Chapter 4
Hydrogen-Like Atom

Abstract As an illustration of the basic principles of the Schrödinger wave mechanics presented in the preceding chapter the bonded (stationary) states and the corresponding energy levels of the *one*-electron (hydrogenic) atom are determined analytically. First, the Hamiltonian of this *two*-particle, central-potential system is separated into parts describing the free movement of the *Center-of-Mass* (CM) and the internal motion of electron relative to nucleus, respectively. In the Cartesian CM coordinates $\boldsymbol{R} = (X, Y, Z)$ the eigenstates of the CM problem are the *plane waves* representing the common eigenvectors with the operator of the system overall momentum $\boldsymbol{P}$. The separation of the spherical coordinates $\boldsymbol{R} = (R, \theta, \phi)$ allows one to uniquely specify the *spherical-waves* of the CM motion as simultaneous eigenvectors of the compatible attributes of the CM angular momentum $\boldsymbol{L}$, viz., the square of its length (L^2) and the selected coordinate (L_z), thus expressing them as products of the associated spherical harmonic (angular part) and the spherical Bessel function (radial part). The analogous separation of the *internal* spherical coordinates $\boldsymbol{r} = (r, \vartheta, \varphi)$ expresses the eigenvectors (orbitals) of the relative-motion Hamiltonian as products of the angular functions representing the simultaneous eigenfunctions of the compatible (commuting) observables l^2 and l_z associated with the electron orbital angular momentum $\boldsymbol{l}$, called the orbital spherical harmonics (the associated Legendre polynomials), and the corresponding radial functions (the Laguerre polynomials). Selected properties of these stationary states and the atomic shell structure they determine are discussed, the relation to Bohr's model of the Old Quantum Theory is examined and the system of atomic units (a.u.), convenient in molecular applications, is introduced.

4.1 Separation of Hamiltonian and Center-or-Mass Motion

The hydrogen-like atom consists of an electron of mass m_e in position $\boldsymbol{r}_e$, which exhibits the elementary negative charge $-e$, moving around the positively charged nucleus $+Ze$ of mass M_n in position $\boldsymbol{R}_n$. It represents one of the very few prototype

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systems, the stationary states of which can be determined analytically by solving the associated eigenvalue problem of the system Coulombic Hamiltonian.

It is convenient to separate the movement of the *Center-of-Mass* (CM) of this *two*-particle system, $M = m_e + M_n$, with the coordinates $\boldsymbol{R} = (m_e\boldsymbol{r}_e + M_n\boldsymbol{R}_n)/M$ and momentum $\boldsymbol{P} = \boldsymbol{p}_e + \boldsymbol{P}_n$, where $\boldsymbol{p}_e$ and $\boldsymbol{P}_n$ denote the momenta of its two constituent parts, from the internal motion described by the electron position relative to nucleus, $\boldsymbol{r} = \boldsymbol{r}_e - \boldsymbol{R}_n$, and the associated relative momentum $\boldsymbol{p} = (M_n\boldsymbol{p}_e - m_e\boldsymbol{P}_n)/M \equiv \mu\dot{\boldsymbol{r}} \cong \boldsymbol{p}_e$, where the system reduced mass $\mu = m_eM_n/M \cong m_e$, due to the dominant mass of the heavy nucleus. This allows one to separate the contributions due to these two sets of coordinates/momenta in the classical Hamiltonian function combining the kinetic energies of individual particles and the potential energy due to their Coulomb interaction, $V(r) = -e^2/r$, which depends only on the interparticle distance $r = |\boldsymbol{r}|$:

$$\begin{aligned} H(\boldsymbol{r}_e, \boldsymbol{p}_e, \boldsymbol{R}_n, \boldsymbol{P}_n) &= \frac{1}{2m_e}p_e^2 + \frac{1}{2M_n}P_n^2 - \frac{e^2}{r} \\ &= \frac{1}{2M}P^2 + \left[\frac{1}{2\mu}p^2 - V(r)\right] = H_{\mathrm{CM}}(\boldsymbol{P}) + h(\boldsymbol{p}, \boldsymbol{r}), \end{aligned} \tag{4.1}$$

It should be observed that the CM movement is free (there is no potential of forces acting on CM in H_{CM}) so that $\boldsymbol{P}$ is conserved in time.

These additive contributions to the classical Hamiltonian function give rise to the corresponding energy operators in the position representation [see (3.35) and (3.37)]:

$$\begin{aligned} \hat{\mathrm{H}}(\boldsymbol{R}, \boldsymbol{r}) &= \frac{\hat{\mathbf{P}}^2(\boldsymbol{R})}{2M} + \left[\frac{\hat{\mathbf{p}}^2(\boldsymbol{r})}{2\mu} + V(r)\right] = \frac{-\hbar^2}{2M}\Delta_{\boldsymbol{R}} + \left[\frac{-\hbar^2}{2\mu}\Delta + V(r)\right] \\ &\equiv \hat{\mathrm{H}}_{\mathrm{CM}}(\boldsymbol{R}) + \hat{\mathrm{h}}(\boldsymbol{r}). \end{aligned} \tag{4.2}$$

Here, the separate Hamiltonians $\hat{\mathrm{H}}_{\mathrm{CM}}(\boldsymbol{R})$ and $\hat{\mathrm{h}}(\boldsymbol{r})$, respectively, denote the energy operators of the free movement of CM and of the relative motion of the electron in the field of its nuclear attractor.

Therefore, the stationary Schrödinger equation (3.104)

$$\hat{\mathrm{H}}(\boldsymbol{R}, \boldsymbol{r})\Phi(\boldsymbol{R}, \boldsymbol{r}) = E\Phi(\boldsymbol{R}, \boldsymbol{r}), \tag{4.3a}$$

where the amplitude wave function is given by the product

$$\Phi(\boldsymbol{R}, \boldsymbol{r}) = \Psi_{\mathrm{CM}}(\boldsymbol{R})\psi(\boldsymbol{r}) \tag{4.3b}$$

which separates the two sets of coordinates, reduces into two simpler eigenvalue problems for the two additive energy components:

$$\hat{\mathrm{H}}_{\mathrm{CM}}(\boldsymbol{R})\Psi_{\mathrm{CM}}(\boldsymbol{R}) = E_{\mathrm{CM}}\Psi_{\mathrm{CM}}(\boldsymbol{R}) \quad \text{and} \quad \hat{\mathrm{h}}(\boldsymbol{r})\psi(\boldsymbol{r}) = \varepsilon\psi(\boldsymbol{r}). \tag{4.4}$$

The system total energy is then given by the sum of their eigenvalues,

$$E = E_{\mathrm{CM}} + \varepsilon, \tag{4.3c}$$

measuring the sharply defined kinetic energy E_{CM} of the free motion of the system as a whole, and the internal energy ε of the relative motion of electron around nucleus.

Obviously, in the Cartesian coordinate system $\boldsymbol{R} = (X, Y, Z)$ the kinetic energy operator $\hat{\mathrm{H}}_{\mathrm{CM}}(\boldsymbol{R})$ commutes with the system overall momentum operator $\hat{\mathbf{P}}(\boldsymbol{R})$, since the square of an operator commutes with the operator itself. Therefore, the solutions of the first of these two Schrödinger equations can be sought as eigenfunctions of $\hat{\mathbf{P}}(\boldsymbol{R})$, i.e., as the states corresponding to the sharply specified momentum, represented by the plane waves of (2.76):

$$\Psi_{\mathrm{CM}}(\boldsymbol{R}) = (2\pi\hbar)^{-3/2}\exp(i\boldsymbol{K}\cdot\boldsymbol{R}), \quad \boldsymbol{K} = \boldsymbol{P}/\hbar, \quad E_{\mathrm{CM}} = \hbar^2K^2/(2M). \tag{4.5}$$

Indeed, operators $\hat{\mathrm{H}}_{\mathrm{CM}}$ and $\hat{\mathbf{P}}$ constitute one of the complete sets of observables for the free motion of this CM "particle," with their common eigensolutions thus providing the full description of this global movement state in quantum mechanics.

4.2 Free Motion in Spherical Coordinates

The alternative set of the complete set of observables commuting with $\hat{\mathrm{H}}_{\mathrm{CM}}(\boldsymbol{R})$ involves the compatible pair of operators associated with the system overall angular momentum $\boldsymbol{L} = \boldsymbol{R} \times \boldsymbol{P}$, say $\hat{\mathbf{L}}^2$ and $\hat{\mathrm{L}}_Z$, $[\hat{\mathbf{L}}^2, \hat{\mathrm{L}}_Z] = 0$ [see (3.71)], which can also be shown to commute with the CM Hamiltonian:

$$[\hat{\mathrm{L}}^2, \hat{\mathrm{H}}_{\mathrm{CM}}] = [\hat{\mathrm{L}}_Z, \hat{\mathrm{H}}_{\mathrm{CM}}] = 0. \tag{4.6}$$

Expressing $L = |\boldsymbol{L}|$ in terms of the lengths of the two defining vectors and the angle α between them gives:

$$L^2 = (RP\ \sin\alpha)^2 = R^2P^2[1 - (\cos\alpha)^2] = R^2P^2 - (\boldsymbol{R}\cdot\boldsymbol{P})^2 \equiv R^2(P^2 - P_R{}^2), \tag{4.7}$$

where $P_R = (\boldsymbol{R}/R)\cdot\boldsymbol{P} \equiv \boldsymbol{e_R}\cdot\boldsymbol{P}$ measures the *radial* component of the total momentum $\boldsymbol{P}$, i.e., its projection onto the unit vector $\boldsymbol{e_R} = \boldsymbol{R}/R$. It can then be verified that the kinetic energy of the CM

$$H_{\mathrm{CM}}(\boldsymbol{P}) = \frac{1}{2M}P^2 = \frac{1}{2M}P_R^2 + \frac{1}{2MR^2}L^2. \tag{4.8}$$

Let us further recall that all quantum mechanical observables must be Hermitian. Therefore, as the momentum operator does not commute with $\boldsymbol{e_R}$ [see (3.56)], in forming the quantum operator corresponding to P_R, one has to symmetrize the defining product, $P_R = ½(\boldsymbol{e_R}\cdot\boldsymbol{P} + \boldsymbol{P}\cdot\boldsymbol{e_R})$, which assures the Hermitian character of the associated operator for the radial component of the overall momentum in the position representation:

$$\hat{\mathrm{P}}_R(\boldsymbol{R}) = \tfrac{1}{2}[\boldsymbol{e_R}\cdot\hat{\mathbf{P}}(\boldsymbol{R}) + \hat{\mathbf{P}}(\boldsymbol{R})\cdot\boldsymbol{e_R}] = -\frac{i\hbar}{2}(\boldsymbol{e_R}\cdot\nabla_{\boldsymbol{R}} + \nabla_{\boldsymbol{R}}\cdot\boldsymbol{e_R}). \tag{4.9}$$

The first part in parentheses measures the component of $\hat{\mathbf{P}}(\boldsymbol{R})$ in direction $\boldsymbol{R}$, which in the spherical coordinates $\boldsymbol{R} = (R, \theta, \phi)$ amounts to the radial differentiation operator

$$\boldsymbol{e_R}\cdot\hat{\mathbf{P}}(\boldsymbol{R}) = -i\hbar\frac{\boldsymbol{R}}{R}\cdot\frac{\partial}{\partial\boldsymbol{R}} = -i\hbar\frac{\partial\boldsymbol{R}}{\partial R}\cdot\frac{\partial}{\partial\boldsymbol{R}} = -i\hbar\frac{\partial}{\partial R}. \tag{4.10}$$

Therefore, the action of $\hat{\mathrm{P}}_R(\boldsymbol{R})$ on the continuous function $f(\boldsymbol{R})$ gives:

$$\begin{aligned}\hat{\mathrm{P}}_R f &= -\frac{i\hbar}{2}\left(\frac{\partial f}{\partial R} + \boldsymbol{e_R}\cdot\nabla_{\boldsymbol{R}}f + f\,\nabla_{\boldsymbol{R}}\cdot\boldsymbol{e_R}\right) = -i\hbar\left(\frac{\partial f}{\partial R} + \frac{f}{R}\right)\\ &= \left(-i\hbar\frac{1}{R}\frac{\partial}{\partial R}R\right)f,\end{aligned} \tag{4.11}$$

thus identifying the radial momentum operator

$$\hat{\mathrm{P}}_R(\boldsymbol{R}) = -i\hbar\frac{1}{R}\frac{\partial}{\partial R}R. \tag{4.12}$$

To summarize, in the adopted spherical coordinates the CM Hamiltonian, which represents in quantum mechanics the physical quantity of (4.8) reads:

$$\hat{\mathrm{H}}_{\mathrm{CM}}(R,\theta,\phi) = \frac{-\hbar^2}{2M}\Delta_{\boldsymbol{R}} = \frac{1}{2M}\hat{\mathrm{P}}_R^2 + \frac{1}{2MR^2}\hat{\mathrm{L}}^2. \tag{4.13}$$

Using next the explicit form of the Laplacian in spherical coordinates,

$$\Delta_{\boldsymbol{R}} = \nabla_{\boldsymbol{R}}^2 = \left(\frac{1}{R}\frac{\partial}{\partial R}R\right)^2 + \frac{1}{R^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right], \tag{4.14}$$

one identifies

$$\hat{\mathrm{L}}^2(\theta,\phi) = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{4.15}$$

In addition, by a straightforward chain-rule transformation of derivatives in (3.70), one finds:

$$\hat{\mathrm{L}}_Z(\phi) = -i\hbar\frac{\partial}{\partial\phi}. \tag{4.16}$$

Therefore, it directly follows from (4.13) and (4.15) that the first commutation relation of (4.6) indeed holds, $\left[\hat{\mathrm{L}}^2,\, \hat{\mathrm{H}}_{\mathrm{CM}}\right] = 0$, since $\hat{\mathrm{L}}^2$ commutes with itself and does not act on the radial coordinate R, thus also commuting with the first, radial part of $\hat{\mathrm{H}}_{\mathrm{CM}}(R,\theta,\phi)$. The second commutation relation of (4.6) directly follows from the commutation relations between observables representing the Cartesian components of $\boldsymbol{L}$ [see (2.34)]:

$$\begin{aligned}
[\hat{\mathrm{L}}^2, \hat{\mathrm{L}}_Z] &= [\hat{\mathrm{L}}_X^2 + \hat{\mathrm{L}}_Y^2 + \hat{\mathrm{L}}_Z^2, \hat{\mathrm{L}}_Z] = [\hat{\mathrm{L}}_X^2 + \hat{\mathrm{L}}_Y^2, \hat{\mathrm{L}}_Z] = [\hat{\mathrm{L}}_X^2, \hat{\mathrm{L}}_Z] + [\hat{\mathrm{L}}_Y^2, \hat{\mathrm{L}}_Z]\\
&= \hat{\mathrm{L}}_X[\hat{\mathrm{L}}_X, \hat{\mathrm{L}}_Z] + [\hat{\mathrm{L}}_X, \hat{\mathrm{L}}_Z]\hat{\mathrm{L}}_X + \hat{\mathrm{L}}_Y[\hat{\mathrm{L}}_Y, \hat{\mathrm{L}}_Z] + [\hat{\mathrm{L}}_Y, \hat{\mathrm{L}}_Z]\hat{\mathrm{L}}_Y\\
&= -i\hbar(\hat{\mathrm{L}}_X\hat{\mathrm{L}}_Y + \hat{\mathrm{L}}_Y\hat{\mathrm{L}}_X) + i\hbar(\hat{\mathrm{L}}_Y\hat{\mathrm{L}}_X + \hat{\mathrm{L}}_X\hat{\mathrm{L}}_Y) = 0,
\end{aligned} \tag{4.17}$$

where we have used the elementary commutators of (3.71):

$$[\hat{\mathrm{L}}_X, \hat{\mathrm{L}}_Z] = -i\hbar\hat{\mathrm{L}}_Y \quad \text{and} \quad [\hat{\mathrm{L}}_Y, \hat{\mathrm{L}}_Z] = i\hbar\hat{\mathrm{L}}_X.$$

It thus follows from (4.6) that the eigenfunctions $\Psi(R,\theta,\phi)$ of $\hat{\mathrm{H}}_{\mathrm{CM}}(R,\theta,\phi)$ should also satisfy the following simultaneous eigenvalue problems:

$$\begin{aligned}
&\hat{\mathrm{H}}_{\mathrm{CM}}(R,\theta,\phi)\Psi(R,\theta,\phi) = E_{\mathrm{CM}}\Psi(R,\theta,\phi), \quad E_{\mathrm{CM}} = \hbar^2K^2/(2M);\\
&\hat{\mathrm{L}}^2(\theta,\phi)\Psi(R,\theta,\phi) = L^2\Psi(R,\theta,\phi) \quad \text{and}\\
&\hat{\mathrm{L}}_Z(\phi)\Psi(R,\theta,\phi) = L_Z\Psi(R,\theta,\phi).
\end{aligned} \tag{4.18}$$

Hence, these common eigenfunctions can be written as products of the radial factor $f_{K,l}(R)$ and one of the angular momentum eigenfunctions $\{Y_l^m(\theta,\phi)\}$, called the *spherical harmonics*,

$$\Psi_{\mathrm{CM}}(R,\theta,\phi) = f_{K,l}(R)Y_l^m(\theta,\phi). \tag{4.19a}$$

The latter represent the common eigenfunctions of the two compatible angular momentum observables:

$$\begin{aligned}
&\hat{\mathrm{L}}^2(\theta,\phi)Y_l^m(\theta,\phi) = l(l+1)\hbar^2Y_l^m(\theta,\phi), \quad && l = 0,1,2,\ldots,\\
&\hat{\mathrm{L}}_Z(\phi)Y_l^m(\theta,\phi) = m\hbar\, Y_l^m(\theta,\phi), && m = -l, -l+1, \ldots, l-1, l,
\end{aligned} \tag{4.20}$$

where the integral quantum numbers l and m determine the allowed spectrum of these physical quantities: $L^2 = l(l+1)\hbar^2$ and $L_Z = m\hbar$.

Inserting the product function of (4.19a) into the Schrödinger equation (4.18) for the CM motion gives the following radial equation for $f_{K,l}(R)$:

$$\left[-\left(\frac{1}{R}\frac{d^2}{dR^2}R\right)+\frac{l(l+1)}{R^2}\right]f_{K,l}(R)=K^2 f_{K,l}(R), \tag{4.21}$$

where we have used the identity

$$\left(\frac{1}{R}\frac{d}{dR}R\right)^2=\frac{1}{R}\frac{d^2}{dR^2}R. \tag{4.22}$$

Upon substituting $z = KR$, this differential equation is transformed into the *spherical Bessel equation*,

$$\frac{d^2 f_{K,l}(z)}{dz^2}+\frac{2}{z}\frac{df_{K,l}(z)}{dz}+\left[1-\frac{l(l+1)}{z^2}\right]f_{K,l}(z)=0, \tag{4.23}$$

the regular solutions of which define the *spherical Bessel functions*:

$$j_l(KR)=\left(-\frac{R}{K}\right)^l\left(\frac{1}{R}\frac{d}{dR}\right)^l j_0(KR), \quad j_0(KR)=\frac{\sin(KR)}{KR}, \tag{4.24}$$

satisfying the following orthogonality relation for the continuous spectrum of K:

$$\int_0^\infty j_l(KR)j_{l'}(K'R)\,R^2dR=\frac{\pi}{2K^2}\delta(K-K')\delta_{l,l'}. \tag{4.25}$$

To summarize, it is natural in the spherical coordinate system to specify the stationary states of the free motion of the CM in the hydrogen-like atom as product of the spherical Bessel function and the spherical harmonic:

$$\Psi_{\mathrm{CM}}(R,\theta,\phi)=j_l(KR)Y_l^m(\theta,\phi). \tag{4.19b}$$

4.3 Eigenfunctions of Angular Momentum Operators

The spherical harmonics can be similarly factorized into eigenfunction of $\hat{\mathrm{L}}_Z(\phi)$,

$$\Phi_m(\phi)=(2\pi)^{-1/2}\exp(im\,\phi), \tag{4.26}$$

and the remaining factor $\Theta_l^m(\theta)$:

$$Y_l^m(\theta,\phi) = \Theta_l^m(\theta)\Phi_m(\phi). \tag{4.27}$$

Substituting this expression into (4.20) and using the explicit form (4.15) of the operator $\hat{\mathrm{L}}^2(\theta,\phi)$ then give the following differential equation for $\Theta_l^m(\theta)$:

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_l^m(\theta)}{\partial\theta}\right) + \left[l(l+1) - \frac{m^2}{\sin^2\theta}\right]\Theta_l^m(\theta) = 0. \tag{4.28}$$

The subsequent substitution $-1 \le x = \cos\theta \le 1$ then transforms the previous equation into a more familiar form of the differential equation defining the *associated Legendre polynomials*,

$$\frac{d}{dx}\left[(1-x^2)\frac{d\Theta_l^m(x)}{dx}\right] + \left[l(l+1) - \frac{m^2}{1-x^2}\right]\Theta_l^m(x) = 0. \tag{4.29}$$

For $m = 0$ it reduces to the differential equation defining the *Legendre polynomials* of order l, $\Theta_l^0(x) \equiv P_l(x)$,

$$\frac{d}{dx}\left[(1-x^2)\frac{dP_l(x)}{dx}\right] + l(l+1)\,P_l(x) = 0. \tag{4.30}$$

Its solutions can be written in the compact (*Rodrigues*) form:

$$P_l(x) = \frac{1}{2^l l!}\frac{d^l}{dx^l}(x^2-1)^l. \tag{4.31}$$

The remaining *associated* Legendre polynomials of degree l and order $|m| \le l$, $\Theta_l^m(x) \equiv N_{l,m}P_l^{|m|}(x)$, which satisfy (4.28) for $m \ne 0$, can then be obtained from these polynomials by repeated differentiations with respect to x:

$$P_l^{|m|}(x) = (-1)^{|m|}(1-x^2)^{|m|/2}\frac{d^{|m|}P_l(x)}{dx^{|m|}}. \tag{4.32}$$

The normalization constant $N_{l,m}$ reflecting the proportionality between $\Theta_l^m(x)$ and $P_l^{|m|}(x)$ is to be determined from the following condition:

$$\int_{-1}^{1}\left(\Theta_l^m(x)\right)^2 dx = 1 \Rightarrow N_{l,m} = \left[\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}\right]^{1/2}. \tag{4.33}$$

The spherical harmonics $\{Y_l^m(\theta,\phi) \equiv Y_l^m(\Omega)\}$ satisfy the usual orthonormality conditions,

$$\int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi\, Y_l^{m^*}(\theta,\phi)\, Y_{l'}^{m'}(\theta,\phi) = \int Y_l^{m^*}(\Omega)\, Y_{l'}^{m'}(\Omega)\, d\Omega = \delta_{l,l'}\delta_{m,m'}, \tag{4.34}$$

involving the integration over the whole range of 4π steradians of the solid angle Ω, i.e., over all possible directions of the unit vector in the physical space:

$$\int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi = \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\phi = \int d\Omega = 4\pi. \tag{4.35}$$

They are automatically satisfied when the two factors in (4.27) are chosen to obey the associated partial relations:

$$\int_0^{\pi} \sin\theta\, d\theta\, \Theta_l^m(\theta)\Theta_{l'}^m(\theta) = \delta_{l,l'} \quad \text{and} \quad \int_0^{2\pi} d\phi\, \Phi_m^*(\phi)\Phi_{m'}(\phi) = \delta_{m,m'}. \tag{4.36}$$

Clearly, the same type of spherical functions describes the eigenstates of the internal (orbital) angular momentum $\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$, associated with the relative motion of electron around the atomic nucleus. The corresponding internal spherical harmonics now depend on the angular coordinates specifying the direction of the relative position vector $\boldsymbol{r} = (r, \vartheta, \varphi)$ of the system electron,

$$Y_l^m(\vartheta,\varphi) = \Theta_l^m(\vartheta)\Phi_m(\varphi), \tag{4.37}$$

and satisfy the associated eigenvalue problems of the compatible operators of the orbital angular momentum of (3.70) and (3.71):

$$\begin{aligned} &\hat{\mathrm{l}}^2(\vartheta,\varphi)Y_l^m(\vartheta,\varphi) = l(l+1)\hbar^2 Y_l^m(\vartheta,\varphi), && l = 0,1,2,\ldots, \\ &\hat{\mathrm{l}}_z(\varphi)Y_l^m(\vartheta,\varphi) = m\hbar\, Y_l^m(\vartheta,\varphi), && m = -l,-l+1,\ldots,l-1,l, \end{aligned} \tag{4.38}$$

The associated commutation relations are given by (3.71) and those involving the internal Hamiltonian $\hat{\mathrm{h}}(\boldsymbol{r}) = \hat{\mathrm{h}}(r,\vartheta,\varphi)$:

$$[\hat{\mathrm{l}}^2, \hat{\mathrm{h}}] = [\hat{\mathrm{l}}_z, \hat{\mathrm{h}}] = 0, \tag{4.39}$$

where in full analogy to (4.13)

$$\hat{\mathrm{h}}(r,\vartheta,\varphi) = \frac{-\hbar^2}{2\mu}\Delta(r,\vartheta,\varphi) + V(r) = \frac{1}{2\mu}\hat{\mathrm{p}}_r^2 + \frac{1}{2\mu r^2}\hat{\mathrm{l}}^2(\vartheta,\varphi) + V(r); \tag{4.40}$$

here, the operator of the radial component of the orbital momentum [see (4.12)],

$$\hat{\mathrm{p}}_r(r) = -i\hbar \frac{1}{r}\frac{\partial}{\partial r} r, \tag{4.41}$$

and the operators of the orbital angular momentum in the spherical coordinates of the system electron read [see (4.15) and (4.16)]:

$$\hat{\mathrm{l}}^2(\vartheta, \varphi) = -\hbar^2 \left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta \frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right], \quad \hat{\mathrm{l}}_z(\varphi) = -i\hbar\frac{\partial}{\partial\varphi}. \tag{4.42}$$

It thus follows from (4.39) that the eigenfunctions of the internal Schrödinger equation (4.4) can be factorized in the form analogous to that in (4.19a):

$$\psi_{n,l,m}(r, \vartheta, \varphi) = R_{n,l}(r) Y_l^m(\vartheta, \varphi). \tag{4.43}$$

These functions represent the simultaneous eigenstates of the associated three (internal) commuting observables:

$$\begin{aligned} &\hat{\mathrm{h}}(r, \vartheta, \varphi)\psi_{n,l,m}(r, \vartheta, \varphi) = \varepsilon_n \psi_{n,l,m}(r, \vartheta, \varphi) \\ &\hat{\mathrm{l}}^2(\vartheta, \varphi)\psi_{n,l,m}(r, \vartheta, \varphi) = l(l+1)\hbar^2 \psi_{n,l,m}(r, \vartheta, \varphi), \quad l = 0, 1, 2, \ldots, \\ &\hat{\mathrm{l}}_z(\varphi)\psi_{n,l,m}(r, \vartheta, \varphi) = m\hbar \psi_{n,l,m}(r, \vartheta, \varphi), \quad m = -l, -l+1, \ldots, l-1, l. \end{aligned} \tag{4.44}$$

4.4 Radial Eigenfunctions and Energy Levels

To obtain the radial functions $\{R_{n,l}(r)\}$ and the admissible energy levels $\{\varepsilon_n\}$ of the *bonded*, stationary states of the internal motions of the electron around the nucleus in the hydrogen-like atom, when $\varepsilon_n < 0$, one substitutes the product function of (4.43) into the first eigenvalue problem of the preceding equation. This gives the radial Schrödinger equation in the form [compare (4.21)]:

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{d^2}{dr^2} r\right) + \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{Ze^2}{r} + |\varepsilon_n|\right] R_{n,l}(r) = 0. \tag{4.45}$$

It can be subsequently simplified by the substitution $U_{n,l}(r) = rR_{n,l}(r)$ and by the introduction of the redefined coefficients in this differential equation: the energy parameter $\kappa_n{}^2 = 2\mu|\varepsilon_n|/\hbar^2$, the energy-scaled (dimensionless) radial distance $\rho_n = 2\kappa_n r$, and a reduced measure of the nuclear charge $\zeta_n = Z/(\kappa_n a_0)$, where $a_0 = \hbar^2/(\mu e^2) = 0.5292 \times 10^{-10}$ m denotes the radius of the first Bohr's orbit in the hydrogen atom,

$$\frac{d^2U_{n,l}(\rho_n)}{d\rho_n^2} - \frac{l(l+1)}{\rho_n^2}U_{n,l}(\rho_n) + \left(\frac{\zeta_n}{\rho_n} - \frac{1}{4}\right)U_{n,l}(\rho_n) = 0. \tag{4.46}$$

In the asymptotic region of very large distances $\rho_n \to \infty$ it thus reduces to a simple differential equation

$$\frac{d^2U_{n,l}(\rho_n)}{d\rho_n^2} = \frac{U_{n,l}(\rho_n)}{4}, \quad \rho_n \to \infty, \tag{4.47}$$

the general solution of which reads: $U_{n,l}(\rho_n) \sim A\exp(-\rho_n/2) + B\exp(\rho_n/2)$, where A and B are integration constants. For this radial function to be finite in this limit $B = 0$, so that $U_{n,l}(\rho_n) \sim A\exp(-\rho_n/2)$ ($\rho_n \to \infty$).

In the other extreme region of $\rho_n \to 0$ the radial equation (4.46) becomes

$$\frac{d^2U_{n,l}(\rho_n)}{d\rho_n^2} = \frac{l(l+1)}{\rho_n^2}U_{n,l}(\rho_n), \quad \rho_n \to 0. \tag{4.48}$$

Inserting into the preceding equation the trial function $U_{n,l}(\rho_n) = {\rho_n}^{\xi}$ then gives the following quadratic equation for the critical exponent ξ:

$$\xi(\xi - 1) = l(l+1) \quad \Rightarrow \quad \{\xi_1 = -l, \xi_2 = l+1\}, \tag{4.49}$$

thus predicting the general solution near the nucleus in the form $U_{n,l}(\rho_n) \sim A'{\rho_n}^{-l} + B'{\rho_n}^{l+1}$. The well-behaving (finite) solution thus results only for $A' = 0$: $U_{n,l}(\rho_n) \sim B'{\rho_n}^{l+1}$ ($\rho_n \to 0$).

The above analysis suggests the following general form of the radial wave function,

$$U_{n,l}(\rho_n) = \exp(-\rho_n/2){\rho_n}^{l+1}V(\rho_n), \tag{4.50a}$$

which automatically guarantees the correct behavior in both these asymptotic regions, including the additional (finite) factor $V(\rho_n)$ defined by the power series:

$$V(\rho_n) = \sum_{i=0}^{\infty} a_i \rho_n^i. \tag{4.50b}$$

Its substitution into (4.46) gives the following differential equation for determining this unknown radial factor:

$$\left[\rho_n \frac{d^2}{d\rho_n^2} + (2l + 2 - \rho_n)\frac{d}{d\rho_n} - (l + 1 - \zeta_n)\right]V(\rho_n) = 0. \tag{4.51}$$

As $V(\rho_n)$ represents the power series this differential equation effectively determines the (energy dependent) recursive relation between the coefficients $\{a_i\}$. Indeed, the left-hand side of this equation also constitutes the power series which vanishes only when coefficients at all powers of ρ_n are simultaneously equal to zero. This requirement generates the following recursion relation between the neighboring coefficients in (4.50b) for the representative term ${\rho_n}^k$:

$$\frac{a_{k+1}}{a_k} = \frac{(k+l+1) - \zeta_n}{(k+1)(k+2l+2)}. \tag{4.52}$$

This power series thus begins with the constant term $a_0 \neq 0$ and it must terminate at some *finite* maximum power. Indeed, if it failed to do so, in the limit of very large values of k, i.e., $k \to \infty$, $a_{k+1}/a_k \to 1/k$, which is characteristic of the power series expansion of the function $\exp(\rho_n) = \sum_{i=0}^{\infty} \frac{1}{i!}\rho_n^i$. Thus, should the power series in (4.50b) fail to terminate, the radial wave function $U_{n,l}(\rho_n)$ would become infinite (ill-behaved) at $\rho_n \to \infty$, diverging as $\exp(\rho_n/2)$.

Therefore, the truncation of this series into the polynomial is the crucial requirement for the radial wave function to well behave at large distances. A reference to (4.52) shows that the series will indeed become the polynomial of degree $k = j$ when $a_{j+1}/a_j = 0$, which takes place only for

$$(j+l+1) \equiv n = \zeta_n \quad \text{or} \quad n^2 = {\zeta_n}^2 = Z^2/({\kappa_n}^2 {a_0}^2) = Z^2\hbar^2/(2\mu|\varepsilon_n|{a_0}^2). \tag{4.53}$$

As, by definition, j is a non-negative integer and $l = 0, 1,\ldots$ [see (4.44)], the *principal* quantum number n, which identifies the electronic “shells,” must also be a positive integer $n = 1, 2, \ldots$. It is subject to the restriction $n > l$, since the degree of the polynomial after which the series expansion terminates $j = n - (l+1) \geq 0$, $V(\rho_n) = V_{n,l}(\rho_n)$, so that there are n values of the angular momentum quantum number l consistent with the given n: $l = 0, 1, \ldots, n-1$.

To summarize, the radial wave function of the internal states of the *one*-electron atom reads:

$$U_{n,l}(\rho_n) = A_{n,l}\exp(-\rho_n/2){\rho_n}^{l+1}V_{n,l}(\rho_n) = A_{n,l}\exp(-\rho_n/2){\rho_n}^{l+1}\sum_{i=0}^{n-l-1} a_i\rho_n^i, \tag{4.54}$$

where $A_{n,l}$ stands for the appropriate normalization constant. The polynomials $V_{n,l}(\rho_n)$, the solutions of the differential equation (4.51), are known as the *associated Laguerre polynomials*:

$$V_{n,l}(\rho_n) = L_{n-l-1}^{2l+1}(\rho_n) = \sum_{i=0}^{n-l-1} \frac{(-1)^i[(n+l)!]^2}{i!(n-l-1-i)!(2l+1+i)!}\rho_n^i. \tag{4.55}$$

Again, the associated Laguerre polynomials $L_p^q(\rho_n)$ of degree p and order q, are compactly represented by the following formulas of Rodrigues in terms of the *Laguerre polynomials* $L_p(\rho_n)$ of degree p:

$$L_p^{q=0}(\rho_n) = L_p(\rho_n) = \exp(\rho_n)\frac{d^p}{d\rho_n^p}[\rho_n^p \exp(-\rho_n)], \tag{4.56}$$

$$L_p^q(\rho_n) = (-1)^q \frac{d^q}{d\rho_n^q} L_{q+p}(\rho_n). \tag{4.57}$$

Thus, the condition of the well-behaved wave function at infinity gives rise to a quantization of the internal energy $\varepsilon_n = -|\varepsilon_n|$ of electron in the hydrogen-like atom:

$$|\varepsilon_n| = \frac{Z^2}{2n^2}\left(\frac{\mu e^4}{\hbar^2}\right) \cong \frac{Z^2}{2n^2}\left(\frac{m_e e^4}{\hbar^2}\right) \equiv \frac{Z^2}{2n^2}\text{hartrees} \equiv \frac{Z^2}{n^2}\text{rydbergs}, \tag{4.58}$$

$$1\ \text{hartree} = 2\ \text{rydbers} = 2|\varepsilon_0| = 27.21161\ \text{eV} = 4.359814 \times 10^{-18}\ \text{J}, \tag{4.59}$$

where we have introduced two popular units of energy used in atomic and molecular physics. For $Z = 1$ this energy spectrum reproduces that following from the historically first quantum model of the hydrogen atom proposed by Bohr in the Old Quantum Theory. One also observes that the scaling factor $\kappa_n = Z/(na_0)$ of the radial distance ρ_n is shell-specific.

4.5 Orbital Degeneracy and Electron Distribution

The energy spectrum of (4.58) becomes very dense for large values of the principal quantum number, with $\varepsilon_\infty = 0$, and becomes continuous for the nonbonded (scattering) states, for $\varepsilon > 0$, when the electron can exhibit the infinite separation from the nucleus. Therefore, such energy-continuum states of the hydrogen-like atom describe the ionization processes, involving a removal of the system electron.

The wave functions of (4.43) define the admissible (linearly independent) bonded states of electron in the hydrogen-like atom. Since the value of the allowed internal energy of (4.58) depends solely on the principal quantum number n the number of combinations of the remaining quantum numbers, the *secondary* (orbital) quantum number l and *magnetic* (azimuthal) quantum number m, which are consistent with the given value of n, determines the system overall orbital degeneracy. For each value of the quantum number associated with the length of the orbital angular momentum, $l = 0, 1,\ldots, n - 1$, which identifies specific atomic "subshells," there are $2l + 1$ admissible values of the azimuthal quantum number m (4.44) determining the spatial orientation of the angular momentum vector (Fig. 1.2). Hence, the total orbital degeneracy g_n of the given eigenvalue ε_n in hydrogen-like atom, i.e., the number of independent stationary (bonded) electronic states belonging to this energy level:

$$g_n = \sum_{l=0}^{n-1} (2l + 1) = n^2. \tag{4.60}$$

This *orbital*-degeneracy is doubled if the two spin states of an electron, $\alpha(\sigma)$ or $\beta(\sigma)$, depending on the discrete spin variable $\sigma = (-½, ½)$, are taken into account, as each *Atomic Orbital* (AO) $\psi_{n,l,m}(r, \vartheta, \varphi)$ can be combined with any of these spin functions into the corresponding *Spin Orbitals* (SOs)

$$\psi^{\sigma}_{n.l,m}(r, \vartheta, \varphi, \sigma) = \begin{cases} \psi^{+}_{n,l,m}(r, \vartheta, \varphi, \sigma) = \psi_{n,l,m}(r, \vartheta, \varphi)\alpha(\sigma) \\ \psi^{-}_{n,l,m}(r, \vartheta, \varphi, \sigma) = \psi_{n,l,m}(r, \vartheta, \varphi)\beta(\sigma) \end{cases}. \tag{4.61}$$

Hence, in hydrogen-like atom all energy levels with $n > 1$ exhibit some *orbital* degeneracy, while the ground 1*s* state,

$$\psi_{1,0,0}(r, \vartheta, \varphi) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} \exp(-Zr/a_0), \tag{4.62}$$

exhibits only the double *spin* degeneracy.

The appearance of the degenerate quantum states can be often ascribed to some apparent symmetry in the physical system. For example, the degeneracy with respect to the magnetic quantum number m reflects the *central* potential feature of the *one*-electron atom. It originates from the absence of the preferred spatial direction and hence from the invariance with regard to rigid rotations about the origin. The degeneracy of states corresponding to different values of l consistent with the given n is peculiar to the Coulomb potential. Any departure from the strict $1/r$ dependence, e.g., in *many*-electron atoms, will remove this ("accidental") degeneracy.

The atomic orbitals of (4.43) are complex for $m \neq 0$, because of the $\Phi_m(\varphi)$ factor in $Y_l^m(\vartheta, \varphi)$ (4.37), with only $m = 0$ functions,

$$\psi_{n,0,0}(r) \equiv ns, \quad \psi_{n,1,0}(r, \vartheta) \equiv np_z, \quad \psi_{n,2,0}(r, \vartheta) \equiv nd_{z^2}, \text{ etc.}, \tag{4.63}$$

which do not depend on the spherical angle φ, are automatically real. However, one can always transform the pair of the complex–conjugate orbital factors $\Phi_m(\varphi) = \Phi^*_{-m}(\varphi)$ for $m > 0$ into two *real* combinations by extracting their real and imaginary parts:

$$\begin{aligned} \mathrm{Re}[\Phi_m(\varphi)] &= \frac{1}{2}[\Phi_m(\varphi) + \Phi_{-m}(\varphi)] = \cos(m\varphi), \\ \mathrm{Im}[\Phi_m(\varphi)] &= \frac{1}{2i}[\Phi_m(\varphi) - \Phi_{-m}(\varphi)] = \sin(m\varphi). \end{aligned} \tag{4.64}$$

Since such real combinations involve functions with the same length of the angular momentum, this physical quantity still remains sharply specified in these combined states. However, the real orbitals are no longer eigenfunctions of the z-component of the angular momentum, as they combine functions with different eigenvalues of this observable. Therefore, in a single measurement of l_z, one has probability ½ of observing either $l_z = m\hbar$ or $l_z = -m\hbar$ and hence $\langle l_z \rangle = 0$ in such linear combinations $\psi_{n,l,\pm m}$ of the complex orbitals $\psi_{n,l,m}$.

The AO parity, i.e., the symmetry (g) or antisymmetry (u) property of $\psi_{n,l,m}$ with respect to the *inversion* operator $\hat{\mathrm{i}}$, which reverses the internal Cartesian coordinates, $\hat{\mathrm{i}}(x, y, z) = (-x, -y, -z)$, is determined solely by the associated property of the spherical harmonic factor $Y_l^m(\vartheta, \varphi)$, since such operation of reversing directions of the coordinate system does not affect the radial distance r. Indeed, in the spherical coordinates $\hat{\mathrm{i}}(r, \vartheta, \varphi) = (r, \pi - \vartheta, \varphi + \pi)$ and hence the action of $\hat{\mathrm{i}}$ on $\Phi_m(\varphi)$ gives:

$$\hat{\mathrm{i}}\ \exp(im\varphi) = [\exp(i\pi)]^m \exp(im\varphi) = (-1)^{|m|} \exp(im\varphi). \tag{4.65}$$

Thus, the magnetic quantum number m itself determines the parity of $\Phi_m(\varphi)$, which is symmetric (g) [antisymmetric (u)] with respect to inversion for the even (odd) values of m.

Next, let us examine the parity of the other, ϑ-dependent part of the angular function, $\Theta_l^m(x) \equiv N_{l,m} P_l^{|m|}(x)$, $x = \cos\vartheta$. Since $\hat{\mathrm{i}} \cos\vartheta = \cos(\pi - \vartheta) = -\cos\vartheta$ and the associated Legendre polynomial of degree l and order m, $P_l^{|m|}(x)$, is obtained by differentiating $(l + |m|)$-times the *even* function $(x^2 - 1)^l$ of the argument x in (4.31) and (4.32), the action of the inversion operation on this angular factor of the wave function gives:

$$\hat{\mathrm{i}} P_l^{|m|}(\cos\vartheta) = (-1)^{l+|m|} \exp(im\varphi) P_l^{|m|}(\cos\vartheta). \tag{4.66}$$

It thus follows from the preceding two equations that the overall parity of the angular function is determined by the parity of the orbital quantum number l:

$$\hat{\mathrm{i}} Y_l^m(\vartheta, \varphi) = (-1)^{l+2|m|} Y_l^m(\vartheta, \varphi) = (-1)^l Y_l^m(\vartheta, \varphi). \tag{4.67}$$

Atomic orbitals posses a number of nodal surfaces on which $\psi_{n,l,m} = 0$, as indeed required to satisfy the orthogonality relations, which guarantee the linear independence of AO. For this purpose it is customary to examine the spatial properties of the *real* AO (4.64),

$$\begin{aligned}\psi_{n,l,\pm m}(r, \vartheta, \varphi) &\propto r^l \exp(\kappa_n r) L_{n-l-1}^{2l+1}(2\kappa_n r) P_l^m(\cos\vartheta) \begin{cases} \cos(m\varphi) \\ \sin(m\varphi) \end{cases} \\ &= R_{n,l}(r) Y_l^{x^a, y^b, z^c},\end{aligned} \tag{4.68}$$

e.g., $\psi_{n,1,\pm 1} = \{np_x, np_y\}$, $\psi_{n,2,\pm 1} = \{nd_{xz}, nd_{yz}\}$, $\psi_{n,2,\pm 2} = \{nd_{xy}, nd_{x^2-y^2}\}$, etc. The angular functions $Y_l^{x^a,y^b,z^c}$ of the real AO are simple functions of the respective integer powers $\{a, b, c\}$ of the electron Cartesian coordinates, which are indicated in their symbolic notation.

By examining the individual factors in the preceding expression, one first realizes that there are $l - m$ values of ϑ for which $P_l^m(\cos\vartheta)$ vanishes and the real/imaginary parts of (4.64) vanish at m values of the azimuth. Moreover, the associated Laguerre polynomial vanishes at $n - l - 1$ values of r; for $l \neq 0$ the radial factor r^l has also the "node" at $r = 0$. Hence, disregarding the latter, the total number of nodal surfaces in AO at finite distances is $n - 1$, including $n - l - 1$ radial and l angular surfaces.

It thus follows from these considerations that only the $l = n - 1$ AO, e.g., 1*s*, 2*p*, 3*d*, 4*f*, etc., have zero radial nodal-surfaces, thus exhibiting only one maximum in their *radial* probability density, which is customarily used to represent the distribution of electrons in atoms. More specifically, using the probability density of finding the electron at point $\boldsymbol{r} = (r, \vartheta, \varphi) = (r, \Omega)$,

$$\rho_{n,l,m}(r,\vartheta,\varphi) = |\psi_{n,l,m}(r,\vartheta,\varphi)|^2 = R_{n,l}^2(r)\left|Y_l^m(\vartheta,\varphi)\right|^2, \tag{4.69}$$

one finds from (4.34) the associated radial probability of locating the electron in the infinitesimal radial range, between the concentric spheres of radii r and $r + dr$,

$$P_{n,l}(r,dr) = r^2 R_{n,l}^2(r)\ dr \int \left|Y_l^m(\Omega)\right|^2 d\Omega = r^2 R_{n,l}^2(r)\ dr, \tag{4.70}$$

where we have recognized the angular normalization of (4.34). Hence, the *radial* probability density reads:

$$\rho_{n,l}^{rad.}(r) \equiv \frac{dP(r,dr)}{dr} = r^2 R_{n,l}^2(r). \tag{4.71}$$

For example, for the ground state of the hydrogen-like atom (4.62), for which $R_{1,0}\ (r) \propto \exp(-Zr/a_0)$ and hence $\rho_{1,0}^{rad.}(r) \propto r^2 \exp(-2Zr/a_0)$, the maximum of the radial distribution is observed at $r_{max.}(Z) = a_0/Z$. This radial probability density also predicts the following average values of r and r^2:

$$\langle r(Z)\rangle = \int_0^\infty r\rho_{1,0}^{rad.}(r)dr = 4\left(\frac{Z}{a_0}\right)^3 \int_0^\infty \exp\left(-\frac{2Zr}{a_0}\right) r^3 dr = \frac{3}{2}\frac{a_0}{Z}, \tag{4.72}$$

$$\langle r^2(Z)\rangle = \int_0^\infty r^2\rho_{1,0}^{rad.}(r)dr = 4\left(\frac{Z}{a_0}\right)^3 \int_0^\infty \exp\left(-\frac{2Zr}{a_0}\right) r^4 dr = 3\left(\frac{a_0}{Z}\right)^2, \tag{4.73}$$

where we have used the typical integral $\int_0^\infty y^n \exp(-by)\, dy = n!/b^{n+1}$. Hence, the square of the dispersion σ_r in the radial distance of this *one*-electron atom reads:

$$\sigma_r^2 = \left\langle r^2(Z) \right\rangle - \langle r(Z) \rangle^2 = \frac{3}{4}\left(\frac{a_0}{Z}\right)^2 \quad \text{or} \quad \sigma_r = \left(\frac{\sqrt{3}}{2}\right)\left(\frac{a_0}{Z}\right). \tag{4.74}$$

Therefore, in the hydrogen atom the maximum radial probability is found at $r_{max.}(Z = 1) = a_0$ as already predicted by Bohr. It should be emphasized, however, that the latter model has invoked the classical ("flat") planetary picture of the electron movements around the nucleus, while the quantum-mechanical perspective predicts the correct spherical distribution of the electron probability density around the nucleus.

The radial densities for the remaining AO in this prototype atomic system are well known and available in practically every textbook of quantum chemistry or elementary quantum mechanics. Let us only recall here that with the increasing principal quantum number $n = 1, 2, 3$, which determines the successive electronic shells, the average distance from the nucleus increases. The atomic subshells, identified by the alternative values of the orbital quantum number l consistent with the given principal quantum number n, exhibit the decreasing trend with increasing l in their most probable and average distances from the nucleus, e.g., $\langle r_{3d} \rangle < \langle r_{3p} \rangle < \langle r_{3s} \rangle$. This observation reflects the intervention of the orthogonality constraints with respect to the stationary states exhibiting the same symmetry and lower energy, for which the electron is on average distributed closer to the nucleus. These requirements effectively shift the probability of the outer subshells away from the nucleus. Indeed, the $3s$ orbital must be orthogonal to both $1s$ and $2s$ states, the $3p$ state is only constrained by its orthogonality to the $2p$ subshell, while $3d$ orbital has no lower-lying analog. Therefore, in the given electronic shell n, the $l = n - 1$ and $l = 0$ subshells always exhibit the minimum and maximum average distance from the nucleus, respectively.

These prototype analytical solutions for the *one*-electron atom can be also regarded as determining a general pattern of the shell structures in N-electron atoms ($N > 1$), in which electrons, occupying N lowest SO, are moving in the effective potential due to the nucleus and the remaining electrons. As this effective attraction by the "screened" nucleus is then no longer of the $1/r$ type, the accidental degeneracy of the hydrogen-like atom is lifted and the subshell energies in *many*-electron atoms depend on both n and l, $\varepsilon = \varepsilon_{n,l}$. In such atomic systems the configuration of the *outer*-most (most polarizable) *valence* shell electrons is decisive for determining the atom propensity to form chemical bonds with other atoms. In such bond-forming processes the distributions of the *inner*-shell electrons remain practically unaffected ("frozen").

It should be finally observed that these "exact" solutions of the Schrödinger equation for the *one*-electron atom, also determining the gross features of the electronic structure of *many*-electron systems, still require several corrections which must be taken into account to relate theoretical predictions to the experimental data. For example, corrections are due to the coupling between the spin and orbital angular momenta and the high speed of the electron, which call for the relativistic approach, the hyperfine structural effects reflect the magnetic properties of the nucleus, and the Lamb shift accounts for the interaction between the electron and electromagnetic field.

4.6 Atomic Units

When describing objects and processes in the atomic scale, it is convenient to use the system of *atomic units* (a.u.), which greatly simplify equations and expressions in molecular quantum mechanics [see (4.58), (4.72), (4.73)]. For example, the proportionality constant in the Coulomb Law determining the potential $V(r)$ of (4.1), $k_C = (4\pi\varepsilon_0)^{-1}$, where ε_0 stands for the electric permittivity of the free space, becomes unity in a.u., $k_C = 1$ a.u. so that $V(r) = -k_C Ze^2/r = -Ze^2/r = -Z/r$ (a.u.), where we have recognized that the magnitude of the electronic charge (proton charge) determines in a.u. the unit of electric charge: $e = 1$. Thus the a.u. of electric permittivity equals $4\pi\varepsilon_0$, or the vacuum permittivity $\varepsilon_0 = (4\pi)^{-1}$ a.u.

This system will be used in the remaining part of the book, unless specified otherwise. It is based upon the underlying units of length, mass, time, and electric charge, which subsequently determine the associated units of the remaining physical quantities, e.g., energy, physical action, angular momentum, etc. Some of these units are summarized in Table 4.1, where the expressions in terms of the universal constants and corresponding values in the *Système International d'Unités* (SI) are also given.

Table 4.1 Atomic units

Property	Unit	Symbol	SI value
Action and angular momentum	Planck's constant	$\hbar$	1.0546×10^{-34} J s
Electric charge	Charge of proton	e	1.6022×10^{-19} C
Electric permittivity	$4\pi\varepsilon_0$	$e^2/(E_h\, a_0)$	1.1127×10^{-10} F m^{-1}
Energy	Hartree, double magnitude of the ground-state energy of hydrogen atom for $\mu = m_e$, i.e., $M_n \to \infty$	$E_h = k_C\, e^2/a_0$ $= k_C{}^2 m_e\, e^4/\hbar^2$	4.3598×10^{-18} J
k_C	Constant in Coulomb Law	$k_C = E_h\, a_0/e^2$	8.9875×10^{9} J m C^{-2}
Length	The first Bohr's radius	$a_0 = \hbar^2/(k_C\, m_e e^2)$	5.2918×10^{-10} m
Mass	Rest mass of electron	m_e	9.1095×10^{-31} kg
Probability density		$a_0{}^{-3}$	6.7483×10^{30} m^{-3}
Time	Time in which one electron on the first Bohr's orbit travels the angle distance of 1 radian	$\tau_0 = a_0/v_0$ $= \hbar^3/(k_C{}^2 m_e e^4)$	2.4189×10^{-17} s
Velocity	Speed of electron on the first Bohr's orbit	$v_0 = a_0/\tau_0$ $= \hbar/(m_e a_0)$ $= k_C\, e^2/\hbar$	2.1877×10^{6} m s^{-1}