Appendix A: Continuum states

This appendix complements what you have already learned about the bound states of quantum systems. It is not a formal part of the present course. However, familiarity with the material it contains is essential for a good understanding of some of the topics studied this year and will therefore be assumed in the examination.

What continuum states are can be more easily understood by comparing the energy eigenstates of a linear harmonic oscillator to those of a free particle. We start with the case of a linear harmonic oscillator. Specifically we consider a particle of mass m confined to the x-axis and of potential energy

$$V(x) = kx^2/2, \tag{A.1}$$

where x is the position of the particle and k is a force constant. The eigenenergies and eigenfunctions of the Hamiltonian of this system are solutions of the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x). \tag{A.2}$$

As you may remember from the level 2 QM course, these eigenenergies are given by the simple formula

$$E_n = \hbar\omega(n+1/2), \qquad n = 0, 1, 2, \ldots, \tag{A.3}$$

where $\omega = (k/m)^{1/2}$. The corresponding eigenfunctions are products of three factors, namely a Gaussian function $\exp(-\alpha^2 x^2/2)$ where α is a constant, a certain polynomial, and a normalization constant N_n. We note the following:

- The energy levels found for this system are discrete, i.e., each eigenenergy E_n is separated from its nearest neighbur by a non-zero energy gap (here this gap is the same for all n, $\hbar\omega$, but for other systems the gap will normally vary from energy level to energy level).

- The corresponding eigenfunctions $\psi_n(x)$ are square-integrable, in the sense that the integrals

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 \, \mathrm{d}x$$

  are finite. (Later on we will see examples of eigenfunctions for which the corresponding integrals diverge, i.e., are infinite.) Since the integrals converge, one can arrange that

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 \, \mathrm{d}x = 1 \tag{A.4}$$

  by a suitable choice of the normalization factors N_n.

- The probability that the particle is at a distance larger than d from the origin when in the eigenstate $\psi_n(x)$ is

$$P_n(d) = \int_{-\infty}^{-d} |\psi_n(x)|^2 \, \mathrm{d}x + \int_{d}^{\infty} |\psi_n(x)|^2 \, \mathrm{d}x. \tag{A.5}$$

Owing to the Gaussian factor $\exp(-\alpha^2 x^2 / 2)$, this probability decreases rapidly for $d \to \infty$. The eigenfunctions $\psi_n(x)$ therefore describe states in which there is a vanishingly small probability that the particle is far away from the origin. These states are similar to the bound states of more complex systems such as atoms, molecules, nuclei, etc., in which the particles forming the system are bound by their mutual interaction and cannot go arbitrarily far apart from each other.

Recall, also, that the eigenfunctions $\psi_n(x)$ form a complete basis set. That is, any square-integrable wave function $\Psi(x, t)$ defined on the infinite interval $-\infty < x < \infty$ can be written as

$$\Psi(x, t) = \sum_{n=0}^{\infty} c_n(t) \psi_n(x) \exp(-iE_n t/\hbar), \tag{A.6}$$

where the coefficients $c_n(t)$ are not functions of x.

We now compare these results to the case of a free particle. As above, we assume that the particle is confined to the x-axis and has a mass m. The time-independent Schrödinger equation now reads[1]

$$-\frac{\hbar^2}{2m} \frac{\mathrm{d}^2 \psi}{\mathrm{d}x^2} = E\psi(x). \tag{A.7}$$

For any value of $E > 0$, the general solution of this equation can be written as a linear combination of the two particular solutions

$$\psi_{k_1}(k, x) = (2\pi)^{-1/2} \exp(ik_1 x) \tag{A.8}$$

and

$$\psi_{k_2}(k, x) = (2\pi)^{-1/2} \exp(ik_2 x), \tag{A.9}$$

where $k_1 = (2mE/\hbar^2)^{1/2}$ and $k_2 = -k_1 = -(2mE/\hbar^2)^{1/2}$. (The $(2\pi)^{-1/2}$ factors have to do with the normalization of these functions, as will become clear

---

[1]Why doesn't this equation contain a potential energy term here? Recall that in 1D, the force acting on a particle of potential energy $V(x)$ is $-\mathrm{d}V/\mathrm{d}x$. Taking $V(x) \equiv 0$ means that the force is zero everywhere, hence that the particle is free. We could equally well have taken $V(x) \equiv V_0$ where V_0 is a non-zero constant, but taking $V(x) \equiv 0$ is simpler. This choice amounts to a choice of the origin of the energy scale and has no impact on the Physics of the problem.

later.) Conversely, for any real, non-zero value of the wave number k (positive or negative) the function

$$\psi_k(x) = (2\pi)^{-1/2} \exp(ikx) \tag{A.10}$$

is a solution of Eq. (A.7) with

$$E = E_k \equiv \frac{\hbar^2 k^2}{2m}. \tag{A.11}$$

In other words, the functions $\psi_k(x)$ and the energies E_k satisfy the eigenvalue equation

$$H\psi_k(x) = E_k\psi_k(x) \tag{A.12}$$

for the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}. \tag{A.13}$$

The functions $\psi_k(x)$ are thus eigenfunctions of this Hamiltonian, and the energies E_k are the corresponding eigenenergies. Very much like the eigenfunctions of the Hamiltonian of a harmonic oscillator, the eigenfunctions $\psi_k(x)$ form a complete basis set. One can indeed show that if $\Psi(x, t)$ is a square-integrable wave function defined on the infinite interval $-\infty < x < \infty$, then there exists a function $c_k(t)$ of k and of x such that

$$\Psi(x, t) = \int_{-\infty}^{\infty} c_k(t)\psi_k(x) \exp(-iE_k t/\hbar)\,\mathrm{d}k. \tag{A.14}$$

Since k varies continuously, this linear combination of eigenfunctions takes the form of an integral, not a discrete sum as in Eq. (A.6). This result is not in contradiction with Eq. (A.6); rather, Eqs. (A.6) and (A.14) give two different ways of representing a same wave function.

> Note 1: A rigorous analysis of the conditions $\Psi(x, t)$ must satisfy for Eq. (A.14) to hold would involve advanced concepts of Fourier analysis and is outside the scope of this course.

However, the eigenfunctions $\psi_k(x)$ and eigenenergies E_k differ in key respects from those found in the case of a harmonic oscillator:

- The possible values of the eigenenergies E_k are not discrete; instead, they are continuously distributed and form a continuum.

- The eigenfunctions $\psi_k(x)$ are not square-integrable: Since $|\psi_k(x)|^2 = (2\pi)^{-1}$ for any value of x, the integral

$$\int_{-\infty}^{\infty} |\psi_k(x)|^2\,\mathrm{d}x$$

diverges. It is therefore not possible to normalize these functions so as to have

$$\int_{-\infty}^{\infty} |\psi_k(x)|^2 \, \mathrm{d}x = 1.$$

The normalization prescription used for such eigenfunctions is examined later in this appendix.

- If, nonetheless, we take it that $|\psi_k(x)|^2$ indicates how the probability of finding the particle varies with position, then one must conclude that in that state the particle can be found anywhere with the same probability, including at points abitrarily far from the origin.

It might seem natural that $|\psi_k(x)|^2$ does not go to zero at large distances since the particle is free and must therefore be in an unbound state, not a bound state. However, one should not conclude from this that a free particle cannot be in a state represented by a square-integrable wave function. To the opposite, one can form square-integrable solutions of the time-dependent Schrödinger equation for a free particle by making linear combinations of the wave functions $\psi_k(x)$ with well-chosen time-dependent coefficients. As k varies continuously, these linear combinations (or "wave packets") are generally integrals, not discrete sums. In particular, one can construct wave functions representing states in which the particle has a vanishingly small probability to be far away from a certain region of space, i.e., localized wave packets. However, the wave functions so obtained are *not* eigenfunctions of the Hamiltonian since they are formed by combining eigenstates of different energies.

The functions $\psi_k(x)$ have a clear physical interpretation despite not being square-integrable. To see this, we first observe that $\psi_k(x)$ is an eigenfunction of the momentum operator ($-i\hbar \mathrm{d}/\mathrm{d}x$ in 1D), since

$$-i\hbar \frac{\mathrm{d}\psi_k}{\mathrm{d}x} = \hbar k \psi_k(x). \tag{A.15}$$

Hence, $\psi_k(x)$ can be understood as describing a state in which the particle has a well-defined momentum, $\hbar k$, and a completely undefined position (if the uncertainty on the momentum is zero, the uncertainty on the position must be infinite).

> Note 2: We follow the usage, widespread in Physics, of saying that functions such as $\psi_k(x)$ are eigenfunctions of the Hamiltonian or eigenfunctions of the momentum operator even though they do not belong to the Hilbert space of square-integrable functions. This usage is not mathematically rigorous but has the merit of simplicity. By saying that $\psi_k(x)$ is an eigenfunction of the Hamiltonian, one means, in this context, that this function satisfies Eq. (A.12) and that it belongs to a set of functions on which any square-integrable wave function can be expanded.

Not all solutions of Eq. (A.12) would be called eigenfunctions. For example, this equation also has solutions for $E \leq 0$, besides the solutions for $E > 0$ mentioned above. The general solution of Eq. (A.12) is

$$\psi(x) = C_1 + C_2 x \qquad (A.16)$$

for $E = 0$ and

$$\psi(x) = C_1 \exp(-|k|x) + C_2 \exp(|k|x) \qquad (A.17)$$

for $E < 0$ (the wave number $k = (2mE/\hbar^2)^{1/2}$ is imaginary when $E < 0$). In both cases, C_1 and C_2 are two arbitrary constants. However, these solutions diverge either when $x \to \infty$ or $x \to -\infty$, with the exception of the $E = 0$ solution for $C_2 = 0$. The latter is included in the integral appearing in Eq. (A.14) (that's $\psi_k(x)$ for $k = 0$). The other solutions do not enter in that equation and for this reason are not considered to be eigenfunctions of this Hamiltonian. For the same reason, the solutions of Eq. (A.2) that diverge for $x \to \pm\infty$ do not appear in Eq. (A.6) and are not considered to be eigenfunctions of the Hamiltonian of the linear harmonic oscillator.

What we have just seen for the case of a free particle in 1D easily generalizes to three dimensions:

- The eigenfunctions of the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 \qquad (A.18)$$

  can be taken to be the plane waves

$$\psi_{\mathbf{k}}(\mathbf{r}) = (2\pi)^{-3/2} \exp(i\mathbf{k} \cdot \mathbf{r}), \qquad (A.19)$$

  where $\mathbf{k}$ is an arbitrary wave vector.

- The corresponding eigenenergies of H,

$$E_{\mathbf{k}} = \frac{\hbar^2 |\mathbf{k}|^2}{2m}, \qquad (A.20)$$

  are distributed continuously from 0 to ∞.

- The functions $\psi_{\mathbf{k}}(\mathbf{r})$ form a complete basis set in the sense that any square-integrable wave function $\Psi(\mathbf{r}, t)$ defined on the three-dimensional space can be written in the form

$$\Psi(\mathbf{r}, t) = \int c_{\mathbf{k}}(t)\psi_{\mathbf{k}}(\mathbf{r}) \exp(-iE_{\mathbf{k}}t/\hbar)\, \mathrm{d}^3 k. \qquad (A.21)$$

Note 3:   Why is the function $(2\pi)^{-3/2}\exp(i\mathbf{k}\cdot\mathbf{r})$ called a plane wave? This function is a solution of the time-independent Schrödinger equation for the energy $E_{\mathbf{k}}$, and therefore the function

$$\Psi_{\mathbf{k}}(\mathbf{r},t) = (2\pi)^{-3/2}\exp(i\mathbf{k}\cdot\mathbf{r})\exp(-iE_{\mathbf{k}}t/\hbar) \qquad\text{(A.22)}$$

is a solution of the time-dependent Schrödinger equation. The name plane wave refers to the fact that $\Psi_{\mathbf{k}}(\mathbf{r},t)$ describes a wave whose phase is constant in the planes perpendicular to the wave vector $\mathbf{k}$. For example, if the wave vector $\mathbf{k}$ lies in the positive x-direction, then $\arg\Psi_{\mathbf{k}}(\mathbf{r},t)$ has the constant value $|\mathbf{k}|x_0 - E_{\mathbf{k}}t/\hbar$ in the plane of equation $x = x_0$.

To recap, the cases of a harmonic oscillator and of a free particle greatly differ in the distribution of their energy levels and in the type of their energy eigenfunctions: the energy levels are discrete and the eigenfunctions are square-integrable for a harmonic oscillator, whereas the energy levels form a continuum and the eigenfunctions are not square-integrable for a free particle.

In the two examples we have just seen, the Hamiltonian supports eigenstates of only one type — either square-integrable eigenstates or non square-integrable eigenstates. A more common situation is that the Hamiltonian supports eigenstates of both types. In general:

1. The Hamiltonian $H = -\hbar^2/(2m)\,\nabla^2 + V(\mathbf{r})$ may have discrete eigenenergies E_n corresponding to square-integrable eigenfunctions $\psi_n(\mathbf{r})$. These eigenfunctions vanish at large distances and represent bound states of the system.

2. The Hamiltonian may also have eigenenergies $E_{\mathbf{k}}$ distributed continuously, not discretely. This is the case, in particular, if $V(\mathbf{r}) \to 0$ for $|\mathbf{r}| \to \infty$. The corresponding eigenfunctions, $\psi_{\mathbf{k}}(\mathbf{r})$, are not square-integrable. They oscillate indefinitely at large distances and represent unbound states. These eigenfunctions are in general much more complicated mathematically than the simple plane waves found in the case of a free particle, but like these plane waves, each of these eigenfunctions can be labelled uniquely by a wave vector $\mathbf{k}$ (ignoring spin). These eigenstates are called continuum states because the energy levels they correspond to form a continuum.

3. The set of the eigenstates of a Hamiltonian is complete only if one includes the continuum eigenstates as well as the bound eigenstates. Therefore the expansion of a wave function $\Psi(\mathbf{r},t)$ over these eigenstates will normally include a sum over the discrete states and an integral over the continuum

states:

$$\Psi(\mathbf{r}, t) = \sum_n c_n(t) \psi_n(\mathbf{r}) \exp(-iE_n t/\hbar) +$$

$$\int c_{\mathbf{k}}(t) \psi_{\mathbf{k}}(\mathbf{r}) \exp(-iE_{\mathbf{k}} t/\hbar) \, \mathrm{d}^3 k. \qquad (A.23)$$

Clearly, there is no integral if the Hamiltonian has only discrete eigenstates and there is no discrete sum if it has only continuum eigenstates.

For example, a hydrogen atom has both bound states in which the electron remains at finite distance from the nucleus and continuum states in which the energy is well defined but the atom is effectively broken up into a nucleus and a quasi-free electron (the electron is free to move to infinity but is still submitted to the Coulomb attraction of the nucleus). The corresponding eigenfunctions can be obtained in closed form in either case; however, whilst the bound state eigenfunctions are relatively simple, as you have seen in the level 2 QM course, the wave functions of the continuum states are much more complicated.

Note 4: When does a given Hamiltonian have a continuous spectrum? The answer is simple: for all practical purposes, it has a continuous spectrum if the corresponding classical system has unbound trajectories. Let us look at the case of a particle (a mass point) of mass m, confined to the x-axis. In Classical Mechanics, the total energy of this particle is given by the equation $E = mv_x^2/2 + V(x)$, where v_x is the velocity of the particle and $V(x)$ is its potential energy. Suppose that $V(x)$ is a finite square potential well:

$$V(x) = \begin{cases} -V_0 & -a \leq x \leq a, \\ 0 & |x| > a, \end{cases} \qquad (A.24)$$

where V_0 and a are two positive constants. If $-V_0 < E < 0$, then this classical particle can be inside the well, (in the region $-a \leq x \leq a$), but not in the regions $x < -a$ or $x > a$. Indeed, for $E < 0$ the potential energy of the particle would be larger than its total energy if it was outside the well. Its kinetic energy would then need to be negative to compensate the excess potential energy, which is impossible. The points $x = -a$ and $x = a$ therefore delimit the region of space in which the particle can be when $-V_0 < E < 0$. However, there is no such limitation when $E > 0$: the particle can have a positive kinetic energy, thus a non-zero velocity, at any value of x, with the consequence that it may go arbitrarily far away from $x = 0$.

The situation is slightly different in Quantum Mechanics, as a quantum mechanical particle can penetrate a finite potential barrier. Suppose that the particle is in a state of well defined energy E, i.e., in an eigenstate of the Hamiltonian. If $E < 0$, there is a non-zero probability that the particle is in the region $x < -a$ or the region $x > a$. The wave function goes rapidly to zero in these classically forbidden regions, though, and therefore the particle has a zero probability to be infinitely far from $x = 0$. Moreover, the corresponding energy levels are discrete because the condition that the wave function goes to zero for $x \to \pm\infty$ can be fulfilled only for certain values of the energy. This restriction does not exist when the classically allowed region extends to the whole x-axis, which is the case when $E > 0$ for this potential.

By contrast, there is no continuum states in the case of a linear harmonic oscillator: since $V(x) \to \infty$ for $x \to \pm\infty$ if $V(x) = kx^2/2$, the classically allowed region is finite for any finite value of the total energy E and the wave function necessarily goes to zero far from the origin.

The calculation of the bound and continuum states supported by a finite square well potential is outlined in Appendix E.

The set of all the energy levels of the Hamiltonian is called the spectrum of the Hamiltonian. As seen above, in many systems the spectrum has a discrete part and a continuous part. The discrete energy levels correspond to eigenfunctions $\psi_n(\mathbf{r})$ representing bound states, while the continuous energy levels correspond to eigenfunctions $\psi_{\mathbf{k}}(\mathbf{r})$ representing unbound continuum states. The eigenfunctions $\psi_n(\mathbf{r})$ are orthogonal to the eigenfunctions $\psi_{\mathbf{k}}(\mathbf{r})$ since they belong to different energy eigenvalues:

$$\int \psi_n^*(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})\,\mathrm{d}^3r = 0 \qquad (A.25)$$

for all n and all $\mathbf{k}$. The eigenfunctions $\psi_n(\mathbf{r})$ are also orthogonal to each other and can be normalized so that

$$\int \psi_{n'}^*(\mathbf{r})\psi_n(\mathbf{r})\,\mathrm{d}^3r = \delta_{n'n}. \qquad (A.26)$$

The continuous energy levels correspond to non-square-integrable eigenfunctions $\psi_{\mathbf{k}}(\mathbf{r})$ which cannot satisfy Eq. (A.26). However, we observe that in the case of

the plane waves defined by Eq. (A.19),

$$
\int \psi_{\mathbf{k}'}^*(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})\,\mathrm{d}^3 r
$$

$$
= \frac{1}{(2\pi)^3}\int \exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}]\,\mathrm{d}^3 r
$$

$$
= \frac{1}{(2\pi)^3}\int \exp[i(k_x-k_x')x + i(k_y-k_y')y + i(k_z-k_z')z]\,\mathrm{d}^3 r
$$

$$
= \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty} \exp[i(k_x-k_x')x]\,\mathrm{d}x
$$

$$
\times \int_{-\infty}^{\infty} \exp[i(k_y-k_y')y]\,\mathrm{d}y \times \int_{-\infty}^{\infty} \exp[i(k_z-k_z')z]\,\mathrm{d}z
$$

$$
= \delta(k_x-k_x')\delta(k_y-k_y')\delta(k_z-k_z'), \tag{A.27}
$$

where (k_x, k_y, k_z), (k_x', k_y', k_z') and (x, y, z) are the Cartesian components of the wave vectors $\mathbf{k}$ and $\mathbf{k}'$ and of the position vector $\mathbf{r}$. In the last step of the calculation we have used a representation of the Dirac delta function you may remember to have seen at level 2,

$$
\frac{1}{2\pi}\int_{-\infty}^{\infty} \exp[i(k-k')x]\,\mathrm{d}x = \delta(k-k'). \tag{A.28}
$$

Similarly, in the more general case where the interaction potential is not everywhere zero, it is possible to define the continuum state eigenfunctions in such a way that, as for these plane waves,

$$
\int \psi_{\mathbf{k}'}^*(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})\,\mathrm{d}^3 r = \delta(k_x-k_x')\delta(k_y-k_y')\delta(k_z-k_z'). \tag{A.29}
$$

Eq. (A.29) can be understood, in an intuitive way, as meaning that continuum states of different wave vectors are orthogonal to each other. This equation can also be taken to be a normalization condition. For example, if we set $\psi_{\mathbf{k}}(\mathbf{r}) = N\exp(i\mathbf{k}\cdot\mathbf{r})$ where N is a real positive constant, then N must be taken to be $(2\pi)^{-3/2}$ in order for Eq. (A.29) to hold.

Note 5:   It is convenient to denote the product

$$
\delta(k_x-k_x')\delta(k_y-k_y')\delta(k_z-k_z')
$$

by the symbol $\delta(\mathbf{k}-\mathbf{k}')$. Correspondingly, one says that continuum eigenfunctions satisfying Eq. (A.29) are "normalized to a delta-function in $\mathbf{k}$-space". Other choices of normalization are also possible but are not used in this course.

Coming back to Eq. (A.23), we note that the coefficients $c_n(t)$ can (in principle) be obtained by projection, as seen at level 2. Namely,

$$c_n(t) = \exp(iE_n t/\hbar) \int \psi_n^*(\mathbf{r})\Psi(\mathbf{r},t)\,\mathrm{d}^3 r. \tag{A.30}$$

Normalizing the eigenfunctions $\psi_{\mathbf{k}}(\mathbf{r})$ according to Eq. (A.29) has the advantage of leading to an almost identical relationship for the continuum state coefficients $c_{\mathbf{k}}(t)$, i.e.,

$$c_{\mathbf{k}}(t) = \exp(iE_{\mathbf{k}} t/\hbar) \int \psi_{\mathbf{k}}^*(\mathbf{r})\Psi(\mathbf{r},t)\,\mathrm{d}^3 r. \tag{A.31}$$

The coefficients $c_n(t)$ and $c_{\mathbf{k}}(t)$ also have similar probabilistic interpretations, but with a key difference: $|c_n(t)|^2$ is a probability but, because the wave vectors $\mathbf{k}$ are continuously distributed, $|c_{\mathbf{k}}(t)|^2$ is a *density* of probability. More precisely:

- $|c_n(t)|^2$ is the probability that at time t the system described by the wave function $\Psi(\mathbf{r},t)$ is in the bound eigenstate n.

- In Cartesian coordinates, $|c_{\mathbf{k}}(t)|^2\,\mathrm{d}^3 k \equiv |c_{\mathbf{k}}(t)|^2\,\mathrm{d}k_x\,\mathrm{d}k_y\,\mathrm{d}k_z$ is the probability that at time t the system is in a continuum eigenstate with a wave vector whose x-component is between k_x and $k_x + \mathrm{d}k_x$, y-component between k_y and $k_y + \mathrm{d}k_y$ and z-component between k_z and $k_z + \mathrm{d}k_z$.

- In spherical polar coordinates, $|c_{\mathbf{k}}(t)|^2\,\mathrm{d}^3 k \equiv |c_{\mathbf{k}}(t)|^2\,k^2 \sin\theta_{\mathbf{k}}\,\mathrm{d}k\,\mathrm{d}\theta_{\mathbf{k}}\,\mathrm{d}\phi_{\mathbf{k}}$ is the probability that at time t the system is in a continuum eigenstate with a wave vector lying in an infinitesimal solid angle of opening $\sin\theta_{\mathbf{k}}\,\mathrm{d}\theta_{\mathbf{k}}\,\mathrm{d}\phi_{\mathbf{k}}$ centered on the direction $(\theta_{\mathbf{k}}, \phi_{\mathbf{k}})$, the norm of this wave vector being between k and $k + \mathrm{d}k$.

Note 6:   Eqs. (A.30) and (A.31) follow from Eqs. (A.23), (A.25), (A.26) and (A.29): Multiplying both sides of Eq. (A.23) by $\psi_{\mathbf{k}}^*(\mathbf{r})$ with $\mathbf{k} = \mathbf{K}$ and integrating the result over space yields

$$\int \psi_{\mathbf{K}}^*(\mathbf{r})\Psi(\mathbf{r},t)\,\mathrm{d}^3 r = \sum_n c_n(t)\exp(-iE_n t/\hbar)\int \psi_{\mathbf{K}}^*(\mathbf{r})\psi_n(\mathbf{r})\,\mathrm{d}^3 r +$$
$$\int c_{\mathbf{k}}(t)\exp(-iE_{\mathbf{k}} t/\hbar)\left[\int \psi_{\mathbf{K}}^*(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})\,\mathrm{d}^3 r\right]\mathrm{d}^3 k. \tag{A.32}$$

Or, taking Eqs. (A.25) and (A.29) into account,

$$\int \psi_{\mathbf{K}}^*(\mathbf{r})\Psi(\mathbf{r},t)\,\mathrm{d}^3 r = c_{\mathbf{K}}(t)\exp(-iE_{\mathbf{K}} t/\hbar). \tag{A.33}$$

Eq. (A.31) follows. Eq. (A.30) is obtained in a similar way.

Note 7:   In most of this Appendix, we have written the wave functions in terms of a single position vector $\mathbf{r}$. All the results mentioned in this course generalize to the case of multi-particle systems in which the wave functions depend on several position vectors.

Appendix B: Working out Eqs. (1.35) and (1.62)

The following identity crops up at various places in the first part of the notes,
in exercises and in past examination questions:

$$\left| \int_{t_0}^{t_1} \exp(i\Omega t)\, \mathrm{d}t \right|^2 = \frac{4\sin^2[\Omega(t_1 - t_0)/2]}{\Omega^2}, \tag{B.1}$$

where Ω is a real constant. In particular, it is used in Eq. (1.35) with $\Omega \equiv \omega_{ba}$.
It is also used in Eq. (1.62) with $\Omega \equiv (\omega_{ba} - \omega)$, $t_0 = 0$ and $t_1 \equiv t$. It can be
established as follows.

We first note that

$$\int_{t_0}^{t_1} \exp(i\Omega t)\, \mathrm{d}t = \frac{\exp(i\Omega t_1) - \exp(i\Omega t_0)}{i\Omega}. \tag{B.2}$$

Taking the modulus squared of this equation gives

$$\begin{aligned}
\left| \int_{t_0}^{t_1} \exp(i\Omega t)\, \mathrm{d}t \right|^2 &= \left| \frac{\exp(i\Omega t_1) - \exp(i\Omega t_0)}{i\Omega} \right|^2 \\
&= \frac{|\exp(i\Omega t_1) - \exp(i\Omega t_0)|^2}{|i\Omega|^2} \\
&= \frac{|\exp(i\Omega t_1) - \exp(i\Omega t_0)|^2}{\Omega^2}. \tag{B.3}
\end{aligned}$$

We now work out the numerator by separating the complex exponentials into
their real and imaginary parts:

$$\begin{aligned}
|\exp(i\Omega t_1) - \exp(i\Omega t_0)|^2 &= |[\cos(\Omega t_1) - \cos(\Omega t_0)] + \\
&\quad i[\sin(\Omega t_1) - \sin(\Omega t_0)]|^2. \tag{B.4}
\end{aligned}$$

Remembering the rule that the modulus squared of a complex number is the sum of the square of the real part and the square of the imaginary part, we then see that

$$|\exp(i\Omega t_1) - \exp(i\Omega t_0)|^2 = [\cos(\Omega t_1) - \cos(\Omega t_0)]^2 + \\ [\sin(\Omega t_1) - \sin(\Omega t_0)]^2. \quad \text{(B.5)}$$

Expanding the squares and making use of standard trigonometric identities then yields

$$|\exp(i\Omega t_1) - \exp(i\Omega t_0)|^2 = 2 - 2\cos(\Omega t_1)\cos(\Omega t_0) - \\ 2\sin(\Omega t_1)\sin(\Omega t_0) \\ = 2 - 2\cos[\Omega(t_1 - t_0)] \\ = 4\sin^2[\Omega(t_1 - t_0)/2]. \quad \text{(B.6)}$$

Eq. (B.2) follows.

> Note 1: Alternatively, we could have made use of the fact that
>
> $$\exp(i\Omega t_1) - \exp(i\Omega t_0) = \exp[i\Omega(t_1 + t_2)/2] \times \\ (\exp[i\Omega(t_1 - t_2)/2] - \exp[-i\Omega(t_1 - t_2)/2]) \\ = 2i\exp[i\Omega(t_1 + t_2)/2]\sin[\Omega(t_1 - t_2)/2]. \quad \text{(B.7)}$$
>
> Taking the modulus squared of this equation gives Eq. (B.6) immediately.

Appendix C: Box-normalized continuum wave functions

This appendix clarifies how the function $\rho_{1D}(E_k)$ is related to a density of states defined as a number of states per unit energy interval (this function is introduced in Section 1.8). It also illustrates how box-normalized functions corresponding to a discrete set of energy levels offer an alternative to delta-normalized functions corresponding to a continuum of energy levels.

Formally, in 1D the eigenfunctions of the Hamiltonian of a free particle of mass m are the plane waves

$$\psi_k(x) = A_k \exp(ikx), \quad \text{(C.1)}$$

where the wave number k could be positive or negative and A_k is a certain normalization factor (A_k may depend on k but not on x). As is mentioned in Appendix A above, setting $A_k \equiv (2\pi)^{-1/2}$ ensures that the wave functions $\psi_k(x)$ are normalized to a delta function in k-space. That is, the functions $\psi_k^{(\delta)}(x)$ defined by the equation

$$\psi_k^{(\delta)}(x) = (2\pi)^{-1/2} \exp(\mathrm{i}kx) \tag{C.2}$$

are such that

$$\int_{-\infty}^{\infty} \psi_{k'}^{(\delta)*}(x)\,\psi_k^{(\delta)}(x)\,\mathrm{d}x = \delta(k - k'). \tag{C.3}$$

We now introduce "box-normalized" continuum wave functions $\psi_k^{(\mathrm{B})}(x)$. Like the delta-normalized functions $\psi_k^{(\delta)}(x)$, these box-normalized functions are solutions of the Schrödinger equation for a free particle:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_k^{(\mathrm{B})}}{\mathrm{d}x^2} = E_k\psi_k^{(\mathrm{B})}(x) \tag{C.4}$$

with $E_k = \hbar^2 k^2/(2m)$. However, instead of letting k take any value, we restrict k to such values that, for any x,

$$\psi_k^{(\mathrm{B})}(x \pm L) \equiv \psi_k^{(\mathrm{B})}(x), \tag{C.5}$$

where L is a certain length. Moreover, we normalize these functions according to the equation

$$\int_{-L/2}^{L/2} |\psi_k^{(\mathrm{B})}(x)|^2\,\mathrm{d}x = 1. \tag{C.6}$$

Functions satisfying this normalization condition are said to be "box normalized".

It is easy to see that the periodic boundary condition set by Eq. (C.5) are met only if $k = 2\pi n/L$, with $n = 0, \pm 1, \pm 2, \ldots$ Moreover, with this choice of normalization,

$$\psi_k^{(\mathrm{B})}(x) = L^{-1/2}\,\exp(\mathrm{i}kx). \tag{C.7}$$

Note 1: In regards to the values of k, note that the general solution of Eq. (C.4) is $A\exp(i|k|x) + B\exp(-i|k|x)$, where A and B are two constant. Requiring that this function has the same value at $x + L$ than at x means that $A\exp(i|k|L)\exp(i|k|x) + B\exp(-i|k|L)\exp(-i|k|x) = A\exp(i|k|x) + B\exp(-i|k|x)$. This relation holds for any value of x only if $\exp(i|k|L) = \exp(-i|k|L) = 1$. Hence $|k| = (2\pi/L)$ times an integer.

In regards to the normalization constant, note that we can choose $\psi_k^{(\mathrm{B})}(x)$ to be of the form of Eq. (C.1). Then the integrand in Eq. (C.6) is simply the constant $|A_k|^2$, and the integral on the left-hand side of this equation is $|A_k|^2 L$, which is 1 if one sets $A_k = L^{-1/2}$.

As in Section 1.8, we are interested in the probability of a bound-free transition induced by a harmonic perturbation of angular frequency ω. Let

us suppose that initially the system is in a state a of wave function $\psi_a(x)$, and make the approximation that the final continuum states can be represented by the wave functions $\psi_k^{(B)}(x)$. Let $P_{ka}(t)$ denote the corresponding probability for a transition to a state of wave number k. Proceedings as in Section 1.6, one finds that

$$P_{ka}(t) \approx (2/\hbar^2)|A_{ka}^{\dagger(B)}|^2 F(t, \omega_{ka} - \omega), \tag{C.8}$$

where the operator $A^{\dagger}$ and the Bohr angular frequency ω_{ka} are defined as in that section, and

$$A_{ka}^{\dagger(B)} = \int_{-L/2}^{L/2} \psi_k^{(B)*}(x) A^{\dagger} \psi_a(x) \, dx. \tag{C.9}$$

(We assume that L is large enough that $\psi_a(x)$ is effectively zero for $|x| > L/2$.) Because the boundary condition restricts the possible values of k, thus the possible values of E_k, the functions $\psi_k^{(B)}(x)$ correspond to discrete energy levels, not to a continuum of energy levels. Therefore, as defined here, $P_{ka}(t)$ is a probability, not a density of probability.

The probability of a transition to any of the states whose wave number lies between a value k_1 and a value k_2 is the sum of P_{ka} over all the values of k for which $k_1 \le k \le k_2$. We will denote this probability by $P^{(B)}(t)$. Thus

$$P^{(B)}(t) = \sum_k P_{ka}(t). \tag{C.10}$$

This sum is discrete since for any finite values of L the allowed values of k are discrete. Since each value of k is in one-to-one correspondence with a value of n (recall that $k = 2\pi n/L$), we can sum over n rather than over k:

$$P^{(B)}(t) = \sum_n P_{ka}(t), \tag{C.11}$$

and it is understood that the sum is over all the values of n such that

$$k_1 \le 2\pi n/L \le k_2. \tag{C.12}$$

In preparation to the next step in the calculation, we write Eq. (C.11) as

$$P^{(B)}(t) = \sum_n P_{ka}(t)\Delta n, \tag{C.13}$$

where Δn is the step between the values of n ($\Delta n = 1$). If L is very large, very many values of n may be encompassed by that sum. We can therefore treat n as a continuous variable and transform the sum into an integral. This gives

$$P^{(B)}(t) = \int P_{ka}(t) \, dn. \tag{C.14}$$

Transforming this integral over n into an integral over energy and making use of Eq. (C.8), we then have

$$P^{(\mathrm{B})}(t) \approx \frac{2}{\hbar^2} \int |A_{ka}^{\dagger(\mathrm{B})}|^2 F(t, \omega_{ka} - \omega) \frac{\mathrm{d}n}{\mathrm{d}E_k} \, \mathrm{d}E_k. \qquad (\mathrm{C}.15)$$

This result may not seem to be identical to the result we would have obtained using delta-normalized functions, namely

$$P^{(\delta)}(t) \approx \frac{2}{\hbar^2} \int |A_{ka}^{\dagger(\delta)}|^2 F(t, \omega_{ka} - \omega) \frac{\mathrm{d}k}{\mathrm{d}E_k} \, \mathrm{d}E_k \qquad (\mathrm{C}.16)$$

with

$$A_{ka}^{\dagger(\delta)} = \int_{-\infty}^{\infty} \psi_k^{(\delta)*}(x) A^\dagger \psi_a(x) \, \mathrm{d}x. \qquad (\mathrm{C}.17)$$

However, since we assume that L is large enough that $\psi_a(x)$ is effectively zero for $|x| > L/2$, and since $\psi_k^{(\mathrm{B})}(x) = (2\pi/L)^{1/2} \psi_k^{(\delta)}(x)$,

$$|A_{ka}^{\dagger(\delta)}|^2 = L/(2\pi) \, |A_{ka}^{\dagger(\mathrm{B})}|^2. \qquad (\mathrm{C}.18)$$

Furthermore, since for the box-normalized functions $k = 2\pi n/L$,

$$\frac{\mathrm{d}k}{\mathrm{d}E_k} = (2\pi/L) \frac{\mathrm{d}n}{\mathrm{d}E_k}. \qquad (\mathrm{C}.19)$$

Eqs. (C.15) and (C.16) are therefore equivalent, provided L is large enough.

You may remember that $\mathrm{d}k/\mathrm{d}E_k$ is the function $\rho_{1\mathrm{D}}(E_k)$ appearing in the Fermi's Golden Rule for 1D systems (see Section 1.8). This function is called the density of states, perhaps confusingly since it does not have the correct physical dimensions to be a number of states per unit energy interval. A better candidate for the latter would be $\mathrm{d}n/\mathrm{d}E_k$, if one discretizes the continuum by imposing periodic boundary conditions. Strictly speaking, $\rho_{1\mathrm{D}}(E_k)$ is a wave-number density. However, the calculation above shows that $\rho_{1\mathrm{D}}(E_k)$ and $\mathrm{d}n/\mathrm{d}E_k$ are basically the same quantity, since they differ by a mere constant factor.

Appendix D: The Born approximation in quantum scattering

This appendix illustrates the use of the Fermi's Golden Rule introduced in Section 1.8. It also extends the theory covered in that section to the 3D case and to the case of free-free transitions.

The question addressed in this appendix is the following: Suppose that a beam of particles hits an obstacle. What is the probability that a particle of that beam is deflected by this interaction? This question is at the focus of quantum scattering theory, a very large and very important part of quantum mechanics. We will address it here through the use of Fermi's Golden Rule, in the approximation where the scattering is described within first order perturbation theory. This approximation, in this context, is called the Born approximation. It is very widely used in Physics. We will not need it elsewhere in this course, but you will probably encounter it in the Nuclear and Particle Physics course.

To be more specific:

- We will assume that neither the particles forming the incident beam nor the atoms, molecules or nuclei they collide with can be excited or de-excited to a different internal state in the collision. I.e., the incident particles and the target can be treated as inert, structureless particles, like mass points in Classical Mechanics. As a consequence, the scattering is necessarily elastic: the particles forming the incident beam have the same energy before and after the collision.

- We will also assume that spin can be ignored. As is explained in Part 4 of these notes, the spin of particles such as electrons, protons or neutrons plays an important role in systems composed of several of these particles. However, we will simply ignore this complication here, and focus on the main point.

- The interaction deflecting the projectiles will be modelled by a potential $V(\mathbf{r})$, where for each projectile $\mathbf{r}$ is the position vector of that projectile.

- We will take the incident beam to be practically mono-energetic, uni-directional and homogeneous (which means that it can thought of as formed by particles which all have the same energy and the same direction of propagation and have a uniform density).

- We will also assume, which is always the case in applications to real scattering experiments, that the radius of the beam is larger than the range of the interaction potential.

These last two assumptions make it possible to represent the incident beam by a simple 3D plane wave,

$$\psi_{\mathbf{k}_i}(\mathbf{r}) = (2\pi)^{-3/2} \exp(i\mathbf{k}_i \cdot \mathbf{r}), \tag{D.1}$$

where the direction of the wave vector $\mathbf{k}_i$ is the initial direction of the incident particles (before scattering), and $\hbar^2|\mathbf{k}_i|^2/2m$ is their energy. (See Appendix A. Here m is the mass of one of these particles.)

The problem then boils down to the following: Suppose that initially we have freely propagating particles of wave vector $\mathbf{k}_i$, and that at time $t = 0$ the Hamiltonian changes abruptly from H_0 to $H_0 + V(\mathbf{r})$, where

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2. \tag{D.2}$$

What is the probability per unit time for a transition to a state of wave vector $\mathbf{k}_f \neq \mathbf{k}_i$? Since the plane wave $\psi_{\mathbf{k}_i}(\mathbf{r})$ describing the initial state is an eigenfunction of H_0, the problem is similar to the one discussed in Section 1.8. However, there are three significant differences:

1. Here the system is three-dimensional, not one-dimensional. The results quoted in Section 1.8 must therefore be generalized to the 3D case.

2. Rather than oscillating harmonically, as is assumed in Section 1.8, our perturbation Hamiltonian,

$$H'(t) = \begin{cases} 0 & t < 0, \\ V(\mathbf{r}) & t \geq 0, \end{cases} \tag{D.3}$$

   is constant in time for $t \geq 0$.

3. The initial state (state a) is a continuum state, not a bound state.

Let us address each of these differences in turn.

We start with the generalization to the 3D case. The key result of Section 1.8 is that for a harmonic perturbation in 1D, the probability for a transition from an initial bound state a to a final continuum state of wave number k_f is given, usually in very good approximation, by the equation

$$P(t) \approx \frac{2\pi}{\hbar}\,\rho_{1D}(E_f)\,|A_{k_f a}^\dagger|^2\,t, \tag{D.4}$$

where $\rho_{1D}(E_f)$ is the density of states at the energy E_f and

$$A_{k_f a}^\dagger = \int_{-\infty}^{\infty} \psi_{k_f}^*(x)\hat{A}^\dagger\psi_a(x)\,\mathrm{d}x. \tag{D.5}$$

In this last equation, $\psi_{k_f}(x)$ is the wave function representing the final continuum state. These results are obtained in the formulation where 1D continuum states are labelled by a wave number k, which can be positive or negative depending on the direction of propagation of the particle, and are represented by wave functions normalized according to the condition

$$\int_{-\infty}^{\infty} \psi_{k'}^*(x)\,\psi_k(x)\,\mathrm{d}x = \delta(k - k'). \tag{D.6}$$

We are particularly interested in the transition rate, $R = \mathrm{d}P/\mathrm{d}t$. In view of Eq. (D.4),

$$R \approx \frac{2\pi}{\hbar}\,\rho_{1\mathrm{D}}(E_\mathrm{f})\,|A^\dagger_{k_\mathrm{f}a}|^2 \tag{D.7}$$

for a 1D system.

In 1D, the final state may have a positive or a negative wave number k, corresponding, respectively to a state in which the particle moves in the positive direction or in the negative direction. The possible directions of propagation are thus *discrete* — either it's the positive direction or it's the negative direction. In 3D, continuum states are labelled by a wave vector, $\mathbf{k}$, not by a wave number, and there is the extra complication that wave vectors are distributed *continuously* in direction. The consequence is that in 3D the equivalent of the rate R of Eq. (D.7) is a differential rate. The calculation yields a certain $\mathrm{d}R(\theta_\mathrm{f}, \phi_\mathrm{f})$, which is the rate of transition to a group of continuum states with an energy around an energy E_f and a wave vector $\mathbf{k}_\mathrm{f}$ with a polar angle θ between θ_f and $\theta_\mathrm{f} + \mathrm{d}\theta_\mathrm{f}$ and a polar angle ϕ between ϕ_f and $\phi_\mathrm{f} + \mathrm{d}\phi_\mathrm{f}$. (Note that θ_f and ϕ_f are the polar angles defining the direction of the wave vector $\mathbf{k}_\mathrm{f}$; they are not polar angles defining the position of a particle.)

If one normalizes the continuum eigenfunctions $\psi_\mathbf{k}(\mathbf{r})$ in such a way that they satisfy the 3D equivalent of Eq. (D.6) (see Appendix A), then the calculation which led to the 1D transition rate can be repeated almost without change. The result is

$$\mathrm{d}R(\theta_\mathrm{f}, \phi_\mathrm{f}) \approx \frac{2\pi}{\hbar}\,\rho_{3\mathrm{D}}(E_\mathrm{f})\,|A^\dagger_{\mathbf{k}_\mathrm{f}a}|^2\,\mathrm{d}\Omega, \tag{D.8}$$

where $\mathrm{d}\Omega$ is the element of solid angle in the direction $(\theta_\mathrm{f}, \phi_\mathrm{f})$:

$$\mathrm{d}\Omega = \sin\theta_\mathrm{f}\,\mathrm{d}\theta_\mathrm{f}\,\mathrm{d}\phi_\mathrm{f}. \tag{D.9}$$

The density of states $\rho_{3\mathrm{D}}(E_\mathrm{f})$ is defined by the equation

$$\rho_{3\mathrm{D}}(E_\mathrm{f}) = k^2 \left.\frac{\mathrm{d}k}{\mathrm{d}E_\mathbf{k}}\right|_{E_\mathbf{k}=E_\mathrm{f}}, \tag{D.10}$$

with $k = |\mathbf{k}|$. Since in our case $E_\mathbf{k} = \hbar^2 k^2/2m$, for us

$$\rho_{3\mathrm{D}}(E_\mathrm{f}) = (2m^3 E_\mathrm{f})^{1/2}/\hbar^3. \tag{D.11}$$

Moreover, the matrix element of $A^\dagger_{\mathbf{k}_\mathrm{f}a}$ appearing in Eq. (D.8) is given by the equation

$$A^\dagger_{\mathbf{k}_\mathrm{f}a} = \int \psi^*_{\mathbf{k}_\mathrm{f}}(\mathbf{r})\hat{A}^\dagger\psi_a(\mathbf{r})\,\mathrm{d}^3 r. \tag{D.12}$$

It is instructive to verify that $\mathrm{d}R(\theta_\mathrm{f}, \phi_\mathrm{f})$ has the physical dimensions of the inverse of a time, as befits a probability per unit time. The calculation involves

working out the physical dimensions of the matrix element $A^\dagger_{\mathbf{k}_{\mathrm{f}}a}$, which can be done as follows: In view of its definition, the operator $A^\dagger$ has necessarily the physical dimensions of an energy. Since $\psi_a(\mathbf{r})$ is meant to represent a bound state wave function normalized according to the equation

$$\int |\psi_a(\mathbf{r})|^2 \, \mathrm{d}^3 r = 1, \tag{D.13}$$

$\psi_a(\mathbf{r})$ must have the physical dimensions of the square root of the inverse of a volume (so that $|\psi_a(\mathbf{r})|^2$ has the physical dimensions of the inverse of a volume, which makes it possible for the whole integral to have no physical dimensions, recall that $\mathrm{d}^3 r$ is a volume). However, as normalized here, the continuum wave function has no physical dimensions (this can be seen immediate in the case where $\psi_{\mathbf{k}}(\mathbf{r})$ is the plane wave $(2\pi)^{-3/2} \exp(i\mathbf{k} \cdot \mathbf{r})$, but this is also true in general). Thus $|A^\dagger_{\mathbf{k}_{\mathrm{f}}a}|^2$ has the physical dimensions of the square of an energy times a volume. Working out the physical dimensions of $\rho_{\mathrm{3D}}(E_{\mathrm{f}})/\hbar$ is comparatively straightforward, and the result is indeed that $\mathrm{d}R(\theta_{\mathrm{f}}, \phi_{\mathrm{f}})$ has the expected physical dimensions of the inverse of a time. We will come back to this point shortly.

Taking into the fact that the perturbation Hamiltonian is now given by Eq. (D.3) is easily done. The change amounts to taking $A^\dagger \equiv V(\mathbf{r})$ and $\omega = 0$ in Eq. (D.8). Because $H'(t)$ is constant for $t > 0$, the energy E_{f} is necessarily equal to the energy of the initial state, $E_{\mathrm{i}} = \hbar k_{\mathrm{i}}^2/2m$, and the rate is given in terms of the matrix elements of $V(\mathbf{r})$,

$$V_{\mathbf{k}_{\mathrm{f}}a} = \int \psi_{\mathbf{k}_{\mathrm{f}}}^*(\mathbf{r}) V(\mathbf{r}) \psi_a(\mathbf{r}) \, \mathrm{d}^3 r. \tag{D.14}$$

However, replacing $\psi_a(\mathbf{r})$ and $\psi_{\mathbf{k}_{\mathrm{f}}}(\mathbf{r})$ by the relevant eigenfunctions of H_0 is more problematic. There is no difficulty for $\psi_{\mathbf{k}_{\mathrm{f}}}(\mathbf{r})$: Since H_0 is the Hamiltonian of a free particle, taking

$$\psi_{\mathbf{k}_{\mathrm{f}}}(\mathbf{r}) \equiv (2\pi)^{-3/2} \exp(i\mathbf{k}_{\mathrm{f}} \cdot \mathbf{r}) \tag{D.15}$$

is completely appropriate. However, simply setting

$$\psi_a(\mathbf{r}) \equiv (2\pi)^{-3/2} \exp(i\mathbf{k}_{\mathrm{i}} \cdot \mathbf{r}) \tag{D.16}$$

for the wave function of the initial state would not be correct dimensionally (recall the dimensional analysis above: it is crucial that $\psi_a(\mathbf{r})$ has the physical dimensions of the square root of the inverse of a volume). This difficulty can be turned around, though. Let us set

$$\psi_a(\mathbf{r}) \equiv L^{-3/2} \exp(i\mathbf{k}_{\mathrm{i}} \cdot \mathbf{r}), \tag{D.17}$$

where L is a certain length (we can choose this length as we want). Then, the integral of $|\psi_a(\mathbf{r})|^2$ over a cube of side L is 1:

$$\int_{L^3} |\psi_a(\mathbf{r})|^2 \, \mathrm{d}^3 r = L^{-3} \int_{L^3} \mathrm{d}^3 r = L^{-3} L^3 = 1. \qquad (\text{D.18})$$

One can interpret this result as meaning that with this normalization, the continuum wave function $\psi_a(\mathbf{r})$ represents a state in which there is one particle in the volume L^3. The corresponding number density of particles, ρ, is thus $1/L^3$. As the particles all move with the velocity $\hbar \mathbf{k}_\mathrm{i}/m$, the number of particles crossing an area A perpendicular to $\mathbf{k}_\mathrm{i}$ in a time t is $\rho|\hbar \mathbf{k}_\mathrm{i}/m|At$. Hence, the corresponding particle flux (number of particles passing the area, per unit area and per unit time), is

$$F = \hbar k_\mathrm{i}/(mL^3). \qquad (\text{D.19})$$

Replacing $\psi_a(\mathbf{r})$ by $L^{-3/2} \exp(i\mathbf{k}_\mathrm{i} \cdot \mathbf{r})$ and $\psi_{\mathbf{k}_\mathrm{f}}(\mathbf{r})$ by $(2\pi)^{-3/2} \exp(i\mathbf{k}_\mathrm{f} \cdot \mathbf{r})$ in Eq. (D.14) yields

$$\mathrm{d}R(\theta_\mathrm{f}, \phi_\mathrm{f}) \approx \frac{2\pi}{\hbar} \rho_\mathrm{3D}(E_\mathrm{f}) \left| \left(\frac{1}{2\pi L} \right)^{3/2} \int \exp(-i\mathbf{k}_\mathrm{f} \cdot \mathbf{r}) \, V(\mathbf{r}) \exp(i\mathbf{k}_\mathrm{i} \cdot \mathbf{r}) \, \mathrm{d}^3 r \right|^2 \, \mathrm{d}\Omega.$$
$$(\text{D.20})$$

Or dividing this transition rate by the flux of incident particles to get a cross section, and also dividing by $\mathrm{d}\Omega$,

$$\begin{aligned}
\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \equiv \frac{1}{F} \frac{\mathrm{d}R}{\mathrm{d}\Omega} &\approx \frac{2\pi}{\hbar} \frac{mL^3}{\hbar k_\mathrm{i}} \frac{\rho_\mathrm{3D}(E_\mathrm{f})}{(2\pi L)^3} \left| \int \exp[i(\mathbf{k}_\mathrm{i} - \mathbf{k}_\mathrm{f}) \cdot \mathbf{r}] \, V(\mathbf{r}) \, \mathrm{d}^3 r \right|^2 \\
&\approx \frac{m^2}{4\pi^2 \hbar^4} \left| \int \exp[i(\mathbf{k}_\mathrm{i} - \mathbf{k}_\mathrm{f}) \cdot \mathbf{r}] \, V(\mathbf{r}) \, \mathrm{d}^3 r \right|^2, \qquad (\text{D.21})
\end{aligned}$$

where in the last step we have made used of Eq. (D.10) and of the fact that $k_\mathrm{f} = k_\mathrm{i}$ (the energy is the same in the initial and the final state since the collision is elastic). Eq. (D.21) is our final result, the differential scattering cross section per unit solid angle, or differential cross section in short, in the Born approximation. We note that this final result does not depend on the arbitrary length L, which we introduced only to facilitate the calculation.

Appendix E: Bound states and continuum states of a finite square well

As is explained in Note 4 of Appendix A, the classical trajectory of a particle is unbound if its total energy is larger than the maximum value of its potential energy, and quantum mechanically these unbound classical trajectories correspond to continuum states. By contrast, the spectrum of Hamiltonian is discrete in the range of total energies for which the particle has only bound classical trajectories. Here we demonstrate this correspondence in the case of a finite square well in 1D. The calculation also brings forth the link between continuum states and quantum scattering explored in detail in the Quantum Theory 3 course. As in Appendix A, we ignore mathematical rigour and treat continuum states as genuine eigenstates of the Hamiltonian even though they do not correspond to square-integrable wave functions.

Our objective is to solve the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x) \tag{E.1}$$

for

$$V(x) = \begin{cases} -V_0 & -a \le x \le a, \\ 0 & |x| > a, \end{cases} \tag{E.2}$$

where V_0 is a positive constant. In view of the form of this potential, we define three regions of the x-axis: the region $x < -a$, the interval $-a \le x \le a$, and the region $x > a$. We will refer to these regions as region I, region II and region III, respectively. In region II ($|x| \le a$), Eq. (E.1) reduces to

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - V_0\psi(x) = E\psi(x), \tag{E.3}$$

or, multiplying each side by $2m/\hbar^2$ and rearranging,

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\kappa^2\psi(x) \tag{E.4}$$

with $\kappa = [2m(E + V_0)/\hbar^2]^{1/2}$. The wave number κ is real and non-zero for any value of $E > -V_0$. The general solution of Eq. (E.4) for these values of E is thus

$$\psi(x) = A_1^{(\mathrm{II})}\exp(i\kappa x) + A_2^{(\mathrm{II})}\exp(-i\kappa x), \tag{E.5}$$

where $A_1^{(\mathrm{II})}$ and $A_2^{(\mathrm{II})}$ are two arbitrary constants. For $|x| > a$, Eq. (E.1) reduces instead to

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi(x) \tag{E.6}$$

with $k = (2mE/\hbar^2)^{1/2}$. Thus k is real when $E > 0$ but imaginary when $E < 0$. Excluding the case where $E = 0$, the general solution of Eq. (E.6) in region I ($x < -a$) is

$$\psi(x) = B_1^{(I)} \exp(ikx) + B_2^{(I)} \exp(-ikx) \qquad (E.7)$$

when $E > 0$ and

$$\psi(x) = C_1^{(I)} \exp(|k|x) + C_2^{(I)} \exp(-|k|x) \qquad (E.8)$$

when $E < 0$, and similarly in region III ($x > a$). $B_1^{(I)}$, $B_2^{(I)}$, $C_1^{(I)}$, $C_2^{(I)}$ and their counterparts for region III are arbitrary constants.

We start with the case where $-V_0 < E < 0$. Classical trajectories for values of the total energy in this range are necessarilly confined to the interval $[-a, a]$, as regions I and III are classically forbidden. We will see that, in Quantum Mechanics, the corresponding energy levels are necessarily discrete.

As seen above, a solution of Eq. (E.1) for a negative value of E has necessarily the form

$$\psi(x) = \begin{cases} C_1^{(I)} \exp(|k|x) + C_2^{(I)} \exp(-|k|x) & x < -a, \\ A_1^{(II)} \exp(i\kappa x) + A_2^{(II)} \exp(-i\kappa x) & -a \leq x \leq a, \\ C_1^{(III)} \exp(|k|x) + C_2^{(III)} \exp(-|k|x) & x > a. \end{cases} \qquad (E.9)$$

However, in order to qualify as an eigenfunction of the Hamiltonian, $\psi(x)$ cannot increase exponentially when $x \to \pm\infty$. The constants $C_2^{(I)}$ and $C_1^{(III)}$ must therefore be zero for the solution to be admissible, with the result that

$$\psi(x) = \begin{cases} C_1^{(I)} \exp(|k|x) & x < -a, \\ A_1^{(II)} \exp(i\kappa x) + A_2^{(II)} \exp(-i\kappa x) & -a \leq x \leq a, \\ C_2^{(III)} \exp(-|k|x) & x > a. \end{cases} \qquad (E.10)$$

Moreover, $\psi(x)$ and $\mathrm{d}\psi/\mathrm{d}x$ must be continuous for all values of x. Requiring that $\psi(x)$ and $\mathrm{d}\psi/\mathrm{d}x$ are continuous both at $x = -a$ and at $x = a$ yields four equations relating the four unknown constants $C_1^{(I)}$, $A_1^{(II)}$, $A_2^{(II)}$ and $C_2^{(III)}$ to each other, i.e.,

$$\begin{aligned}
\mathrm{e}^{-i\kappa a} A_1^{(II)} &+ \mathrm{e}^{i\kappa a} A_2^{(II)} - \mathrm{e}^{-|k|a} C_1^{(I)} & &= 0, \\
i\kappa\mathrm{e}^{-i\kappa a} A_1^{(II)} &- i\kappa\mathrm{e}^{i\kappa a} A_2^{(II)} - |k|\mathrm{e}^{-|k|a} C_1^{(I)} & &= 0, \\
\mathrm{e}^{i\kappa a} A_1^{(II)} &+ \mathrm{e}^{-i\kappa a} A_2^{(II)} & -\mathrm{e}^{-|k|a} C_2^{(III)} &= 0, \\
i\kappa\mathrm{e}^{i\kappa a} A_1^{(II)} &- i\kappa\mathrm{e}^{-i\kappa a} A_2^{(II)} & +|k|\mathrm{e}^{-|k|a} C_2^{(III)} &= 0.
\end{aligned} \qquad (E.11)$$

This homogeneous system of four linear algebraic equations has a solution other than the trivial solution $C_1^{(I)} = A_1^{(II)} = A_2^{(II)} = C_2^{(III)} = 0$ only if its

determinant is zero, which happens only for certain, discrete values of E. Since $\psi(x)$ goes exponentially to zero for $|x| \to \infty$, we see that these discrete eigenenergies correspond to square-integrable wave functions in which the particle is unlikely to be far away from the well (far away meaning $|x| \gg 1/|k|$ here). These eigenstates are analogous to the bound states of atomic hydrogen you studied at level 2, in which the electron and the proton are effectively bound to each other by their electrostatic interaction.

We turn now to the case where $E > 0$. Classical trajectories for positive total energies are unbound. We will see that the corresponding energy levels form a continuum.

A solution of Eq. (E.1) for a positive value of E has necessarily the form

$$\psi(x) = \begin{cases} B_1^{(I)} \exp(ikx) + B_2^{(I)} \exp(-ikx) & x < -a, \\ A_1^{(II)} \exp(i\kappa x) + A_2^{(II)} \exp(-i\kappa x) & -a \leq x \leq a, \\ B_1^{(III)} \exp(ikx) + B_2^{(III)} \exp(-ikx) & x > a. \end{cases} \qquad \text{(E.12)}$$

It is not possible to find values of the constants $B_1^{(I)}$, $B_2^{(I)}$, $B_1^{(III)}$ and $B_2^{(III)}$ for which solutions of that form would go to zero for $x \to \infty$. However, a solution of Eq. (E.1) which oscillates like $\exp(ikx)$ or $\exp(-ikx)$ for $x \to \infty$ still qualifies as an eigenfunction of the Hamiltonian. Here, too, $\psi(x)$ and $\mathrm{d}\psi/\mathrm{d}x$ must be continuous both at $x = -a$ and at $x = a$. This requirement introduces four constraints on the values of the six arbitrary constants appearing in Eq. (E.12). As these constraints are fewer in number than the arbitrary constants, they can be satisfied for *any* value of E (as long as this value is positive, that is). For instance, we can reduce the number of unknowns by setting $B_1^{(III)} = 1$ and $B_2^{(III)} = 0$, in which case the matching conditions yield the following system of algebraic equations:

$$\begin{aligned} \mathrm{e}^{-i\kappa a} A_1^{(II)} &+ \mathrm{e}^{i\kappa a} A_2^{(II)} - \mathrm{e}^{-ika} B_1^{(I)} - \mathrm{e}^{ika} B_2^{(I)} = 0, \\ i\kappa \mathrm{e}^{-i\kappa a} A_1^{(II)} &- i\kappa \mathrm{e}^{i\kappa a} A_2^{(II)} - ik\mathrm{e}^{-ika} B_1^{(I)} + ik\mathrm{e}^{ika} B_2^{(I)} = 0, \\ \mathrm{e}^{i\kappa a} A_1^{(II)} &+ \mathrm{e}^{-i\kappa a} A_2^{(II)} = \mathrm{e}^{ika}, \\ i\kappa \mathrm{e}^{iaa} A_1^{II)} &- i\kappa \mathrm{e}^{-i\kappa a} A_2^{(II)} = ik\mathrm{e}^{ika}. \end{aligned} \qquad \text{(E.13)}$$

The determinant of this nonhomogeneous system of equations is non-zero, and therefore the system has a solution, for any $E > 0$.

The form of this solution is worth noting. Since $B_2^{(III)} = 0$ and $B_1^{(III)} \neq 0$, the wave function $\psi(x)$ is simply $\exp(ikx)$ in region III (within a constant factor), which represents a state in which the particle moves in the positive x-direction away from the well. The corresponding values of $B_1^{(I)}$ and $B_2^{(I)}$ are generally both non-zero, however; hence, in region I, $\psi(x)$ is a linear combination of the plane waves $\exp(ikx)$ and $\exp(-ikx)$, which propagate in opposite

directions. The wave function $\psi(x)$ can therefore be understood as representing a state in which a plane wave propagating with positive velocity along the negative x-axis is partly transmitted and partly reflected as it impinges on the potential well. An analogous situation for an atom of hydrogen would one in which an unbound electron, initially in a state of a well defined wave vector, scatters off a proton. In general, continuum states are widely used to describe scattering processes in Quantum Mechanics.

Appendix F: The classical Hamiltonian of a charged particle in an EM field

This appendix is addressed to students who have taken a course in Lagrangian and Hamiltonian Mechanics. Its objective is to explain how to write the classical Lagrangian and the classical Hamiltonian of a charged particle in an electromagnetic field.

For the sake of simplicity, we only consider the case of a system composed of a single particle. A force $\mathbf{F}$ acting on this particle is said to derive from a velocity-independent potential if it can be written as $\mathbf{F} = -\boldsymbol{\nabla}V$, where the potential energy V which does *not* explicitly depend on the velocity of the particle. If the total force acting on the particle derives from a velocity-independent potential, the Lagrangian function, L, can always be taken to be the difference between the kinetic energy and the potential energy: $L = T - V$. Lagrange's equations are then equivalent to Newton's equation. This remains true even if the particle is submitted to holonomic constraints, as these constraints can be fully taken into account by adopting appropriate generalized co-ordinates. However, not all systems of practical interest can be described in terms of holonomic constraints and velocity-independent potentials. The Lorentz force, for example, does not derive from such a potential. As is shown below, the case of a charged particle moving in an electromagnetic field is nonetheless amenable to a Lagrangian description, provided the Lagrangian function is properly defined.

Consider a particle of mass m and charge q, of Cartesian coordinates $x(t)$, $y(t)$, $z(t)$, moving with velocity $\mathbf{v}$ in a potential $V(x,y,z)$, an electric field $\boldsymbol{\mathcal{E}}(x,y,z,t)$ and a magnetic field $\boldsymbol{\mathcal{B}}(x,y,z,t)$. The force experienced by this particle is $q(\boldsymbol{\mathcal{E}} + \mathbf{v} \times \boldsymbol{\mathcal{B}}) - \boldsymbol{\nabla}V$. Its x-coordinate varies in time according to the equation

$$m\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = q[\mathcal{E}_x + (\mathbf{v} \times \boldsymbol{\mathcal{B}})_x] - \frac{\partial V}{\partial x}, \tag{F.1}$$

and similarly for its y-coordinate and its z-coordinate. Describing the field by a scalar potential $\phi(x, y, z, t)$ and a vector potential $\mathbf{A}(x, y, z, t)$ and recalling how the E- and B-fields are written in terms of these functions, we can also write Eq. (F.1) as follows:

$$m\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -q\frac{\partial \phi}{\partial x} - q\frac{\partial A_x}{\partial t} + q[\mathbf{v} \times (\boldsymbol{\nabla} \times \mathbf{A})]_x - \frac{\partial V}{\partial x}. \tag{F.2}$$

Let us expand the term involving the curl of the vector potential. Since

$$
\begin{aligned}
(\boldsymbol{\nabla} \times \mathbf{A})_x &= \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}, \\
(\boldsymbol{\nabla} \times \mathbf{A})_y &= \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}, \\
(\boldsymbol{\nabla} \times \mathbf{A})_z &= \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y},
\end{aligned}
\tag{F.3}
$$

and with the Cartesian components of the velocity vector denoted, as usual, by $\dot{x}$, $\dot{y}$ and $\dot{z}$, we have

$$
\begin{aligned}
{[}\mathbf{v} \times (\boldsymbol{\nabla} \times \mathbf{A}){]}_x &= \dot{y}(\boldsymbol{\nabla} \times \mathbf{A})_z - \dot{z}(\boldsymbol{\nabla} \times \mathbf{A})_y \\
&= \dot{y}\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right) - \dot{z}\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right).
\end{aligned}
\tag{F.4}
$$

We will prove that equation (F.2) is equivalent to the Lagrange's equation for the x-coordinate,

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{x}} = \frac{\partial L}{\partial x}, \tag{F.5}$$

if the Lagrangian function is

$$L = T - V - q\phi + q\mathbf{A} \cdot \mathbf{v}. \tag{F.6}$$

First of all, note that V, ϕ and $\mathbf{A}$ may depend explicitly on x but not on $\dot{x}$; the only terms depending explicitly on the $\dot{x}$ is the kinetic energy, $T = (m/2)(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$, and the term in $A_x\dot{x}$ appearing in the scalar product $\mathbf{A} \cdot \mathbf{v}$. Hence,

$$\frac{\partial L}{\partial x} = -\frac{\partial V}{\partial x} - q\frac{\partial \phi}{\partial x} + q\frac{\partial A_x}{\partial x}\dot{x} + q\frac{\partial A_y}{\partial x}\dot{y} + q\frac{\partial A_z}{\partial x}\dot{z} \tag{F.7}$$

and

$$\frac{\partial L}{\partial \dot{x}} = m\dot{x} + qA_x. \tag{F.8}$$

We obtain, by employing the chain rule,

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{x}} = m\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} + q\left(\frac{\partial A_x}{\partial x}\dot{x} + \frac{\partial A_x}{\partial y}\dot{y} + \frac{\partial A_x}{\partial z}\dot{z} + \frac{\partial A_x}{\partial t}\right). \tag{F.9}$$

The equivalence of equations (F.2) and (F.5) is readily established by using equations (F.7) and (F.9) in equation (F.5), simplifying, and using equation (F.4) to re-express the result in the form of equation (F.2).

Of course, a similar calculation can be done for the y and the z variables. The conclusion is that the Lagrange's equations for the Lagrangian (F.6) predict the same trajectory as Newton's equation.

It is worth noting, from equation (F.8), that the canonical momentum (or generalized momentum) conjugate to x is $m\dot{x} + qA_x$, rather than $m\dot{x}$ as would be the case if the particle was free. The canonical momentum vector, $\mathbf{p}$, has the Cartesian components $p_x = m\dot{x} + qA_x$, $p_y = m\dot{y} + qA_y$, and $p_z = m\dot{z} + qA_z$.

The energy function is defined by the relation

$$h = \dot{x}p_x + \dot{y}p_y + \dot{z}p_z - L = \mathbf{v} \cdot \mathbf{p} - L. \tag{F.10}$$

Expressing $\dot{x}$, $\dot{y}$ and $\dot{z}$ as functions of p_x, p_y and p_z in h yields the Hamiltonian

$$H = (\mathbf{p} - q\mathbf{A}) \cdot \mathbf{p}/m -$$
$$[(m/2)(\mathbf{p} - q\mathbf{A})^2/m^2 - V - q\phi + q\mathbf{A} \cdot (\mathbf{p} - q\mathbf{A})/m]. \tag{F.11}$$

The right-hand side of equation (F.11) can be rearranged into the simpler form

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\phi + V. \tag{F.12}$$

The non-relativistic quantum theory of the interaction of matter with light is based on the quantum-mechanical analogue of equation (F.12): formally, one passes to the quantum-mechanics Hamiltonian by replacing the classical canonical momentum vector $\mathbf{p}$ by the operator $-i\hbar\boldsymbol{\nabla}$.

Appendix G: Coherent vs. incoherent fields

The difference between a coherent and an incoherent superposition of two field modes may be clarified by considering the following example (this issue crops up in Section 2.6 of the course notes). Consider a homogeneous field composed of two components propagating in the z-direction, one with an electric field $\mathcal{E}_0\,\hat{\boldsymbol{\epsilon}}\,\sin[\omega_1(t - z/c) - \varphi_1]$ and the other with an electric field $\mathcal{E}_0\,\hat{\boldsymbol{\epsilon}}\,\sin[\omega_2(t - z/c) - \varphi_2]$ (thus two components of same polarization and same electric field amplitude but different frequencies). Taken individually, each one of these two components has an intensity

$$I_0 = \frac{1}{2}\,\epsilon_0\,c\,\mathcal{E}_0^2.$$

The total intensity of the field would thus be $2\,I_0$ if there would be no interference between these components. However, if they act coherently, the total electric field would be

$$\mathcal{E}_0\,\hat{\boldsymbol{\epsilon}}\,\sin[\omega_1(t-z/c)-\varphi_1]+\mathcal{E}_0\,\hat{\boldsymbol{\epsilon}}\,\sin[\omega_2(t-z/c)-\varphi_2]=$$
$$\mathcal{E}_{\mathrm{tot}}(t)\,\hat{\boldsymbol{\epsilon}}\,\sin\left[\frac{(\omega_1+\omega_2)(t-z/c)}{2}+\frac{\varphi_1+\varphi_2}{2}\right]$$

with

$$\mathcal{E}_{\mathrm{tot}}(t)=2\,\mathcal{E}_0\,\cos\left[\frac{(\omega_1-\omega_2)(t-z/c)}{2}+\frac{\varphi_1-\varphi_2}{2}\right].$$

The field would then have a total intensity

$$I_{\mathrm{tot}}(t)=4\,I_0\cos^2\left[\frac{(\omega_1-\omega_2)(t-z/c)}{2}+\frac{\varphi_1-\varphi_2}{2}\right],$$

which oscillates between 0 and $4\,I_0$ around an average value of $2\,I_0$. This oscillation of the intensity depends on the relative phase of the two fields, $\varphi_1-\varphi_2$, and is well defined if the field is coherent (i.e., if $\varphi_1-\varphi_2$ is a constant). By contrast, an *inc*oherent superposition of these two components could be thought of as being a superposition in which $\varphi_1-\varphi_2$ varies rapidly and randomly. This fast variation would wash the oscillation of $I_{\mathrm{tot}}(t)$ away, and the total intensity would effectively be $2\,I_0$ at all times. There is no interference between the frequency components if the field is incoherent; they act independently of each other, as if they were alone and not part of a superposition.

Appendix H: The parity of the spherical harmonics

This Appendix gives a proof of the following parity relation, which is used in Section 2.9:

$$Y_{lm}(\pi-\theta,\phi+\pi)=(-1)^l\,Y_{lm}(\theta,\phi). \tag{H.1}$$

This proof is based on the fact that for any l, $Y_{ll}(\theta,\phi)=N_{ll}\sin^l\theta\exp(il\phi)$, where N_{ll} is a normalization constant. Let us consider two right-handed systems of coordinates, one defined by the usual x-, y- and z-axes, and another rotated with respect to the first one. The joint eigenfunctions of the operators $\mathbf{L}^2$ and L_z are the spherical harmonics $Y_{lm}(\theta,\phi)$ where θ and ϕ are the polar angles defined as usual. The choice of the z-axis being arbitrary, we can also define the joint eigenfunctions of $\mathbf{L}^2$ and $\mathbf{L}'_z$, the latter being the projection of $\mathbf{L}$ on the z-axis of the rotated coordinate system. In terms

of the polar angles θ' and ϕ' in the rotated coordinate system, these joint eigenfunctions can be taken to be the spherical harmonics $Y_{lm}(\theta', \phi')$. In particular, $Y_{ll}(\theta', \phi') = N_{ll} \sin^l \theta' \exp(il\phi')$.

A given direction correspond to angles θ and ϕ in the original system of coordinates and to angles θ' and ϕ' in the rotated system. The values of the latter depend on the values of θ and ϕ as well as on the angles by which the second system is rotated with respect to the first one. Therefore $Y_{ll}(\theta', \phi')$ is a function of θ and ϕ, through θ' and ϕ'. Depending on the rotation, this function may be quite complicated. However, since it is a function of θ and ϕ, it can be expressed as a linear combination of the spherical harmonics $Y_{lm}(\theta, \phi)$:

$$Y_{ll}(\theta', \phi') = \sum_{\lambda\mu} c_{\lambda\mu} Y_{\lambda\mu}(\theta, \phi). \tag{H.2}$$

Since the spherical harmonics $Y_{ll}(\theta', \phi')$ and $Y_{\lambda\mu}(\theta, \phi)$ are eigenfunctions of $\mathbf{L}^2$, the equation is possible only if the coefficients $c_{\lambda\mu}$ are zero for $\lambda \neq l$. Thus

$$Y_{ll}(\theta', \phi') = \sum_{\mu} c_{l\mu} Y_{l\mu}(\theta, \phi). \tag{H.3}$$

Now, under a reflection through the origin, $\theta \to \pi - \theta$, $\phi \to \phi + \pi$, $\theta' \to \pi - \theta'$ and $\phi' \to \phi' + \pi$. Hence

$$Y_{ll}(\pi - \theta', \phi' + \pi) = \sum_{\mu} c_{l\mu} Y_{l\mu}(\pi - \theta, \phi + \pi). \tag{H.4}$$

But $Y_{ll}(\pi - \theta', \phi' + \pi) = (-1)^l Y_{ll}(\theta', \phi')$, since $\sin(\pi - \theta') = \sin \theta'$ and $\exp[il(\phi' + \pi)] = \exp(il\pi) \exp(il\phi') = (-1)^l \exp(il\phi')$. We conclude from this that

$$\sum_{\mu} c_{l\mu} Y_{l\mu}(\pi - \theta, \phi + \pi) = (-1)^l \sum_{\mu} c_{l\mu} Y_{l\mu}(\theta, \phi). \tag{H.5}$$

This identity must hold for any value θ, for any value of ϕ and for any rotation. This is possible only if $Y_{l\mu}(\pi - \theta, \phi + \pi) = (-1)^l Y_{l\mu}(\theta, \phi)$ for each value of μ individually. Q.E.D.

Appendix I: About certain two-electron integrals frequently encountered in Atomic Physics

Calculations concerning atoms or molecules with several electrons often involve integrals such as

$$\int \psi_a^*(\mathbf{r}_1, \mathbf{r}_2) V_{\text{ee}}(\mathbf{r}_1, \mathbf{r}_2) \psi_b(\mathbf{r}_1, \mathbf{r}_2)\, \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2,$$

where $\psi_a(\mathbf{r}_1, \mathbf{r}_2)$ and $\psi_b(\mathbf{r}_1, \mathbf{r}_2)$ are two two-electron wave functions and

$$V_{\text{ee}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{I.1}$$

Calculating such integrals is made much easier, in many cases, by passing to spherical polar coordinates $(r1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$ and using the fact that

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{l,m}^*(\theta_1, \phi_1) Y_{l,m}(\theta_2, \phi_2). \tag{I.2}$$

In this equation, $r_<$ and $r_>$ denote, respectively, the smaller of r_1 and r_2 and the larger of r_1 and r_2, and the $Y_{l,,m}(\theta, \phi)$ functions are the usual spherical harmonics.

Note 1:   Eq. (I.2) is nothing else than a form of the following equation:

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l(\cos\theta_{12}), \tag{I.3}$$

where θ_{12} is the angle between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. The coefficients of this expansion, i.e., the functions $P_l(\cos\theta_{12})$ of θ_{12}, are polynomials in $\cos\theta_{12}$ called Legendre polynomials. Eq. (I.2) is obtained by expanding each of the polynomials in spherical harmonics, using the relation

$$P_l(\cos\theta_{12}) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_{l,m}^*(\theta_1, \phi_1) Y_{l,m}(\theta_2, \phi_2). \tag{I.4}$$

As an example of the use of Eq. (I.2) in this context, let us calculate the integral

$$I = (4\pi)^{-2} \int \exp(-\alpha_1 r_1 - \alpha_2 r_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \exp(-\beta_1 r_1 - \beta_2 r_2)\, \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2, \tag{I.5}$$

where α_1, α_2, β_1 and β_2 are constants. More explicitely,

$$I = (4\pi)^{-2} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \int_0^{\infty} dr_1 \, r_1^2 \, \exp(-\lambda r_1) \int_0^{\infty} dr_2 \, r_2^2 \, \exp(-\mu r_2) \frac{r_<^l}{r_>^{l+1}}$$

$$\times \int_0^{\pi} d\theta_1 \, \sin\theta_1 \int_0^{2\pi} d\phi_1 \, Y_{l,m}^*(\theta_1, \phi_1) \int_0^{\pi} d\theta_2 \, \sin\theta_2 \int_0^{2\pi} d\phi_2 \, Y_{l,m}(\theta_2, \phi_2), \quad (I.6)$$

with $\lambda = \alpha_1 + \beta_1$ and $\mu = \alpha_2 + \beta_2$. Since $Y_{0,0}(\theta_1, \phi_1) = Y_{0,0}^*(\theta_2, \phi_2) = (4\pi)^{-1/2}$,

$$\int_0^{\pi} d\theta_1 \, \sin\theta_1 \int_0^{2\pi} d\phi_1 \, Y_{l,m}^*(\theta_1, \phi_1) \int_0^{\pi} d\theta_2 \, \sin\theta_2 \int_0^{2\pi} d\phi_2 \, Y_{l,m}(\theta_2, \phi_2)$$

$$= (4\pi)^{1/2} \int_0^{\pi} d\theta_1 \, \sin\theta_1 \int_0^{2\pi} d\phi_1 \, Y_{l,m}^*(\theta_1, \phi_1) Y_{0,0}(\theta_1, \phi_1)$$

$$\times (4\pi)^{1/2} \int_0^{\pi} d\theta_2 \, \sin\theta_2 \int_0^{2\pi} d\phi_2 \, Y_{0,0}^*(\theta_2, \phi_2) Y_{l,m}(\theta_2, \phi_2). \quad (I.7)$$

Therefore, in view of the orthonormality of the spherical harmonics,

$$\int_0^{\pi} d\theta_1 \, \sin\theta_1 \int_0^{2\pi} d\phi_1 \, Y_{l,m}^*(\theta_1, \phi_1) \int_0^{\pi} d\theta_2 \, \sin\theta_2 \int_0^{2\pi} d\phi_2 \, Y_{l,m}(\theta_2, \phi_2)$$

$$= 4\pi \, \delta_{l,0}\delta_{m,0}. \quad (I.8)$$

The double sum in Eq. (I.6) thus collapses to just one term, that with $l = m = 0$, with the result that

$$I = \int_0^{\infty} dr_1 \, r_1^2 \, \exp(-\lambda r_1) \int_0^{\infty} dr_2 \, r_2^2 \, \exp(-\mu r_2) \frac{1}{r_>}. \quad (I.9)$$

Now, $r_> = r_2$ when $r_2 > r_1$ and $r_> = r_1$ when $r_2 < r_1$. Thus

$$I = \int_0^{\infty} dr_1 \, r_1 \, \exp(-\lambda r_1) \int_0^{r_1} dr_2 \, r_2^2 \, \exp(-\mu r_2) +$$

$$\int_0^{\infty} dr_1 \, r_1^2 \, \exp(-\lambda r_1) \int_{r_1}^{\infty} dr_2 \, r_2 \, \exp(-\mu r_2). \quad (I.10)$$

This double integral can also be written as

$$I = -\frac{\partial^3}{\partial\lambda\partial\mu^2} \int_0^{\infty} dr_1 \, \exp(-\lambda r_1) \int_0^{r_1} dr_2 \, \exp(-\mu r_2)$$

$$- \frac{\partial^3}{\partial\lambda^2\partial\mu} \int_0^{\infty} dr_1 \, \exp(-\lambda r_1) \int_{r_1}^{\infty} dr_2 \, \exp(-\mu r_2). \quad (I.11)$$

The calculation is straightforward, if a little long. One eventually finds

$$I = 2 \frac{\lambda^2 + 3\lambda\mu + \mu^2}{\lambda^2(\lambda + \mu)^3\mu^2}. \quad (I.12)$$

(As stated above, $\lambda = \alpha_1 + \beta_1$ and $\mu = \alpha_2 + \beta_2$.)