles are such at the deepest level. There is no way, even as a matter of principle, to ever tell e.g. two electrons apart, as they both are present at all points of space, with a certain probability amplitude. QM implements perfect indistinguishableness through symmetry: any many-particles ket has a definite symmetry “character” for the permutation operator $P_{ij}$ swapping the $i$th and $j$th identical particles. As this permutation symmetry is a discrete symmetry which, if applied twice, leads back to the initial state, the eigenvalues of $P_{ij}$ can only be $+1$ or $-1$.

The particles for whose swap the overall system ket $|a\rangle$ is symmetric are called **bosons**. The eigenvalue of $P_{ij}$ is $+1$, i.e. $P_{ij}|a\rangle = |a\rangle$.

The particles for whose swap the overall ket $|a\rangle$ is antisymmetric are called **fermions**. Here the eigenvalue of $P_{ij}$ is $-1$, i.e. $P_{ij}|a\rangle = -|a\rangle$.

All elementary particles of “matter” (electrons, protons, neutrons$^5$ . . .) are examples of fermions, all of spin $1/2$. Elementary bosons are carriers of “interactions”. For example, photons (spin 1) are the quanta of the electromagnetic field, see Sect. 4.3.2.2. A simple general rule connects the spin of a particle kind to its permutational symmetry: **integer-spin particles are bosons, half odd-integer particles are fermions**.

$^5$ Contrary to electrons, protons and neutrons are not quite elementary, since they are bound states of triplets of elementary spin-$1/2$ quarks, and they follow the rule for composite particles sketched below.
A collection of bosons and fermions lumped together can behave as a single point-like particle. This occurs when the internal dynamics is associated to high excitation energy, so that the lump remains in its ground state (possibly degenerate according to the projection of the lump’s total angular momentum). It is important to know the eigenvalue for the permutation of two such identical lumps (composite bosons/fermions). This is simply answered by counting the number of \((-1)\)’s generated by the permutations of pairs of identical fermions. For example, hydrogen atoms in the same hyperfine state are identical bosons, since a \(-1\) is generated by the permutation of the two electrons and a second \(-1\) is generated by the permutation of the two protons, in total \((-1) \cdot (-1) = +1\). Likewise, the \(^{13}\)C isotope of carbon is a fermion (6 protons + 7 neutrons + 6 electrons), while \(^{238}\)U is a boson (92 protons + 146 neutrons + 92 electrons). Similarly, identical nuclei are bosons or fermions according to whether they contain an even or odd number of nucleons (protons plus neutrons); for example the deuteron nucleus \(D^+\), a bound proton and neutron in a \(i = 1\) nuclear-spin state, is a boson. Due to the angular-momentum composition rule (B.72), all composite particles fulfill the general spin rule.

The permutational symmetry is crucial to understand the dynamics of many electrons and, in particular, the structure of many-electron atoms. As discussed in greater detail below, antisymmetry obliges \(N\) electrons to span \(N\) quantum states, thus effectively avoiding one another. In practice, the geometrical constraint of antisymmetry is often more effective than the dynamical electron–electron repulsion (1.6) in keeping electrons apart.

Without permutational antisymmetry all electrons would occupy the same 1s shell in the atomic ground state. If that happened (as it could if electrons were distinguishable particles—or bosons—rather then fermions), then the atomic ionization energies should increase roughly as \(Z^2\) and the size of atoms should decrease roughly as \(Z^{-1}\). In stark contrast, relatively mild non-monotonic \(Z\) dependence of both these properties (Figs. 2.14 and 2.15) are observed: in particular, the first ionization energy and the atomic size exhibit a weak general tendency to respectively decrease and increase with \(Z\).

**Fig. 2.14** As a function of the atomic number \(Z\), the first-ionization energy of neutral atoms \((N = Z)\), i.e. the minimum energy required to remove one electron from the atom.
Fig. 2.15 Empirical atomic radii, as a function of $Z$. The vertical bars represent the standard deviation. The labels $TM1$, $TM2$ and $TM3$ mark the ranges of the first, second and third transition series, respectively (Data from Ref. [19])

2.2.2 The Independent-Particles Approximation

The exact solution of the Schrödinger equation associated to Hamiltonian (1.1) requires the determination of a $N$-electron wavefunction. For increasing $N$, this becomes soon a formidable task, because the $N$-electron wavefunction describes the correlated motion of all the $N$ electrons, and thus depends intricately on all position and spin coordinates of the $N$ electrons. The amount of information carried by a generic $N$-electron wavefunction is exponentially large with $N$: there is no way to store (let alone compute!) the full wavefunction for the ground state of many interacting electrons.

Most approximate methods on the market exploit the observation that a basis of the Hilbert space of $N$-particle states can be built as a product of single-particle basis states. Consider the complete set of orthonormal states $\{|\alpha\rangle\}$ for a single particle, where $\alpha$ takes all possible values allowed to a full set of quantum numbers, e.g. $n$, $l$, $m_l$, $m_s$ in the example of an electron in an atom. Then the tensor product

$$|\alpha_1, \alpha_2, \ldots, \alpha_N\rangle = |\alpha_1\rangle \otimes |\alpha_2\rangle \otimes \cdots |\alpha_N\rangle,$$

realizes a basis for $N$ particles when all possible choices of $\alpha_1, \alpha_2, \ldots, \alpha_N$ are explored. For indistinguishable particles, the correct permutational symmetry is imposed to the product state (2.60) by taking the properly symmetrized linear combination

$$|\alpha_1, \alpha_2, \ldots, \alpha_N\rangle^{S/A} = \frac{1}{\sqrt{N!}} \sum_P (\pm 1)^{|P|} P|\alpha_1, \alpha_2, \ldots, \alpha_N\rangle$$

$$= \frac{1}{\sqrt{N!}} \sum_P (\pm 1)^{|P|} |\alpha_{P_1}, \alpha_{P_2}, \ldots, \alpha_{P_N}\rangle.$$  (2.61)
Here $P$ indicates a generic permutation of the $N$ states $\alpha_j$, and the sum extends over all $N! P$ permutations; for example, $\mathcal{N}_P = N!$ if the states $\alpha_j$ happen to be all different. $\{P\}$ in the exponent indicates the parity of the permutation $P$, i.e. the number of pair swaps composing $P$. The fully symmetrized basis state $|\alpha_1, \alpha_2, \ldots, \alpha_N\rangle^S$ realizes the correct permutational symmetry of $N$ bosons; the antisymmetric combination $|\alpha_1, \alpha_2, \ldots, \alpha_N\rangle^A$ involving nontrivial $(-1)$ signs can play the role of basis state for $N$ fermions. For bosons, no restriction applies to the quantum numbers $\alpha_j$; any number of them may coincide. Instead, for fermions, all quantum numbers must necessarily be different. If two were equal, say $\alpha_i = \alpha_j$, in the sum (2.61), the kets $|\alpha_p_1, \ldots, \alpha_p_i, \ldots, \alpha_p_j, \ldots, \alpha_p_N\rangle$ and $|\alpha_p_1, \ldots, \alpha_p_j, \ldots, \alpha_p_i, \ldots, \alpha_p_N\rangle$ would be equal, but with opposite parity phase factor $(-1)^{|P|}$, so that they all cancel in pairs in the sum, and the total ket $|\alpha_1, \ldots, \alpha_i, \ldots, \alpha_j, \ldots, \alpha_N\rangle^A$ vanishes. As a result, the product basis kets for $N$ fermions are characterized by $N$ different quantum numbers: this property expresses the Pauli exclusion principle, according to which two identical fermions can never occupy the same quantum state.

The wavefunction representation of a $N$-fermion basis ket is obtained starting from the eigenket of position and spin of the $j$th fermion, shorthanded to $|w_j\rangle = |r_j, \sigma_j\rangle$. The corresponding $N$-fermions product converts to a bra as $\langle w_1, w_2, \ldots w_N |$, and is then to be properly antisymmetrized. The wavefunction associated to Eq. (2.61) is then

$$
\Psi_{\alpha_1, \ldots, \alpha_N}(w_1, \ldots, w_N) = A(w_1, w_2, \ldots, w_N|\alpha_1, \alpha_2, \ldots, \alpha_N)^A
$$

$$
= \frac{1}{N!} \sum_{P} (-1)^{|P|} \sum_{P'} \frac{1}{N!} \sum_{P} (-1)^{|P|} |w_{p_1}', \ldots, w_{p_N}', \alpha_{p_1}, \ldots, \alpha_{p_N}\rangle
$$

$$
= \frac{1}{N!} \sum_{P} (-1)^{|P|} \sum_{P} (-1)^{|P|} \psi_{\alpha_{p_1}}(w_{p_1}') \ldots \psi_{\alpha_{p_N}}(w_{p_N}')
$$

$$
= \sum_{P} (-1)^{|P|} \psi_{\alpha_{p_1}}(w_1) \ldots \psi_{\alpha_{p_N}}(w_N), \tag{2.62}
$$

where the sum over permutations of the variables $w_j$ generates $N!$ identical copies of the same wavefunction, and is therefore eliminated. The sum in the last expression is the determinant of the matrix whose elements are $\psi_{\alpha_i}(w_j)$:

$$
\Psi_{\alpha_1, \ldots, \alpha_N}(w_1, \ldots, w_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_{\alpha_1}(w_1) & \psi_{\alpha_1}(w_2) & \cdots & \psi_{\alpha_1}(w_N) \\
\psi_{\alpha_2}(w_1) & \psi_{\alpha_2}(w_2) & \cdots & \psi_{\alpha_2}(w_N) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_{\alpha_N}(w_1) & \psi_{\alpha_N}(w_2) & \cdots & \psi_{\alpha_N}(w_N)
\end{vmatrix}. \tag{2.63}
$$

This basis wavefunction is called a Slater determinant.\(^6\)

\(^6\) In Eq. (2.63) we introduce an extra normalization factor $(N!)^{-1/2}$. This standard factor allows one to carry out integration (e.g. for wavefunction normalization) over an unrestricted domain of all $w_j$ variables, instead of the appropriate “hyper-triangle” $w_1 > w_2 > \cdots > w_N$. 

An (anti)symmetrized product ket (2.61) contains an amount of information only directly, rather than exponentially, proportional to the number \( N \) of identical particles, and is thus substantially simpler than a general boson/fermion ket. Despite their simplicity, the kets of Eq. (2.61) constitute a basis of the Hilbert space of the proper symmetry: any physical \( N \)-boson/\( N \)-fermion ket \( |a^{B/F}\rangle \), e.g. an exact energy eigenstate of \( N \) interacting identical particles, can be expressed as a linear combination of the factorized basis kets:

\[
|a^{B/F}\rangle = \sum_{\alpha_1,\alpha_2,\ldots,\alpha_N} c_{\alpha_1,\alpha_2,\ldots,\alpha_N}^{a} |\alpha_1, \alpha_2, \ldots, \alpha_N\rangle^{S/A},
\]

where \( c_{\alpha_1,\alpha_2,\ldots,\alpha_N}^{a} \) are the complex coefficients defining the linear combination. The number of these coefficients grows exponentially with \( N \): the amount of information of the correlated state \( |a^{B/F}\rangle \) is now encoded in its expansion coefficients \( c_{\alpha_1,\alpha_2,\ldots,\alpha_N}^{a} \).

Several approximate methods of solution of the Schrödinger problem for many-electron systems replace the (lowest) exact eigenstate with one (as smart as possible) basis state \( |\alpha_1, \alpha_2, \ldots, \alpha_N\rangle^{A} \) constructed with single-particle states \( |\alpha_1\rangle, |\alpha_2\rangle, \ldots \), solutions of some appropriate single-electron Hamiltonian. This scheme is named independent-particles approximation.

For atoms, the simplest approach along this line consists in neglecting the electron–electron Coulomb interaction \( V_{ee} \) of Eq. (1.6) altogether. In this approximation, the Schrödinger problem for the \( N \) electrons factorizes exactly: each electron moves independently of the others in the field \( V_{ne} \) of the nucleus of charge \( Zq_e \). Neglecting relativistic corrections, the single-electron eigenstates \( |\alpha_j\rangle \) are represented by hydrogenic wavefunctions of the kind (2.27), as defined in Eqs. (2.11)–(2.13), with the appropriate \( Z \).\(^7\) In this atomic context \( \alpha_j \) stands for a set of quantum numbers \( n_j, l_j, m_{lj}, m_{sj} \). Choose a list of \( N \) different \( \alpha_j \): the generic \( N \)-electron eigenstate is \( |\alpha_1, \alpha_2, \ldots, \alpha_N\rangle^{A} \), as in Eq. (2.61). The example of a possible \( N = 4 \)-electron state is

\[
|1, 0, 0, \uparrow, 3, 1, 1, \uparrow, 3, 1, 0, \uparrow, 3, 1, -1, \downarrow\rangle^{A}.
\]

The standard spectroscopic notation \( 1s3p^{3} \) for this state lists the occupied single-particle orbitals, with the corresponding electron numbers as exponents: all information about the \( m_{lj} \)'s and \( m_{sj} \)'s is omitted. In contrast, the box notation \( 1s\Box[3p\Box[\Box[\Box]]] \) contains all details.

The total energy \( E_{\text{tot}} \) of an atomic state is minus the work needed to decompose the atom from that given bound state to an isolated nucleus plus the \( N \) individual electrons at rest at infinite reciprocal distance. The total energy of non-interacting electrons is simply the sum of their single-electron energies.

\(^7\) We neglect all reduced-mass effects, assuming an infinite nuclear mass. The finiteness of the nuclear mass could introduce tiny correlations in the electronic motions, which would add to those of Coulombic origin.
The eigenstate (2.65) is not the one with the lowest possible energy. The ground state can be obtained by minimizing the energy of each single-particle orbital, without violating the Pauli principle. For \( N = 4 \), the lowest energy is realized by any of \( 1s^2 2s^2 \), \( 1s^2 2s^2 2p \) plus 11 similar states, \( 1s^2 2p^2 \) plus 14 similar states: a total of \( (1s^2 2s^2) + 12 (1s^2 2s 2p) + 15 (1s^2 2p^2) = 28 \) individual states, all with energy

\[
E_{1s^2 2s^2}^{\text{tot}} = 2\varepsilon_1 + 2\varepsilon_2 = -2 \frac{E_{\text{Ha}}}{2} \left( \frac{Z^2}{1^2} + \frac{Z^2}{2^2} \right) = -\frac{5}{4} Z^2 E_{\text{Ha}}. \tag{2.66}
\]

The excited state (2.65) has significantly higher total energy \( E_{1s3p}^{\text{tot}} = -\frac{2}{3} Z^2 E_{\text{Ha}} \).

Real electrons do interact with each other. In a neutral atom, the electron–electron repulsion (1.4) is of the same order of magnitude as the attraction (1.6) to the nucleus, which means that the brutal simplification of a complete neglect of \( V_{ee} \) is a very poor approximation, doomed to yield unphysical predictions. Since the maximum occupation of the \( n \)th hydrogenic level \( 2n^2 \) grows rapidly, the minimum energy required to remove an electron from a neutral atom (the first ionization energy) increases with \( Z \) only marginally more slowly than \( Z^2 \), at variance with experiment (Fig. 2.14). Moreover, in this model any atom (regardless of \( Z \)) would be able to accept any number \( N \) of electrons, always forming bound states. Experimentally, however, only certain atoms can form negatively-charged ionic bound states, but never with more than 1 extra charge \( (N \leq Z + 1) \). The main reason for the failures of this model is illustrated in Fig. 2.16: in reality while an electron is removed from the atom, it does not feel the bare nuclear attraction \( -Ze^2/r \) but rather, due to electron–electron repulsion and according to the divergence law of electromagnetism, the substantially weaker combined effect of the nuclear charge and that of the other \( N-1 \) electrons, \( V(r) \simeq (-Z + N - 1) e^2/r \). This phenomenon of screening decreases the ionization energy substantially, and must be included for a fair description of the atomic wavefunction.

The following section sketches a simple but instructive theory for the simplest many-electron atom, He \( (Z = N = 2) \), for which significant insight is obtained by treating \( V_{ee} \) as a perturbation to the uncorrelated electron states. Perturbative methods fail for \( N \geq 3 \): Sect. 2.2.4 sketches a more systematic method for a much improved independent-electron method, which includes screening.

**Fig. 2.16** When one electron moves away from an atom/ion, the nucleus of charge \( Z q_e \) and the remaining \( (N-1) \) electrons attract it as if effectively they were a point charge \( (Z - N + 1) q_e \).
2.2.3 The 2-Electron Atom

In the simplest nontrivial case of \( N = 2 \) electrons (relevant for the He atom, and for the Li\(^{+}\), Be\(^{2+}\) ... ions), the independent-electron wavefunction reads

\[
\Psi_{\alpha_1, \alpha_2}(w_1, w_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{\alpha_1}(w_1) & \psi_{\alpha_1}(w_2) \\ \psi_{\alpha_2}(w_1) & \psi_{\alpha_2}(w_2) \end{vmatrix} = \frac{\psi_{\alpha_1}(w_1)\psi_{\alpha_2}(w_2) - \psi_{\alpha_1}(w_2)\psi_{\alpha_2}(w_1)}{\sqrt{2}}.
\]

(2.67)

In the cases where the orbital quantum numbers coincide (\( n_1 = n_2, l_1 = l_2, m_{l_1} = m_{l_2} \)), the orbital part can be factorized in the Slater determinant. Only spin remains in the antisymmetric combination:

\[
\Psi_{n, l, m_1, \uparrow, n, l, m_2, \downarrow}(w_1, w_2) = \psi_{n, l, m_1}(r_1) \psi_{n, l, m_2}(r_2) \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_{\uparrow}(\sigma_1) \chi_{\uparrow}(\sigma_2) \\ \chi_{\downarrow}(\sigma_1) \chi_{\downarrow}(\sigma_2) \end{vmatrix}.
\]

(2.68)

Here the Slater determinant is simply \( \chi_{\uparrow}(\sigma_1) \chi_{\downarrow}(\sigma_2) - \chi_{\uparrow}(\sigma_2) \chi_{\downarrow}(\sigma_1) \). This combination of the two electron spin wavefunctions is an eigenstate of the square modulus of the total spin \( S = s_1 + s_2 \), with null eigenvalue \( |S|^2 = S(S+1)\hbar^2 = 0 \). Eigenstates of \( |S|^2 \), like the one of Eq. (2.68), are useful because the matrix elements of the (hitherto neglected) Coulomb repulsion between states of different \( S \) vanish since \( V_{ee} \) is an orbital operator, which does not act on spin. The other \( S = 0 \) states (spin singlets), those involving two different sets of orbital quantum numbers, are:

\[
\Psi_{n_1, l_1, m_{l_1}, n_2, l_2, m_{l_2}}^{S=0}(w_1, w_2)
= \frac{\psi_{n_1, l_1, m_{l_1}}(r_1) \psi_{n_2, l_2, m_{l_2}}(r_2) + \psi_{n_1, l_1, m_{l_1}}(r_2) \psi_{n_2, l_2, m_{l_2}}(r_1)}{\sqrt{2}} \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_{\uparrow}(\sigma_1) \chi_{\uparrow}(\sigma_2) \\ \chi_{\downarrow}(\sigma_1) \chi_{\downarrow}(\sigma_2) \end{vmatrix}.
\]

(2.69)

Note that the \( S = 0 \) states of Eq. (2.69) are not single Slater determinants of the type of Eq. (2.67). The singlet states are characterized by an orbital part of the wavefunction which is symmetric under permutation \( P_{12} \), with the spin part taking care of the required antisymmetry.

The singlet states (2.68) and (2.69) are \( S = 0 \) eigenstates of \( |S|^2 \). The other value of \( S \) allowed by Eq. (B.72) is \( S = 1 \). The spin part of the wavefunctions of the \( S = 1 \) spin-triplet states is any of:

\[
\begin{align*}
\mathcal{P}^S=1, M_S=1(\sigma_1, \sigma_2) &= \chi_{\uparrow}(\sigma_1) \chi_{\uparrow}(\sigma_2) \\
\mathcal{P}^S=1, M_S=0(\sigma_1, \sigma_2) &= \frac{1}{\sqrt{2}}[\chi_{\uparrow}(\sigma_1) \chi_{\downarrow}(\sigma_2) + \chi_{\downarrow}(\sigma_2) \chi_{\uparrow}(\sigma_1)] \\
\mathcal{P}^S=1, M_S=-1(\sigma_1, \sigma_2) &= \chi_{\downarrow}(\sigma_1) \chi_{\downarrow}(\sigma_2)
\end{align*}
\]

(2.70)
Table 2.1: The characters of the fixed-total-spin-$S$ two-electron basis states

<table>
<thead>
<tr>
<th></th>
<th>$S = 0$—spin-singlet states</th>
<th>$S = 1$—spin-triplet states</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orbital quantum number</td>
<td>Any</td>
<td>$(n_1, l_1, m_{l_1}) \neq (n_2, l_2, m_{l_2})$</td>
</tr>
<tr>
<td>Orbital wavefunction</td>
<td>Symmetric</td>
<td>Antisymmetric</td>
</tr>
<tr>
<td>Spin quantum numbers</td>
<td>$\uparrow$ and $\downarrow$ (different)</td>
<td>Any</td>
</tr>
<tr>
<td>Spin wavefunction</td>
<td>Antisymmetric</td>
<td>Symmetric</td>
</tr>
</tbody>
</table>

which are all symmetric for $P_{12}$. Therefore the orbital part takes care of antisymmetry:

$$
\psi_{S=1, M_{S}}^{n_1, l_1, m_{l_1}, n_2, l_2, m_{l_2}}(w_1, w_2) = \frac{\psi_{n_1, l_1, m_{l_1}}(r_1) \psi_{n_2, l_2, m_{l_2}}(r_2) - \psi_{n_1, l_1, m_{l_1}}(r_2) \psi_{n_2, l_2, m_{l_2}}(r_1)}{\sqrt{2}} \mathcal{S}^{S=1, M_S}(\sigma_1, \sigma_2).
$$

(2.71)

In these states, at least one of the orbital quantum numbers for the two electrons needs to be different: $(n_1, l_1, m_{l_1}) \neq (n_2, l_2, m_{l_2})$, or else the wavefunction vanishes.

Table 2.1 summarizes the basic properties of the singlet ($S = 0$) and triplet ($S = 1$) basis states $|n_1, l_1, m_{l_1}, n_2, l_2, m_{l_2}, S, M_S\rangle$ for two electrons. These spin-symmetrized states are convenient 0th-order states for a perturbation theory in $V_{ee}$, see Appendix B.39. They are eigenstates of $T_e + V_{ne}$: like in the example of Eq. (2.66), the “unperturbed” energies

$$
E_{n_1, n_2}^{\text{tot}}(0) = -\frac{E_{\text{Ha}}}{2} \left( \frac{Z^2}{n_1^2} + \frac{Z^2}{n_2^2} \right) = -2 E_{\text{Ha}} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right),
$$

(2.72)

where the last expression refers to He ($Z = 2$). The ground state $n_1 = n_2 = 1$ (in spectroscopic notation $1s^2$) is necessarily a spin singlet and has energy $E_{1,1}^{\text{tot}}(0) = -4 E_{\text{Ha}} \simeq -109 \text{ eV}$.

As a next step, following standard perturbation theory (Appendix B.9) the effect of $V_{ee}$ is accounted for by evaluating its diagonal matrix elements over the zeroth order eigenkets. Equation (B.85) provides the first-order (additive) correction $E_{n_1, l_1}^{\text{tot}}(1) = (V_{ee})$ to the eigenenergies:

$$
E_{n_1, l_1, m_{l_1}, n_2, l_2, m_{l_2}, S, M_S}^{\text{tot}}(1) = \langle n_1, l_1, m_{l_1}, n_2, l_2, m_{l_2}, S, M_S | V_{ee} | n_1, l_1, m_{l_1}, n_2, l_2, m_{l_2}, S, M_S \rangle.
$$

(2.73)

Since the electron–electron repulsion is positive, this correction is always positive. The detailed calculation of these Coulomb integrals is a rather intricate mathematical exercise, with instructive qualitative outcomes. The largest of these $E_{n_1, l_1}^{\text{tot}}(1)$
corrections occurs for the most localized wavefunction, the one where the two
electrons stay very close together, both in the 1s level: the ground state 1s^2. The
average inter-electron distance is approximately a_0, thus the Coulomb integral
E_{1,0,0,0,0,0}^{\text{tot}(1)} is of order \sim e^2/a_0 = E_{\text{Ha}}. The precise value obtained from integra-
tion [5] is \frac{5}{4} E_{\text{Ha}} \simeq 34\text{eV}. This correction brings the estimated ground-state energy
of He to \( E_{1,1}^{\text{tot}(0)} + E_{1,0,0,0,0,0}^{\text{tot}(1)} = -74.8\text{eV} \), in fair agreement with the experi-
mental value \(-79.00\text{eV} \) (minus the sum of the first and second ionization energies
of He).

For the optically most relevant states, those with one electron sitting in 1s and
the other in an excited state \( n_2[l_2] \), the first-order correction accounts for several
experimental observations:

- All Coulomb integrals are smaller than the one for the ground state, and tend to
decrease for increasing \( n_2 \): the Coulomb correction become less and less important
as the electrons move apart from each other.
- The Coulomb integrals at given \( n_2 \) depend weakly on \( l_2 \): they usually increase
for increasing \( l_2 \). By looking at the hydrogenic radial distributions Fig. 2.7, one
can note that indeed the electrons, on average, sit slightly closer when \( l_2 \) is larger.
This is an important novelty, since it breaks the H-atom \( l \)-degeneracy of the shells,
putting \( E_{ns} < E_{np} < E_{nd} < \ldots \), in accord to experimental finding (Fig. 2.17).

---

**Fig. 2.17** Energy levels of atomic He, with several optical transitions. While
one electron remains in the \( n_1 = 1 \) single-electron state, the quantum numbers
\( n = n_2 \) and \( l_2 \) refer to the other (excited) electron. Note that each triplet state sits
systematically lower than the corresponding singlet. The energy zero is the ground
state 1s^2, and the horizontal dashed line at 24.59 eV marks the first-ionization
threshold. (Inspired by Fig. 4.4 of Ref. [3]; data from Ref. [20])
The Coulomb integrals depend on $S$, clearly not through the spin wavefunction which has nothing to do with the purely spatial operator $V_{ee}$, but through the different electron–electron correlation in the $P_{12}$-symmetric ($S = 0$) or $P_{12}$-antisymmetric ($S = 1$) spatial wavefunction. In particular, Eq. (2.71) shows that the triplet wavefunction $\Psi^{S=1, M_S}_{n_1,l_1,m_{l_1}, n_2,l_2,m_{l_2}}(w_1, w_2)$ vanishes for $r_1 \to r_2$. On the contrary, the singlet wavefunction $\Psi^{S=0}_{n_1,l_1,m_{l_1}, n_2,l_2,m_{l_2}}(w_1, w_2)$ is finite at $r_1 = r_2$. Therefore, on average, the electrons in a spin-triplet state avoid each other more effectively than in the spin-singlet state with the same orbital quantum numbers. Indeed, Coulomb integrals are systematically smaller for $S = 1$ than for $S = 0$ states, as explicit evaluation of the integral (2.73) shows. This result accounts for the experimental observation that each triplet state always lies below the corresponding singlet (Fig. 2.17). This kind of Coulomb splitting between states which differ uniquely for their total spin, here $S = 0$ or 1, is called exchange splitting.

The perturbative approach presented here is useful mostly as a conceptual tool, to understand qualitative trends, and general concepts such as those listed above. Perturbation theory is relatively successful for the 2-electron atom, but for $N > 2$ electrons the repulsion that a given electron experiences from the other $N - 1$ electrons is comparable to the attraction generated by the nucleus, and any attempt to treat it as a small perturbation fails. A better approximate approach, based on a mean-field self-consistent evaluation of the electron–electron repulsion, yields fair quantitative accuracy for any $N$ and is commonly used to date. The reliability of this and similar self-consistent field methods have made them standard tools for understanding experiments and making predictions of atomic properties of matter from first principles.

### 2.2.4 The Hartree-Fock Method

The problem of describing at best the ground state of a $N$-electron problem in terms of a single Slater determinant belongs to the general framework of variational problems, see Appendix B.5. The simple idea is that the average energy $E^{\text{var}}[\alpha] = \langle \alpha | H_{\text{tot}} | \alpha \rangle$ of any state $| \alpha \rangle$ is greater than or equal to that of the ground state. The lower $E^{\text{var}}[\alpha]$ is, the closer $| \alpha \rangle$ gets to the ground state. When for $| \alpha \rangle$ we take a generic Slater determinant, the “best” state in its class is the result of the minimization of the energy

---

8 This means that the fixed-spin states include a degree of geometric correlation of the electronic motion induced by the symmetry properties of the spatial wavefunction. Employing a basis where the perturbation $V_{ee}$ is diagonal within each unperturbed degenerate space follows the same strategy as the adoption (Appendix B.8.1 and Sect. 2.1.7) of the $| l, s, j, m_j \rangle$ basis to have $H_{e-o}$ diagonal within the degenerate multiplets.
under arbitrary variations of the $N$ single-particle wavefunctions $\psi_{\alpha_i}$ composing the Slater determinant. We only require the $\psi_{\alpha_i}$ to remain mutually orthonormal $\int dw \psi_{\alpha_i}^\ast (w) \psi_{\alpha_j} (w) = \delta_{ij}$. In Eq. (2.74), the “one-particle term” $H_1(w) = \left[-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{|r|}\right] \otimes \mathbb{I}_{\text{spin}}$ would describe the individual motion of each electron in the field of the nucleus, and $v_{ee}(w, w') = \frac{e^2}{|r-r'|} \otimes \mathbb{I}_{\text{spin}}$ represents the electron–electron Coulomb repulsion of electrons at locations $r$ and $r'$.

Finding a minimum of $E^{\text{var}}$ is the problem of minimizing a functional, i.e. a function whose independent variables are (a set of) functions. This constrained minimization problem is formally solved if the $\psi_{\alpha_i}$ satisfy the set of coupled nonlinear integro-differential equations called Hartree-Fock (HF) equations:

$$H_1(w) \psi_{\alpha}(w) + \sum_{\beta} |\psi_{\beta}(w')|^2 v_{ee}(w, w') dw' \psi_{\alpha}(w)$$

$$- \int \sum_{\beta} \psi_{\beta}^\ast (w') v_{ee}(w, w') \psi_{\beta}(w) \psi_{\alpha}(w') dw' = \varepsilon_{\alpha} \psi_{\alpha}(w).$$ (2.75)

Each numbered term in Eq. (2.75) derives from a corresponding term in the total energy (2.74). If one pretends that all $\psi_{\beta}$ functions are given known functions (rather than the unknown functions they really are), then equations (2.74) become linear in $\psi_{\alpha}$. These equations for $\psi_{\alpha}$ have then a Schrödinger-like form. Term 1 contains the kinetic energy plus the Coulomb attraction of the nucleus; term 2 represents the Coulomb repulsion of the average charge distribution of all electrons ($\sum_{\beta} |\psi_{\beta}(w')|^2$ represents the number-density distribution of the $N$ electrons at position $w'$); term 3 is a nonclassical nonlocal exchange term which, in particular, removes the unphysical repulsion of the electron with itself introduced by term 2 (observe that the $\alpha = \beta$ terms in the sums of terms 2 and 3 cancel).\(^\text{9}\) The HF equations realize a

\(^9\) In the $\beta$ sum of term 3, only $m_{s\beta} = m_{s\alpha}$ terms survive, as $v_{ee}$ is purely orbital and does not modify spin.
natural way to deal with the electron–electron repulsion as accurately as possible at the mean-field level.

Terms 2 and 3 of Eq. (2.75) depend explicitly on the (unknown) wavefunctions \( \psi_\beta \). The standard strategy (Fig. 2.18) for the solution of the HF equation is based on initially assuming that all \( \psi_\beta \) in Eq. (2.75) are known: start from some arbitrary initial set of \( N \) orthonormal one-electron wavefunctions, put them in place of all \( \psi_\beta \)'s in Eq. (2.75), thus generating a first approximation for the effective potential energy acting on the single electrons; solve (usually numerically) the linear equations for \( \psi_\alpha \); from the list of solutions, take the \( N \) eigenfunctions with lowest single-particle eigenenergy \( \varepsilon_\beta \); re-insert them into the equations (2.75) in place of the \( \psi_\beta \)'s thus generating a better approximation for the effective potential energy; iterate this procedure as long as needed. Usually, after several iterations (of the order of 10, depending on the starting \( \psi_\beta \)), self-consistency is reached, i.e. the wavefunctions do not change appreciably from one iteration to the next. The converged wavefunctions allow one to compute several observable quantities, and in particular the total HF energy given by Eq. (2.74). The sum of the nuclear potential plus the repulsion of the charge distribution of the other electrons represents the self-consistent potential energy \( V_{\text{HF}} \) driving the motion of the electrons.

Until now, no assumption has been made about the symmetry of \( V_{\text{HF}}(w) \), which is safe in a general context. In practice, a simplifying approximation is usually made when applying HF to atoms: that the electron charge distribution and therefore the self-consistent \( V_{\text{HF}} \) are spherically symmetric functions, like the attraction to the
nucleus $V_{ne}$. This approximation allows one to separate variables in Eq. (2.75), like in the Schrödinger problem for the one-electron atom, and write each HF single-particle solution $\psi_\alpha$ as the product of a radial wavefunction $R_{nl}(r)$ times a spherical harmonic $Y_{lm} \chi_{ms}(\sigma)$, as in Eq. (2.27). In the spherical approximation, one-electron wavefunctions are labeled by hydrogen-like quantum numbers $\alpha = (n, l, m_l, m_s)$: here quantum numbers $l, m_l, m_s$ label exactly the same angular and spin dependence as in Eq. (2.27) for the one-electron atom. In contrast, the radial wavefunctions $R_{nl}(r)$ differ from those of Eq. (2.13), and are usually determined numerically. Despite their differences, the HF radial functions and those of the one-electron atom share the following properties: (i) the number of radial nodes $(n-l-1)$ defines $n$, and (ii) near the nucleus $R_{nl}(r) \propto r^l$.

The $N$-electron ground state is built by filling the single-electron levels starting from 1s, 2s, 2p,... upward. As expected, the spherically symmetric self-consistent potential $V_{HF}(r)$ felt by each electron behaves as $\simeq (N - 1 - Z) e^2 / r$ for large $r$ and as $\simeq -Ze^2 / r$ for small $r$, see Fig. 2.19. Because the potential has not a simple Coulomb shape, the single-electron levels do not coincide with the energies of the one-electron atom, Eq. (2.10), and importantly their energy depends on $l$, not only on $n$. Indeed, an $ns$ orbital, with larger probability than $np$ near the nucleus (where the effective HF potential is more strongly attractive), is placed lower in energy. Thus the Hartree-Fock method accounts quite naturally for the observed $l$-ordering $ns$, $np$, $nd$,... of the single-electron levels observed in the atomic spectra (e.g. for He in Fig. 2.17). Moreover, the faster-than-Coulombic raise of the effective potential of many-electron atoms induces a $n$-dependence of the shell energy which is more rapid than the $n^{-2}$ of the one-electron atom.

Figure 2.20 reports the filled single-electron radial distribution associated to the HF wavefunctions for the Ar atom. The typical radii of the individual shells vary

---

**Fig. 2.19** A sketch of the radial dependence of the one-electron Hartree-Fock effective potential energy multiplied by $r$ for atomic oxygen, $N = Z = 8$ (solid line). This quantity interpolates between the hydrogen $-1$ value (dashed) at large distance, and the value $-8$ generated by the bare oxygen nucleus in the context of a O$^{7+}$ ion (dotted) at small distance.
Fig. 2.20  The radial distributions of a many-electron atom (Ar, \( N = Z = 18 \)) computed by means of the HF self-consistent method.  

(a) The radial probability distribution for each one of the filled single-electron states. Note that the characteristic radius of the innermost shell \( n = 1 \) is \( \approx a_0/Z \), while the outer filled shell \( (n = 3) \) is slightly larger than \( a_0 \).  

(b) The total radial probability distribution \( P(r) \) and effective integrated charge \( Z_{\text{eff}}(r) \) generating the effective one-electron HF potential acting on each electron (Data from Ref. [1]).

substantially with \( n \), from \( \approx a_0/Z \) of 1s, to a few times \( a_0 \) for the 3p valence shell. As a result, 3 peaks associated to each of the filled shells emerge prominently in the total probability distribution \( P(r) \), Fig. 2.20b.

The independent-electron self-consistent spherical-field HF model has become far more than just an approximation to the actual atomic state: it provides the ordinary language of atomic physics. The electron occupancies of the single-electron orbitals composing the Slater determinant with the largest overlap to the actual correlated many-electron atomic eigenstate are adopted routinely as a label of that eigenstate. For example, the standard notation for the electronic ground-state configuration of Mg is \( 1s^22s^22p^63s^2 \).
2.2.5 Electronic Structure Across the Periodic Table

Let us now examine electronic configurations across the periodic table in the light of the HF theory. The 1s\(^2\) ground configuration of He has total energy \(E_{1s^2}^{\text{tot}} = -77.8\) eV according to HF, \(\sim 1.2\) eV above the measured ground-state energy; the radial dependence of the one-electron wavefunction is of course nonhydrogenic. In Lithium, a third electron adds into 2s (configuration 1s\(^2\)2s). The HF ground-state total energy is \(-7.4328\) \(E_{\text{Ha}}\) [5], to be compared with the experimental (1\(^{\text{st}}\) + 2\(^{\text{nd}}\) + 3\(^{\text{rd}}\)) ionization energy 7.4755 \(E_{\text{Ha}}\), with an error of about 1 eV. The first ionization potential can be computed by subtracting the total energy given by a self-consistent calculation for the positive ion, \(N = Z - 1\): for Li, one obtains a ionization potential of 5.34 eV, in good accord with the experimental value 5.39 eV. This value is much smaller than that of He (24.59 eV). The reason is that the binding of the \(n = 2\) shell is much weaker than 1s. Beryllium has a 1s\(^2\)2s\(^2\) ground state. For all these atoms \((N \leq 4)\) involving only s orbitals, the spherical approximation is appropriate.

Starting from Boron, electrons occupy progressively a degenerate p sub-shell: as the p orbitals are non spherically symmetric, the spherical approximation for the self-consistent field is questionable. The 2p sub-shell is completely filled as Neon \((N = Z = 10)\), the next noble gas, is reached. Again Ne is a spherically symmetrical atom, since \(\sum |Y_{l,m_l}(\theta, \phi)|^2\) is independent of \(\theta\) and \(\phi\). The ionization potential of Ne is again very large, but not as much as that of He (see Fig. 2.21). The next atom, Na, involves one electron in the 3s sub-shell, which is located much higher in energy than 2p. Again the ionization potential has a dip, as shown in Fig. 2.14, which can be interpreted as the starting of a new shell which is only weakly bound. As \(Z = N\) further increases, the filling of the \(n = 3\) shell proceeds fairly smoothly, with 3s and 3p becoming more and more strongly bound until the next noble gas Ar is reached.\(^{10}\) For \(Z\) this large, the \(l\)-dependence of the single-particle HF energy is so strong that the HF self-consistent field puts the 4s sub-shell lower than 3d. Indeed experiment shows that potassium has ground state 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)4s rather than 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)3d. The physical properties of this atom are similar to those of other alkali metals (Li, Na).

After filling 4s at \(Z = 20\) (Ca), and before involving 4p, electrons start to fill the 3d shell. Note however a few inversions (as in Cr and Cu) indicating that 4s and 3d are very close in energy, and subtler effects of electron correlation play a relevant role. Further intersections associated to a strong \(l\)-dependence of energy occur as 4d, 4f and 5d are being filled, as reported in the periodic table. Similar properties of all elements with a given number of s or p electrons in the outermost shell suggest the overall arrangement of the periodic table. The “low-energy” properties of atoms

\(^{10}\) For argon, \(Z = 18\), the HF approximation finds a total energy of \(-526.817\) \(E_{\text{Ha}}\), which is 0.791 \(E_{\text{Ha}} = 21.5\) eV in excess of the experimental energy [21]. The absolute error is rather large, which indicates that the neglect of dynamical correlations in the electronic motion is a serious drawback of HF. However, the relative error is \(\sim 0.15\)% only, and the excess energy per electron amounts to approximately 1 eV, indicating that this mean-field approximation captures the bulk of the electron–electron repulsion.
Fig. 2.21 An energy diagram comparing the observed ground state and lowest excitations of the $1 \leq Z \leq 11$ atoms. The zero of the energy scale (top of the figure) is set for each atom at the ground energy of the monocation. The energy spread of the atomic multiplets for fixed configuration, highlighted by the *vertical arrows*, is due to Coulomb exchange and correlation energy.

The size of the atoms (a not especially well-defined property) computed with HF is in relatively good accord with the empirical trends of Fig. 2.15. In particular, noble gases are especially small and alkali atoms especially large relative to other atoms of similar $Z$; on the whole, the size of neutral atoms tends to increase slowly with $Z$. Cations (=positive ions) can be produced with any charge $Z - N$; the size of these species decreases as shells empty up and screening is less and less effective. A cation with $N$ electrons often exhibits the same formal ground electronic configuration as the neutral atom ($Z = N$): this holds especially for small charging, $N \approx Z$. However all single-electron wavefunctions shrink closer to the nucleus in cations than in the neutral atom. Anions (=negative ions) are stable in gas phase only for certain atoms and only up to a maximum charging of 1 electron (i.e. $N \leq Z + 1$). The HF model signals that a certain ionic configuration is unstable by never reaching self consistence. The HF stability or lack thereof often agrees with experiment.
For example all halogens (F, Cl, Br, I, At), thanks to their almost complete relatively “deep” in energy np\textsuperscript{5} shell (Fig. 2.21), have positive electron affinity (defined as the ionization potential of the negative ion), which means that their negative ion is stable against the loss of the extra electron.

Beside ionic states, HF permits also to compute (to some extent) excited states and excitation energies. For example, after computing the ground-state properties of Na, by filling the \( N = 11 \) lowest single-electron levels as 1s\(^2\)2s\(^2\)2p\(^6\)3s, one could run a new self-consistent calculation putting the 11th valence electron in 3p rather than in 3s (configuration 1s\(^2\)2s\(^2\)2p\(^6\)3p). The self-consistent field turns out different, and the total energy is larger. The difference in total energy between the two calculations is a fair estimate of the excitation energy, here of the 3s\( \rightarrow \)3p transition of Na, approximately 2 eV, see Fig. 2.24.

### 2.2.6 Fundamentals of Spectroscopy

The main observation needed to understand the spectra of many-electron atoms is that the dipole operator driving electromagnetic transitions is a one-electron operator. In concrete, it the sum of the individual dipoles of the single electrons:

\[
d = \sum_i d_i = -q_e \sum_i r_i. \tag{2.76}
\]

Consider initial and final states described in the HF model as two antisymmetrized states as in Eq. (2.61). Between two such states, the matrix element of one such operator is\(^{11}\)

\[
\langle \beta_1, \ldots, \beta_N | \sum_i d_i | \alpha_1, \ldots, \alpha_N \rangle^A
\]

\[
= \frac{1}{N!} \sum_{i} \sum_{P \ P'} (\beta_{P_1} | \alpha_{P'_1} \rangle \ldots (\beta_{P_i} | \alpha_{P'_i} \rangle \ldots (\beta_{P_N} | \alpha_{P'_N} \rangle
\]

\[
= \frac{1}{N!} \sum_{i \ P} \sum_{P\ P'} \delta_{P_1, P'_1} \ldots \delta_{P_{i-1}, P'_{i-1}} \langle \beta_{P_i} | d_i | \alpha_{P'_i} \rangle \ldots \delta_{P_N, P'_N}
\]

\[
= \frac{1}{N!} \sum_{i \ P} \langle \beta_{P_i} | d_i | \alpha_{P_i} \rangle = \sum_i \langle \beta_i | d_i | \alpha_i \rangle.
\]

\(^{11}\) The first simplification comes because all one-electron angular products vanish unless all \( \beta_{P_k} = \alpha_{P'_k} \). This statement is rigorous under the simplifying assumption that the single-electron basis states composing the initial state \( | \alpha_1, \ldots, \alpha_N \rangle^A \) are essentially equal to those composing the final state \( | \beta_1, \ldots, \beta_N \rangle^A \). The second simplification is due to the \( N - 1 \) Kronecker deltas forcing the \( P' \) permutation to match \( P \). The final elimination of the sum over \( P \) is due to this sum leading to \( N! \) copies of the same matrix elements.
This calculation relates the \(N\)-electron electric-dipole matrix element to that of one-electron states. When \(\langle \beta_i | d | \alpha_i \rangle\) vanishes, because it violates the one-electron electric-dipole selection rules of Sect. 2.1.9, the overall matrix element vanishes.

In concrete: dipole-allowed transitions occur only between \(N\)-electron states differing in one electron that makes a dipole-allowed transition, with the other \(N - 1\) electrons remaining in their initial single-particle state. With this condition, any of the \(N\) electrons in the initial states \(|\alpha_i\rangle\) can make its own transition to any initially empty state. The angular part of all one-electron wavefunction is a standard spherical harmonic \(Y_{lm}\). Therefore the electric-dipole selection rules (\(\Delta l = \pm 1, \Delta s = 0\)) derived for the one-electron atom in Sect. 2.1.9 continue to hold for the electron executing the transition. Here we report a few examples of allowed transitions of beryllium: \(1s^22s^2 \rightarrow 1s^22s2p\), \(1s^22s2p \rightarrow 1s^22s4d\), and \(1s^22s^2 \rightarrow 1s2s^23p\); and a few examples of forbidden transitions: \(1s^22s^2 \not\rightarrow 1s^22s3d\), \(1s^22s^2 \not\rightarrow 1s^22p^2\), and \(1s^22s^2 \not\rightarrow 1s2s2p3p\). Further rules discussed in Sect. 2.2.9 restrict dipole-allowed transitions depending on changes of total angular momenta obtained by coupling the spins and orbital angular momenta of individual electrons following the schemes of Sect. 2.2.8.3.

\section*{2.2.7 Core Levels and Spectra}

A result of HF theory is that the screening of the deep (strongly bound) single-particle levels is scarce, so that their energy is highly negative, and decreases essentially as \(\propto -Z^2\). Indeed, in the independent-electron language, it should be possible to excite electrons from the deep core levels \(1s, 2s, \ldots\) For example for Na, a configuration such as \(1s^12s^22p^63s^2\) could be investigated, where an inner \(1s\) electron has been promoted to the outer \(3s\) shell. Producing this state requires a huge excitation energy (of the order of \(40 \, E_H\)), to the extent that one might suspect that such a highly unbound state has no right to exist. Indeed, the atom in this state has plenty of electric-dipole-allowed transitions to get rid of big chunks of this excitation energy, to states at much lower energy, such as \(1s^22s^22p^53s^2\). According to Eq. (2.45), the decay transition rate is very large as it grows with the third power of the energy associated to the transition, which dominates over the reduction in dipole matrix element due to the small size of the initial shell, to a total \(\sim Z^{4-5}\) dependence—see Eq. (2.55). Accordingly, the spectral broadening due to the short lifetime of core states is often huge, exceeding \(h\gamma \approx 1\, \text{eV}\). Despite such huge broadening, core-hole states are not just a theoretical prediction of the independent-electron model, but they are routinely observed in UV and X-ray spectroscopies.

Many experiments probing core spectra with photons can be classified as absorption or emission, with the same conceptual scheme of Figs. 1.3 and 1.4. Absorption data (Fig. 2.22) show a remarkable regularity of the spectra above \(\approx 100\, \text{eV}\), and systematic changes of peak positions and intensities as \(Z\) is increased. A characteristic feature of X-ray absorption spectra is the asymmetry of the peaks, which exhibit a sharp edge at the low-energy side and a broad slow decrease at the high-energy side.
This edge occurs because below the minimum excitation energy for the core state no absorption takes place, while above threshold, the core electron may be promoted to several empty bound and unbound states of the atom (whether in gas or condensed phase), leading to continuum absorption. The slow intensity decay above edge is due to an increase of the ejected-electron kinetic energy (which equals the difference between the absorbed photon energy and the energy of the atomic excited core state): the final state becomes increasingly orthogonal to the initial core level, and correspondingly the dipole matrix element (2.46) decreases. For this same reason, an X-ray photon hitting an atom is much more likely to extract a core electron than a weakly-bound outer-shell electron.

Emission spectra show the same simplicity and regularity as absorption spectra. Initial atomic excitations are usually prepared by collisions with high-energy electrons. The subsequent emission involves transitions only from levels for which enough energy is made available by excitation. For example, if 2 keV electrons are used to excite the sample, emission involving the 1s shell is observed for all Z ≤ 14 (Si), but not for P and higher-Z atoms (see Fig. 2.22).

Yet another uncalled-for traditional notation haunts core states and X-ray spectra: a hole (=missing electron) in shell n = 1, 2, 3, 4,... is labeled K, L, M, N,... The substructures related to states of different l and j acquire a Roman counting subscript (e.g. L_{III} for 2p^2P_{3/2}), as in Fig. 2.23. Dipole-allowed transitions in emission are organized in series according to the initial shell, with a Greek-letter subscript for the final shell. For example, the transition K → L (in other words the decay 1s2s2p^6 \cdots → 1s2s2p^5 \cdots) produces the Kα emission line, K → M is Kβ, and L → M is Lα.

In the days of the great discoveries of chemistry and physics, when the structure and classification of atoms were being understood, H. G.-J. Moseley acquired and compared characteristic emission spectra of many elements: he showed that the Kα

---

**Fig. 2.22** The observed absorption coefficient of all atoms in the third row of the periodic table, showing, for increasing Z, the regular displacement of the K edge (at the right), and a gradual buildup of the L edge (at the left)
inverse wavelength (equivalently, energy) is roughly proportional to $Z^2$. This inverse wavelength fits an approximate phenomenological law:

$$\frac{1}{\lambda_{K\alpha}} \approx C (Z - a)^2. \quad (2.77)$$

In this phenomenological dependence, the proportionality constant $C$ is close to $E_{\text{Ha}}/(4\pi\hbar c) \simeq 1.097 \times 10^7 \text{ m}^{-1}$, and the quantity $a$, accounting for screening, is approximately 2. The discovery of this regularity permitted Moseley to identify the correct value of $Z$ of each atomic species, thus correcting several mistakes in the early attempts to construct the periodic table of the elements.

The decent accuracy of Moseley’s fit suggests that one could estimate the core-level energy positions (within, say, 20%) without going through a full self-consistent HF calculation. Indeed, the energy of a core level is close to that of a hydrogenic state in an effective $-Z_{\text{eff}} e^2/r$ Coulomb potential, where the value of $Z_{\text{eff}}$ is the average of the effective potential, like the curve of Fig. 2.19, weighted by the radial distribution $P(r)$ of the single-electron wavefunction of that level. Accordingly, the energy of a core shell can be estimated by means of Eq. (2.10), replacing $Z$ with $Z_{\text{eff}} \simeq Z - 2$ for the $K$ shell, $Z_{\text{eff}} \simeq Z - 10$ for the $L$ shell, and in general $Z_{\text{eff}} \simeq Z$ (number of electrons in inner shells up to and including the target shell).

Nowadays, X-ray spectroscopies are used routinely in research and applications, including position-sensitive analytic tools, local probes of the near chemical environment of different atomic species, and many others. Many more applications of X-ray spectroscopies are reported in the scientific literature and at the web sites of X-ray photon facilities [22].
2.2.8 Optical Spectra

The systematic regularity of the core spectra is lost rapidly when the visible and soft-UV range is explored. Different atoms exhibit vastly different spectra. A few trends and similarities can be recognized.

In the LS scheme, atomic states are labeled $^{2S+1}[L]_{J}$ to collect their total angular momenta. An optional “o” apex can be added to indicate that the overall parity $(-1)\sum_{J}l_{J}$ of that state is odd.

2.2.8.1 Alkali Atoms

The alkali atoms have $Z-1$ electrons filling a number of close shells (=completely filled shells) which are energetically well separated ($\sim 20$ eV) from the outermost half-occupied $n_{0}s$ level. The latter is very shallow, with a binding energy ranging from 5.4 eV in Li to 3.9 eV in Cs. The electrons in the inner shells form an essentially “frozen” spherically symmetric core (null spin and orbital angular momentum), which provides an effective potential (Fig. 2.19) for the motion of the outer electron. Like for hydrogen, the ground-state label is $^2S_{1/2}$, because the angular momenta of the alkali atoms coincide with those of the valence electron.

The outer electron is the protagonist of all excitations in the optical spectra of the alkali elements. These spectra resemble the spectrum of a one-electron atom, the main difference being the sizable energy gaps between states characterized by the same $n$ but different $l$, see Fig. 2.24. In both emission and absorption, dipole-allowed optical transitions appear as diagonal lines in such level schemes, namely $s\leftrightarrow p$, $p\leftrightarrow d$, and $d\leftrightarrow f$, like in Fig. 2.17. A characteristically bright transition in the visible (Li and Na) or near IR (K, Rb, and Cs) spectrum originates from the $\sim 2$ eV $n_{0}s\leftrightarrow n_{0}p$ separation, and finds no similarity in hydrogen. This $n_{0}s\rightarrow n_{0}p$ transition is especially intense due to the large electric-dipole matrix element involving strongly overlapping and fairly extended wavefunctions.

Spin-orbit affects all non-s states. The natural generalization of Eqs. (2.32) and (2.35) to a generic radial potential yields a microscopic estimate of the relevant $\xi_{nl}$ for a given shell:

$$\xi_{nl} = \frac{\hbar^2}{2m_c^2\alpha^2} \left\langle n, l \right| \frac{1}{r} \frac{dV_{\text{eff}}(r)}{dr} \left| n, l \right\rangle = Z_{\text{eff}}^{s-o} \alpha^2 E_{\text{Ha}} \frac{1}{n^3(l+1)(2l+1)}.$$  

(2.78)

where $Z_{\text{eff}}^{s-o}$ is implicitly defined by this equation and provides rough estimates of $\xi_{nl}$. Due to the strong localization of the mean field $r^{-1} dV_{\text{eff}}(r)/dr$ near the origin, the effective charge $Z_{\text{eff}}^{s-o}$ is usually larger than that introduced above for the estimate of the level position: $Z_{\text{eff}} < Z_{\text{eff}}^{s-o} < Z$. The spin-orbit level splittings induces splittings of all optical transitions. Table 2.2 reports the observed spin-orbit splittings of the lowest excited $p$ state of the alkali atoms. These splittings are generally larger than those of H: for example the 3p splitting originates a well-resolved
2.2 Many-Electron Atoms

Fig. 2.24 The observed level scheme of lithium and sodium, compared to the levels of hydrogen. For a easier comparison, for each atom the scale reference energy is set at the ground state of its monocation, like in Fig. 2.21. Note the significant dependence of energy not only on \( n \) but also on \( l \). The \( 2s \leftrightarrow 2p \) transition of Li (red lines at 670.776 and 670.791 nm) and the \( 3s \leftrightarrow 3p \) transition of Na (yellow ”D-lines” at 588.995 and 589.592 nm) are characteristically bright optical transitions in the visible range (Data from Ref. [20]).

![Energy levels of Li and Na compared to H](image)

Table 2.2 The spin-orbit splittings and effective charge of the lowest excited p level of the alkali atoms

<table>
<thead>
<tr>
<th>Element</th>
<th>H</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Z )</td>
<td>1</td>
<td>3</td>
<td>11</td>
<td>19</td>
<td>37</td>
<td>55</td>
</tr>
<tr>
<td>Single-electron excited level ( np )</td>
<td>2p</td>
<td>2p</td>
<td>3p</td>
<td>4p</td>
<td>5p</td>
<td>6p</td>
</tr>
<tr>
<td>Spin-orbit splitting ( \frac{1}{2} \xi_{np} ) (meV)</td>
<td>0.045</td>
<td>0.042</td>
<td>2.1</td>
<td>7.2</td>
<td>29.5</td>
<td>68.7</td>
</tr>
<tr>
<td>( Z_{eff} s-o )</td>
<td>1</td>
<td>0.98</td>
<td>3.5</td>
<td>6.0</td>
<td>10.0</td>
<td>14.2</td>
</tr>
</tbody>
</table>

doublet structure in the optical spectrum of sodium vapors (the characteristic yellow 3s–3p lines of wavelengths 588.99 and 589.59 nm). Remarkably, the spin-orbit splitting of Li 2p is smaller than that of H 2p: the reason is that most of the Li 2p wavefunction lies well outside the compact 1s screening shell.

The fine-structure splittings of higher excited non-s states are smaller than those of the \( n0p \) states, see Fig. 2.25. In the Li spectrum all doublets are split with the smaller \( J \) at lower energy, as expected by \( \xi_{nl} > 0 \), Eq. (2.78). However, the spectra of Na and K display an inverted splitting of the \( l \geq 2 \) doublets, due to nontrivial exchange and correlation effects (neglected in the mean-field HF approximation) of the valence and core electrons [6] prevailing over the weak spin-orbit interaction.
Fig. 2.25  The fine structure of a few low-energy excited levels of sodium. All splittings are widely expanded to make them visible. The regular $P_{1/2} - P_{3/2}$ splitting of the p states is governed by the spin-orbit interaction. Note the inverted splitting of the $D_{5/2} - D_{3/2}$ doublets. The reference energy is the same as in Fig. 2.24.

Within the HF model, Eq. (2.78) can be used to estimate the spin-orbit energy $\xi_{nl}$ for any shell of any atom, not just for the excited shells of alkali atoms. For example, the large effective $Z_{\text{eff}}$ accounts for the colossal spin-orbit splittings (tens or hundreds eV) of the core shells of heavy atoms, observed in X-ray spectra (e.g. the $L_{\text{II}} - L_{\text{III}}$ splitting shown in Figs. 2.22 and 2.23).

2.2.8.2 Atoms with Elementary Ground States

For a number of atoms, the occupancies of the single orbitals are sufficient to determine uniquely all global symmetry properties of the atomic ground state, in particular its total angular momentum $J$ (thus its degeneracy).

The ground-state symmetry of noble gases, alkali earth and, in general, all atoms in close-shell configurations, including Zn, Cd, Hg, Yb, and No is trivial, as all orbital and spin angular-momentum component cancel: these atoms all qualify as nondegenerate spherically symmetric $1S_0$.

Likewise, the ground state of alkali metals is simply $2S_{1/2}$, with a twofold degeneracy associated to spin, but no orbital degeneracy.

B, Sc, and atoms in the same groups IIIIB and IIIA, with a single electron in a degenerate p or d shell (and all inner shells complete), are only marginally more complicated: here the total spin and orbital angular momenta equal those of the lone electron. Spin-orbit coupling splits the two levels with $J = L \pm 1/2$, putting $J = L - 1/2$ lower. Accordingly, the ground state of B is $2P_{1/2}$ and that of Sc is $2D_{3/2}$.

The last relatively simple class is that of the halogen atoms (group VIIIB, $p^5$ configuration), characterized by a single hole in an otherwise full shell. Here, unsurprisingly, this hole carries the same spin and orbital angular momentum ($S = 1/2$ and $L = 1$) as one electron in that shell. However, the effective spin-orbit interaction for
the hole is reversed in sign. Once this is agreed upon, the ground-state symmetry of all halogens is $2P_{3/2}$. Similarly, the symmetry of the $4f^{13}$ ground state of Tm is $^2F_{7/2}$.

### 2.2.8.3 Atoms with Incomplete Degenerate Shells

Things get intricate when several electrons occupy a degenerate shell, but are too few to fill it completely. The HF independent-electron quantum state usually predicts incorrect degeneracies. For example, the two 2p electrons of carbon can settle in any of the 15 Slater-determinant states sketched in Fig. 2.26. HF puts all the six $M_S = \pm 1$ states of the leftmost and rightmost column at the same energy, and the remaining nine $M_S = 0$ states in the three central columns at a higher energy. This splitting is due to the exchange term in Eq. (2.75). However, the actual ground state of C is not 6-fold degenerate! The $M_S = \pm 1$ are the high-$|S_z|$ components of a $^3P$ spin and orbital triplet, consisting of $3 \times 3 = 9$ states. The three missing $M_S = 0$ states could be obtained as suitable linear combinations of the nine $M_S = 0$ Slater determinant, which, as such, are not $S^2$ eigenstates. These combinations are not single Slater determinants, and therefore the HF method cannot be applied to these combinations.
Fig. 2.27 The observed ordering of the $p^2$ multiplets of carbon and silicon follow Hund’s rules. Labels adopt the LS coupling scheme. Degeneracies $(2J + 1)$ are indicated at the left without specific adaptations. The 6 remaining $M_S = 0$ combinations are excited states, identified in Fig. 2.27. The splittings among these states is due to mechanisms discussed in the following.

In general, $N$ electrons can occupy $d = 2(2l+1)$ degenerate spin-orbitals in \( \binom{d}{N} \) different ways, corresponding to physically different (orthonormal) quantum states. The degeneracy of these states is partly (but generally incorrectly) lifted by the HF method. In an actual atom, the splitting of these multiplets is governed by (i) Coulomb exchange (mostly accounted for by HF) and correlation (i.e. the effects of the residual electron–electron interaction ignored at the HF level, inducing correlated electronic motion), and (ii) the spin-orbit interaction.

In the outer atomic shells and for $Z$ smaller than $\sim 30$, spin-orbit energy is a comparatively small ($\xi \ll 1$ eV) and thus initially negligible interaction. Coulomb repulsion induce much larger splittings of the order of one to several eV (see the He results, Sect. 2.2.3). The Coulomb interaction (and also its residual part, i.e. the part not accounted for by the HF mean field) is spherically symmetric: it thus commutes with total $|S|^2$ and $|L|^2$. These operators thus provide a proper labeling of states in the degenerate state. Table 2.3 reports a complete list of the “multiplet” states labeled by their total spin and orbital angular momentum.

Coulomb exchange&correlation acts on the degenerate HF states very much like the full Coulomb repulsion does in He (Sect. 2.2.3). It first of all splits states of different total spin $S$: low-spin states sit higher in energy because the correlated motion of the electrons takes them, on average, nearer to one another. The ground state will therefore have the highest possible spin: this result agrees with the empirical first Hund’s rule.

In degenerate configurations there can occur several states of the same $S$, but different orbital angular momentum $L$. Electrons avoid one another more efficiently when they rotate all together cooperatively, in states with high $L$. Accordingly, the state with the largest possible $L$ among those with given $S$ sits lowest in energy. This is known as second Hund’s rule.

Finally, once the total $L$ and $S$ are determined, the hitherto neglected spin-orbit interaction couples them together to a total angular momentum $J$. The allowed values of $J$ are given by the usual rule (B.72), and the question of which of them is lowest in energy is decided by the sign of the effective spin-orbit parameter for that partly filled shell. While the true spin-orbit parameter is necessarily positive [see Eq. (2.78)],
Table 2.3 All terms into which Coulomb exchange&correlation splits a degenerate $|l|^{N}$ configuration, for $l = 0$ to 3 and all possible fillings $N$

| $|l|^{N}$ | $S = 0$ | $1/2$ | 1 | $3/2$ | 2 | $5/2$ | 3 | $7/2$ |
|---|---|---|---|---|---|---|---|---|
| s | $2S$ | | | | | | | |
| p, p$^5$ | $2P$ | | | | | | | |
| p$^2$, p$^4$ | $^1SD$ | $^3P$ | | | | | | |
| p$^3$ | $^2PD$ | $^4S$ | | | | | | |
| d, d$^9$ | $^2D$ | | | | | | | |
| d$^2$, d$^8$ | $^1SDG$ | $^3PF$ | | | | | | |
| d$^3$, d$^7$ | | | $^2PDFGH$ | | | $^4PF$ | | |
| | | 2 | | | | | | |
| d$^4$, d$^6$ | $^1SDFGI$ | | | | | | | $^5D$ |
| | | | | | | | | |
| d$^5$ | | | | $^2SPDFGH$ | | $^4PDFG$ | | $^6S$ |
| | | | | | | | | |
| f, f$^{13}$ | | | | | | $^2F$ | | |
| f$^2$, f$^{12}$ | $^1SDGI$ | | | | | | $^3PFH$ | |
| f$^3$, f$^{11}$ | | | $^2PDFGHKL$ | | | $^4SDFGI$ | | |
| | | | | | | | | |
| f$^4$, f$^{10}$ | $^1SDFGHIKLN$ | | | | | $^3PDFGHKLM$ | | $^5SDFGI$ |
| | | | | | | | | |
| f$^5$, f$^{9}$ | | | $^2PDFGHIKLMO$ | | | $^4SPDFGHKLM$ | | $^6PFH$ |
| | | | | | | | | |
| f$^6$, f$^{8}$ | $^1SDFGHIKLMNOQ$ | | | | | | $^3PDFGHKLMNO$ | | $^5SPDFGHIKL$ | | $^7F$ |
| | | | | | | | | | | | | |
| f$^7$ | | | | $^2SDFGHIKLMNOQ$ | | $^4SPDFGHIKLMN$ | | $^6PDFGH$ | | $^8S$ |
| | | | | | | | | | | | | |

When several states with the same $2S+1|L|$ occur in the configuration, the number of occurrences is noted below the letter $|L|$ denoting the total orbital angular momentum. In LS (Russell-Saunders) coupling, weak spin-orbit interaction splits further states characterized by different $J$, e.g. $^2P \rightarrow ^2P_{1/2}, ^2P_{3/2}$, not detailed here. After Ref. [5]
the effective parameter for the coupling of total $L$ with total $S$ may as well be negative, as discussed above for the halogens. Indeed the sign of the effective spin-orbit reverses when more than $2l + 1$ electrons occupy a shell with room for $2(2l + 1)$ electrons. Accordingly, the third Hund’s rule states that the lowest-energy state has $J = |L - S|$ for a less-than-half-filled shell and $J = L + S$ when the shell is more than half filled.

In the $p^2$ example, the 15 states of Fig. 2.26 combine themselves into 9 spin-orbit split triplet states $^3P_0$, $^3P_1$, $^3P_2$, plus 6 singlet states $^1D_2$, $^1S_0$. No other state is compatible with Pauli’s principle [1]. The Hund-rules ordering of these states is illustrated in Fig. 2.27.

Similar Hund-rules level ordering is usually observed also in configurations involving several incomplete shells, as occur in atomic excited states—see Fig. 2.28b. The observed multiplets of states corresponding to each configuration are scattered

---

**Fig. 2.28** The conceptual sequence of splittings of LS multiplets caused by interactions of decreasing strength. **a** The $6 \times (6 - 1)/2! = 15$ states of two “equivalent” electrons in a $np^2$ configuration, including Coulomb and spin-orbit splittings plus those induced by a weak external magnetic field (Zeeman limit). **b** The $6 \times 10 = 60$ states of two “nonequivalent” (different $n$ and/or $l$) electrons in a $3d4p$ configuration, as occurs in the spectrum of excited Ti.
over ranges shown as brackets in Fig. 2.21 for a few low-Z atoms. The low-energy multiplets scatter out by several eV, while more excited multiplets scatter less, because the Coulomb repulsion is smaller for more extended wavefunctions. Note also that Hund’s rules are phenomenological results, not exact laws of nature. Their predictions are occasionally violated. For example, for the 3d²4s² configuration of Ti Hund’s rules predict an ordering ³F < ³P < ¹G < ¹D < ¹S, while in reality ¹D lies below ³P.

The described scheme of coupling all \( s_i \) together to a total \( S \) and all \( l_i \) together to a total \( L \) (followed by spin-orbit coupling of \( S \) and \( L \) together) is called Russell-Saunders or LS coupling. It provides a satisfactory basis of coupled states for low-Z atoms, where Coulomb exchange and correlation dominates over spin orbit. For increasing \( Z \) the spin-orbit interaction grows rapidly, while electron–electron repulsion remains in the few eV range, and even weakens due to the valence orbitals spreading out. For very large \( Z \geq 50 \) spin-orbit dominates: \( H_{s-o} \) must be accounted for before Coulomb terms. The spin-orbit interaction couples the spin and orbital moment of each electron to an individual \( j_i = l_i \pm \frac{1}{2} \). These individual total angular momenta are then coupled to a total \( J \) by smaller Coulomb terms. This ordering of the couplings of the angular momenta is called jj coupling, and provides another basis for the many-electron states. While the LS basis is almost diagonal for small \( Z \), the jj basis is almost diagonal for large \( Z \) (see Fig. 2.29). For intermediate \( Z \), both basis are nondiagonal: the matrix of Coulomb exchange and correlation plus spin-orbit interaction should be diagonalized to express the proper eigenstates as linear combinations of the states of either basis.

**Fig. 2.29** A level correlation diagram, illustrating, for increasing \( Z \), the effect of the increasing relative magnitude of spin-orbit over Coulomb exchange and correlation energies: atomic spectra evolve from the pure LS coupling of carbon (\( Z = 6 \)) to the intermediate coupling (exchange & correlation and spin-orbit of the same order) of germanium (\( Z = 32 \)) to the jj coupling (dominating spin-orbit) of lead (\( Z = 82 \)).
2.2.8.4 Many-Electron Atoms in Magnetic Fields

When a uniform magnetic field acts on a many-electron atom, two very different behaviors are observed depending on whether the atom carries a magnetic moment or not. Atoms with total angular momentum $J = 0$ carry no permanent magnetic dipole available to align with the field: the field induces a small magnetic moment $\sim \mu_B (\mu_B B)/\Delta$, where $\Delta$ is the energy gap between the ground state and the lowest excitation. We will ignore such tiny effects. Instead, open-shell atoms with $J \neq 0$ carry a magnetic moment $\mu = -g_J\mu_B J/\hbar$, with a tendency to align to the field.

For LS coupling, the appropriate Landé g-factor $g_J$ is determined by Eq. (B.78), with the total angular momenta $J, L,$ and $S$ in place of the single-electron $j, l,$ and $s$. As discussed in Sect. 2.1.10, this total magnetic moment, derived by the coupling of orbital and spin contributions, is relevant in the limit of weak external magnetic field (Zeeman limit). In practical experiments this is the relevant limit for many-electron atoms, due to the $Z^4$ increase of the spin-orbit energy $\xi$, often exceeding the maximum field accessible in the lab (of the order of 10 T). Also the opposite strong-field (Paschen-Back) limit can be realized, since in highly-excited states, an electron close to dissociation is weakly affected by the nuclear field.

The simplest splitting pattern—three equally spaced lines, corresponding to $\Delta M_J = 1, 0$ and $-1$—is called regular Zeeman splitting. An example is shown in Fig. 2.30. It occurs when the initial and final g-factors are equal (typically $g = g_L = 1$). This in principle occurs when either $S = 0$ or $L = 0$. However, $L = 0$ is most unlikely, as the electron making the transition changes its $l$ by unity, thus transitions $L_i = 0 \rightarrow L_f = 0$ seldom occur. In practice, regular Zeeman splitting is observed in optical transitions between spin-singlet states ($S = 0$). In all other cases, the Zeeman spectrum shows more complicated patterns due to the different initial and final g-factors (anomalous Zeeman spectrum, see Fig. 2.31).

The most direct experiment to investigate the ground-state degeneracy and magnetic moment of many-electron atoms is the Stern-Gerlach one (Sect. 2.1.5). The amount of deflection of the atoms in a field gradient measures the $z$ component of the magnetic moment, and therefore the Landé g-factor $g_J$, according to Eq. (2.26):

![Fig. 2.30](image-url) A regular Zeeman spectrum, with its interpretation. It occurs in transitions between $S = 0$ states, which have the same initial and final Landé g-factors. For example, it is observed in the $2s3d^1D_2 \rightarrow 2s2p^1P_1$ emission of Be
\[ F_z = \mu_z \frac{\partial B_z}{\partial z} = -\mu_B \ g_J \ M_J \frac{\partial B_z}{\partial z}. \]  

(2.79)

The number of sub-beams into which the inhomogeneous field splits the original beam measures directly the number of allowed \( M_J \) values, i.e. the ground-state degeneracy \( 2J + 1 \).

### 2.2.9 Electric-Dipole Selection Rules

As discussed in Sect. 2.2.6, the main selection rule requires that a single electron jumps to another state satisfying

\[ \Delta l = \pm 1 \quad \text{(for the one electron making the transition).} \] 

(2.80)

A few extra electric-dipole selection rules for the total quantum numbers \( J, L \), and \( S \) of many-electron atoms in LS coupling also apply. They are summarized below:

- Parity changes \( \Delta S = 0 \)  
  (2.81)

- \( \Delta L = 0, \pm 1 \)  
  (2.83)
As both $S$ and $L$ are good quantum numbers only in the limit of very small spin-orbit, in practice selection rules (2.82) and (2.83) are only approximate.

Figure 2.29 draws the allowed transitions in characteristic examples of LS coupling and $jj$ coupling. In this latter scheme, specific dipole selection rules apply, which are described in advanced atomic-physics textbooks [6].

The present Chapter summarizes a few main concepts and experimental evidence in the field of atomic spectroscopy which, in the context of a general course in physics of matter, provide a minimal background and language for understanding and describing the microscopic atomic structure, which lays at the root of the physics of matter. Important conceptual points (e.g. the seniority scheme for the labeling of LS states when $L$, $S$ and $J$ are not sufficient), and modern spectroscopic techniques (e.g. Auger) are omitted altogether. These and other more advanced subjects, including countless analytic chemical and astrophysical applications of atomic physics, are dealt with in specific textbooks [5–7].

**Problems**

A ★ marks advanced problems.

2.1 A beam of oxygen atoms emerges from an oven with approximately equal populations of its $1s^22s^22p^2$ triplet states: $^3P_0$, $^3P_1$, $^3P_2$. The average kinetic energy is $E_{\text{kin}} = 0.2$ eV. These atoms are sent through a $l = 0.3$ m long Stern-Gerlach magnet, where a field gradient $\partial B/\partial z = 150$ T/m is present. Successively, the beam crosses a region of length $l' = 0.5$ m where the magnetic field is negligible. Compute the total number of beam components detected at the end of the SG apparatus and the distance between the most widely spaced components.

2.2 The two lowest electric-dipole optically allowed transitions starting from the ground state of the Ne atom are observed at energies 16.8 and 19.8 eV. Determine the electronic configuration and the corresponding spectroscopic term of both final excited states involved in these transitions. Describe how these absorption lines change if a uniform magnetic field of 1 T acts on a gaseous Ne sample.

2.3 Construct the scheme of the core levels of Sn, indicating the excitation energies in eV. The $K$ edge is observed at $\lambda_K = 0.425$ Å, and the wavelengths of the first two lines of the $K$ series are: $K_{\alpha} = 0.517$ Å, $K_{\beta} = 0.437$ Å. Evaluate the minimum excitation energy needed to observe the $L$ series emission lines after excitation. Evaluate the maximum kinetic energies of photoelectrons produced by the excitation of shells $K$, $L$, $M$ of Sn induced by 32 keV X rays.

2.4 Two hydrogen atoms are excited in the quantum states described by the following wavefunctions:
\[
(a) \quad \psi_{300} = \frac{1}{9\sqrt{3\pi} a_0^{3/2}} \left( 3 - 2 \frac{r}{a_0} + \frac{2 r^2}{9 a_0^2} \right) e^{-r/3a_0}
\]

and

\[
(b) \quad \psi_{210} = \frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta,
\]

where \(a_0\) is the Bohr radius. For each, evaluate the decay probability rate \(\gamma\) to the ground state

\[
\psi_{100} = \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}
\]

in the electric-dipole approximation.

[Recall that in this approximation \(\gamma_{if} = (3\pi \varepsilon_0)^{-1} \hbar^{-4} c^{-3} (\varepsilon_i - \varepsilon_f)^3 |\langle f | d | i \rangle|^2\), where the Cartesian components of \(d\) are \(-q_e r \sin \theta \cos \phi\), \(-q_e r \sin \theta \sin \phi\), and \(-q_e r \cos \theta\).]

2.5 The 7 valence electrons of the \(\text{Fe}^{+}\) ion in its ground state assume the configuration \(3d^6 4s\). Evaluate the ground-state magnetic moment and the number of components in which the spin-orbit interaction splits the lowest-energy (according to the first and second of Hund’s rules) degenerate configuration.

2.6 Determine the number of absorption lines that a gas-phase sample of atomic chlorine at 1,000 K exhibits in the \(3s^2 3p^5 (2P) \rightarrow 3s^2 3p^4 4s (2P)\) transition. Assume a significant thermal population of the excited state of the \(3s^2 3p^5 (2P)\) configuration, given that this excited state sits 109.4 meV above the ground state. If this sample is immersed in a static uniform magnetic field \(|B| = 1.5\ T\), how many distinct sub-lines does each of the lines determined above split into?

2.7 The three components of the ground configuration \(3d^2 4s^2 3\ F\) of atomic titanium are at energies 0, 0.02109, and 0.04797 eV. The absorption spectrum of Ti vapor at 1,000 K involves lines related to transitions starting from the ground-state components to \(3d^2 4s 4p\) levels, which are organized as three groups of states of total orbital angular momentum \(L = 2, 3\) and 4. Establish the quantum numbers of the final states of the electric-dipole allowed transitions in each of the three groups. Considering now uniquely the transitions starting from the ground state \(3\ F_2\), identify the most intense transition in each group.

2.8* Evaluate the magnitude of the magnetic moment \(|\mu|\) of atomic \(\text{Sc}, \text{V}, \text{and Mn}\) in their respective ground states \(3d 4s^2, 3d^3 4s^2, 3d^5 4s^2\). Beams of such atoms with equal kinetic energy are sent through one Stern-Gerlach apparatus. Identify for which of these three elements the least-deflected beam component is deflected the most.

2.9 A 30 keV X-ray beam hits a palladium target. Among the photoemitted electrons several are measured at values of kinetic energy: 5, 650, 26,396, 26,670, and 26,827 eV. Given these data, evaluate the core-shell energies of Pd, assign the departing shell for the electrons of the smallest kinetic energy and evaluate
the effective charge $Z_{\text{eff}}$ (with three significant digits) relevant for the motion of an electron in that shell, consistently with the measured photoelectron energies.

2.10 Helium atoms in the excited state 1s2s($^3S_1$) are generated and accumulated in a storage vessel for (on average) one hour. They leave it through a tiny orifice at an average speed 2,000 m/s, and into a Stern-Gerlach apparatus characterized by a length 0.5 m and a field gradient $\partial B/\partial z = 9 \text{T/m}$. Given that the lifetime $\tau$ of the metastable 1s2s($^3S_1$) state is 8,000 s, evaluate the fraction of deflected atoms with a $M_J = 1$ component of total angular momentum over the total number of atoms leaving the storage vessel in a given time. Evaluate also the angular deflection of that component.

2.11 A 10 keV photon beam hits a cesium target. Part of the photoemitted electrons is collimated by suitably placed slits and sent into a transverse-field analyzer characterized by $|B| = 0.1 \text{T}$. Electrons circulating with radii 2.3 and 3.2 mm. Based on these data, assign the core shells from which the electrons are emitted and evaluate their excitation energy.

2.12 * In the standard formulation of the hydrogen-atom problem, the nucleus is taken as a point charge producing a potential energy $V_{\text{Coul}}(r) = -e^2/r$ for the electron at distance $r$. In fact the nucleus has a finite size. Modeling it as a uniform sphere of positive charge, of radius $r_n = 0.9 \text{ fm}$, the potential energy changes to $V_{\text{true}}(r) = -3e^2/(2r_n) + e^2r^2/(2r_n^3)$ inside the nucleus (no change outside, of course). Evaluate the effect of this modification on the hydrogen ground-state energy to first order in perturbation theory. [Suggestion: approximate $\exp(x) \simeq 1$ when $|x| \ll 1$.]
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