# Chapter 13
# Other Examples of the Schrödinger Equation

## 13.1 Introduction

A number of properties of the one-dimensional, time-independent Schrödinger equation can be worked out without specifying the form of the coefficient. To this purpose one examines the two fundamental solutions, which are real because the coefficient is such. One finds that the fundamental solutions do not have multiple zeros and do not vanish at the same point; more precisely, the zeros of the first and second fundamental solution separate each other. It is also demonstrated that the character of the fundamental solutions within an interval is oscillatory or non oscillatory depending on the sign of the equation's coefficient in such an interval. After completing this analysis, the chapter examines an important and elegant solution method, consisting in factorizing the operator. The theory is worked out for the case of localized states, corresponding to discrete eigenvalues. The procedure by which the eigenfunctions' normalization is embedded into the solution scheme is also shown. The chapter continues with the analysis of the solution of a Schrödinger equation whose coefficient is periodic; this issue finds important applications in the case of periodic structures like, e.g., crystals. Finally, the solution of the Schrödinger equation for a particle subjected to a central force is worked out; the equation is separated and the angular part is solved first, followed by the radial part whose potential energy is specified in the Coulomb case. The first complements deal with the operator associated to the angular momentum and to the solution of the angular and radial equations by means of the factorization method. The last complement generalizes the solution method for the one-dimensional Schrödinger equation in which the potential energy is replaced with a piecewise-constant function, leading to the concept of transmission matrix.

## 13.2 Properties of the One-Dimensional Schrödinger Equation

In the general expression (11.44) for the transmission coefficient, the fundamental solutions $u$, $v$ appear in the denominator. It is then necessary to investigate the zeros of the solutions of (11.28). Due to the $u(0) = 1$ prescription, the possible zeros of $u$ belong to the interval $0 < x \leq s$, while those of $v$ belong to the interval $0 \leq x \leq s$.



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If one or more zero exist, they can not be multiple. In fact, if $u$ had a multiple zero at $x_m$ it would be $u(x_m) = 0$, $u'(x_m) = 0$, hence $u = 0$ would be a solution of (11.28) compatible with such conditions. In fact, because of the uniqueness of the solution, $u = 0$ would be the only solution. Observing that $u$ is continuous, this would contradict the condition $u(0) \neq 0$. Similarly, if $v$ had a multiple zero it would vanish identically. Remembering that the derivative of the solution is continuous, this would contradict the condition $v'(0) = 1$ of (11.40). Another property is that $u$ and $v$ cannot vanish at the same point. This is apparent from the relation $W(x) = u\,v' - u'\,v = 1$ demonstrated in Sect. A.12. For the same reason, $u'$ and $v'$ cannot vanish at the same point.

If one of the solutions, say $u$, has more than one zero in $0 < x \leq s$, then the following property holds: between two consecutive zeros of $u$ there is one and only one zero of $v$. Let $x_L, x_R$ be two consecutive zeros of $u$, with $0 < x_L < x_R \leq s$. The property is demonstrated by showing, first, that a contradiction would arise if there were no zeros of $v$ between $x_L$ and $x_R$ (that is to say, at least one zero must exist there) and, second, that if a zero of $v$ exists between $x_L$ and $x_R$, it must be unique [102]. To proceed one considers the function $u/v$ in the interval $x_L \leq x \leq x_R$. By definition $u/v$ vanishes at the boundaries of such an interval while, as shown above, $v$ cannot vanish at the boundaries. If one assumes that there are no zeros of $v$ inside the interval, then $u/v$ exists everywhere in the interval, and is also everywhere continuous with a continuous first derivative because $u$ and $v$ are solutions of the second-order differential Eq. (11.28). As $u/v$ vanishes at $x_L$ and $x_R$, its derivative must vanish at least once in the open interval $x_L < x < x_R$. However, this is impossible because $\mathrm{d}(u/v)/\mathrm{d}x = -W/v^2 = -1/v^2 \neq 0$. This shows that $v$ must have at least one zero between $x_L$ and $x_R$. Such a zero is also unique because, if $v$ had two zeros in $x_L < x < x_R$, then by the same reasoning $u$ would have one zero between them, so $x_L$ and $x_R$ would not be consecutive. The property may be restated as *the zeros of two real linearly-independent solutions of a second-order linear differential equation separate each other*. The property does not hold for complex solutions.

So far the properties demonstrated in this section did not consider the sign of the coefficient $q(x) = 2\,m\,(E - V)/\hbar^2$ of (11.28). The coefficient separates the interval $0 \leq x \leq s$ into subintervals where $q$ is alternatively positive or negative. If $q$ is continuous the extrema of the subintervals are the zeros of $q$, otherwise they may be discontinuity points of $q$. In either case the behavior of the solution $u$ within each subinterval depends on the sign of $q$ there. To show this, consider the function $\mathrm{d}(u\,u')/\mathrm{d}x = (u')^2 - q\,u^2$, where the expression at the right hand side has been found by means of (11.28). If $q \leq 0$ in the subinterval, then $\mathrm{d}(u\,u')/\mathrm{d}x$ is non negative. It follows that $u\,u'$ is a non-decreasing function in the subinterval, hence it has one zero at most. Remembering that $u$ and $u'$ can not vanish at the same point, one of the following holds: *i)* neither $u$ nor $u'$ vanish in the subinterval, *ii)* either $u$ or $u'$ vanishes once in the subinterval. For a given interval a function is called *non oscillatory* if its derivative vanishes at most once. It follows that the solution $u$ is non oscillatory in those subintervals where $q \leq 0$. The case $V = V_0 > E > 0$ in the interval $0 < x < s$, considered in Sect. 11.3.1, is of this type.

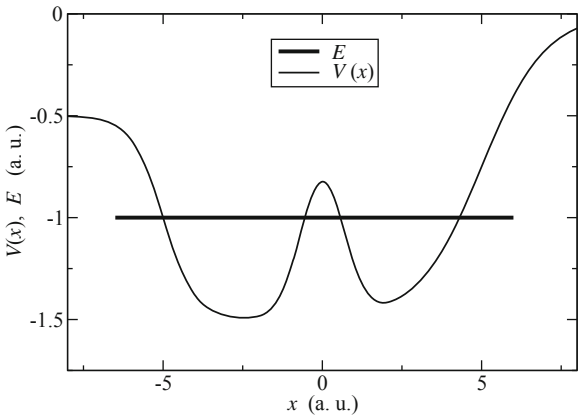


**Fig. 13.1** Form of the potential energy that gives rise to localized states (Sect. 13.3). Only one state $E$ is shown

## 13.3 Localized States—Operator's Factorization

It may happen that the form of the potential energy $V$ in the interval $0 \leq x \leq s$ is such that $V$ has one or more negative minima (Fig. 13.1). In this case negative eigenvalues of $E$ may exist, giving rise to localized states. To treat this case one must preliminarily observe that the eigenfunctions do not vanish identically outside the interval $0 \leq x \leq s$, because the minima of $V$ are finite. As a consequence, it is convenient to replace the above interval with $x_1 \leq x \leq x_2$, where the two boundaries may be brought (independently from each other) to $-\infty$ or $+\infty$, respectively. Letting

$$\lambda = \frac{2m}{\hbar^2} E, \qquad r_l(x) = -\frac{2m}{\hbar^2} V, \tag{13.1}$$

the Schrödinger Eq. (11.28) becomes

$$w'' + r_l\, w + \lambda\, w = 0. \tag{13.2}$$

The integer index $l = 0, 1, \ldots$ is attached to $r(x)$ for convenience. In fact, in typical applications the form of the potential energy in (13.1) may be prescribed by a previous separation procedure in which the index is involved. As will be shown after the analysis of the solution procedure, index $l$ may eventually be disposed of. For the time being, the solutions of (13.2) must be considered as dependent on the eigenvalue $\lambda$ and on the index $l$, namely, $w = w_{\lambda l}(x)$. Also, for a given pair $\lambda$, $l$ the eigenfunctions are non degenerate due to the normalization condition. As a consequence, two eigenfunctions belonging to the same pair differ by a multiplicative constant at most.

### *13.3.1 Factorization Method*

A possible method for solving (13.2) is expanding $w$ into a power series, replacing the series into (13.2), collecting the terms of equal power, and letting their coefficients

vanish. This provides a recurrence relation involving the coefficients of the series; then, the latter is suitably truncated to obtain a square-integrable solution. Another method for solving (13.2), that greatly reduces the calculation effort and brings about a procedure of supreme elegance, is the operator's factorization. The conditions that make the factorization possible are illustrated in [52] and are briefly reported here. In essence they amount to finding a function $g_l(x)$ and a parameter $L_l$ such that (13.2) may be recast as

$$\left(g_{l+1} + \frac{\mathrm{d}}{\mathrm{d}x}\right)\left(g_{l+1} - \frac{\mathrm{d}}{\mathrm{d}x}\right) w_{\lambda l} = (\lambda - L_{l+1})\, w_{\lambda l}, \tag{13.3}$$

$$\left(g_l - \frac{\mathrm{d}}{\mathrm{d}x}\right)\left(g_l + \frac{\mathrm{d}}{\mathrm{d}x}\right) w_{\lambda l} = (\lambda - L_l)\, w_{\lambda l}. \tag{13.4}$$

Note that both (13.3) and (13.4) must be identical to (13.2). An additional constraint is that, for a given integer $n$, it must be $L_{n+1} > L_{l+1}$, $l = 0, 1, \ldots, n-1$. To proceed, the boundary conditions $w_{\lambda l}(x_1) = w_{\lambda l}(x_2) = 0$ will be assumed. If one or both boundaries are at infinity, the condition $\int |w_{\lambda l}|^2 \, \mathrm{d}x < \infty$ will also be assumed. Now, imposing that (13.3) is identical to (13.2) yields $g_{l+1}^2 + g_{l+1}' + L_{l+1} = -r_l$ whence, letting $l \leftarrow l - 1$,

$$g_l^2 + g_l' + L_l = -r_{l-1}. \tag{13.5}$$

Similarly, imposing that (13.4) is identical to (13.2) leads to

$$g_l^2 - g_l' + L_l = -r_l. \tag{13.6}$$

Adding (13.6) to (13.5) and subtracting (13.6) from (13.5) yields, respectively,

$$g_l^2 + L_l = -\frac{1}{2}(r_{l-1} + r_l), \qquad g_l' = -\frac{1}{2}(r_{l-1} - r_l). \tag{13.7}$$

Differentiating the first relation of (13.7) with respect to $x$ and replacing $g_l'$ from the second one provides

$$g_l = \frac{1}{2}\,\frac{r_{l-1}' + r_l'}{-2\, g_l'} = \frac{1}{2}\,\frac{r_{l-1}' + r_l'}{r_{l-1} - r_l}. \tag{13.8}$$

Finally, replacing (13.8) into the first relation of (13.7),

$$L_l = -\frac{1}{2}(r_{l-1} + r_l) - \frac{1}{4}\left(\frac{r_{l-1}' + r_l'}{r_{l-1} - r_l}\right)^2. \tag{13.9}$$

In conclusion, the factorization is possible if $L_l$ given by (13.9) is independent of $x$. In this case, $g_l$ is given by (13.8). As $r_l$ is real, both $L_l$ and $g_l$ are real as well.

### 13.3.2 First-Order Operators

If the factorization (13.3, 13.4) succeeds, it is useful to define the first-order, real operators

$$\mathcal{A}_l^+ = g_l + \frac{\mathrm{d}}{\mathrm{d}x}, \qquad \mathcal{A}_l^- = g_l - \frac{\mathrm{d}}{\mathrm{d}x}, \tag{13.10}$$

so that (13.3, 13.4) are rewritten as

$$\mathcal{A}_{l+1}^+ \mathcal{A}_{l+1}^- w_{\lambda l} = (\lambda - L_{l+1})\, w_{\lambda l}, \qquad \mathcal{A}_l^- \mathcal{A}_l^+ w_{\lambda l} = (\lambda - L_l)\, w_{\lambda l}. \tag{13.11}$$

The two operators (13.10) are mutually adjoint. In fact, for any pair of functions $f_1$, $f_2$ fulfilling the same boundary conditions as $w_{\lambda l}$ one finds

$$\int_{x_1}^{x_2} f_1^*\, \mathcal{A}_l^+ f_2 \,\mathrm{d}x = \left[f_1^*\, f_2\right]_{x_1}^{x_2} + \int_{x_1}^{x_2} (\mathcal{A}_l^- f_1)^*\, f_2 \,\mathrm{d}x, \tag{13.12}$$

where the integrated part vanishes due to the boundary conditions. From the above result one finds a property of the eigenvalue $\lambda$. In fact, multiplying (13.11) by $w_{\lambda l}^*$ and integrating, one finds

$$\int_{x_1}^{x_2} |\mathcal{A}_{l+1}^- w_{\lambda l}|^2 \,\mathrm{d}x = (\lambda - L_{l+1}) \int_{x_1}^{x_2} |w_{\lambda l}|^2 \,\mathrm{d}x, \tag{13.13}$$

where (13.12) has been used after letting $f_1 = w_{\lambda l}$, $f_2 = \mathcal{A}_{l+1}^- w_{\lambda l}$. From (13.13) it follows that, if $w_{\lambda l}$ is an eigenfunction, that is, if $w_{\lambda l}$ does not vanish identically, then the case $\lambda < L_{l+1}$ is impossible. In fact, the integral at the right hand side of (13.13) is strictly positive, while that at the left hand side is non negative. There remain two possibilities, namely:

1. $\mathcal{A}_{l+1}^- w_{\lambda l}$ does not vanish identically, whence both integrals of (13.13) are stricly positive. It follows that $\lambda > L_{l+1}$. Also, as will be shown later, $\mathcal{A}_{l+1}^- w_{\lambda l}$ is another eigenfunction of (13.2). The opposite is also true, namely, $\lambda > L_{l+1}$ implies that $\mathcal{A}_{l+1}^- w_{\lambda l}$ does not vanish identically.
2. $\mathcal{A}_{l+1}^- w_{\lambda l}$ vanishes identically, whence $\lambda = L_{l+1}$. The opposite is also true, namely, $\lambda = L_{l+1}$ implies that $\mathcal{A}_{l+1}^- w_{\lambda l}$ vanishes identically. In this case $\mathcal{A}_{l+1}^- w_{\lambda l}$ is not an eigenfunction of (13.2).

The discussion above allows one to identify the eigenvalue $\lambda$. In fact, there must be a value of the index $l$, say $l = n$, such that the equality $\lambda = L_{n+1}$ holds. It follows that the eigenvalue is identified by the index $n$, $\lambda = \lambda_n$.

As mentioned before the condition $L_{n+1} > L_{l+1}$, $l = 0, 1, \ldots, n-1$ holds. As a consequence, the eigenfunction corresponding to the pair $\lambda_n, l$ may be indicated with $w_{nl}$ instead of $w_{\lambda l}$. In particular, the eigenfunction corresponding to $l = n$ is $w_{nn}$. As shown in case 2 above, such an eigenfunction corresponds to the equality $\lambda_n = L_{n+1}$ which, in turn, implies the condition $\mathcal{A}_{n+1}^- w_{nn} = 0$. Remembering the second relation

of (13.10), such a condition yields the first-order equation $(g_{n+1} - \mathrm{d}/\mathrm{d}x)\ w_{nn} = 0$, whose solution is real and reads

$$w_{nn} = c_{nn}\ \exp\left[\int_{x_1}^{x} g_{n+1}(\xi)\,\mathrm{d}\xi\right], \quad \frac{1}{c_{nn}^2} = \int_{x_1}^{x_2} \exp\left[\int_{x_1}^{x} 2\,g_{n+1}(\xi)\,\mathrm{d}\xi\right]\mathrm{d}x, \tag{13.14}$$

with $c_{nn} = \sqrt{c_{nn}^2} > 0$.

### 13.3.3 The Eigenfunctions Corresponding to $l < n$

The result given in (13.14) shows that, if the factorization is achieved, the eigenfunction corresponding to $l = n$ is found by solving a first-order equation. It remains to determine the eigenfunctions corresponding to $l = 0, 1, \ldots, n-1$. For this, left multiplying the first relation in (13.11) by $\mathcal{A}_{l+1}^-$, letting $l \leftarrow l+1$ in the second relation of (13.11), and remembering that $\lambda = L_{n+1}$, one finds

$$\mathcal{A}_{l+1}^- \mathcal{A}_{l+1}^+ \mathcal{A}_{l+1}^- w_{nl} = (L_{n+1} - L_{l+1})\,\mathcal{A}_{l+1}^- w_{nl}, \tag{13.15}$$

$$\mathcal{A}_{l+1}^- \mathcal{A}_{l+1}^+ w_{\lambda,l+1} = (L_{n+1} - L_{l+1})\,w_{n,l+1}. \tag{13.16}$$

The above show that both $w_{n,l+1}$ and $\mathcal{A}_{l+1}^- w_{nl}$ are eigenfunctions of the operator $\mathcal{A}_{l+1}^- \mathcal{A}_{l+1}^+$ belonging to the same eigenvalue. As the eigenfunctions are non degenerate, it must be

$$\mathcal{A}_{l+1}^- w_{nl} = \text{const} \times w_{n,l+1}, \tag{13.17}$$

where the constant may be determined by imposing the normalization condition. The result shows that, if $w_{n0}$ is known, one may calculate a sequence of eigenfunctions belonging to $\lambda_n = L_{n+1}$ (apart from the normalization constant) by successive applications of first-order operators: $\mathcal{A}_1^- w_{n0} = \text{const} \times w_{n1}$, $\mathcal{A}_2^- w_{n1} = \text{const} \times w_{n2}, \ldots$. The process stops for $l = n$ because, as shown earlier, $\mathcal{A}_{n+1}^- w_{nn} = 0$ is not an eigenfunction anymore, so any further application of the operator beyond $l = n$ provides a sequence of zeros. In a similar manner, left multiplying the second relation in (13.11) by $\mathcal{A}_l^+$ and letting $l \leftarrow l-1$ in the first relation of (13.11), one finds

$$\mathcal{A}_l^+ \mathcal{A}_l^- w_{n,l-1} = (L_{n+1} - L_l)\,w_{n,l-1}, \tag{13.18}$$

$$\mathcal{A}_l^+ \mathcal{A}_l^- \mathcal{A}_l^+ w_{nl} = (L_{n+1} - L_l)\,\mathcal{A}_l^+ w_{nl}. \tag{13.19}$$

From the above one finds that both $w_{n,l-1}$ and $\mathcal{A}_l^+ w_{nl}$ are eigenfunctions of the operator $\mathcal{A}_l^+ \mathcal{A}_l^-$ belonging to the same eigenvalue, whence

$$\mathcal{A}_l^+ w_{nl} = \text{const} \times w_{n,l-1}. \tag{13.20}$$

The result shows that, if $w_{nn}$ is known, one may calculate a sequence of eigenfunctions belonging to $\lambda_n = L_{n+1}$ (apart from the normalization constant) by successive applications of first-order operators: $\mathcal{A}_n^+ w_{nn} = \text{const} \times w_{n,n-1}$, $\mathcal{A}_{n-1}^+ w_{n,n-1} = \text{const} \times w_{n,n-2}, \ldots$. The process stops for $l = 0$ which, by hypothesis, is the minimum of $l$. The derivation also shows that, since $w_{nn}$ and the operators are real, all the eigenfunctions found using the factorization method are real as well.

### 13.3.4 Normalization

The results of this section may be summarized as follows: (13.17) shows that the application of the first-order operator $\mathcal{A}_{l+1}^-$ to an eigenfunction of indices $n, l$ provides an eigenfunction of indices $n, l+1$. Similarly, (13.20) shows that the application of the first-order operator $\mathcal{A}_l^+$ to an eigenfunction of indices $n, l$ provides an eigenfunction of indices $n, l-1$. These results may be described as a process of going up or down along a ladder characterized by an index $n \geq 0$, whose steps are numbered by a second index $l = 0, 1, \ldots, n$. It follows that by applying two suitably-chosen operators one may go up and down (or down and up) one step in the ladder and return to the same eigenfunction apart from a multiplicative constant. This is indeed true, as shown by (13.11), that also indicate that the multiplicative constant to be used at the end of the two steps starting from $w_{nl}$ is $L_{n+1} - L_l$ when the operators' index is $l$. It follows that the constants in (13.17, 13.20) must be chosen as $\sqrt{L_{n+1} - L_{l+1}}$ and $\sqrt{L_{n+1} - L_l}$, respectively. This provides a method for achieving the normalization of the eigenfunctions, starting from an eigenfunction $w_{nn}$ normalized to unity as in (13.14). For this one defines the auxiliary, mutually adjoint operators

$$\mathcal{B}_{nl}^+ = \frac{\mathcal{A}_l^+}{\sqrt{L_{n+1} - L_l}}, \qquad \mathcal{B}_{nl}^- = \frac{\mathcal{A}_l^-}{\sqrt{L_{n+1} - L_l}}, \tag{13.21}$$

so that (13.11) become

$$\mathcal{B}_{n,l+1}^+ \mathcal{B}_{n,l+1}^- w_{nl} = w_{nl}, \qquad \mathcal{B}_{nl}^- \mathcal{B}_{nl}^+ w_{nl} = w_{nl}. \tag{13.22}$$

Thanks to the auxiliary operators the multiplicative constant at the end of the two steps becomes unity. Remembering that the eigenfunctions and operators are real, multiplying both of (13.22) by $w_{nl}$ and integrating yields

$$\int_{x_1}^{x_2} (\mathcal{B}_{n,l+1}^- w_{nl})^2 \, \mathrm{d}x = \int_{x_1}^{x_2} (\mathcal{B}_{nl}^+ w_{nl})^2 = \int_{x_1}^{x_2} w_{nl}^2 \, \mathrm{d}x, \tag{13.23}$$

On the other hand, replacing the constant in (13.17), (13.20) with $\sqrt{L_{n+1} - L_{l+1}}$, $\sqrt{L_{n+1} - L_l}$, respectively, one derives

$$\mathcal{B}_{n,l+1}^- w_{nl} = w_{n,l+1}, \qquad \mathcal{B}_{nl}^+ w_{nl} = w_{n,l-1}. \tag{13.24}$$

Comparing (13.24) with (13.23) shows that, if one of the eigenfunctions of the ladder is normalized to unity, all the others have the same normalization. In particular, if $w_{nn}$ is normalized to unity as in (13.14), then the whole ladder of normalized eigenfunction is found by repeatedly applying the same procedure:

$$\mathcal{B}^+_{nn} w_{nn} = w_{n,n-1}, \quad \mathcal{B}^+_{n,n-1} w_{n,n-1} = w_{n,n-2}, \quad \ldots, \quad \mathcal{B}^+_{n1} w_{n1} = w_{n0}. \tag{13.25}$$

## 13.4 Schrödinger Equation with a Periodic Coefficient

An important case of (11.28) occurs when the coefficient $q$ is periodic [37], with a period that will be denoted with $2\,\omega$. The independent variable (not necessarily a Cartesian one) will be denoted with $z$:

$$w''(z) + q(z)\, w(z) = 0, \qquad q(z + 2\,\omega) = q(z), \tag{13.26}$$

where primes indicate derivatives. Here the variable $z$ is considered real; the theory, however, can be extended to the case of a complex variable. Let $u(z)$, $v(z)$ be fundamental solutions (Sect. 11.4), with $u(0) = 1$, $u'(0) = 0$, $v(0) = 0$, $v'(0) = 1$. As (13.26) holds for any $z$, it holds in particular for $z + 2\,\omega$. From the periodicity of $q$ it follows

$$w''(z + 2\,\omega) + q(z)\, w(z + 2\,\omega) = 0, \tag{13.27}$$

namely, $w(z + 2\,\omega)$ is also a solution. Similarly, $u(z + 2\,\omega)$, $v(z + 2\,\omega)$ are solutions. As the equation has only two independent solutions it must be

$$u(z + 2\,\omega) = a_{11}\, u(z) + a_{12}\, v(z), \qquad v(z + 2\,\omega) = a_{21}\, u(z) + a_{22}\, v(z), \tag{13.28}$$

with $a_{ij}$ suitable constants. The values of the latter are readily related to those of $u, v$ by letting $z = 0$ and using the initial conditions: $u(2\,\omega) = a_{11}$, $u'(2\,\omega) = a_{12}$, $v(2\,\omega) = a_{21}$, $v'(2\,\omega) = a_{22}$. As the Wronskian of $u, v$ equals unity it follows $a_{11} a_{22} - a_{12} a_{21} = 1$. One now seeks a constant $s$ such that

$$u(z + 2\,\omega) = s\, u(z), \qquad v(z + 2\,\omega) = s\, v(z). \tag{13.29}$$

This is equivalent to diagonalizing (13.28), namely, $s$ must fulfill for any $z$ the following relations:

$$(a_{11} - s)\, u(z) + a_{12}\, v(z) = 0, \qquad a_{21}\, u(z) + (a_{22} - s)\, v(z) = 0. \tag{13.30}$$

Equating to zero the determinant of the coefficients in (13.30) yields

$$s = \frac{a_0}{2} \pm \sqrt{\frac{a_0^2}{4} - 1}, \qquad a_0 = a_{11} + a_{22}. \tag{13.31}$$

If $a_0 = 2$ the two solutions of (13.31) are real and take the common value $s^- = s^+ = 1$. In this case, as shown by (13.29), the functions $u, v$ are periodic with period $2\,\omega$.

Similarly, if $a_0 = -2$ the two solutions of (13.31) are real and take the common value $s^- = s^+ = -1$. In this case, as shown by (13.29), the functions $u$, $v$ are periodic with period $4\,\omega$, whereas their moduli $|u|$, $|v|$ are periodic with period $2\,\omega$. As the moduli $|u|$, $|v|$ do not diverge as further and further periods are added to $z$, the case $a_0 = \pm 2$ is stable. If $a_0 > 2$ the two solutions of (13.31) are real and range over the intervals $0 < s^- < 1$ and, respectively, $s^+ > 1$. In particular it is $s^- \to 0$ for $a_0 \to \infty$. If $a_0 < -2$ the two solutions of (13.31) are real and range over the intervals $s^+ < -1$ and, respectively, $-1 < s^- < 0$. In particular it is $s^- \to 0$ for $a_0 \to -\infty$. From the relations (13.29) it follows that the moduli of the solutions corresponding to $s^+$ diverge: in fact one has $u(z + n\,2\,\omega) = (s^+)^n\,u(z)$ and $v(z + n\,2\,\omega) = (s^+)^n\,v(z)$, so the case $|a_0| > 2$ is unstable. When $|a_0| < 2$ the two solutions are complex, namely, $s^\pm = \exp(\pm \mathrm{i}\,\mu)$ with $\tan^2 \mu = 4/a_0^2 - 1$. As the modulus of the solutions is unity, the case $|a_0| < 2$ is stable.

The discussion about stability may seem incomplete because the possible cases depend on the value of $a_0 = a_{11} + a_{22} = u(2\,\omega) + v'(2\,\omega)$, which depends on the fundamental solutions that are yet to be found. On the other hand, the analysis of stability must eventually reduce to considering only the properties of the coefficient of (13.26). In fact, it can be shown that if $q(z)$ is positive for all values of $z$ and the absolute value of $2\,\omega \int_0^{2\,\omega} q(z)\,\mathrm{d}z$ is not larger than 4, then $|a_0| < 2$ [74]. Multiplying both sides of the first relation in (13.29) by $\exp[-\alpha\,(z+2\,\omega)]$, with $\alpha$ an undetermined constant, yields

$$\tilde{u}(z + 2\,\omega) = s\,\exp(-2\,\omega\alpha)\,\tilde{u}(z), \qquad \tilde{u}(z) = \exp(-\alpha\,z)\,u(z). \tag{13.32}$$

A similar treatment is applied to $v(z)$, to yield another auxiliary function $\tilde{v}$. Now one exploits the undetermined constant to impose that the auxiliary functions be periodic of period $2\,\omega$: for this one lets $s\exp(-2\,\omega\,\alpha) = 1$, whence

$$\alpha = \frac{\log s}{2\,\omega}. \tag{13.33}$$

The constant $\alpha$ defined by (13.33) is termed *characteristic exponent* or *Floquet exponent*. Three of the cases listed in the discussion above about stability, namely, $s^\pm = \exp(\pm \mathrm{i}\,\mu)$, $s^\pm = 1$, and $s^\pm = -1$ lead now to the single expression $\alpha^\pm = \pm \mathrm{i}\,\mu/(2\,\omega)$, with $0 \le \mu \le \pi$, showing that $\alpha$ is purely imaginary. The cases $0 < s^- < 1$ and $s^+ > 1$ lead to real values of $\alpha$ (negative and positive, respectively) and, finally, the cases $s^+ < -1$ and $-1 < s^- < 0$ lead to complex values of $\alpha$. Considering the stable cases only, one transforms (13.26) by replacing $w(z)$ with, e.g., $\tilde{u}(z)\,\exp[\pm \mathrm{i}\,\mu\,z/(2\,\omega)]$ to find

$$\tilde{u}''(z) \pm 2\,\mathrm{i}\,\frac{\mu}{2\,\omega}\,\tilde{u}'(z) + \left[q(z) - \frac{\mu^2}{4\,\omega^2}\right]\tilde{u}(z) = 0. \tag{13.34}$$

The coefficients and the unknown function of (13.34) are periodic functions of period $2\,\omega$. As a consequence it suffices to solve the equation within the single period, say, $0 \le z \le 2\,\omega$. An example is given in Sect. 17.8.4; a different approach leading to the generalization to three dimensions is shown in Sect. 17.6.

## 13.5 Schrödinger Equation for a Central Force

In the investigation about the properties of atoms it is important to analyze the dynamics of particle subjected to a central force in the case where the motion is limited. The treatment based on the concepts of Classical Mechanics is given in Sects. 3.4 (where the general properties are illustrated), 3.7 (for the two-particle interaction), 3.8 (for a Coulomb field in the repulsive case), and 3.13.6 (for a Coulomb field in the attractive case). To proceed one considers a particle of mass[1] $m_0$ acted upon by a force deriving from a potential energy of the central type, $V = V(r)$, and expresses the time-independent Schrödinger equation $-\hbar^2/(2\,m_0)\,\nabla^2 w + V(r)\,w = E\,w$ in spherical coordinates $r$, $\vartheta$, $\varphi$ (Sect. B.1). Remembering the transformation (B.25) of the $\nabla^2$ operator one obtains

$$\frac{1}{r}\,\frac{\partial^2(r\,w)}{\partial r^2} + \frac{1}{r^2}\,\hat{\Omega} w + \frac{2\,m_0}{\hbar^2}\,[E - V(r)]\,w = 0, \tag{13.35}$$

where operator $\hat{\Omega}$ is defined as

$$\hat{\Omega} = \frac{1}{\sin^2\vartheta}\left[\sin\vartheta\,\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\,\frac{\partial}{\partial\vartheta}\right) + \frac{\partial^2}{\partial\varphi^2}\right]. \tag{13.36}$$

The $r$ coordinate is separated by letting $w = \varrho(r)\,Y(\vartheta,\varphi)$ in (13.35) and dividing both sides by $w/r^2$:

$$r^2\left[\frac{1}{r\,\varrho}\,\frac{\mathrm{d}^2(r\,\varrho)}{\mathrm{d}r^2} + \frac{2\,m_0}{\hbar^2}\,(E - V)\right] = -\frac{1}{Y}\,\hat{\Omega} Y. \tag{13.37}$$

Each side of (13.37) must equal the same dimensionless constant, say, $c$, whence the original Schrödinger equation separates into the pair

$$\hat{\Omega} Y = -c\,Y, \quad \left[-\frac{\hbar^2}{2\,m_0}\,\frac{\mathrm{d}^2}{\mathrm{d}r^2} + V_e(r)\right] r\,\varrho = E\,r\,\varrho, \quad V_e = V + \frac{c\,\hbar^2}{2\,m_0\,r^2}. \tag{13.38}$$

The first equation in (13.38), called *angular equation*, does not depend on any parameter specific to the problem in hand. As a consequence, its eigenvalues $c$ and eigenfunctions $Y$ can be calculated once and for all. Being the equation's domain two dimensional, the eigenfunctions $Y$ are expected to depend onto two indices, say, $l$, $m$. After the angular equation is solved, inserting each eigenvalue $c$ into the second equation of (13.38), called *radial equation*, provides the eigenvalues and eigenfunctions of the latter. For the radial equation, the solution depends on the form

[1] To avoid confusion with the azimuthal quantum number $m$, the particle's mass is indicated with $m_0$ in the sections dealing with the angular momentum in the quantum case.

of $V(r)$. It is also worth noting the similarity of $V_e$ with its classical counterpart (3.5), that reads

$$V_e = V + \frac{M^2}{2\,m_0\,r^2}, \qquad M^2 = \text{const.} \tag{13.39}$$

To tackle the solution of the angular equation $\hat{\Omega} Y = -c\,Y$ one associates an operator $\mathcal{L}_x$, $\mathcal{L}_y$, $\mathcal{L}_z$ to each component of the classical angular momentum $\mathbf{M} = \mathbf{r} \wedge \mathbf{p}$, and another operator $\mathcal{L}^2$ to its square modulus $M^2$. The procedure, illustrated in Sect. 13.6.1, shows that the three operators $\mathcal{L}_x$, $\mathcal{L}_y$, $\mathcal{L}_z$ do not commute with each other, whereas $\mathcal{L}^2$ commutes with each of them. Also, it is found that $\mathcal{L}^2$ is proportional to $\hat{\Omega}$, specifically, $\mathcal{L}^2 = -\hbar^2\,\hat{\Omega}$. In conclusion, the Schrödinger equation in the case of a central force reads

$$\mathcal{H} w = E\,w, \qquad \mathcal{H} = -\frac{\hbar^2}{2\,m\,r}\,\frac{\partial^2}{\partial r^2}\,r + \frac{\mathcal{L}^2}{2\,m_0\,r^2} + V(r). \tag{13.40}$$

As the $r$ coordinate does not appear in $\mathcal{L}^2$, the latter commutes with $\mathcal{H}$; moreover, $\mathcal{L}^2$ does not depend on time. As a consequence, its expectation value is a constant of motion (Sect. 10.7). Similarly, $\mathcal{L}_z$ commutes with $\mathcal{L}^2$ and does not contain $r$ or $t$, so it commutes with $\mathcal{H}$ as well and its expectation value is also a constant of motion. As $\mathcal{H}$, $\mathcal{L}^2$, and $\mathcal{L}_z$ commute with each other, they have a common set of eigenfunctions.

### 13.5.1 Angular Part of the Equation

The conservation of the expectation values of $\mathcal{L}^2$ and $\mathcal{L}_z$ is the counterpart of the classical result of the conservation of $M^2$ and $M_z$ (Sect. 2.8). In contrast, the expectation values of $\mathcal{L}_x$ and $\mathcal{L}_y$ are not constants of motion. To determine the eigenfunctions $w$ of $\mathcal{H}$, $\mathcal{L}^2$ and $\mathcal{L}_z$ it is convenient to solve the eigenvalue equation for $\mathcal{L}_z$ first:

$$\mathcal{L}_z w = L_z\,w, \qquad -\mathrm{i}\,\hbar\,\frac{\partial w}{\partial \varphi} = L_z\,w, \qquad w = v(r,\vartheta)\,\exp\left(\mathrm{i}\,L_z\,\varphi/\hbar\right), \tag{13.41}$$

with $v$ yet undetermined. For an arbitrary value of $L_z$, the exponential part of $w$ is a multi-valued function of $\varphi$. This is not acceptable because $w$ should not vary when $\varphi$ is changed by integer multiples of $2\pi$. A single-valued function is achieved by letting $L_z/\hbar = m$, with $m$ an integer. In conclusion, the eigenvalues and eigenfunctions of $\mathcal{L}_z$ are

$$L_z = m\,\hbar, \qquad w = v(r,\vartheta)\,\exp\left(\mathrm{i}\,m\,\varphi\right). \tag{13.42}$$

Combining (13.42) with (13.36) provides

$$\hat{\Omega} w = \frac{\exp\left(\mathrm{i}\,m\,\varphi\right)}{\sin^2\vartheta}\left[\sin\vartheta\,\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\,\frac{\partial}{\partial\vartheta}\right) - m^2\right] v(r,\vartheta). \tag{13.43}$$

**Table 13.1** The lowest-order spherical harmonics

| $Y_l^m$ | Form of the function |
|---|---|
| $Y_0^0$ | $1/\sqrt{4\,\pi}$ |
| $Y_1^{-1}$ | $\sqrt{3/(8\,\pi)}\,\sin\vartheta\,\exp(-\mathrm{i}\,\varphi)$ |
| $Y_1^0$ | $-\sqrt{3/(4\,\pi)}\,\cos\vartheta$ |
| $Y_1^1$ | $-\sqrt{3/(8\,\pi)}\,\sin\vartheta\,\exp(\mathrm{i}\,\varphi)$ |

This result shows that in (13.40) the factor $\exp(\mathrm{i}\,m\,\varphi)$ cancels out, so that $\hat{\Omega}$ actually involves the angular coordinate $\vartheta$ only. This suggests to seek the function $v(r,\vartheta)$ by separation. Remembering that $w$ was originally separated as $w = \varrho(r)\,Y(\vartheta,\varphi)$ one finds

$$v(r,\vartheta) = \varrho(r)\,P(\vartheta), \qquad Y(\vartheta,\varphi) = P(\vartheta)\,\exp(\mathrm{i}\,m\,\varphi). \tag{13.44}$$

As the separation transforms $\hat{\Omega}Y = -cY$ into $\hat{\Omega}P = -cP$, the equation to be solved for a given integer $m$ reduces to

$$\frac{1}{\sin^2\vartheta}\left[\sin\vartheta\,\frac{\mathrm{d}}{\mathrm{d}\vartheta}\left(\sin\vartheta\,\frac{\mathrm{d}}{\mathrm{d}\vartheta}\right) - m^2\right]P = -cP. \tag{13.45}$$

From $\mathcal{L}^2 = -\hbar^2\,\hat{\Omega}$, it follows that the eigenvalue of $\mathcal{L}^2$ is $\lambda = \hbar^2\,c$. The eigenvalues $c$ of (13.45) are found by the factorization method described in Sect. 13.3.1; they have the form $c = l\,(l+1)$, with $l$ a non-negative integer, called *orbital* (or *total*) *angular momentum quantum number*. For a given $l$, the allowed values of $m$, called *azimuthal* (or *magnetic*) *quantum number*, are the $2\,l+1$ integers $-l,\ldots,0,\ldots,l$. The details of the eigenvalue calculation are given in Sect. 13.6.2.

The factorization method provides also the eigenfunctions of $\mathcal{L}^2$ and $\mathcal{L}_z$, that are called *spherical harmonics* and, as expected, depend on the two indices $l$, $m$. The details of the calculation of the eigenfunctions $Y_l^m$ are given in Sect. 13.6.3. The lowest-order spherical harmonics are shown in Table 13.1. As the eigenfunctions fulfill the equations

$$\mathcal{L}^2 Y_l^m = \hbar^2\,l\,(l+1)\,Y_l^m, \qquad \mathcal{L}_z Y_l^m = \hbar\,m\,Y_l^m, \tag{13.46}$$

the only possible results of a measurement of $M^2$ are $\hbar^2\,l\,(l+1)$, with $l = 0,1,2,\ldots$ and, for a given $l$, the only possible results of a measurement of $M_z$ are $\hbar\,m$, with $m = -l,\ldots,-1,0,1,\ldots,l$. It follows that the only possible results of a measurement of $M$ are $\hbar\,\sqrt{l\,(l+1)}$. For any $l > 0$ it is $\max(|M_z|) = \hbar\,l < \hbar\,\sqrt{l\,(l+1)} = M$; as a consequence, for $l > 0$ the angular momentum $\mathbf{M}$ lies on a cone centered on the $z$ axis. The half amplitude $\alpha = \arccos[m/\sqrt{l(l+1)}]$ of such a cone is strictly positive, showing that the other two components $M_x$, $M_y$ can not vanish together when $M \neq 0$. A geometrical construction describing the relation between $\mathbf{M}$ and $M_z$ is given in Fig. 13.2. The groups of states corresponding to the orbital quantum numbers $l = 0,1,2,3$ are denoted with special symbols and names, that originate from spectroscopy [7, Chap. 15] and are listed in Table 13.2. For $l \geq 4$ the symbols continue in alphabetical order ("g", "h", ...), while no special names are used.

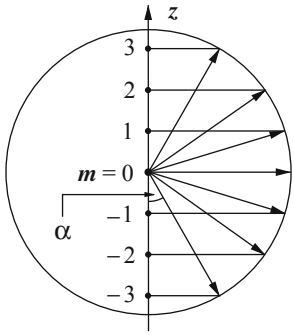


**Fig. 13.2** Geometrical construction showing the relation between **M** and $M_z$. The $l = 3$ is case considered, whence one finds $m = -3, \ldots, 0, \ldots, 3$ and $\sqrt{l\,(l+1)} \simeq 3.46$

**Table 13.2** Symbols and names for the states corresponding to $l = 0, 1, 2, 3$

| $l$ | $m$ | Symbol | Name |
|---|---|---|---|
| 0 | 0 | s | Sharp |
| 1 | −1, 0, 1 | p | Principal |
| 2 | −2, −1, 0, 1, 2 | d | Diffuse |
| 3 | −3, −2, −1, 0, 1, 2, 3 | f | Fundamental |

### 13.5.2 Radial Part of the Equation in the Coulomb Case

To solve the radial part of the Schrödinger equation (second and third relation in (13.38)) one uses the eigenvalue $c = l\,(l+1)$ to find

$$\left[-\frac{\hbar^2}{2\,m_0}\,\frac{\mathrm{d}^2}{\mathrm{d}r^2} + V_e(r)\right] r\,\varrho(r) = E\,r\,\varrho(r), \qquad V_e = V + \frac{\hbar^2\,l\,(l+1)}{2\,m_0\,r^2}. \tag{13.47}$$

As anticipated above, the solution of (13.47) depends on the form of $V(r)$. Of particular interest is the Coulomb potential (3.31), that is considered here in the attractive case

$$V(r) = -\frac{Z\,q^2}{4\,\pi\,\varepsilon_0\,r}, \tag{13.48}$$

with $\varepsilon_0$ the vacuum permittivity, $q > 0$ the elementary electric charge, and $Z\,q$ the charge whence the central force originates. This form of the potential energy is typical of the case of an electron belonging to a hydrogen or hydrogen-like atom. As usual, the arbitrary constant inherent in the definition of the potential energy is such that $\lim_{r\to\infty} V = 0$. As a consequence, the electron is bound if $E < 0$ (in other terms, according to the definition given in Sect. 3.13.6, the classical motion is limited).

The eigenvalues $E$ of (13.47, 13.48) are found by the factorization method described in Sect. 13.3.1; they have the form

$$E = E_n = -\frac{m_0}{2\,\hbar^2}\left(\frac{Z\,q^2}{4\,\pi\,\varepsilon_0}\right)^2 \frac{1}{n^2}, \tag{13.49}$$

where $n$ is an integer, called *principal quantum number*, fulfilling the relation $n \geq l + 1$. The details of the eigenvalue calculation are given in Sect. 13.6.4. As $l \geq 0$, the minimum value of $n$ is 1. For a given $n$ the possible values of the orbital quantum number are $l = 0, 1, \ldots, n-1$; also, as found earlier, for each $l$ the possible values of the azimuthal quantum number are $m = -l, \ldots, 0, \ldots, l$. It follows that, for a given $n$ the number of different pairs $l, m$ is

$$\sum_{l=0}^{n-1} (2\,l + 1) = n^2, \tag{13.50}$$

namely, each eigenvalue $E_n$ of the energy corresponds to $n^2$ possible combinations[2] of the eigenvalues of $M$ and $M_z$. As for the radial part of the equation, the factorization method provides also the eigenfunctions of (13.47); the details are given in Sect. 13.6.5.

## 13.6 Complements

### *13.6.1 Operators Associated to Angular Momentum*

Consider the classical angular momentum $\mathbf{M} = \mathbf{r} \wedge \mathbf{p}$ (Sect. 2.6), whose components in rectangular coordinates are given by (2.38), namely,

$$M_x = y\,p_z - z\,p_y, \qquad M_y = z\,p_x - x\,p_z, \qquad M_z = x\,p_y - y\,p_x. \tag{13.51}$$

The operators corresponding to (13.51) are

$$\begin{cases} \mathcal{L}_x = -\mathrm{i}\,\hbar\,(y\,\partial/\partial z - z\,\partial/\partial y) \\ \mathcal{L}_y = -\mathrm{i}\,\hbar\,(z\,\partial/\partial x - x\,\partial/\partial z) \\ \mathcal{L}_z = -\mathrm{i}\,\hbar\,(x\,\partial/\partial y - y\,\partial/\partial x) \end{cases} \tag{13.52}$$

It is easily found that $\mathcal{L}_x$, $\mathcal{L}_y$, $\mathcal{L}_z$ are Hermitean and fulfill the relations

$$\begin{cases} \mathcal{L}_x\,\mathcal{L}_y - \mathcal{L}_y\,\mathcal{L}_x = \mathrm{i}\,\hbar\,\mathcal{L}_z \\ \mathcal{L}_y\,\mathcal{L}_z - \mathcal{L}_z\,\mathcal{L}_y = \mathrm{i}\,\hbar\,\mathcal{L}_x \\ \mathcal{L}_z\,\mathcal{L}_x - \mathcal{L}_x\,\mathcal{L}_z = \mathrm{i}\,\hbar\,\mathcal{L}_y \end{cases} \tag{13.53}$$

namely, $\mathcal{L}_x$, $\mathcal{L}_y$, $\mathcal{L}_z$ do not commute with each other. Left multiplying the third relation in (13.53) by $\mathcal{L}_x$ and the second one by $\mathcal{L}_y$ provides, respectively,

$$\mathcal{L}_x^2\,\mathcal{L}_z = \mathcal{L}_x\,\mathcal{L}_z\,\mathcal{L}_x - \mathrm{i}\,\hbar\,\mathcal{L}_x\,\mathcal{L}_y, \qquad \mathcal{L}_y^2\,\mathcal{L}_z = \mathcal{L}_y\,\mathcal{L}_z\,\mathcal{L}_y + \mathrm{i}\,\hbar\,\mathcal{L}_y\,\mathcal{L}_x. \tag{13.54}$$

[2] The actual degree of degeneracy of $E_n$ is $2\,n^2$, where factor 2 is due to spin (Sect. 15.5.1).

Similarly, right multiplying the third relation in (13.53) by $\mathcal{L}_x$ and the second one by $\mathcal{L}_y$,

$$\mathcal{L}_z\,\mathcal{L}_x^2 = \mathcal{L}_x\,\mathcal{L}_z\,\mathcal{L}_x + \mathrm{i}\,\hbar\,\mathcal{L}_y\,\mathcal{L}_x, \qquad \mathcal{L}_z\,\mathcal{L}_y^2 = \mathcal{L}_y\,\mathcal{L}_z\,\mathcal{L}_y - \mathrm{i}\,\hbar\,\mathcal{L}_x\,\mathcal{L}_y. \tag{13.55}$$

The operator associated to $M^2 = M_x^2 + M_y^2 + M_z^2$ is $\mathcal{L}^2 = \mathcal{L}_x^2 + \mathcal{L}_y^2 + \mathcal{L}_z^2$ whence, using (13.54, 13.55),

$$\mathcal{L}^2\,\mathcal{L}_z - \mathcal{L}_z\,\mathcal{L}^2 = (\mathcal{L}_x^2 + \mathcal{L}_y^2)\,\mathcal{L}_z - \mathcal{L}_z\,(\mathcal{L}_x^2 + \mathcal{L}_y^2) = 0. \tag{13.56}$$

Similarly,

$$\mathcal{L}^2\,\mathcal{L}_x - \mathcal{L}_x\,\mathcal{L}^2 = 0, \qquad \mathcal{L}^2\,\mathcal{L}_y - \mathcal{L}_y\,\mathcal{L}^2 = 0. \tag{13.57}$$

In conclusion, the components $\mathcal{L}_x$, $\mathcal{L}_y$, $\mathcal{L}_z$ do not commute with each other, while the square modulus of the angular momentum commutes with any single component of it. To check whether $\mathcal{L}^2$ or any of the components $\mathcal{L}_x$, $\mathcal{L}_y$, $\mathcal{L}_z$ commute with the Hamiltonian operator of a central force, it is necessary to express all operators in spherical coordinates. To this purpose, using $\mathcal{L}_z$ by way of example, one finds

$$-\frac{\mathcal{L}_z}{\mathrm{i}\,\hbar} = x\,\frac{\partial}{\partial y} - y\,\frac{\partial}{\partial x} = r\,\sin\vartheta\,\cos\varphi\,\frac{\partial}{\partial y} - r\,\sin\vartheta\,\sin\varphi\,\frac{\partial}{\partial x}. \tag{13.58}$$

The partial derivatives $\partial/\partial x$ and $\partial/\partial y$ in terms of the spherical coordinates are extracted from (B.4); in particular, the first one reads $\partial/\partial x = \sin\vartheta\,\cos\varphi\,\partial/\partial r + (1/r)\,\cos\vartheta\,\cos\varphi\,\partial/\partial\vartheta - (1/r)\,(\sin\varphi/\sin\vartheta)\,\partial/\partial\varphi$, while the expression of $\partial/\partial y$ is obtained from that of $\partial/\partial x$ by replacing $\cos\varphi$ with $\sin\varphi$ and $\sin\varphi$ with $-\cos\varphi$. When such expressions of the partial derivatives are used within (13.58), several terms cancel out to finally yield the relation

$$\mathcal{L}_z = -\mathrm{i}\,\hbar\,\frac{\partial}{\partial\varphi} \tag{13.59}$$

which, consistently with the classical one, $M_z = p_\varphi$ (Sect. 2.8), shows that the operator associated to the $z$ component of the angular momentum is conjugate to the generalized coordinate $\varphi$. The quantum relation can thus be derived directly from the classical one by letting $\mathcal{L}_z = \hat{p}_\varphi = -\mathrm{i}\,\hbar\,\partial/\partial\varphi$. As already noted in Sect. 2.8, the remaining components of $M_x$, $M_y$ are not conjugate momenta. The expression of $\mathcal{L}_x$ in spherical coordinates reads

$$\mathcal{L}_x = \mathrm{i}\,\hbar\,\left(\sin\varphi\,\frac{\partial}{\partial\vartheta} + \frac{\cos\vartheta}{\sin\vartheta}\,\cos\varphi\,\frac{\partial}{\partial\varphi}\right), \tag{13.60}$$

while that of $\mathcal{L}_y$ is obtained from (13.60) by replacing $\cos\varphi$ with $\sin\varphi$ and $\sin\varphi$ with $-\cos\varphi$. Combining the above finding, one calculates the expression of $\mathcal{L}^2 = \mathcal{L}_x^2 + \mathcal{L}_y^2 + \mathcal{L}_z^2$, that turns out to be

$$\mathcal{L}^2 = -\frac{\hbar^2}{\sin^2\vartheta}\,\left[\sin\vartheta\,\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\,\frac{\partial}{\partial\vartheta}\right) + \frac{\partial^2}{\partial\varphi^2}\right] = -\hbar^2\,\hat{\Omega}. \tag{13.61}$$

### 13.6.2 Eigenvalues of the Angular Equation

The solution of the angular equation is found by the factorization method described in Sect. 13.3.1. Remembering that $\mathcal{L}_z$ and $\mathcal{L}^2$ commute, the whole eigenfunction $Y = P(\vartheta)\,\exp(\mathrm{i}\,m\,\varphi)$, introduced in Sect. 13.5 and common to both operators, will be used here. The following hold:

$$\mathcal{L}_z Y = L_z\,Y, \qquad \mathcal{L}^2 Y = \lambda\,Y, \tag{13.62}$$

with $L_z = m\,\hbar$, $m$ an integer. Applying the operator $\mathcal{L}_x \pm \mathrm{i}\,\mathcal{L}_y$ to the first equation in (13.62) yields $\left(\mathcal{L}_x \pm \mathrm{i}\,\mathcal{L}_y\right)\,\mathcal{L}_z Y = m\,\hbar\,\left(\mathcal{L}_x \pm \mathrm{i}\,\mathcal{L}_y\right)\,Y$, where the upper (lower) signs hold together. Due to the commutation rules (13.53) the left hand side of the above transforms into

$$\left(\mathcal{L}_z\mathcal{L}_x - \mathrm{i}\,\hbar\,\mathcal{L}_y\right)\,Y \pm \mathrm{i}\,\left(\mathcal{L}_z\mathcal{L}_y + \mathrm{i}\,\hbar\,\mathcal{L}_x\right)\,Y = \mathcal{L}_z\left(\mathcal{L}_x \pm \mathrm{i}\,\mathcal{L}_y\right)\,Y \mp \hbar\,\left(\mathcal{L}_x \pm \mathrm{i}\,\mathcal{L}_y\right)\,Y,$$

whence the first eigenvalue equation in (13.62) becomes

$$\mathcal{L}_z\,\left(\mathcal{L}_x \pm \mathrm{i}\,\mathcal{L}_y\right)\,Y = (m \pm 1)\,\hbar\,\left(\mathcal{L}_x \pm \mathrm{i}\,\mathcal{L}_y\right)\,Y. \tag{13.63}$$

Iterating the above reasoning shows that, if $Y$ is an eigenfunction of $\mathcal{L}_z$ belonging to the eigenvalue $m\,\hbar$, then $(\mathcal{L}_x + \mathrm{i}\,\mathcal{L}_y)Y$, $(\mathcal{L}_x + \mathrm{i}\,\mathcal{L}_y)^2 Y, \ldots$ are also eigenfunctions of $\mathcal{L}_z$ which belong, respectively, to $(m+1)\,\hbar$, $(m+2)\,\hbar, \ldots$, and so on. Similarly, $(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y)Y$, $(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y)^2 Y, \ldots$ are also eigenfunctions of $\mathcal{L}_z$ belonging, respectively, to $(m-1)\,\hbar$, $(m-2)\,\hbar, \ldots$, and so on. At the same time, due to the commutativity of $\mathcal{L}^2$ with $\mathcal{L}_x$ and $\mathcal{L}_y$, it is

$$\left(\mathcal{L}_x \pm \mathrm{i}\,\mathcal{L}_y\right)\,\mathcal{L}^2 Y = \mathcal{L}^2\,\left(\mathcal{L}_x \pm \mathrm{i}\,\mathcal{L}_y\right)\,Y = \lambda\,\left(\mathcal{L}_x \pm \mathrm{i}\,\mathcal{L}_y\right)\,Y, \tag{13.64}$$

showing that $(\mathcal{L}_x \pm \mathrm{i}\,\mathcal{L}_y)Y$ is also an eigenfunction of $\mathcal{L}^2$, belonging to the same eigenvalue as $Y$. By induction, $(\mathcal{L}_x \pm \mathrm{i}\,\mathcal{L}_y)^2 Y, \ldots$ are also eigenfunctions of $\mathcal{L}^2$, belonging to the same eigenvalue as $Y$. To summarize, if $Y = P(\vartheta)\,\exp(\mathrm{i}\,m\,\varphi)$ is an eigenfunction common to operators $\mathcal{L}_z$ and $\mathcal{L}^2$, belonging to the eigenvalues $L_z = m\,\hbar$ and $\lambda$, respectively, then,

1. $(\mathcal{L}_x + \mathrm{i}\,\mathcal{L}_y)Y$ is another eigenfunction of $\mathcal{L}^2$ still belonging to $\lambda$, and is also an eigenfunction of $\mathcal{L}_z$ belonging to $(m+1)\,\hbar$. Similarly, $(\mathcal{L}_x + \mathrm{i}\,\mathcal{L}_y)^2 Y$ is still another eigenfunction of $\mathcal{L}^2$ belonging to $\lambda$, and is also an eigenfunction of $\mathcal{L}_z$ belonging to $(m+2)\,\hbar$, and so on.
2. $(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y)Y$ is another eigenfunction of $\mathcal{L}^2$ still belonging to $\lambda$, and is also an eigenfunction of $\mathcal{L}_z$ belonging to $(m-1)\,\hbar$. Similarly, $(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y)^2 Y$ is still another eigenfunction of $\mathcal{L}^2$ belonging to $\lambda$, and is also an eigenfunction of $\mathcal{L}_z$ belonging to $(m-2)\,\hbar$, and so on.

By this reasoning, starting from a given pair $\lambda$, $Y$ it seems possible to construct as many degenerate eigenfunctions of $\mathcal{L}^2$ as we please. This, however, leads to

unbounded eigenvalues of $\mathcal{L}_z$, which are not admissible as shown below. As a consequence, the procedure depicted here can be applied only a finite number of times. To demonstrate that the eigenvalues of $\mathcal{L}_z$ are bounded one starts from the relation $\mathcal{L}^2 = \mathcal{L}_x^2 + \mathcal{L}_y^2 + \mathcal{L}_z^2$ and from a given pair $\lambda$, $Y$. As $Y$ is also an eigenfunction of $\mathcal{L}_z$ belonging to, say, $m\,\hbar$, an application of $\mathcal{L}^2$ to $Y$ followed by a left scalar multiplication by $Y^*$ yields, thanks to (13.62),

$$\lambda - m^2\hbar^2 = \frac{\langle \mathcal{L}_x Y | \mathcal{L}_x Y \rangle + \langle \mathcal{L}_y Y | \mathcal{L}_y Y \rangle}{\langle Y | Y \rangle} \geq 0, \tag{13.65}$$

where the hermiticity of $\mathcal{L}_x$, $\mathcal{L}_y$ has been exploited. Inequality (13.65) provides the upper bound for $|m|$. To find the acceptable values of $m$ one defines $m^+ = \max(m)$, and lets $Y^+$ be an eigenfunction of $\mathcal{L}^2$ and $\mathcal{L}_z$ belonging to $\lambda$ and $m^+\,\hbar$, respectively. From (13.63) one obtains $\mathcal{L}_z\,(\mathcal{L}_x + \mathrm{i}\,\mathcal{L}_y)Y^+ = (m^+ + 1)\,\hbar\,(\mathcal{L}_x + \mathrm{i}\,\mathcal{L}_y)Y^+$ but, as the eigenvalue $(m^+ + 1)\hbar$ is not acceptable, it must be $(\mathcal{L}_x + \mathrm{i}\,\mathcal{L}_y)Y^+ = 0$. Similarly, letting $m^- = \min(m)$, and letting $Y^-$ be an eigenfunction of $\mathcal{L}^2$ and $\mathcal{L}_z$ belonging to $\lambda$ and $m^-\,\hbar$, respectively, it must be $(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y)Y^- = 0$. Due to the commutation rules it is $(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y)\,(\mathcal{L}_x + \mathrm{i}\,\mathcal{L}_y) = \mathcal{L}_x^2 + \mathcal{L}_y^2 - \hbar\,\mathcal{L}_z$, whence

$$\mathcal{L}^2 = (\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y)\,(\mathcal{L}_x + \mathrm{i}\,\mathcal{L}_y) + \hbar\,\mathcal{L}_z + \mathcal{L}_z^2. \tag{13.66}$$

Application of (13.66) to $Y^+$ and $Y^-$ yields

$$\begin{cases} \mathcal{L}^2 Y^+ = \left(\mathcal{L}_z^2 + \hbar\,\mathcal{L}_z\right)\,Y^+ = \hbar^2\,m^+\,\left(m^+ + 1\right)\,Y^+ \\ \mathcal{L}^2 Y^- = \left(\mathcal{L}_z^2 - \hbar\,\mathcal{L}_z\right)\,Y^- = \hbar^2\,m^-\,\left(m^- - 1\right)\,Y^- \end{cases} \tag{13.67}$$

By construction, $Y^+$ and $Y^-$ belong to the same eigenvalue of $\mathcal{L}^2$; as a consequence it must be $m^+\,\left(m^+ + 1\right) = m^-\,\left(m^- - 1\right)$. A possible integer solution of the above is $m^- = m^+ + 1$ which, however, is not acceptable because $m^+ = \max(m)$. The only acceptable solution left is $m^- = -m^+$. In conclusion, letting $l = m^+$ (so that $m^- = -l$) and using (13.67), the eigenvalues of $\mathcal{L}^2$ take the form

$$\lambda = \hbar^2\,l\,(l+1), \tag{13.68}$$

with $l$ a non-negative integer. For a given $l$, the allowed values of $m$ are the $2\,l + 1$ integers $-l, \ldots, 0, \ldots, l$.

### *13.6.3 Eigenfunctions of the Angular Equation*

Due to the findings illustrated in Sect. 13.6.2, the eigenfunctions of $\hat{\Omega}$, whose form is $Y(\vartheta, \varphi) = P(\vartheta)\,\exp(\mathrm{i}\,m\,\varphi)$, depend on the two indices $l, m$ and, for this reason, will be indicated with $Y_l^m$. In particular, the eigenfunction $Y^+$ introduced in Sect. 13.6.2, which belongs to $l = \max(m)$ and fulfills the equation $(\mathcal{L}_x + \mathrm{i}\,\mathcal{L}_y)Y = 0$, will be

indicated with $Y_l^l$. Similarly, as $P$ depends on $l$ and may depend on $m$ as well, it will be indicated with $P_l^m$. The eigenfunction $Y_l^l$ is readily found by solving the first-order equation $(\mathcal{L}_x + \mathrm{i}\,\mathcal{L}_y)Y_l^l = 0$, where operator $\mathcal{L}_x$ is expressed in terms of $\varphi$, $\vartheta$ through (13.60), and $\mathcal{L}_y$ is obtained from (13.60) by replacing $\cos\varphi$ with $\sin\varphi$ and $\sin\varphi$ with $-\cos\varphi$. After eliminating the factor $\hbar\,\exp[\mathrm{i}\,(l+1)\,\varphi]$ one finds a differential equation for $P_l^l$, that reads

$$\frac{\mathrm{d}P_l^l}{\mathrm{d}\vartheta} - l\,\frac{\cos\vartheta}{\sin\vartheta}\,P_l^l = 0, \qquad \frac{1}{P_l^l}\,\frac{\mathrm{d}P_l^l}{\mathrm{d}\vartheta} = \frac{l}{\sin\vartheta}\,\frac{\mathrm{d}\sin\vartheta}{\mathrm{d}\vartheta}. \tag{13.69}$$

In conclusion it is found, with $a$ an arbitrary constant,

$$P_l^l = a\,(\sin\vartheta)^l\,, \qquad Y_l^l = a\,\exp(\mathrm{i}\,l\,\varphi)\,(\sin\vartheta)^l\,. \tag{13.70}$$

Then, remembering the discussion of Sect. 13.6.2, the remaining $2\,l$ eigenfunctions $Y_l^{l-1}, \ldots, Y_l^0, \ldots, Y_l^{-l}$ are found by successive applications of

$$\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y = -\hbar\,\exp(-\mathrm{i}\,\varphi)\left(\frac{\partial}{\partial\vartheta} - \mathrm{i}\,\frac{\cos\vartheta}{\sin\vartheta}\,\frac{\partial}{\partial\varphi}\right), \tag{13.71}$$

with the help of the auxiliary relations $-\mathrm{i}\,\partial Y_l^l/\partial\varphi = l\,Y_l^l$ and

$$\left(\frac{\partial}{\partial\vartheta} + l\,\frac{\cos\vartheta}{\sin\vartheta}\right) Y_l^l = \frac{\partial[(\sin\vartheta)^l\,Y_l^l]/\partial\vartheta}{(\sin\vartheta)^l} = a\,\frac{\exp(\mathrm{i}\,l\,\varphi)}{(\sin\vartheta)^l}\,\frac{\mathrm{d}}{\mathrm{d}\vartheta}\,(\sin\vartheta)^{2l}\,. \tag{13.72}$$

In fact, combining $\mathcal{L}_z\left[\left(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y\right)Y_l^m\right] = (m-1)\,\hbar\left[\left(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y\right)Y_l^m\right]$ with $\mathcal{L}_z\,Y_l^m = m\,\hbar\,Y_l^m$ provides the recursive relation $Y_l^{m-1} = \left(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y\right)Y_l^m$. In particular, letting $m = l, m = l-1, \ldots$ yields

$$Y_l^{l-1} = \left(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y\right)Y_l^l, \qquad Y_l^{l-2} = \left(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y\right)Y_l^{l-1}, \qquad \ldots \tag{13.73}$$

where $Y_l^l$ is given by (13.70) while

$$\left(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y\right)Y_l^l = Y_l^{l-1} = a\,\frac{\exp[\mathrm{i}\,(l-1)\,\varphi]}{(\sin\vartheta)^{l-1}}\,\frac{-\hbar}{\sin\vartheta}\,\frac{\mathrm{d}}{\mathrm{d}\vartheta}\,(\sin\vartheta)^{2l}\,. \tag{13.74}$$

The denominator $(\sin\vartheta)^l$ in the above has been split into two parts for the sake of convenience. The next functions are found from

$$\begin{aligned} Y_l^{l-s-1} &= \left(\mathcal{L}_x - \mathrm{i}\,\mathcal{L}_y\right)Y_l^{l-s} = \frac{-\hbar}{\exp(\mathrm{i}\,\varphi)}\left[\frac{\partial}{\partial\vartheta} + (l-s)\,\frac{\cos\vartheta}{\sin\vartheta}\right]Y_l^{l-s} = \\ &= \frac{\exp(-\mathrm{i}\,\varphi)}{(\sin\vartheta)^{l-s-1}}\,\frac{-\hbar}{\sin\vartheta}\,\frac{\partial}{\partial\vartheta}\left[(\sin\vartheta)^{l-s}\,Y_l^{l-s}\right], \end{aligned} \tag{13.75}$$

where the product $(\sin\vartheta)^{l-s}\,Y_l^{l-s}$ is taken from the previously-calculated expression of $Y_l^{l-s}$. Iterating the procedure yields

$$Y_l^{l-s} = a\,\frac{\exp[\mathrm{i}\,(l-s)\varphi]}{(\sin\vartheta)^{l-s}}\,\underbrace{\frac{-\hbar}{\sin\vartheta}\,\frac{\mathrm{d}}{\mathrm{d}\vartheta}\cdots\frac{-\hbar}{\sin\vartheta}\,\frac{\mathrm{d}}{\mathrm{d}\vartheta}}_{s\ \text{times}}\,(\sin\vartheta)^{2l}. \tag{13.76}$$

As $Y_l^{l-s}$ is a solution of the linear, homogeneous equations $\mathcal{L}_z Y = L_z Y$ and $\mathcal{L}^2 Y = \lambda Y$, the constant $a\,\hbar^s$ that builds up in the derivation can be dropped. Letting $m = l - s$ one finds

$$Y_l^m = c_{lm} \frac{\exp(\mathrm{i}\, m\, \varphi)}{(\sin\vartheta)^m} \underbrace{\frac{-1}{\sin\vartheta}\frac{\mathrm{d}}{\mathrm{d}\vartheta} \cdots \frac{-1}{\sin\vartheta}\frac{\mathrm{d}}{\mathrm{d}\vartheta}}_{l-m \text{ times}} (\sin\vartheta)^{2l}, \tag{13.77}$$

where the coefficient $c_{lm}$ has been added for normalization purposes. One may recast (13.77) in a more compact form by letting $\zeta = \cos\vartheta$, whence $-1 \le \zeta \le 1$ and $\mathrm{d}\zeta = -\sin\vartheta\,\mathrm{d}\vartheta$. As a consequence,

$$Y_l^m = c_{lm} \frac{\exp(\mathrm{i}\, m\, \varphi)}{(1-\zeta^2)^{m/2}} \frac{\mathrm{d}^{l-m}}{\mathrm{d}\zeta^{l-m}} (1-\zeta^2)^l. \tag{13.78}$$

The eigenfunctions $Y_l^m$ are square integrable and mutually orthogonal [78, App. B.10]. To examine some of their properties it is convenient to introduce some special functions; to begin with, the *associate Legendre functions* are defined in the interval $-1 \le \zeta \le 1$ by

$$P_l^m(\zeta) = \frac{(-1)^m}{2^l\, l!} (1-\zeta^2)^{m/2} \frac{\mathrm{d}^{l+m}}{\mathrm{d}\zeta^{l+m}} (\zeta^2 - 1)^l, \tag{13.79}$$

with $l = 0, 1, \ldots$ and, for each $l$, $m = -l, \ldots, -1, 0, 1, \ldots, l$. As $(1-\zeta^2)^{m/2}$ and $(\zeta^2-1)^l$ are even functions of $\zeta$, $P_l^m$ is even (odd) if $l+m$ is even (odd): $P_l^m(-\zeta) = (-1)^{l+m} P_l^m(\zeta)$. Furthermore, it is

$$P_l^m(\zeta) = (-1)^m \frac{(l+m)!}{(l-m)!} P_l^{-m}. \tag{13.80}$$

Replacing $m$ with $-m$ in (13.79) shows that $Y_l^m$ is proportional to $P_l^{-m}$ which, in turn, is proportional to $P_l^m$ due to (13.80). In conclusion, using $\zeta = \cos\vartheta$,

$$Y_l^m(\vartheta, \varphi) = c_{lm} \exp(\mathrm{i}\, m\, \varphi)\, P_l^m(\cos\vartheta), \tag{13.81}$$

with $0 \le \vartheta \le \pi$ and $0 \le \varphi \le 2\pi$. As for the indices it is $l = 0, 1, \ldots$ and $m = -l, \ldots, -1, 0, 1, \ldots, l$. The functions $Y_l^m$ defined by (13.81) are called *spherical harmonics*. Combining the definition of $Y_l^m$ with the properties of $P_l^m$ shown above yields $Y_l^{-m} = (-1)^m (Y_l^m)^*$. Note that $Y_l^m$ and $Y_l^{-m}$ are linearly independent, whereas $P_l^m$ and $P_l^{-m}$ are not. Letting

$$c_{lm} = \left[ \frac{(2l+1)(l-m)!}{4\pi\,(l+m)!} \right]^{1/2}, \tag{13.82}$$

the set made of the spherical harmonics is orthonormal, namely,

$$\int_0^{2\pi} \int_0^{\pi} \left(Y_\lambda^\mu\right)^* Y_l^m \,\mathrm{d}\vartheta\,\mathrm{d}\varphi = \begin{cases} 1, & \lambda = l \text{ and } \mu = m \\ 0, & \text{otherwise} \end{cases} \tag{13.83}$$

and complete (Sect. 8.4.3), namely,

$$F(\vartheta,\varphi)=\sum_{l=0}^{\infty}\sum_{m=-l}^{l} a_{lm}\,Y_l^m(\vartheta,\varphi),\qquad a_{lm}=\int_0^{2\pi}\int_0^{\pi}\left(Y_l^m\right)^*\,F\,\mathrm{d}\vartheta\,\mathrm{d}\varphi, \quad (13.84)$$

where $F$ is a sufficiently regular function of the angles. The inner sum of (13.84),

$$Y_l(\vartheta,\varphi)=\sum_{m=-l}^{l} a_{lm}\,Y_l^m(\vartheta,\varphi) \quad (13.85)$$

is also called *general spherical harmonic of order l*, whereas the special case $m=0$ of the associate Legendre function,

$$P_l^0(\zeta)=\frac{1}{2^l\,l\,!}\,\frac{\mathrm{d}^l}{\mathrm{d}\zeta^l}(\zeta^2-1)^l, \quad (13.86)$$

is a polynomial of degree $l$ called *Legendre polynomial*.

### 13.6.4 Eigenvalues of the Radial Equation—Coulomb Case

The case $E<0$ of the radial Eq. (13.47) is considered here, corresponding to a limited motion. As a consequence, the eigenvectors are expected to depend on a discrete index, and the eigenfunctions are expected to be square integrable. Calculating the derivative and multiplying both sides of (13.47) by $-2\,m_0/(\hbar^2\,r)$ yields

$$\frac{\mathrm{d}^2\varrho}{\mathrm{d}r^2}+\frac{2}{r}\,\frac{\mathrm{d}\varrho}{\mathrm{d}r}-\frac{2\,m_0}{\hbar^2}\,V_e\,\varrho+\frac{2\,m_0}{\hbar^2}\,E\,\varrho=0. \quad (13.87)$$

To proceed one scales the independent variable by multiplying both sides of (13.87) by $a^2$, where $a$ is a length. The term involving $V_e$ becomes

$$-a^2\,\frac{2\,m_0}{\hbar^2}\,V_e\,\varrho=\left[\frac{2\,m_0\,Z\,q^2\,a}{4\,\pi\,\varepsilon_0\,\hbar^2\,(r/a)}-\frac{l\,(l+1)}{(r/a)^2}\right]\varrho, \quad (13.88)$$

where both fractions in brackets are dimensionless. As $a$ may be chosen arbitrarily, it is convenient to select for it a value that makes the first fraction equal to $2/(r/a)$, namely,

$$a=\frac{4\,\pi\,\varepsilon_0\,\hbar^2}{m_0\,Z\,q^2}. \quad (13.89)$$

As a consequence, the term involving $E$ becomes

$$a^2\,\frac{2\,m_0}{\hbar^2}\,E\,\varrho=\lambda\,\varrho,\qquad \lambda=\left(\frac{4\,\pi\,\varepsilon_0}{Z\,q^2}\right)^2\,\frac{2\,\hbar^2}{m_0}\,E. \quad (13.90)$$

Adopting the dimensionless variable $x = r/a$ and using the relations $a^2\,\mathrm{d}^2\varrho/\mathrm{d}r^2 = \mathrm{d}^2\varrho/\mathrm{d}x^2$, $(2\,a^2/r)\,\mathrm{d}\varrho/\mathrm{d}r = (2/x)\,\mathrm{d}\rho/\mathrm{d}x$ yields the radial equation in scaled form,

$$\frac{\mathrm{d}^2\varrho}{\mathrm{d}x^2} + \frac{2}{x}\,\frac{\mathrm{d}\varrho}{\mathrm{d}x} + \left[\frac{2}{x} - \frac{l\,(l+1)}{x^2}\right]\varrho + \lambda\,\varrho = 0. \tag{13.91}$$

The range of the independent variable is $0 \le x < \infty$, so the equation has a double pole in the origin: it is necessary to select solutions that vanish in the origin in such a way as to absorb the pole (more on this in Sect. 13.6.5). The replacement $\varrho = \sigma/x$ gives (13.91) the simpler form

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}x^2} + \left[\frac{2}{x} - \frac{l\,(l+1)}{x^2}\right]\sigma + \lambda\,\sigma = 0, \tag{13.92}$$

which is identical to (13.2). The factorization of (13.92) is then accomplished following the scheme shown in Sect. 13.3, and is based upon the function $g_l = l/x - 1/l$; in this case operators (13.10) and parameter (13.9) read, respectively,

$$\mathcal{A}_l^+ = \frac{l}{x} - \frac{1}{l} + \frac{\mathrm{d}}{\mathrm{d}x}, \qquad \mathcal{A}_l^- = \frac{l}{x} - \frac{1}{l} - \frac{\mathrm{d}}{\mathrm{d}x}, \qquad L_l = -1/l^2. \tag{13.93}$$

The latter depends only on $l$ and fulfills the relation $L_{n+1} > L_{l+1}, l = 0, 1, \ldots, n-1$. As a consequence, remembering the second relation in (13.90), the eigenvalues[3] $\lambda = \lambda_n = L_{n+1}$ of (13.92) and those of (13.87) are, respectively,

$$\lambda_n = -\frac{1}{(n+1)^2}, \qquad E_n = -\left(\frac{Z\,q^2}{4\,\pi\,\varepsilon_0}\right)^2 \frac{m_0/(2\,\hbar^2)}{(n+1)^2}, \qquad n = 0, 1, \ldots. \tag{13.94}$$

### 13.6.5 Eigenfunctions of the Radial Equation—Coulomb Case

The eigenfunction corresponding to $l = n$ is found by applying (13.14). As the eigenfunction is indicated here with $\sigma_{nn}$, one must solve $\mathcal{A}_{n+1}^-\sigma_{nn} = 0$, namely, using (13.93), $[(n+1)/x - 1/(n+1) - \mathrm{d}/\mathrm{d}x]\,\sigma_{nn} = 0$, whose solution is

$$\sigma_{nn} = c_{nn}\,x^{n+1}\,\exp\left(-\frac{x}{n+1}\right), \qquad n = 0, 1, \ldots, \tag{13.95}$$

which vanishes both in the origin and at infinity, this fulfilling the requirements stated in Sect. 13.6.4. The eigenfunction (13.95) is also square integrable with, from (C.88, C.90),

$$\frac{1}{c_{nn}^2} = \int_0^\infty x^{2n+2}\exp\left(-\frac{2x}{n+1}\right)\mathrm{d}x = (2n+2)\,!\,\left(\frac{n+1}{2}\right)^{2n+3}. \tag{13.96}$$

[3] In (13.49) a more convenient notation is used, obtained from (13.94) through the replacements $n+1 \leftarrow n' \leftarrow n$, with $n' = 1, 2, \ldots$.

Combining the first definition in (13.21) with the third relation in (13.93), the auxiliary operator $\mathcal{B}^+_{nl}$ reads

$$\mathcal{B}^+_{nl} = \frac{l\,(n+1)}{\sqrt{(n+1-l)(n+1+l)}}\,\mathcal{A}^+_l. \tag{13.97}$$

Then, from the second of (13.24), the normalized eigenfunctions corresponding to $l < n$ are found recursively from

$$\sigma_{n,n-1} = \mathcal{B}^+_{nn}\sigma_{nn}, \qquad \sigma_{n,n-2} = \mathcal{B}^+_{n,n-1}\sigma_{n,n-1}, \qquad \ldots \tag{13.98}$$

The last eigenfunction found by the recursive procedure is $\sigma_{n0} = \mathcal{B}^+_{n1}\sigma_{n1}$ as expected. In fact, a further iteration would not yield an eigenfunction because $\mathcal{B}^+_{n0} = 0$.

The eigenfunction of (13.87) corresponding to the lowest total energy $E_{\min} = E(n = 0)$ is found by combining (13.95, 13.96) with $\sigma = \varrho/x$ and $x = r/a$, this yielding $\varrho(r) = (1/2)\,\exp(-r/a)$. There is only one spherical harmonic compatible with this energy eigenvalue, specifically, $Y^0_0 = 1/\sqrt{4\,\pi}$ (Table 13.1). Thus, the product $w(E_{\min}) = (c/2)\,\exp(-r/a)/\sqrt{4\,\pi}$, with $c$ a normalization constant, is the eigenfunction of the Schrödinger Eq. (13.35) corresponding to the lowest total energy. The normalization constant is necessary because $\varrho$ is obtained from scaling another function $\sigma$, originally normalized to unity. Taking the Jacobian determinant $J = r^2\,\sin\vartheta$ from (B.3) one finds

$$\frac{1}{c^2} = \frac{1}{16\,\pi}\int_0^\infty\int_0^\pi\int_0^{2\,\pi}\exp\left(-\frac{2\,r}{a}\right)r^2\,\sin\vartheta\,\mathrm{d}r\,\mathrm{d}\vartheta\,\mathrm{d}\varphi = \frac{a^3}{16}, \tag{13.99}$$

whence $w(E_{\min}) = \exp(-r/a)/\sqrt{\pi\,a^3}$.

### 13.6.6 Transmission Matrix

The one-dimensional, time-independent Schrödinger Eq. (11.28) is solvable analytically in a limited number of cases, some of which have been illustrated in the sections above. When the analytical solution is not known one must resort to approximate methods; an example is given here, with reference to a finite domain $0 \le x \le s$. The latter is tessellated by selecting $N$ points $x_1 < x_2 < \ldots < x_N$, internal to the domain, called *nodes*. The boundaries of the domain are indicated with $0 = x_0 < x_1$ and $s = x_{N+1} > x_N$. The segment bounded by $x_i$ and $x_{i+1}$ is indicated with $h_{i+1}$ and is called *element*. The same symbol indicates the length of the element, $h_{i+1} = x_{i+1} - x_i$. Finally, a subdomain $\Omega_i$, called *cell*, is associated to each node. For the internal nodes $x_1, \ldots, x_N$ the cell is bounded by $x_i - h_i/2$ and $x_i + h_{i+1}/2$. The same symbol is used to indicate also the cell length, $\Omega_i = (h_i + h_{i+1})/2$ (Fig. 13.3). The left boundary $x_0$ is associated to the cell $\Omega_0$ of length $h_1/2$ placed on the right of $x_0$, while the right boundary $x_{N+1}$ is associated to the cell $\Omega_{N+1}$ of length $h_{N+1}/2$ placed on the left of $x_{N+1}$.

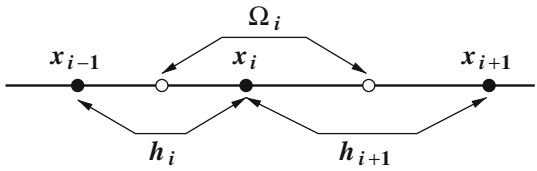


**Fig. 13.3** Illustration of the concepts of node, element, and cell (Sect. 13.6.6)

The approximation methods that are applicable to a given tessellation are numerous. The method depicted in this section replaces the coefficient $q(x)$ of (11.28) over each element $h_i$ with an approximating function $q_i(x)$ such that the solution $w_i(x)$ to (11.28) over $h_i$ can be found analytically. The approximating functions $q_i$ may differ from an element to another, this yielding different analytical solutions. Then, the continuity of the analytical solutions and their derivatives is imposed at each node; finally, the same continuity is imposed at the boundaries 0 and $s$, where the form of the wave function is supposed to be known.

To proceed, consider an internal node $i = 1, 2, \ldots, N$ and the two elements $h_i$, $h_{i+1}$ adjacent to it. The solutions $w_i$, $w_{i+1}$ over the two elements is expressed in terms of the fundamental solutions $u$, $v$ (compare with Sect. 11.4):

$$w_i(x) = a_i^u u_i(x) + a_i^v v_i(x), \qquad w_{i+1}(x) = a_{i+1}^u u_{i+1}(x) + a_{i+1}^v v_{i+1}(x), \quad (13.100)$$

with $a_i^u, a_i^v, a_{i+1}^u, a_{i+1}^v$ undetermined constants. The fundamental solutions fulfill the boundary conditions

$$u_{i+1}(x_i) = 1, \qquad u'_{i+1}(x_i) = 0, \qquad v_{i+1}(x_i) = 0, \qquad v'_{i+1}(x_i) = 1, \quad (13.101)$$

$i = 1, 2, \ldots, N$, where primes indicate derivatives. Imposing the continuity of $w$, $w'$ at $x_i$ yields

$$a_{i+1}^u = a_i^u u_i(x_i) + a_i^v v_i(x_i), \qquad a_{i+1}^v = a_i^u u'_i(x_i) + a_i^v v'_i(x_i). \quad (13.102)$$

Letting

$$\mathbf{a}_i = \begin{bmatrix} a_i^u \\ a_i^v \end{bmatrix}, \qquad \mathbf{N}_i = \begin{bmatrix} u_i(x_i) & v_i(x_i) \\ u'_i(x_i) & v'_i(x_i) \end{bmatrix}, \quad (13.103)$$

the relations (13.102) take the form

$$\mathbf{a}_{i+1} = \mathbf{N}_i \, \mathbf{a}_i . \quad (13.104)$$

Matrix $\mathbf{N}_i$ is known by construction, and provides the link between the unknown vectors $\mathbf{a}_i$ and $\mathbf{a}_{i+1}$. Vector $\mathbf{a}_i$ belongs to element $h_i$ only, whereas matrix $\mathbf{N}_i$ belongs to element $h_i$ (due to $u_i$, $v_i$) and also to node $x_i$ (because $u_i$, $v_i$ are calculated at $x_i$). Iterating (13.104) yields

$$\mathbf{a}_{N+1} = \mathbf{N}_I \mathbf{a}_1, \qquad \mathbf{N}_I = \mathbf{N}_N \mathbf{N}_{N-1} \ldots \mathbf{N}_2 \mathbf{N}_1 . \quad (13.105)$$

Remembering the discussion in Sect. A.12 one finds $\det\mathbf{N}_i = W = 1$, whence $\det\mathbf{N}_I = \det\mathbf{N}_N \ldots \det\mathbf{N}_1 = 1$. Now it is necessary to link the solution over $h_1$ with that over $x < 0$, which is given by (11.30). Although the two functions $\exp(\pm \mathrm{i}\, k_L\, x)$ in the latter are not fundamental solutions, it is convenient to keep the form (11.30) because $a_2/a_1$ provides the information about the reflection coefficient directly. Letting

$$\mathbf{a}_L = \begin{bmatrix} a_1 \\ a_2 \end{bmatrix}, \qquad \mathbf{N}_L = \begin{bmatrix} 1 & 1 \\ \mathrm{i}\, k_L & -\mathrm{i}\, k_L \end{bmatrix}, \tag{13.106}$$

the continuity of $w$ and $w'$ at $x = 0$ yields $\mathbf{a}_1 = \mathbf{N}_L\, \mathbf{a}_L$. Similarly, it is necessary to link the solution over $h_{N+1}$ with that over $x > s$, which is given by (11.31). Again, the two functions $\exp(\pm \mathrm{i}\, k_R\, x)$ in the latter are not fundamental solutions, however, they are kept here because $a_5/a_1$ provides the information about the transmission coefficient directly. Letting

$$\mathbf{a}_R = \begin{bmatrix} a_5 \\ a_6 \end{bmatrix}, \qquad \mathbf{N}_R = \begin{bmatrix} \exp(\mathrm{i}\, k_R\, s) & \exp(-\mathrm{i}\, k_R\, s) \\ \mathrm{i}\, k_R\, \exp(\mathrm{i}\, k_R\, s) & -\mathrm{i}\, k_R\, \exp(-\mathrm{i}\, k_R\, s) \end{bmatrix}, \tag{13.107}$$

the continuity of $w$ and $w'$ at $x = s$ yields $\mathbf{N}_R\, \mathbf{a}_R = \mathbf{N}_{N+1}\, \mathbf{a}_{N+1}$, with $\det\mathbf{N}_{N+1} = 1$, $\det\mathbf{N}_L = -2\,\mathrm{i}\, k_L$, $\det\mathbf{N}_R = -2\,\mathrm{i}\, k_R$. Combining the relations found so far,

$$\mathbf{a}_R = \mathbf{N}\, \mathbf{a}_L, \qquad \mathbf{N} = \mathbf{N}_R^{-1}\, \mathbf{N}_{N+1}\, \mathbf{N}_I\, \mathbf{N}_L, \tag{13.108}$$

where

$$\mathbf{N}_R^{-1} = \begin{bmatrix} \exp(-\mathrm{i}\, k_R\, s)/2 & \exp(-\mathrm{i}\, k_R\, s)/(2\,\mathrm{i}\, k_R) \\ \exp(\mathrm{i}\, k_R\, s)/2 & \mathrm{i}\, \exp(\mathrm{i}\, k_R\, s)/(2\, k_R) \end{bmatrix}, \qquad \det\mathbf{N}_R^{-1} = -\frac{1}{2\,\mathrm{i}\, k_R}. \tag{13.109}$$

whence $\det\mathbf{N} = \det\mathbf{N}_R^{-1} \det\mathbf{N}_{N+1} \det\mathbf{N}_I \det\mathbf{N}_L = k_L/k_R$. Matrix $\mathbf{N}$ (also called *transmission matrix* in [15]) provides the link between $\mathbf{a}_L$ and $\mathbf{a}_R$. Splitting the first relation of (13.108) into its components gives

$$a_5 = N_{11}\, a_1 + N_{12}\, a_2, \qquad a_6 = N_{21}\, a_1 + N_{22}\, a_2. \tag{13.110}$$

If the particle is launched, e.g., from $-\infty$ one lets $a_6 = 0$, whence

$$\frac{a_2}{a_1} = -\frac{N_{21}}{N_{22}}, \qquad \frac{a_5}{a_1} = \frac{\det\mathbf{N}}{N_{22}} = \frac{k_L/k_R}{N_{22}}. \tag{13.111}$$

Combining (13.111) with (11.35) yields[4] $|N_{21}|^2 + k_L/k_R = |N_{22}|^2$.

[4] Within a numerical solution of the Schrödinger equation, the relation $|N_{21}|^2 + k_L/k_R = |N_{22}|^2$ may be exploited as a check for the quality of the approximation.

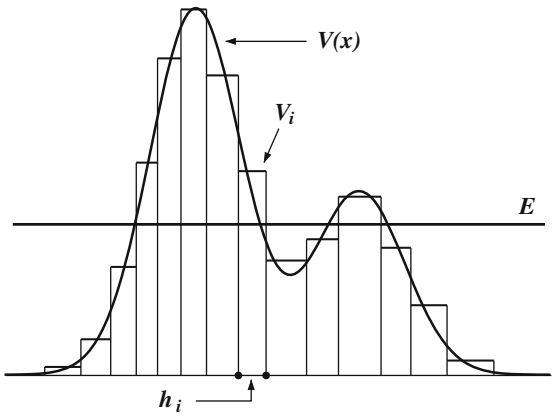


**Fig. 13.4** Example of a potential energy $V(x)$ replaced with a piecewise-constant function $V_i$ (Sect. 13.6.6)

The derivation of the transmission matrix has been carried out here without specifying the form of the fundamental solutions $u_i$, $v_i$ over the corresponding element $h_i$. In the practical cases, to easily find an analytical solution over each element one approximates the coefficient $q(x)$ of (11.28) with a constant, $q_i = \text{const}$ in $h_i$; this is equivalent to replacing the potential energy $V(x)$ with a piecewise-constant function $V_i$ (Fig. 13.4). Depending on the sign of $q_i = 2\,m\,(E - V_i)/\hbar^2$ the possible cases for $u_i$, $v_i$ are:

$$\begin{cases} q_i = -\alpha_i^2 < 0 & u_i = \cosh\left[\alpha_i\,(x - x_{i-1})\right] & v_i = \sinh\left[\alpha_i\,(x - x_{i-1})\right]/\alpha_i \\ q_i = k_i^2 > 0 & u_i = \cos\left[k_i\,(x - x_{i-1})\right] & v_i = \sin\left[k_i\,(x - x_{i-1})\right]/k_i \\ q_i = 0 & u_i = 1 & v_i = x - x_{i-1} \end{cases} \tag{13.112}$$

with $\alpha_i$, $k_i$ real. As the potential energy is replaced with a piecewise-constant function, the accuracy of the approximation is not very high.

## Problems

**13.1** Letting $Z = 1$ in (13.49) one finds the expression of the energy levels of the hydrogen atom in a bound state, consistently with that obtained from the Bohr hypothesis (Sect. 7.4.4). Use the same equation to calculate the minimum energy that must be given to the electron to extract it from the hydrogen atom (*ionization energy*).

**13.2** With reference to the hydrogen atom, calculate the expectation value of the radius $r$ corresponding to the eigenfunction $w(E_{\min}) = \exp(-r/a)/\sqrt{\pi\,a^3}$ found in Sect. 13.6.5.