

1.7: Space Dependence

In contrast to the simple and universal time dependence (62) of the stationary states, the spatial distributions of their wavefunction $\psi_n(\mathbf{r})$ need to be calculated from the problem-specific stationary Schrödinger equation (65). The solution of this equation for various particular cases is a major focus of the next two chapters. For now, let us consider just the simplest example, which nevertheless will be the basis for our discussion of more complex problems: let a particle be confined inside a rectangular hardwall box. Such confinement may be described by the following potential energy profile: ⁵⁴

$$U(\mathbf{r}) = \begin{cases} 0, & \text{for } 0 < x < a_x, \quad 0 < y < a_y, \quad \text{and } 0 < z < a_z \\ +\infty, & \text{otherwise} \end{cases} \quad (1.7.1)$$

The only way to keep the product $U(\mathbf{r})\psi_n$ in Eq. (65) finite outside the box, is to have $\psi = 0$ in these regions. Also, the function has to be continuous everywhere, to avoid the divergence of the kinetic-energy term $(-\hbar^2/2m)\nabla^2\psi_n$. Hence, in this case we may solve the stationary Schrödinger equation (60) just inside the box, i.e. with $U = 0$, so that it takes a simple form

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n = E_n\psi_n, \quad (1.7.2)$$

with zero boundary conditions on all the walls. ⁵⁵ For our particular geometry, it is natural to express the Laplace operator in the Cartesian coordinates $\{x, y, z\}$ aligned with the box sides, with the origin at one of the corners of its rectangular $a_x \times a_y \times a_z$ volume, so that our boundary problem becomes:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi_n = E_n\psi_n, \text{ for } 0 < x < a_x, \quad 0 < y < a_y, \quad \text{and } 0 < z < a_z, \\ \text{with } \psi_n = 0 \text{ for } : x = 0 \text{ and } a_x; \quad y = 0 \text{ and } a_y; \quad z = 0 \text{ and } a_z.$$

This problem may be readily solved using the same variable separation method as was used in Sec. 5 - now to separate the Cartesian spatial variables from each other, by looking for a partial solution of Eq. (78) in the form

$$\psi(\mathbf{r}) = X(x)Y(y)Z(z). \quad (1.7.3)$$

(Let us postpone assigning function indices for a minute.) Plugging this expression into Eq. (78b) and dividing all terms by the product XYZ , we get

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} - \frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2} - \frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2Z}{dz^2} = E. \quad (1.7.4)$$

Now let us repeat the standard argumentation of the variable separation method: since each term on the left-hand side of this equation may be only a function of the corresponding argument, the equality is possible only if each of them is a constant - in our case, with the dimensionality of energy. Calling these constants E_x , etc., we get three similar 1D equations

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} = E_x, \quad -\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2} = E_y, \quad -\frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2Z}{dz^2} = E_z, \quad (1.7.5)$$

with Eq. (80) turning into the following energy-matching condition:

$$E_x + E_y + E_z = E. \quad (1.7.6)$$

All three ordinary differential equations (81), and their solutions, are similar. For example, for $X(x)$, we have the following 1D Helmholtz equation

$$\frac{d^2X}{dx^2} + k_x^2X = 0, \quad \text{with } k_x^2 \equiv \frac{2mE_x}{\hbar^2}, \quad (1.7.7)$$

and simple boundary conditions: $X(0) = X(a_x) = 0$. Let me hope that the reader knows how to solve this well-known 1D boundary problem - describing, for example, the usual mechanical waves on a guitar string. The problem allows an infinite number of sinusoidal standing-wave eigenfunctions, ⁵⁶

$$X \propto \sin k_x x, \quad \text{with } k_x = \frac{\pi n_x}{a_x}, \quad \text{so that } X = \left(\frac{2}{a_x}\right)^{1/2} \sin \frac{\pi n_x x}{a_x}, \quad \text{with } n_x = 1, 2, \dots, \quad (1.7.8)$$

corresponding to the following eigenenergies:

$$E_x = \frac{\hbar^2}{2m} k_x^2 = \frac{\pi^2 \hbar^2}{2ma_x^2} n_x^2 \equiv E_{x1} n_x^2. \quad (1.7.9)$$

Figure 8 shows these simple results, using a somewhat odd but very graphic and common representation, in that the eigenenergy values (frequently called the energy levels) are used as horizontal axes for plotting the eigenfunctions - despite their completely different dimensionality.

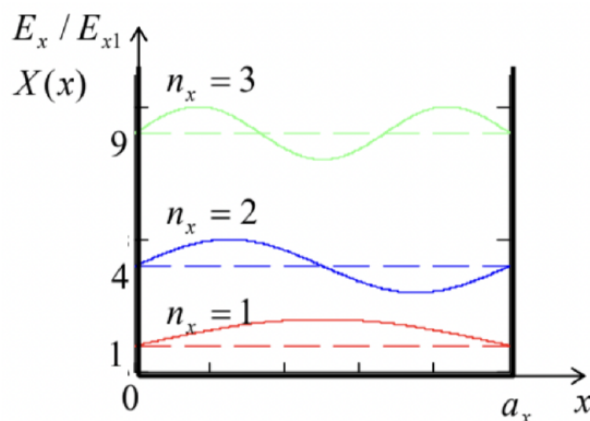


Fig. 1.8. The lowest eigenfunctions (solid lines) and eigenvalues (dashed lines) of Eq. (83) for a potential well of length a_x . Solid black lines show the effective potential energy profile for this 1D eigenproblem.

Due to the similarity of all Eqs. (81), $Y(y)$ and $Z(z)$ are absolutely similar functions of their arguments, and may also be numbered by integers (say, n_y and n_z) independent of n_x , so that the spectrum of values of the total energy (82) is

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{a_x^2} + \frac{n_y^2}{a_y^2} + \frac{n_z^2}{a_z^2} \right) \quad (1.7.10)$$

Thus, in this 3D problem, the role of the index n in the general Eq. (69) is played by a set of three independent integers $\{n_x, n_y, n_z\}$. In quantum mechanics, such integers play a key role and thus have a special name, the quantum numbers. Using them, that general solution, for our current simple problem may be represented as the sum

$$\Psi(\mathbf{r}, t) = \sum_{n_x, n_y, n_z=1}^{\infty} c_{n_x, n_y, n_z} \sin \frac{\pi n_x x}{a_x} \sin \frac{\pi n_y y}{a_y} \sin \frac{\pi n_z z}{a_z} \exp \left\{ -i \frac{E_{n_x, n_y, n_z}}{\hbar} t \right\}, \quad (1.7.11)$$

with the front coefficients that may be readily calculated from the initial wavefunction $\Psi(\mathbf{r}, 0)$, using Eq. (68) - again with the replacement $n \rightarrow \{n_x, n_y, n_z\}$.

This simplest problem is a good illustration of typical results the wave mechanics gives for spatially-confined motion, including the discrete energy spectrum, and (in this case, evidently) orthogonal eigenfunctions. Perhaps most importantly, its solution shows that the lowest value of the particle's kinetic energy (86), reached in the so-called ground state (in our case, the state with $n_x = n_y = n_z = 1$) is above zero for any finite size of the confining box. An example of the opposite case of a continuous spectrum for the unconfined motion of a free particle is given by the plane waves (29). With the account of relations $E = \hbar\omega$ and $\mathbf{p} = \hbar\mathbf{k}$, such wavefunction may be viewed as the product of the time-dependent factor (62) by the eigenfunction,

$$\psi_{\mathbf{k}} = a_{\mathbf{k}} \exp\{i\mathbf{k} \cdot \mathbf{r}\}, \quad (1.7.12)$$

which is the solution of the stationary Schrödinger equation (78a) if it is valid in the whole space.⁵⁷ The reader should not be worried too much by the fact that the fundamental solution (86) in free space is a traveling wave (having, in particular, a non-zero value of the probability current \mathbf{j}), while those inside a quantum box are standing waves, with $\mathbf{j} = 0$, even though the free space may be legitimately considered as the ultimate limit of a quantum box with volume $V = a_x \times a_y \times a_z \rightarrow \infty$. Indeed, due to the linearity of wave mechanics, two traveling-wave solutions (88) with equal and opposite values of the momentum (and hence with the same energy) may be readily combined to give a standing-wave solution,⁵⁸ for example, $\exp\{i\mathbf{k} \cdot \mathbf{r}\} + \exp\{-i\mathbf{k} \cdot \mathbf{r}\} = 2 \cos(\mathbf{k} \cdot \mathbf{r})$, with the net current $\mathbf{j} = 0$. Thus, depending on the convenience for a particular problem, we may represent its general solution as a sum of either travelingwave or standing-wave eigenfunctions. Since in the

unlimited free space, there are no boundary conditions to satisfy, the Cartesian components of the wave vector \mathbf{k} in Eq. (88) can take any real values. (This is why it is more convenient to label these wavefunctions, and the corresponding eigenenergies,

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} \geq 0 \quad (1.7.13)$$

with their wave vector \mathbf{k} rather than an integer index.) However, one aspect of continuous-spectrum systems requires a bit more caution with mathematics: the summation (69) should be replaced by the integration over a continuous index or indices - in our current case, the three Cartesian components of the vector \mathbf{k} . The main rule of such replacement may be readily extracted from Eq. (84): according to this relation, for standing-wave solutions, the eigenvalues of k_x are equidistant, i.e. separated by equal intervals $\Delta k_x = \pi/a_x$, with similar relations for other two Cartesian components of vector \mathbf{k} . Hence the number of different eigenvalues of the standing-wave vector \mathbf{k} (with $k_x, k_y, k_z \geq 0$), within a volume $d^3k \gg 1/V$ of the \mathbf{k} space is $dN = d^3k / (\Delta k_x \Delta k_y \Delta k_z) = (V/\pi^3) d^3k$. Frequently, it is more convenient to work with traveling waves (88); in this case we should take into account that, as was just discussed, there are two different traveling wave numbers (say, $+k_x$ and $-k_x$) corresponding to each standing wave vector's $k_x > 0$. Hence the same number of physically different states corresponds to a $2^3 = 8$ -fold larger \mathbf{k} space or, equivalently, to an 8-fold smaller number of states per unit volume d^3k :

$$dN = \frac{V}{(2\pi)^3} d^3k \quad (1.7.14)$$

For $dN \gg 1$, this expression is independent of the boundary conditions, and is frequently represented as the following summation rule

$$\lim_{k^3 V \rightarrow \infty} \sum_{\mathbf{k}} f(\mathbf{k}) = \int f(\mathbf{k}) dN = \frac{V}{(2\pi)^3} \int f(\mathbf{k}) d^3k, \quad (1.7.15)$$

where $f(\mathbf{k})$ is an arbitrary function of \mathbf{k} . Note that if the same wave vector \mathbf{k} corresponds to several internal quantum states (such as spin - see Chapter 4), the right-hand side of Eq. (91) requires its multiplication by the corresponding degeneracy factor of orbital states.⁵⁹

⁵⁴ Another common name for such potentials, especially of lower dimensionality, is the potential well, in our current case "rectangular" one: with a flat "bottom" and vertical, infinitely high "walls". Note that sometimes, very unfortunately, such potential profiles are called "quantum wells". (This term seems to imply that the particle's confinement in such a well is a phenomenon specific for quantum mechanics. However, as we will repeatedly see in this course, the opposite is true: quantum effects do as much as they only can to overcome the particle's confinement in a potential well, letting it partly penetrate in the "classically forbidden" regions beyond the well's walls.)

⁵⁵ Rewritten as $\nabla^2 f + k^2 f = 0$, Eq. (78a) is just the Helmholtz equation, which describes waves of any nature (with the wave vector \mathbf{k}) in a uniform, isotropic, linear medium - see, e.g., EM Secs. 7.5-7.9 and 8.5.

⁵⁶ The front coefficient in the last expression for X ensures the (ortho)normality condition (66).

⁵⁷ In some systems (e.g., a particle interacting with a potential well of a finite depth), a discrete energy spectrum within a certain energy interval may coexist with a continuous spectrum in a complementary interval. However, the conceptual philosophy of eigenfunctions and eigenvalues remains the same even in this case.

⁵⁸ This is, of course, the general property of waves of any physical nature, propagating in a linear medium - see, e.g., CM Sec. 6.5 and/or EM Sec. 7.3.

⁵⁹ Such factor is similar to the front factor 2 in Eq. (1) for the number of electromagnetic wave modes, in that case describing two different polarizations of the waves with the same wave vector.