

Chapter 2

The Periodic Table, Molecules, and Bonds

2.1 Atoms: Building up the Periodic Table

In this chapter we show how the Schrödinger equation—together with a few additional concepts—can allow us to build (conceptually) the periodic table of the elements. In turn, this will give us some ideas about the nature of atomic orbitals, concept that constitutes the basic building block underlying the formation of atomic bonds in molecules and crystals.

First, we need to introduce the concept of *quantum number*. The example of a particle in a three-dimensional (3D) box will illustrate this. For simplicity, we treat the simpler case of a free particle. Any text on Quantum Mechanics could—and should—be consulted to have a more complete picture and set of examples [1–5].

2.1.1 Free Particles in Three Dimensions

The Schrödinger equation describing a particle of mass m in absence of any potential is

$$-\frac{\hbar^2 \nabla^2}{2m} \Psi(\mathbf{r}, t) = i \hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t). \quad (2.1)$$

In order to solve this partial differential equation we use a technique called “separation of variables.” Let us look for a solution of the form

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) T(t), \quad (2.2)$$

that is, we look for a solution expressed as the product of a function ψ that depends only on the spatial coordinates \mathbf{r} , and a function T that depends only on time. Thanks to the linearity of the Schrödinger equation, the most general solution satisfying the required boundary and initial conditions can always be written as a linear combination of solutions of this type. Therefore, the particular choice given by Eq. (2.2) does not restrict the generality of the solution we can obtain.

Inserting Eq. (2.2) into Eq. (2.1) and dividing by Ψ , we obtain

$$-\frac{1}{\psi(\mathbf{r})} \frac{\hbar^2 \nabla^2}{2m} \psi(\mathbf{r}) = i \hbar \frac{1}{T(t)} \frac{dT(t)}{dt}. \quad (2.3)$$

Note now that the left-hand side (lhs) of this equation is a function of the spatial coordinates \mathbf{r} only, whereas the right-hand side (rhs) depends only on t . Since \mathbf{r} and t are independent variables, we are free to change them as we please. Therefore, the equality expressed by Eq. (2.3) can hold only if both sides of the equation are equal to a constant. Therefore, calling this constant E , must we have

$$\frac{dT(t)}{dt} + i\frac{E}{\hbar} T(t) = 0, \quad (2.4)$$

and

$$-\frac{\hbar^2 \nabla^2}{2m} \psi(\mathbf{r}) = E \psi(\mathbf{r}). \quad (2.5)$$

Equation (2.4) has a general solution $T(t) = Ae^{-i\omega t}$, where A is a constant to be determined by the initial conditions, and $\hbar\omega = E$. Note that, since the lhs of Eq. (2.5) is just the Hamiltonian of the system, this equation is exactly the eigenvalue equation for the operator $\hat{\mathbf{H}}$ of the simple system. Therefore, we can identify the search for the solution ψ as the search for the eigenvectors of the Hamiltonian, and E as their eigenvalues. Therefore, E is just the energy of the particle.

We conclude that our solution has the form $\Psi(\mathbf{r}, t) = Ae^{-i\omega t} \psi(\mathbf{r})$. This represents an eigenvector of the Hamiltonian, $|\psi\rangle$, in the Hilbert space $L^2(\mathbb{R}^3)$, that rotates in time with radian frequency ω . The wavefunction $\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle$ satisfies the “time-independent” Schrödinger equation, Eq. (2.5).

Assuming that the potential energy of the particle is just a constant, V_0 , we can determine $\psi(\mathbf{r})$ by following the same procedure of “separation of variables.” We express the Laplacian and the spatial coordinate \mathbf{r} in terms of their components:

$$-\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} \psi(x, y, z) + \frac{\partial^2}{\partial y^2} \psi(x, y, z) + \frac{\partial^2}{\partial z^2} \psi(x, y, z) \right] + V_0 \psi(x, y, z) = E \psi(x, y, z). \quad (2.6)$$

Now, let us look for a solution of the form:

$$\psi(x, y, z) = \psi_x(x) \psi_y(y) \psi_z(z), \quad (2.7)$$

where ψ_x , ψ_y , and ψ_z are three different functions in one variable only. Inserting this into Eq. (2.6), we obtain

$$-\frac{\hbar^2}{2m} \left[\psi_y(y) \psi_z(z) \frac{d^2 \psi_x(x)}{dx^2} + \psi_x(x) \psi_z(z) \frac{d^2 \psi_y(y)}{dy^2} + \psi_x(x) \psi_y(y) \frac{d^2 \psi_z(z)}{dz^2} \right] = E \psi_x(x) \psi_y(y) \psi_z(z). \quad (2.8)$$

Dividing both sides by $\psi_x(x) \psi_y(y) \psi_z(z)$:

$$-\frac{\hbar^2}{2m} \left[\frac{1}{\psi_x(x)} \frac{d^2 \psi_x(x)}{dx^2} + \frac{1}{\psi_y(y)} \frac{d^2 \psi_y(y)}{dy^2} + \frac{1}{\psi_z(z)} \frac{d^2 \psi_z(z)}{dz^2} \right] = E. \quad (2.9)$$

This equation tells us that the sum of three functions of different variables (x , y , and z) must always be equal to a constant (E) for all possible values of x , y , and z . This is possible only if each function is equal to a constant, that is

$$-\frac{\hbar^2}{2m} \frac{1}{\psi_x(x)} \frac{d^2 \psi_x(x)}{dx^2} = E_x, \quad (2.10)$$

$$-\frac{\hbar^2}{2m} \frac{1}{\psi_y(y)} \frac{d^2 \psi_y(y)}{dy^2} = E_y, \quad (2.11)$$

$$-\frac{\hbar^2}{2m} \frac{1}{\psi_z(z)} \frac{d^2 \psi_z(z)}{dz^2} = E_z. \quad (2.12)$$

We have indicated with E_x , E_y , and E_z three arbitrary constants subject to the condition $E_x + E_y + E_z = E$. Rewriting Eq. (2.10) as

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi_x(x)}{dx^2} = E_x \psi_x(x), \quad (2.13)$$

its general solution has the form:

$$\psi_x(x) = A_x e^{ik_x x}, \quad (2.14)$$

where A_x is an arbitrary multiplicative constant that will be determined below by “normalizing” the wavefunction. In this equation

$$k_x = \frac{1}{\hbar} \sqrt{2mE_x}. \quad (2.15)$$

is the wavenumber along the x -axis. We can proceed in an analogous way for the y - and z -components, so that the full wavefunction has the form:

$$\psi(\mathbf{r}) = A_x A_y A_z e^{i(k_x x + k_y y + k_z z)} = A e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (2.16)$$

having defined the *wavevector* \mathbf{k} as the vector with components (k_x, k_y, k_z) , and A is an arbitrary constant.

Recalling that $\Psi(\mathbf{r}, t) = A e^{-i\omega t} \psi(\mathbf{r})$, Eq. (2.16) describes the particle as a “plane-wave” propagating in the direction of the wavevector \mathbf{k} with wavenumber (number of wavelengths per unit length along the direction of propagation) given by the magnitude k of \mathbf{k} and with phase velocity ω/k . Note that its momentum \mathbf{p} will be $\hbar\mathbf{k}$, and the energy of the particle is $E = \hbar^2 k^2 / (2m)$.

2.1.2 Particles in a Three-Dimensional Box

Consider again Eq. (2.5) or (2.6), but assume now that the particle is confined in a cubic box with side length L ; i.e., the potential vanishes for $-L/2 < x < L/2$, $-L/2 < y < L/2$, and $-L/2 < z < L/2$, but it is infinite otherwise. Therefore, we must look for solutions of a form similar to what we have just found for a free particle, but subject to the condition that the wavefunction vanishes at the boundary, and outside, of the box. Therefore, we must look for solutions $\psi_x(x)$, $\psi_y(y)$, and $\psi_z(z)$ of the form:

$$\psi_x(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n_x \pi x}{L}\right)$$

where n_x is an integer, with similar expressions being valid for y and z . The full wavefunction will now be

$$\psi(\mathbf{r}) = \left(\frac{8}{\Omega}\right)^{1/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right), \quad (2.17)$$

where $\Omega = L^3$ is the volume of the box and the energy of the particle will be

$$E_{n_x, n_y, n_z} = \frac{(n_x^2 + n_y^2 + n_z^2) \hbar^2 \pi^2}{2mL^2}.$$

Note that the normalization constant $A = (8/\Omega)^{1/2}$ in this case has been fixed by requiring that there is unit probability of finding the electron inside the box:

$$\int_{\Omega} d\mathbf{r} |\psi(\mathbf{r})|^2 = 1.$$

If we were considering a particle in one dimension, the particle would have only one degree of freedom and we would need only a single “quantum number,” say, n_x , to label the energy levels. In 3D, instead, the particle has 3 degrees of freedom and we now need three quantum numbers, n_x , n_y , and n_z to label the possible states (that is, the possible “types” of wavefunction) of the particle.

2.1.3 The Hydrogen Atom

The case of the H atom is conceptually similar to the case of the particle in a cubic box. Unfortunately, it is significantly more complicated from a mathematical perspective, because the potential confining the particle (the Coulomb potential energy is $-e^2/(4\pi\epsilon_0 r)$) is not “flat,” but depends on the distance r from the nucleus. Indeed, the time-independent Schrödinger equation we must solve is

$$\left[-\frac{\hbar^2 \nabla^2}{2m_e} + V(r) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (2.18)$$

where $V(r) = -e^2/(4\pi\epsilon_0 r)$. We have used the notation m_e for the mass of the particle, since we are specifically interested in an electron around a proton. Also, we have attempted to minimize the confusion caused by the fact that the symbol m will be used below to label a quantum number. It is true that the potential is not constant, so separating variables in Cartesian coordinates would not work: We would not be able to re-express this equation as the sum of terms that depends on a single variable, as we found in Eq. (2.9). However, the potential energy V depends only on the radial coordinate r , not the polar and azimuthal angles θ and ϕ . This spherical symmetry can be exploited to separate variables if we employ spherical coordinates. Thus, we look for solutions of the form:

$$\psi(\mathbf{r}) = \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi). \quad (2.19)$$

The “radial function” $R(r)$ describes the way the wavefunction spreads away from the nucleus. The “angular functions” $\Theta(\theta)$ and $\Phi(\phi)$ describe how the wavefunction is distributed as a function of the polar and azimuthal angles.

Rewriting Eq. (2.18) in spherical coordinates,

$$\begin{aligned} & \frac{1}{r^2 \sin \theta} \left[\sin \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] - \frac{2m_e V(r)}{\hbar^2} \psi \\ &= -\frac{2m_e E}{\hbar^2} \psi. \end{aligned} \quad (2.20)$$

and inserting Eq. (2.19), we have

$$\begin{aligned} & \frac{1}{r^2} \Theta \Phi \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{R\Phi}{r^2 \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{R\Theta}{r^2 \sin^2 \theta} \frac{d^2 \Phi}{d\phi^2} - \frac{2m_e V(r)}{\hbar^2} R\Theta \Phi \\ &= -\frac{2m_e E}{\hbar^2} R\Theta \Phi. \end{aligned} \quad (2.21)$$

Now, following the same procedure we have followed before in Cartesian coordinates, let's divide by $R\Theta\Phi$ the expression above:

$$\frac{1}{Rr^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{1}{r^2 \sin \theta} \frac{1}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} - \frac{2m_e V(r)}{\hbar^2} = -\frac{2m_e E}{\hbar^2}. \quad (2.22)$$

Multiplying by $r^2 \sin^2 \theta$ and rearranging the result, we obtain

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = r^2 \sin^2 \theta \left\{ \frac{1}{Rr^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{1}{r^2 \sin \theta} \frac{1}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) - \frac{2m_e [V(r) - E]}{\hbar^2} \right\}. \quad (2.23)$$

Now we follow the “usual” reasoning: The lhs is a function of ϕ alone, while the rhs is a function of r and θ . Since we can vary r , θ , and ϕ independently, the only way Eq. (2.23) can hold is for both sides to be equal to a constant. Let's call this constant m^2 (where m is to be viewed, for now, as a general complex number). Thus,

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m^2, \quad (2.24)$$

so that the “azimuthal” factor Φ must be of the form:

$$\Phi(\phi) \sim e^{\pm im\phi}, \quad (2.25)$$

up to a normalization constant. Since we require periodic (and so, single-valued in real space) solutions, we see that m must be an integer. This condition should remind us of the De Broglie and Bohr's arguments to explain the discrete nature of the atomic spectra by requiring that an integer number of wavelengths must “fit” into an orbit. Note also how the eigenvalue problem given by Eq. (2.24) [and, more generally, Eq. (2.20)] is defined not only by the differential equation, but also by the boundary conditions, and so by the space of functions we intend to confine our attention to; namely, differentiable, integrable over the entire space and single-valued/periodic, in our case. This is another way of expressing physically sensible boundary conditions. Returning to Eq. (2.23) and using Eq. (2.24), we see that

$$\begin{aligned} & \frac{1}{Rr^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{1}{r^2 \sin \theta} \frac{1}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \\ &+ \frac{1}{r^2 \sin \theta} \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} - \frac{m^2}{r^2 \sin^2 \theta} - \frac{2m_e [V(r) - E]}{\hbar^2} = 0. \end{aligned} \quad (2.26)$$

Multiplying this equation by r^2 , we can rewrite it as

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2m[V(r) - E]}{\hbar^2} r^2 = -\frac{1}{\sin \theta} \frac{1}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{m^2}{\sin^2 \theta}. \quad (2.27)$$

Once more, we see that the lhs is a function of r alone, while the rhs depends only on θ . Thus, both sides must be equal to a constant, say K . Therefore, we reach the two equations:

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2m_e[V(r) - E]}{\hbar^2} r^2 R = KR, \quad (2.28)$$

and

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{m^2 \Theta}{\sin^2 \theta} = -K\Theta. \quad (2.29)$$

We can now proceed in two ways, the first restricted to the case at hand, the second path being more general and being related with the *angular momentum operators*. Let's discuss them both. In order to proceed from Eq. (2.29), we'll skip some details here and simply state without proof that requiring Θ to be single-valued implies that K must be of the form $l(l+1)$, where l is a positive integer, much like requiring Φ to be single-valued resulted in an integer m before. Moreover, the integer m must take values of magnitude smaller than l (i.e., $m = 0, \pm 1, \pm 2, \dots, \pm l$).

** We should stop here for a brief comment. The statement above is the essence of what is called the theory of "orthogonal polynomials." The text by Arfken [6] gives an exceptionally clear overview of the topic. When trying to solve many types of ordinary differential equations of the form $Q(x)y(x)'' + P(x)y(x)' + \lambda y(x) = 0$, it is convenient to expand the unknown solution, $y(x)$, in a power series of x ; that is, $y(x) = \sum_n a_n x^n$. Inserting this series into the original differential equation, one can equate terms of the same power of x and obtain a set of recursive relations that the coefficients a_n must satisfy in order for $y(x)$ to be a solution. One finds that when the parameter λ takes discrete values, λ_N , then one can terminate the series at the term x^N , all coefficients a_n vanishing for $n \geq N$, for finite N . This results in the generation of polynomials $y_N(x)$, that constitute a basis set on the functional space considered; for example, in the Hilbert space $L^2(\mathbb{R})$ of all square-integrable complex functions of a real variable. These can be orthogonalized or orthonormalized using the Gram-Schmidt procedure. Hermite, Legendre, Jacobi, Laguerre, and Chebyshev polynomials belong to this class. In the context of Quantum Mechanics, usually the parameter λ is related to the eigenvalue of the Hamiltonian and the resulting discrete set of values λ_N yields the discrete spectrum, the polynomials y_N being related to the eigenvectors. We will encounter shortly two examples of such functions, the Legendre and Laguerre polynomials.*

Returning to Eq. (2.29), with these considerations we see that it must take the form:

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{m^2 \Theta}{\sin^2 \theta} + l(l+1)\Theta = 0. \quad (2.30)$$

Setting $x = \cos \theta$ transforms this equation into what is known as the "associated Legendre" equation whose solutions are the "associated Legendre polynomials"

$$P_l^m(x) = (1-x^2)^{m/2} \frac{d^m}{dx^m} P_l(x), \quad (2.31)$$

where the functions $P_l(x)$ are the Legendre polynomials. Thus, we have found that the full angular dependence of our solution has the form:

$$Y_l^m(\theta, \phi) = P_l^m(\cos \theta) e^{im\phi}. \quad (2.32)$$

Properly normalized, so that

$$\int_0^\pi d\theta \int_0^{2\pi} d\phi |Y_l^m(\theta, \phi)|^2 = 1, \quad (2.33)$$

these functions are called “spherical harmonics.”

The second way to proceed from Eq. (2.29) is to consider the angular momentum operators. In Classical Mechanics the orbital angular momentum of a particle is defined as

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \quad (2.34)$$

so that the z -component, for example, will be

$$L_z = xp_y - yp_x. \quad (2.35)$$

The quantum-mechanical equivalent will be the operator

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \quad (2.36)$$

Note that from the basic commutation rules between the position and the momentum operators,

$$[\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij}, \quad [\hat{x}_i, \hat{x}_j] = [\hat{p}_i, \hat{p}_j] = 0, \quad (2.37)$$

(where we have used the notation $x_1 = x$, $x_2 = y$, and $x_3 = z$ and similarly for p_1 , etc.) we have

$$[\hat{L}_z, \hat{x}] = i\hbar \hat{y}, \quad [\hat{L}_z, \hat{p}_x] = i\hbar \hat{p}_y, \quad (2.38)$$

$$[\hat{L}_z, \hat{y}] = -i\hbar \hat{x}, \quad [\hat{L}_z, \hat{p}_y] = -i\hbar \hat{p}_x, \quad (2.39)$$

and:

$$[\hat{L}_i, \hat{L}_j] = i\hbar \epsilon_{ijk} \hat{L}_k, \quad (2.40)$$

where $\epsilon_{ijk} = 1$ when (i, j, k) is a cyclical permutation of $(1, 2, 3)$, $\epsilon_{ijk} = -1$ for an anti-cyclical permutation, $\epsilon_{ijk} = 0$ otherwise. Defining the square magnitude of the total angular momentum,

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \quad (2.41)$$

we have

$$[\hat{L}^2, \hat{L}_j] = 0. \quad (2.42)$$

So, since \hat{L}^2 commutes with any \hat{L}_i , we can select a basis of common eigenstates of \hat{L}^2 and \hat{L}_z , that is

$$\hat{L}^2 |\psi\rangle = \alpha |\psi\rangle, \quad (2.43)$$

and

$$\hat{L}_z|\psi\rangle = \beta|\psi\rangle. \quad (2.44)$$

In the spherical-coordinates representation we have

$$\hat{L}^2 = \hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right], \quad (2.45)$$

and

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}. \quad (2.46)$$

Using these expressions, we see that Eq. (2.44) reduces to Eq. (2.24), so that m must be an integer (positive or negative). Then, Eq. (2.43) becomes identical to Eq. (2.29) with $K = l(l+1)$.

* This last conclusion can also be reached in another very elegant way that bypasses the need to consider orthogonal polynomials. We present it here, because a similar, purely algebraic, technique will be used to deal with the harmonic oscillator when we shall discuss elementary excitations and second quantization. Define the “raising/lowering” operators:

$$\hat{L}_{\pm} = \hat{L}_x \pm i \hat{L}_y \quad (2.47)$$

It is easy to see, using the commutation rules we have derived above, that

$$[\hat{L}^2, \hat{L}_{\pm}] = 0, \quad (2.48)$$

(where, for clarity, we should recall that $\hat{\mathbf{L}} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$, so that $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$), and

$$[\hat{L}_z, \hat{L}_{\pm}] = \pm \hbar \hat{L}_{\pm}. \quad (2.49)$$

Applying \hat{L}_{\pm} on an eigenstate $|\psi\rangle$ of \hat{L}_z with eigenvalue β , using Eq. (2.49), we have

$$\hat{L}_z \hat{L}_{\pm} |\psi\rangle = [\hat{L}_{\pm} \hat{L}_z \pm \hbar] |\psi\rangle = (\beta \pm \hbar) |\psi\rangle. \quad (2.50)$$

This expression shows that the operators \hat{L}_{\pm} raise (+) or lower (−) the eigenstate $|\psi\rangle$ of \hat{L}_z to another eigenstate of \hat{L}_z , now with a larger/smaller eigenvalue ($\beta \pm \hbar$). Since the total angular momentum is finite, the eigenvalues β of \hat{L}_z must span in discrete steps the range $(-m\hbar, m\hbar)$, where m is an integer, for this raising/lowering process to terminate upwards or downwards. Therefore, the states $|\psi\rangle$ can be labeled as $|\alpha, m\rangle$, where α is a yet-to-be-determined eigenvalue of \hat{L}^2 . To determine α , a little algebra using the commutation rule, Eq. (2.48), and the definitions of \hat{L}^2 and \hat{L}_{\pm} , shows that we must have $\alpha = l(l+1)\hbar^2$, where l is a positive integer, including 0, and that m must be smaller than l . Thus, we can recast Eqs. (2.43) and (2.44) as

$$\hat{L}^2 |l, m\rangle = l(l+1)\hbar^2 |l, m\rangle, \quad (2.51)$$

and

$$\hat{L}_z |l, m\rangle = m\hbar |l, m\rangle, \quad (2.52)$$

with $l = 0, 1, 2, 3, \dots$ and m can take the $2l+1$ values $-l, -l+1, \dots, -1, 0, 1, l-1, l$.

Leaving now the abstract algebraic domain and returning to the real-space representation of the eigenstates, we see that the spherical harmonics are eigenfunctions of the angular momentum operator corresponding to a total angular momentum $\sqrt{l(l+1)}\hbar$ with projection $m\hbar$ over the z -axis (the polar axis). Note also that the spherical harmonics satisfy the orthogonality condition:

$$\int_0^\pi d\theta \int_0^{2\pi} d\phi Y_l^m(\theta, \phi) Y_{l'}^{*m'}(\theta, \phi) = \delta_{mm'} \delta_{ll'}. \quad (2.53)$$

Returning to the radial function R , this must obey Eq. (2.28) with $K = l(l+1)$:

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2m_e[V(r) - E]}{\hbar^2} r^2 R - l(l+1)R = 0. \quad (2.54)$$

Now we can make use of the fact that we are dealing with a Coulomb potential and set $V(r) = -e^2/(4\pi\epsilon_0 r)$. Thus, the radial wavefunction $R(r)$ must satisfy the equation:

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m_e E}{\hbar^2} r^2 R - l(l+1)R + \frac{2m_e}{\hbar^2} \frac{e^2}{4\pi\epsilon_0} r R = 0. \quad (2.55)$$

Let us now introduce the new dependent variable $u(r) = rR(r)$, which obeys the equation:

$$-\frac{\hbar^2}{2m_e} \frac{d^2 u}{dr^2} + \frac{\hbar^2 l(l+1)}{2m_e r^2} u - \frac{e^2}{4\pi\epsilon_0 r} u = Eu. \quad (2.56)$$

Defining the independent variable

$$\rho = \frac{(8m_e |E|)^{1/2} r}{\hbar}, \quad (2.57)$$

and a measure λ of the binding energy of the particle,

$$\lambda = \frac{e^2}{4\pi\epsilon_0 \hbar} \left(\frac{m_e}{2|E|} \right)^{1/2}, \quad (2.58)$$

Eq. (2.56) becomes

$$\frac{d^2 u}{d\rho^2} - \frac{l(l+1)}{\rho^2} u + \left(\frac{\lambda}{\rho} - \frac{1}{4} \right) u = 0. \quad (2.59)$$

Clearly, at large ρ the solution behaves as $u \sim \exp(\pm \rho/2)$, the minus sign being the only physically meaningful choice. Thus, setting

$$u(\rho) = F(\rho) \exp(-\rho/2), \quad (2.60)$$

Eq. (2.59) implies

$$\frac{d^2 F}{d\rho^2} - \frac{dF}{d\rho} + \left[\frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2} \right] F = 0. \quad (2.61)$$

Following the general procedure outlined when discussing orthogonal polynomials, one can show that the solutions of this equation (closely related to the so-called associated Laguerre polynomials) have an acceptable behavior in the limit $\rho \rightarrow \infty$ only for integer values of λ (say, $\lambda = n$, where n is an integer) larger than l so that the “radial” component of the wavefunction will be defined by the two integers n and $l < n$. The index n is directly related to the energy E via Eq. (2.58).

As a result of this discussion, we see a situation similar to what we saw before in the case of the 3D particle in the cubic box: We need three quantum numbers to label the eigenvectors (with eigenfunctions $\psi_{nlm}(\mathbf{r}) = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi) = R_{nl}(r)Y_l^m(\theta, \phi)$), and eigenvalues (energy levels) of the Hamiltonian: The “principal” (or “radial”) quantum number, n , can take the values:

$$n = 1, 2, 3, \dots \infty.$$

Usually (that is, in the absence of magnetic fields and ignoring weaker perturbations), the electron energy depends only on this number via Eq. (2.58): When $\lambda = n$,

$$E_n = \frac{m_e e^4}{2(4\pi\hbar)^2 n^2}, \quad (2.62)$$

in agreement with the early result of Bohr’s model. The quantum numbers l and m are related to the angular momentum: as we saw, $l(l+1)\hbar^2$ is its squared magnitude and $m\hbar$ its component along the polar axis. These can take the values:

$$\begin{aligned} l &= 0, 1, \dots, n-1, \quad (n \text{ total number of values}) \\ m &= -l, -l+1, \dots, 0, 1, \dots, l-1, l, \quad (2l+1 \text{ total number of values}). \end{aligned}$$

For $l = 0$, we must also have $m = 0$. In this case the wavefunction does not depend on the angles θ and ϕ . These are fully spherically symmetric wavefunctions (for every n) and are called *s*-waves. For $l = 1$ we can have three different wavefunctions for $m = -1, 0, +1$. These are called *p*-waves and can be expressed as functions shaped like “lobes” pointing along the *x*-, *y*-, or *z*-axis. For $l = 2$ we can have five states ($m = -2, -1, 0, +1, +2$), called *d*-waves. For $l = 3$ we have seven *f*-waves, and so on.

2.1.4 Periodic Table

We are now ready to build the periodic table of the elements. We shall do it as if we were building an onion, one “shell” at a time, from the inside out. We shall call “shell” each layer defined by a common quantum number n , “subshells” those with common angular quantum number l . The word “orbital” or “state” denotes any combination of quantum numbers.

Before building atoms, though, we need to know two additional facts: The existence of an additional electronic degree of freedom (“spin”) and of “Pauli’s exclusion principle.” They will be discussed at length later. For now, we consider them qualitatively.

Regarding spin, in addition to the three degrees of freedom that all particles have in three dimensions (3D), most particles also possess an additional “internal” degree of freedom, s , which one can visualize as the particle “spinning” around a polar axis, much like a spinning top or the planets. Thus, spin is an internal angular momentum of the particle. As we just saw for the orbital angular momentum, spin can also take only discrete values in integer or semi-integer multiple of the reduced Planck constant. Photons, some nuclei, and some elementary particles have integer values of spin ($s = 0$ or $n\hbar$, where n is an integer.). For reasons we shall see later, these particles are called “Bosons.”

Electrons, protons, and neutrons have half-integer spin ($s = (n\hbar/2)$). They are called “Fermions.” Electrons have spin $\hbar/2$ (usually said “spin one-half”). Every electron can exist in two different spin states: Spin “pointing up” ($s = \hbar/2$) or “pointing down” ($s = -\hbar/2$). Both are states with angular momentum of magnitude $\hbar/2$, but they differ in the direction of rotation around their axis.

Regarding Pauli’s principle, in order to explain the periodic table and the electronic structure of the atoms, the German physicist Wolfgang Pauli had to invoke a new postulate (later demonstrated rigorously): Given an energy level, characterized by a set of quantum numbers, it can be occupied only by one Fermion (so, electrons). Therefore, a given hydrogen state characterized by the quantum numbers (n, l, m) , can be empty or occupied by one or two electrons (in which case an electron will have spin up, the other spin down). Attempting to add a third electron would violate Pauli’s principle.

Let’s start with the simplest element, H. Its nucleus has a single positively charged proton and it is surrounded by a single electron. The lowest possible orbital the electron can occupy is the “ground state” ($n = 1$, $l = 0$, and $m = 0$). We use the notation $1s^1$, meaning that in the orbital $1(n = 1)$, which is an s -wave ($l = 0$), we have one electron (the superscript “1”). Note that the electron is bound rather weakly to the nucleus: the ionization energy, E_1 in Eq. (2.62) is about 13.6 eV. This quantity is called a “Rydberg” and is indicated by the symbol “Ry”. We shall use it very frequently in later chapters. Therefore, H loses its electron quite easily; that is, it is easily ionized. This trait is common to all elements with only one electron in the outermost shell. These elements are very reactive (think of hydrogen reacting with oxygen!).

The next simplest element is He. Solving the Schrödinger equation for this atom already introduces enormous complications. The wavefunction we must find is now a function of six variables, $\psi(\mathbf{r}_1, \mathbf{r}_2)$, \mathbf{r}_1 and \mathbf{r}_2 being the coordinates of the two electrons. Unlike the case of the hydrogen atom, in which the potential energy is given, now the potential energy must include also the electrostatic potential felt by each electron due to the charge of the other electron. The potential energy due to the Coulomb interaction with the charge of the nucleus and with the “time averaged” charge distribution of the other electron is called the “Hartree” energy. However, more subtle contributions to this potential energy come from the fact that Pauli’s principle can also be reformulated by requiring that the total wavefunction be antisymmetric under exchange of the two electrons, that is, $\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)$. This property will also be discussed at length in later chapters, since it affects very strongly the electronic properties of crystals. For now, we simply observe that this “antisymmetrization” makes electron with spins pointing in the same direction repel each other; the opposite is true for electrons with spins pointing in the opposite direction. The Coulomb repulsion between the electrons, therefore, will be modified by this effect and the additional (positive or negative) change in energy is called the “exchange” energy. An additional correction (the “correlation” energy) will be discussed in later chapters. What matters now is that the Hartree and exchange energies depend on the spatial distribution of the electrons, $|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2$. So, the potential energy entering the Schrödinger equation depends on the wavefunction itself. This renders the Schrödinger equation nonlinear and only approximate or numerical solutions can be found. The case of heavier atoms, so with a much larger number of electrons, is, of course, extremely complicated. In later chapters we will see how one can handle such a situation even in crystals, systems with an extremely large number of electrons. Here, we should just keep these facts in mind and we shall deal with the problem at a qualitative level.

Returning to the He atom, its nucleus now has two protons (so that the “atomic number” of He is $Z = 2$). Two neutrons are required to prevent the Coulomb repulsion between the protons from causing a disintegration of the nucleus itself. (These are forces of a different nature, the *strong nuclear forces* that we will ignore in this book.) Two electrons orbit the nucleus and, in the configuration of the lowest possible energy, both are in the lowest-energy “shell,” provided they align their spins in opposite directions. We use the notation $1s^2$. Note that we have fully populated the first “shell.” If we were to ionize negatively the atom by adding another electron, this would have to occupy the next higher-energy shell, $n = 2$, because there is no more room in the $n = 1$ shell. Thus, the third electron would have to go farther away from the nucleus. So, He does not easily acquire another electron.

On the other hand, stripping one electron away from the He atom is energetically very expensive, since both electrons sit quite close to the doubly charged nucleus. Therefore, helium does not “like” to lose or gain electrons (that is, becoming ionized). He, like all elements which have a fully occupied shell, is chemically inert.

The third element, Li, has three protons in its nucleus ($Z = 3$), so it must have three electrons orbiting it in order to be charge neutral. The third electron, as we just saw, must occupy the $n = 2$ shell, so Li will have the electronic configuration $1s^2 2s^1$. It is a very reactive metal, for the reasons we discussed dealing with H: It is very easy to strip away the lone outer electrons, leaving behind a positive Li ion.

We now keep populating the $n = 2$ shell, adding another electron in the s orbital (beryllium, Be, $1s^2 2s^2$ with $Z = 4$), then 6 more into the 3 p orbitals, adding electrons with spin up and spin down in sequence. As we move from the reactive metals (Li and Be), we build elements with 3 “outer” electrons (boron, B, $1s^2 2s^2 2p^1$), 4 outer electrons (carbon, C, $1s^2 2s^2 2p^2$), 5 (nitrogen, N, $1s^2 2s^2 2p^3$), 6 (oxygen, O, $1s^2 2s^2 2p^4$), and 7 outer electrons (fluorine, F, $1s^2 2s^2 2p^5$). As we do so, we move from elements which like to lose electrons, to those who like to gain them. Eventually, with neon (Ne, $Z = 10$, $1s^2 2s^2 2p^6$) we complete the $n = 2$ shell and we hit another inert gas, like He, unlikely to react chemically. The eight slots we have filled while populating the $n = 2$ shell are the eight columns of the periodic table. The chemical properties of any two elements having the same number of electrons in the outer shell are very similar. So, as we fill the $n = 3$ shell, we start from sodium (column I, Na, $Z = 11$, $1s^2 2s^2 2p^6 3s^1$) which, having only one electron in the outer shell, behaves like Li. And we end up with argon (column VIII, Ar, $Z = 18$, $1s^2 2s^2 2p^6 3s^2 3p^6$) which is another inert gas like He and Ne.

Things get a little more complicated now, because the energy of the $4s$ shell is lower than that of the $3d$ shell. This is caused by the perturbation of the Coulomb energy (Hartree, exchange, and correlation) due to the many electrons present in the system, so that the energetic “ladder” expected from an analogy with the eigenlevels of the H atom fails significantly. The dependence of the energy level on the quantum number l , for example, is a manifestation of this fact. So, with potassium (K) and calcium (Ca) we fill the $4s$ shell, but then we go back filling the $3d$ shell. The fact remains that—up until further complications caused by the f states of transition metals—each element belongs to its own column which determines the chemical properties via the number of electrons in the outer shell.

Of interest to us are silicon (Si, $Z = 14$, $1s^2 2s^2 2p^6 3s^2 3p^2$) and germanium (Ge, $Z = 32$, $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$) which, like C, belong to the IV column. Their 4 outer electrons are $s^2 p^2$ and can easily “hybridize” into 4 sp^3 orbitals, forming the tetrahedral structure required to bond atoms in their cubic crystal form. Elements of column III (B, Al, Ga, and In) have outer electrons arranged as $s^2 p^1$, that is, one fewer electron than in Si and Ge. Elements of column V (N, P, As, and Sb) have outer electrons arranged as $s^2 p^3$, that is, one more electron than in Si and Ge.

Finally, electrons in fully occupied shells are called “core electrons.” They do not contribute to the chemical activity of the element. Electrons in the outer shell are called “valence electrons.”

2.2 Molecules and Bonds

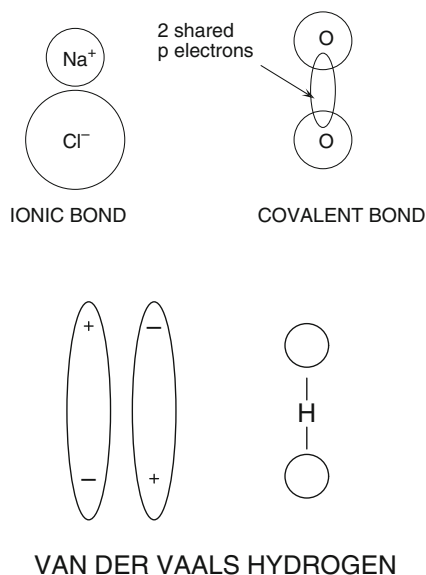
The nature of chemical bonds, molecular orbitals, hybridization, and such, has been subject, and still is, of too many studies and even controversy. Being interested in solids and electronic transport in crystals, we can only give here a bird’s eye view. Excellent texts such as Pauling’s [7] and Harrison’s [8] give a comprehensive and detailed account from the perspective of a chemist (Pauling, arguably one of the fathers of the concept of chemical bond in light of Quantum Mechanics) and of a physicist (Harrison).

If we bring several atoms together, interesting things happen, depending on the electronic populations of the outer shell.

1. *Nothing.* For example, bringing 2 Ne atoms together, both atoms retain their electronic configuration unaltered, as they are both in a configuration of a completely filled outer shell with 8 electrons (2 in s orbitals, 6 in p orbitals). This is why elements of the VIII column are called “inert” elements (or gases).
2. *Formation of an ionic bond.* Let’s consider Na and Cl. Na has 1 electron in the outer s shell, Cl 7 valence electrons (2 in the s shell, 5 in the p shell). Energetically, it is advantageous for Na to release its electron (weakly bound, as the core electrons shield the nuclear charge), while Cl “loves” to acquire that electron to complete the filling of its outer shell. Thus, the sodium atom becomes positively ionized (Na^+) and the chlorine atom becomes negatively ionized (Cl^-). Now we have a positive (Na^+) and negative (Cl^-) particle which are attracted by the strong Coulomb force. The two ions are said to have formed an “ionic bond” and stick together in the NaCl molecule (regular kitchen salt when in crystalline form). Semiconducting crystals, like GaAs (Ga in column III, As in column V, so this is a so-called III–V compound semiconductor), are bound in large part by ionic bonds. Water (H_2O) is similarly formed, although now the charge transfer takes place among three atoms: The 2 H atoms give their electrons to O which has 6 valence electrons, and so it fills its outer shell. Thus, we now have two positively charged H^+ ions bound to a doubly ionized O^{2-} ion. Ionic bonds are usually quite strong with “binding energies” of several eV, i.e., of the order of 1–10 eV.
3. *Formation of a covalent bond.* Let’s consider two oxygen atoms brought together. They are in the $2s^2 2p^4$ configuration in the outer shell. They would both “love” to fill their outer shells by adding two electrons. They can do that by sticking together and sharing their two outer electrons, thus forming the O_2 molecule. They form a “covalent bond.” The situation with Si and Ge is somewhat more complicated. They have 4 electrons in their outer shells ($s^2 p^2$). They can “hybridize” to form 4 sp^3 orbitals. These are linear combinations of the s orbital and of the 3 p orbitals that, when Si atoms are arranged in a crystal, form a state with lower energy than the separate s and p orbitals. These hybrid orbitals are arranged in a tetragonal fashion, so that each Si atom has four neighbor Si atoms to form covalent bonds. Therefore, the Si_2 molecule cannot exist, but several Si atoms can form a “network” of tetragonal bonds and form a covalent crystal. Covalent bonds are, usually, the strongest bonds.
4. *Metallic bond.* When we bring together a large number of metallic atoms (say, Li or Be), the weakly bound single electrons belonging to each one of the many atoms are “shared” among all ions. The ions form a “lattice” (as we shall see below dealing with crystals), the shared electrons keeping the lattice together. The metallic bond has a strength comparable to that of ionic bonds.
5. *Hydrogen bond.* This is still a poorly understood bond present in water-ice, and, for example, binding the bases to the chain of DNA molecules. A H atom between two molecules acts as a bridge binding (somewhat weakly) the molecules together, as its lone electrons “resonates” between them.
6. *Van der Waals force.* Although generally a weaker effect, another type of interaction affects solids and some relatively chemically inactive molecules. When brought together, rather than exchanging or sharing electrons, atoms or molecules “polarize” their electronic clouds. The resulting interaction is between electric dipoles with opposite orientation. The force decays very quickly with distance. This is an interaction typical of flat surfaces (think of two sheets of glass) and polymers.

Illustrations of the ionic, covalent and Van der Waals bond are shown in Fig. 2.1. Note also that, although we have made a sharp distinction between ionic and covalent bonds, in many cases both types of bonds contribute: For example, in III–V compound semiconductors, a large charge transfer causes ionicity of the bonds, but the fact that most of these crystallize into the face-centered cubic

Fig. 2.1 Cartoon representation of chemical bonds: in an ionic bond, two atoms with large electron affinities exchange charge, resulting in two ionized atoms that are attracted by the resulting Coulomb force. In a covalent bond, atoms with similar or identical electron affinities share their valence electrons in a bonding orbital



structure resulting from sp^3 hybridization shows that the bond is also largely covalent. Such bonds are often characterized by specifying the degree of ionicity.

We have outlined why the chemical properties of the elements are fully determined by the valence electrons. The number of electrons in the outer shell also determines the chemical valence of the atom. As a general rule, electrons with fewer than 3 electrons in the outer (incomplete) shell have a chemical valence equal to the number of electrons. For example, Li (one electron in the outer shell) has valence I, Ga (3 electrons in the outer shell) has valence III. If the outer shell contains 6 electrons or more, the valence of the element is 8 minus the number of electrons. Elements with a more complicated electronic structure of the outer shell(s) can exhibit several different chemical valence numbers.

Finally, it is important to realize that during the formation of a bond, the electronic orbitals change their structure. For example, during the formation of the O_2 molecule the electrons "shared" by the two oxygen atoms will "orbit" both cores (nuclei+core electrons), forming new orbitals by a "linear superposition" of the wavefunctions of the $2p$ orbitals of each atom. As shown in the figure below, out of these two "single atom" orbitals we form two molecular orbitals: A lower-energy "bonding orbital" and a higher-energy "antibonding orbital," respectively, at a slightly lower and higher energy than the original single-atom orbitals. The bonding orbital is occupied by the two shared electrons and it exhibits a larger charge density (that is, a larger $|\psi|^2$) between the atoms. In other words, there is a large probability of finding the electrons between the atoms. Thus, this orbital contributes to keeping the atoms together. The antibonding orbital is empty and it is associated with a charge density (again, $|\psi|^2$), which is larger away from the bond. A bonding and an antibonding orbital are illustrated in Fig. 2.2.

Very large molecules may consist of a very large number of atoms. For example, polymers, such as the polyparaphenylene (PPP) chain of C atom illustrated in Fig. 2.3. In such a chain, each C atom on the "center" atomic line is bound to three more C atoms in hybrid sp^2 orbitals (note that the notation used here differs from the notation used before: The superscript "2" now indicates that 2 p orbitals make up the hybrid orbital): The outer s orbital and three p orbitals split into three linear combinations of the lone s and two p bonding orbitals, and a single p_z orbital that "sticks out" of the plane of the molecule. For C atoms on the outer lines of the chain, two such sp^2 orbitals bond each C atom to its two neighbors; the remaining sp^2 orbital is "terminated" by an H atom. The out-of-plane p_z orbitals hybridize into a set of bonding π orbitals that extend throughout the chain (the use of Greek letters is briefly explained at the end of the chapter). Higher-energy orbitals (the $3s$ and $3p$)

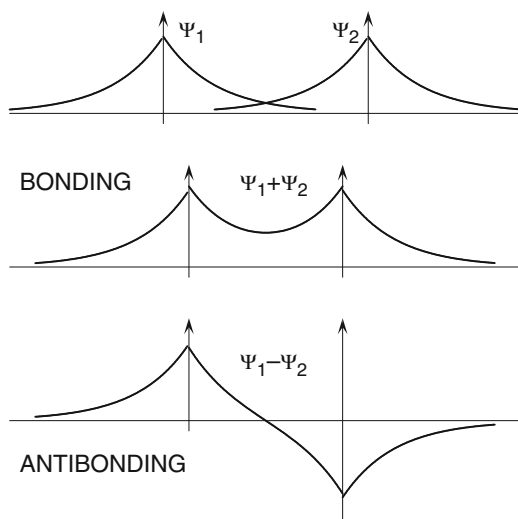


Fig. 2.2 Schematic representation of bonding and antibonding states in a diatomic molecule: Two molecular orbitals can result from the linear superposition of the two outer-shell wavefunctions of the two atoms, a bonding orbital with a large electron charge density between the atoms, charge that contributes to the bonding and has a lower Coulomb energy; and an antibonding, higher-energy orbital. The Van der Waals interaction between two molecules stems from the mutually induced charge polarization and resulting Coulomb attraction. In a H-bond, a hydrogen atom acts as a bridge, being shared by the two atoms or molecules

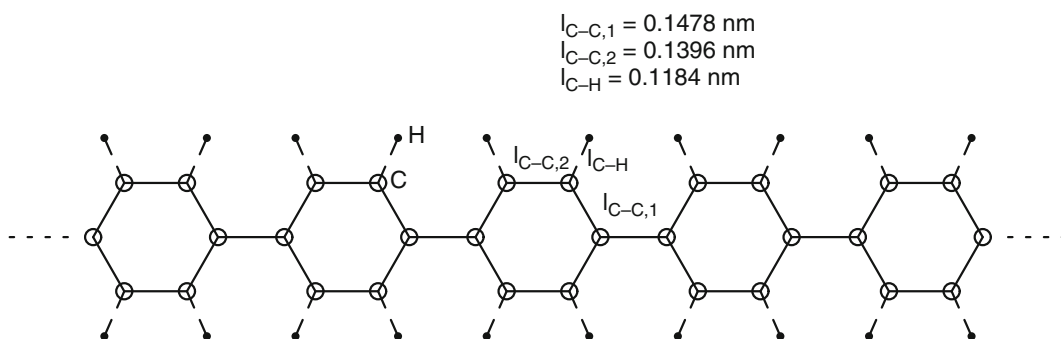


Fig. 2.3 The polyparaphenylene (PPP) chain. The *circles* denote C atoms, the little dots at the edges of the chain denote H atoms. The lines connecting the atoms are sp^2 hybrid atomic orbitals. The remaining p_z orbitals in the outer shells of the C atoms “stick” in and out of the page. They “fuse” together into a molecular π bonding orbital that extends throughout the entire chain. They are the highest-occupied molecular orbitals, HOMO. The next higher-energy molecular orbitals, σ^* and π^* , are, instead, empty antibonding orbitals. They are the lowest-unoccupied molecular orbitals, LUMO

hybridize into antibonding σ and π bonds. In this case, the polymers exhibit an energy difference between the highest-energy occupied (hybridized) molecular orbital (HOMO) and the lowest-energy unoccupied molecular orbital (LUMO). Such a molecule will be electrically insulating, since only electrons occupying the delocalized LUMO (that is, spread among many atoms) can move if driven by an electric field, but there are no electrons in these states. Other examples of molecules may be found in which the valence hybridized orbitals are only partially occupied, so these molecules will be good conductors, behaving as metals. These considerations will be repeated almost verbatim when dealing with insulators and conductors in the context of crystals (solids). Strands of DNA, or even larger proteins, can fall into any of these categories. Their electrical properties are now being exploited

to “mark” them for medical or biological purposes, “sense” them in diagnostics, such as detecting the change of conductivity induced by a mismatched basis in a DNA sequence. Also, electronic devices based on single molecules are an extremely active area of research. A complete discussion of these topics is, clearly, outside the scope of this text, although the connections are many: understanding their physical principles, their atomic and electronic structure, and their electronic and electrical properties requires concepts, mathematical and numerical techniques that are very similar, often identical, to those discussed here. The text by Helgaker et al. [9] constitutes an excellent and relatively recent overview of this fast-developing field.

Finally, note how hybrid molecular orbitals are termed with the Greek letter(s) associated with the Latin character of the atomic orbital that enters the hybridization (*s* atomic orbitals hybridize into σ molecular orbitals, *p* can enter into π -bonds as well as σ -bonds).

Problems

2.1. (The de Broglie Hypothesis and the Bohr Atom) The *de Broglie’s assumption* to explain atomic spectra (among other things) consists in assuming that *all* forms of matter behave as particles or waves, depending on the situation. For a particle of mass *m*, the wavelength λ of the associated “pilot wave” will be given by

$$p = mv = \frac{h}{\lambda}$$

Consider how de Broglie’s suggestion may explain some features of the hydrogen atom:

- Show that the de Broglie assumption, together with the “quantization condition” that the circular orbit be an integer multiple of the length of the electron wavelength (that is, $n\lambda = 2\pi r$, where *r* is the radius of the orbit, *n* an integer), implies that only discrete orbits are allowed.
- Calculate the total energy (kinetic plus potential) in each orbit characterized by an integer *n*. Show that the result is identical to what is shown in Eq. (2.62).

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