Chapter 3. Higher Dimensionality Effects

The coverage of multi-dimensional problems of wave mechanics in this course is minimal: it is limited to a few phenomena (such as the AB effect and Landau levels) that cannot take place in one dimension due to topological reasons, and a few key 3D problems (such as the Born approximation in scattering theory and the Bohr atom) whose solutions are necessary for numerous applications.

3.1. Quantum interference and the AB effect

In the past two chapters, we have already discussed some effects of the de Broglie wave interference. For example, standing waves inside a quantum well, or even on the top of a tunnel barrier, may be considered as a result of the incident and reflected waves. However, there are some remarkable new effects made possible by the spatial separation of such traveling waves, and such separation requires a higher (either 2D or 3D) dimensionality. A good example of such separation is provided by the Young-type experiment (Fig. 1) in which particles are passed through two narrow holes (or slits) in an otherwise opaque partition.

If the particles emitted by the source do not interact (which is always true if the emission rate is sufficiently low), the average rate of particle counting by the detector is proportional to the probability density \( w(r, t) = \Psi(r, t) \Psi^*(r, t) \) to find a single particle at the detector’s location \( r \), where \( \Psi(r, t) \) is the solution of the single-particle Schrödinger equation (1.25). Let us describe this experiment for the case when the particles may be represented by monochromatic waves of energy \( E \) (e.g., very \( r \)-long wave packets), so that the wavefunction may be taken in the form given by Eqs. (1.56) and (1.61): \( \Psi(r, t) = \psi(r) \exp\{-iEt/\hbar\} \). In this case, in the free-space parts of the system, \( \psi(r) \) satisfies the stationary Schrödinger equation (1.60) with Hamiltonian (1.27a):

\[
-\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi . \tag{3.1a}
\]

With the standard definition \( k \equiv (2mE)^{1/2}/\hbar \), it may be rewritten as the 3D Helmholtz equation

\[
\nabla^2 \psi + k^2 \psi = 0 \tag{3.1b}
\]
– an evident 3D generalization of Eqs. (1.75) or (2.81).

The opaque parts of the partition may be well described as classically forbidden regions, so if their size scale \( a \) is much larger than the wavefunction penetration depth \( \delta \) (2.67), we can use on their surface \( S \) the same boundary conditions as for the quantum barrier of infinite height:

\[
\psi \big|_S = 0.
\]  

Equations (1) and (2) formulate the standard boundary problem of the theory of propagation of scalar waves of any nature. For an arbitrary geometry, such problem does not have a simple analytical solution. However, for a conceptual discussion of interference we use certain natural assumptions that will allow us to find its particular, approximate solution.

First, let us discuss wave emission, into free space, by a small-size source located at the origin. Naturally, the emitted wave should be spherically-symmetric: \( \psi(r) = \psi(r) \). Using the well-known expression for the Laplace operator in spherical coordinates, \(^1\) we then reduce Eq. (1) to an ordinary differential equation

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) + k^2 \psi = 0.
\]  

Let us introduce a new function, \( f(r) = r \psi(r) \). Plugging the reciprocal relation \( \psi = f/r \) into Eq. (3), we see that it is reduced to the 1D wave equation,

\[
\frac{d^2 f}{dr^2} + k^2 f = 0,
\]  

whose solutions were discussed in detail in Sec. 2.2. For a fixed \( k \), the general solution of Eq. (4) is

\[
f = f_+ e^{ikr} + f_- e^{-ikr}
\]  

so that the full wavefunction

\[
\psi(r) = \frac{f_+}{r} e^{ikr} + \frac{f_-}{r} e^{-ikr}, \quad \text{i.e.} \quad \Psi(r,t) = \frac{f_+}{r} e^{i(kr-\omega t)} + \frac{f_-}{r} e^{-i(kr+\omega t)}, \quad \text{with} \; \omega \equiv \frac{E}{\hbar} = \frac{hk^2}{2m}.
\]  

If the source is located at point \( r' \neq 0 \), the obvious generalization of Eq. (6)

\[
\Psi(r,t) = \frac{f_+}{R} e^{i(kR-\omega t)} + \frac{f_-}{R} e^{-i(kR+\omega t)}, \quad \text{with} \; R \equiv |R|, \quad R \equiv r - r'.
\]  

The first term of this solution describes a spherically-symmetric wave propagating from the source outward, while the second one, a wave converging onto the source point \( r' \) from large distances. Though the latter solution is possible at some very special circumstances (say, when the outgoing wave is reflected back from a spherical shell), for our problem, only the outgoing waves are relevant, so that we may keep only the first term (proportional to \( f_+ \)) in Eq. (7). Note that factor \( R \) is the denominator (that was absent in 1D geometry) has a simple physical sense: it provides the independence of the full probability current \( I = 4\pi R^2 j(R) \), with \( j(R) \propto k\Psi \Psi^* \propto 1/R^2 \), of the distance \( R \) between the observation point and the source.

\(^1\) See, e.g., MA Eq. (10.9).
Now let us assume that the partition’s geometry is not too complicated – for example, it is planar as shown in Fig. 1, and consider the region of the particle detector location far behind the partition (at \( z >> 1/k \)), and at a relatively small angle to it: \( |x| << z \). Then it should be physically clear that the spherical waves (7) emitted by each point inside the slit cannot be perturbed too much by the opaque parts of the partition, and their only role is the restriction of the set of such emitting points by the area of the slits. Hence, an approximate solution of the boundary problem is given by the following Huygens principle: the wave behind the partition looks as if it was the sum of contributions (7) of point sources located in the slits, with each source’s strength \( f \) proportional to the amplitude of the wave arriving at this pseudo-source from the real source – see Fig. 1. This principle finds its confirmation in strict wave theory, which shows\(^2\) that with our assumptions, the solution of the boundary problem (1)-(2) may be presented as the following Kirchhoff integral:

\[
\psi(r) = c \int_{\text{slits}} \frac{\psi(r')}{R} e^{ikR} d^2r', \quad \text{with} \quad c = \frac{k}{2\pi i}.
\]  

(3.8)

If the source is also far from the partition, its wave front is almost parallel to the slit plane, and the slits are not too broad, we can take \( \psi(r') \) constant (\( \psi_{1,2} \)) at each slit, so that Eq. (8) is reduced to

\[
\psi(r) = a''_1 \exp\{ikl''_1\} + a''_2 \exp\{ikl''_2\}, \quad \text{with} \quad a''_{1,2} = \frac{cA_{1,2}}{l''_{1,2}} \psi_{1,2},
\]  

(3.9)

where \( A_{1,2} \) are the slit areas. The wavefunctions on the slits be calculated approximately\(^3\) by applying the same Eq. (7) to the space before the slits: \( \psi_{1,2} \approx (f/\ell_{1,2}) \exp\{ik\ell_{1,2}\} \). As a result, Eq. (9) may be rewritten as

\[
\psi(r) = a_1 \exp\{ikl_1\} + a_2 \exp\{ikl_2\}, \quad \text{with} \quad l_{1,2} \equiv l'_{1,2} + l''_{1,2}, \quad a_{1,2} \equiv \frac{cfA_{1,2}}{l''_{1,2}}.
\]  

(3.10)

(As Fig. 1 shows, each of \( l_{1,2} \) is the length of the full classical path of the particle from the source, through the corresponding slit, and further to the observation point \( r \) – see Fig. 1).

According to Eq. (10), the resulting rate of particle counting is proportional to

\[
w(r) = \psi(r)\psi^*(r) = |a_1|^2 + |a_2|^2 + 2|a_1a_2|\cos\varphi_{1,2},
\]  

(3.11)

where

\[
\varphi_{1,2} \equiv k(l_{2} - l_{1})
\]  

(3.12)

is the difference of the total wave phase accumulations along each of two alternative trajectories. The last expression may be evidently generalized as

\(^2\) For a proof of Eq. (8), see, e.g., EM Sec. 8.5.

\(^3\) A possible (and reasonable) concern about the application of Eq. (7) to the field in the slits is that it ignores the effect of opaque parts of the partition. However, as we know from Chapter 2, the main role of the classically forbidden region is providing the reflection of the incident wave towards its source (i.e. to the left in Fig. 1). As a result, the contribution of this reflection to the field inside the slits is insignificant is \( A_{1,2} >> \lambda^2 \), and even in the opposite case provides just some rescaling of the amplitudes \( a_{1,2} \), which is unimportant for our conceptual discussion.
with integration along the virtually closed contour \( C \) (see the dashed line in Fig. 1), i.e. from point 1, in the positive (i.e. counterclockwise) direction to point 2. (From our experience with the 1D WKB approximation we may expect such generalization to be valid even if \( k \) changes, sufficiently slowly, along the paths.)

\[
\varphi_{12} = \oint_C \mathbf{k} \cdot d\mathbf{r}, 
\]

(3.13)

Our result (11) shows that the counting rate oscillates as a function of the difference \( (l_2 - l_1) \) that in turn changes with detector’s position, giving the famous interference pattern, with the amplitude proportional to the product \( |a_1 a_2| \), and hence vanishing if any of the slits is closed. For a wave theory, this is a well-known result,\(^4\) but for particle physics, is was (and still is :-) rather shocking. Indeed, our analysis pertains to a very low particle emission/detection rate, so that there is no other way to interpret it rather than resulting from particle’s interference with itself, or rather the interference of its wavefunction parts passing through each of two slits.

Let us now discuss a very interesting effect of magnetic field on the quantum interference. In order to make the discussion simpler, let us consider an alternative version of the two-slit experiment, in which each of alternative path is fixed to a narrow channel using a partial confinement – see Fig. 2. (In this arrangement, moving the particle detector without changing channels’ geometry, and hence local values of \( k \) may be more problematic in experimental practice, so let us think about its position \( \mathbf{r} \) fixed.)

In this case, because of the effect of the walls providing the path confinement, we cannot use expressions (10) for amplitudes \( a_{1,2} \). However, from the discussions in Sec. 1.6 and Sec. 2.2, it should be clear that the first of expressions (10) remains valid, though may be with a value of \( k \) specific for each channel.

The benefit of this geometry is that we can now apply magnetic field \( \mathcal{B} \), perpendicular to the plane of particle motion, that would pierce contour \( C \), but would not touch the particle propagation channels. In classical physics, magnetic field’s effect on a particle with electric charge \( q \) is described by the Lorentz force:\(^5\)

\[
\mathbf{F}_B = q \mathbf{v} \times \mathcal{B},
\]

(3.14)

\(^4\) See, e.g., a detailed discussion in EM Sec. 8.4.

\(^5\) See, e.g., Sec. 5.1. Note that Eq. (14), as well as all other formulas of this course, are in the SI units; in Gaussian units, all terms which include either \( \mathcal{B} \) or \( \mathbf{A} \) should be divided by \( c \), the speed of light in free space.
where $B$ is the field value at the point of its particle’s location, so that for the experiment shown in Fig. 2, $F_B = 0$, and the field would not affect the particle motion at all. In quantum mechanics, this is not so, and the field does affect the probability density $w$, even if $B = 0$ in all points where the wavefunction $\psi(r)$ is not equal to zero.

In order to describe this surprising effect, let us first develop a general framework for account of effects of electromagnetic fields on a quantum particle, which will also give us some important by-product results. In order to do that, we need to calculate the Hamiltonian operator of a charged particle in the field. For an electrostatic field, this hardly present any problem. Indeed, from classical electrodynamics we know that such field may be presented as a gradient of its electrostatic potential $\phi$, \[ E = -\nabla \phi(r), \] so that the force exerted by the field on a particle with electric charge $q$, \[ F = q\phi, \] may be described by adding the potential energy of the field, \[ U(r) = q\phi(r), \] to other (possible) components of the full potential energy of the particle. As we have already discussed, such a function of coordinates may be included to the Hamiltonian operator just by adding it to the kinetic energy operator (1.27).

However, magnetic field’s effect is peculiar: since its Lorentz force (14) cannot do any work on the particle: \[ dW_B = F_B \cdot dr = F_B \cdot dv = q\mathbf{v} \times \mathbf{B} \cdot dv = 0, \] the field cannot be presented by any potential energy, so it may not be immediately clear how to account for it in the Hamiltonian. Help comes from the analytical-mechanics approach to classical electrodynamics: in the non-relativistic limit, the Hamiltonian function of a particle in electromagnetic field looks superficially like that in electrostatic field only: \[ H = \frac{mv^2}{2} + U = \frac{p^2}{2m} + q\phi; \] however, the momentum $p = mv$ that participates in this expression is now the difference \[ p = \mathbf{P} - q\mathbf{A}. \] Here $\mathbf{A}$ is the vector-potential, defined by the well-known relations for the electric and magnetic field: \[ \mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}, \] while $\mathbf{P}$ is the canonical momentum whose Cartesian components may be calculated (in classics) from the Lagrangian function, using the standard formula of analytical mechanics,

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6 See, e.g., EM Sec. 9.7.
7 See, e.g., EM Sec. 6.7, in particular Eqs. (6.106).
8 Just for reader’s reference, the classical Lagrangian corresponding to Hamiltonian (19) is
To emphasize the difference between the two momenta, \( \mathbf{p} = m \mathbf{v} \) is frequently called the \textit{kinematic momentum} (or “mv-momentum”). The distinction between \( \mathbf{p} \) and \( \mathbf{P} = \mathbf{p} + q \mathbf{A} \) becomes even more clear if we notice that vector-potential is not \textit{gauge-invariant}: according to the second of Eqs. (21), at the so-called \textit{gauge transformation}

\[
\mathbf{A} \rightarrow \mathbf{A} + \nabla \chi ,
\]

with an arbitrary single-valued scalar \textit{gauge function} \( \chi = \chi(r, t) \), the magnetic field does not change. Moreover, according to the first of Eqs. (21), if we make the simultaneous replacement

\[
\phi \rightarrow \phi - \frac{\partial \chi}{\partial t} ,
\]

the gauge transformation does not affect the electric field either. With that, the gauge function does not change the classical particle’s equation of motion, and hence the velocity \( \mathbf{v} \) and momentum \( \mathbf{p} \). Hence, the kinematic momentum is gauge-invariant, while \( \mathbf{P} \) is not, because it changes by \( q \nabla \chi \).

Now the standard way of transfer to quantum mechanics is to treat the canonical rather than kinematic momentum according to correspondence postulate discussed in Sec. 1.2. This means that in the coordinate representation, the operator of this variable is given by Eq. (1.26):\(^9\)

\[
\hat{\mathbf{P}} = -i \hbar \nabla .
\]

Hence the Hamiltonian operator corresponding to the classical function (19) is

\[
\hat{H} = \frac{1}{2m} \left( -i \hbar \nabla - q \mathbf{A} \right)^2 + q \phi = -\frac{\hbar^2}{2m} \left( \nabla - iq \frac{\hbar}{\mathbf{A}} \right)^2 + q \phi ,
\]

so that the Schrödinger equation of a particle moving in electromagnetic field (but otherwise free) is

\[
-\frac{\hbar^2}{2m} \left( \nabla - iq \frac{\hbar}{\mathbf{A}} \right)^2 \psi + q \phi \psi = E \psi ,
\]

We may now repeat all the calculations of Sec. 1.4 for the case \( \mathbf{A} \neq 0 \), and readily get the following generalized expression for the probability current density:

\[
\mathbf{j} = \frac{\hbar}{2im} \left[ \psi^* \left( \nabla - iq \frac{\hbar}{\mathbf{A}} \right) \psi - \text{c.c} \right] = \frac{1}{2m} \left[ \psi^* \hat{\mathbf{P}} \psi - \text{c.c} \right] = \frac{\hbar}{m} | \psi |^2 \left( \nabla \phi - \frac{q}{\hbar} \mathbf{A} \right) .
\]

- see EM Sec. 9.7. Note that this function includes \( \mathbf{A} \) within a term that cannot be interpreted as either the purely kinetic energy (as the first term) or the purely potential energy (as the last term with the minus sign).

\(^9\) The validity of this choice is clear from the fact that if the \textit{kinetic} momentum was described by this differential operator, the Hamiltonian operator corresponding to the classical Hamiltonian function (19) would not include the magnetic field at all, and hence solutions of the corresponding Schrödinger equation could not satisfy the correspondence principle.
We see that the current density is gauge-invariant (as required for any observable) only if the wavefunction’s phase $\varphi$ changes as

$$\varphi \rightarrow \varphi + \frac{q}{\hbar} \chi.$$  

(3.29)

This may be a point of concern: since the quantum interference is described by the spatial dependence of phase $\varphi$, can the observed interference pattern depend on the gauge function choice (which would not make sense)? Fortunately, this is not true, because the spatial phase difference between two interfering paths, participating in Eq. (11), is gauge-transformed as

$$\varphi_{12} \rightarrow \varphi_{12} + \frac{q}{\hbar} (\chi_2 - \chi_1).$$  

(3.30)

But $\chi$ has to be a single-valued function of coordinates, hence in the limit when points 1 and 2 coincide, $\chi_1 = \chi_2$, so that $\Delta \varphi$ (and hence the interference pattern) is gauge-invariant.

However, the difference $\varphi$ may be affected by the magnetic field, even if it is localized outside the channels in which the particle propagates. Indeed, in this case the field cannot affect particle’s velocity and current density $j$:

$$j(r)|_{\beta=0} = j(r)|_{\beta=0},$$  

(3.31)

so that the last form of Eq. (28) yields

$$\nabla \varphi(r)|_{\beta=0} = \nabla \varphi(r)|_{\beta=0} + \frac{q}{\hbar} A.$$  

(3.32)

Integrating this equation along contour $C$ (Fig. 2), for the phase difference between points 1 and 2 we get

$$\varphi_{12}|_{\beta=0} = \varphi_{12}|_{\beta=0} + \frac{q}{\hbar} \oint_C A \cdot d\mathbf{r},$$  

(3.33)

where the integral should be taken along the same virtually closed contour $C$ as before (in Fig. 2, from point 1, counterclockwise along the dashed line to point 2). But from the classical electrodynamics we know\(^\text{10}\) that as points 1 and 2 are overlapped, i.e. contour $C$ becomes closed, the last integral is just the magnetic flux $\Phi \equiv \oint B \cdot d\mathbf{a}$ through any smooth surface limited by contour $C$, so that Eq. (33) may be presented as

$$\varphi_{12}|_{\beta=0} = \varphi_{12}|_{\beta=0} + \frac{q}{\hbar} \Phi.$$  

(3.34a)

In terms of the interference pattern, this means a shift of interference fringes, proportional to the magnetic flux (Fig. 3). This phenomenon is usually called the “Aharonov-Bohm” (or just the $AB$) effect.\(^\text{11}\) For particles with a single elementary charge, $q = \pm e$, this result is frequently presented as

\(^{10}\) See, e.g., EM Sec. 5.3.

\(^{11}\) I personally prefer the latter, less personable name, because the effect had been actually predicted by W. Ehrenberg and R. Siday in 1949, before it was rediscovered by Y. Aharonov and D. Bohm in 1959. To be fair to Aharonov and Bohm, it was their work that triggered a wave of interest to the phenomenon, resulting in its first
\[ \varphi_{12} \Big|_{\varphi=0} = \varphi_{12} \Big|_{\varphi=0} \pm 2\pi \frac{\Phi}{\Phi_0}, \]  

(3.34b)

where the fundamental constant \( \Phi_0 \equiv 2\pi\hbar/e = h/e \approx 4.14 \times 10^{-15} \) Wb has the meaning of flux necessary to change \( \varphi_{12} \) by \( 2\pi \), i.e. shift the interference pattern (11) by one period, and is called the normal magnetic flux quantum, because of the reasons we will soon discuss.

The AB effect may be “almost explained” classically, in terms of Faraday’s electromagnetic induction. Indeed, a change \( \Delta\Phi \) of magnetic flux in time causes a vortex-like electric field \( \Delta\mathbf{E} \) around it. That field is not restricted to the magnetic field’s location, i.e. may reach particle’s trajectories. The field’s magnitude (or rather of its integral along contour \( C \)) may be readily calculated by integration of the first of Eqs. (21):

\[ \Delta V \equiv \oint_C \mathbf{E} \cdot d\mathbf{r} = -\frac{d\Phi}{dt}, \]  

(3.35)

I hope that in this expression the reader readily recognizes the integral (“undergraduate”) form of Faraday’s induction law. Now let us assume that the variable separation described in Sec. 1.5 may be applied to the end points 1 and 2 of particle’s alternative trajectories as two independent systems, and that the magnetic flux’ change by certain amount \( \Delta\Phi \) does not change the spatial parts \( \psi_f \) of wavefunctions of these systems. Then change (35) leads to the change of potential energy difference \( \Delta U = q\Delta V \) between the two points, and repeating the arguments that were used in Sec. 2.3 at the discussion of the Josephson effect, we may rewrite Eq. (2.53) as

\[ \frac{d\varphi_{12}}{dt} = -\frac{\Delta U}{h} = -\frac{q}{h} \Delta V = \frac{q}{h} \frac{d\Phi}{dt}. \]  

(3.36)

Integrating this relation over the time of magnetic field’s change, we get

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12 This assumption may seem a bit of a stretch, but the resulting relation (37) may be indeed proven for a rather realistic model, though that would take more time and space that I can afford.
Δφ_{12} = \frac{q}{\hbar} \Delta \Phi , \quad (3.37)

- superficially, the same result as given by Eq. (34).

However, this interpretation of the AB effect is limited. Indeed, it requires the particle to be in the system (on the way from the source to the detector) during the flux change, i.e. when the induced electric field \( \varepsilon \) may affect its dynamics. On the contrary, Eq. (34) predicts that the interference pattern would shift even if the field change has been made when there is no particle in the system, and hence field \( \varepsilon \) could not be felt by it. Experiment confirms the latter conclusion. Hence, there is *something* in the space where a particle propagates (i.e., outside of the magnetic field region), which transfers information about even the static magnetic field to the particle. The standard interpretation of this surprising fact is as follows: the vector-potential \( A \) is not just a convenient mathematical tool, but a physical reality (just as its electric counterpart \( \phi \)), despite the large freedom of choice we have in prescribing specific spatial and temporal dependences of these potentials without affecting any observable – see Eqs. (23)-(24).

Let me briefly discuss the very interesting form the AB effect takes in superconductivity. In this case, our results require two changes. The first one is simple: since superconductivity may be interpreted as the Bose-Einstein condensate of Cooper pairs with electric charge \( q = 2e \), \( \Phi_0' \) has to be replaced by the so-called *superconducting flux quantum*\(^\text{13}\)

\[
\Phi_0 \equiv \frac{\pi \hbar}{e} \approx 2.07 \times 10^{-15} \text{ Wb} = 2.07 \times 10^{-7} \text{ Gs cm}^2 . \quad (3.38)
\]

Second, since the pairs are Bose particles and are all condensed in the same quantum state, described by the same wavefunction, the total electric current density, proportional to the probability current density \( j \), may be extremely large – in real superconducting materials, up to \(~10^{12} \text{ A/m}^2\). In these conditions, one cannot neglect the contribution of that current into the magnetic field and hence its flux \( \Phi \), which (according to the Lenz rule of the Faraday induction law) tries to compensate changes in external flux. In order to see possible results of this contribution, let us consider a closed superconducting loop (Fig. 4).

Due to the Meissner effect (which is just another version of the flux self-compensation), current and magnetic field penetrate inside the superconductor by only a small distance (called the *London

\(^\text{13}\) One more bad, though common, term – a wire can (super)conduct, but a quantum hardly can!
penetration depth) $\delta_L \sim 10^{-7} \text{ m}$.\(^{14}\) If the loop is made of a superconducting wire that is considerably thicker than $\delta_L$, we can draw a contour deep inside the wire, at that the current density is negligible. According to Eq. (28), everywhere at the contour,

$$\nabla \varphi - \frac{q}{\hbar} A = 0. \tag{3.39}$$

Integrating this equation along the contour as before (from point 1 to the virtually coinciding point 2), we need to have the phase difference $\varphi_{12} = 2\pi n$, because the wavefunction $\psi \propto \exp\{i\varphi\}$ in the initial and final points 1 and 2 should be “essentially” the same, i.e. produce the same observables. As a result, we get

$$\Phi = \oint_{C} A \cdot dr = \frac{2\pi\hbar}{q} n = \frac{\pi\hbar}{e} n = n\Phi_0. \tag{3.40}$$

This is the famous flux quantization effect,\(^{15}\) which justifies the term “magnetic flux quantum” for the constant $\Phi_0$ given by Eq. (38).

Here I have to mention in passing very interesting effects of “partial flux quantization”, that arise when a superconductor loop is closed by a Josephson junction, forming the so-called Superconductor Quantum Interference Device - “SQUID”. Such devices are used, in particular, for supersensitive magnetometry and ultrafast, low-power computing.\(^{16}\)

3.2. Landau levels and quantum Hall effect

In the last section, we have used the Schrödinger equation (27) for analysis of static magnetic field effects in “almost-1D”, circular geometries shown in Figs. 1, 2, and 4. However, this equation describes very interesting effects in higher dimensions as well, especially in the 2D case. Let us consider a uniform 2D quantum well (say, parallel to the $[x, y]$ plane), with strong confinement in the perpendicular direction $z$. According to the discussion in Sec. 1.6, energy-relaxed particles will always reside in the lowest energy subband, with constant quantization energy ($E_z$).\(^{1}\) Adding this shift to well’s flat floor $U(x, y) = \text{const}$, and taking the resulting constant energy as the reference, for the 2D motion of the particle in the well, we reduce Eq. (27) to the similar equation, but with the Laplace operator acting only in directions $x$ and $y$:

$$- \frac{\hbar^2}{2m} \left( n_x \frac{\partial}{\partial x} + n_y \frac{\partial}{\partial y} - i \frac{q}{\hbar} A \right)^2 \psi = E \psi. \tag{3.41}$$

Let us find its solutions for the simplest case when the applied static magnetic field is uniform and perpendicular to the plane:

$$\mathbf{B} = B \mathbf{n}_z. \tag{3.42}$$

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\(^{14}\) For more detail, see EM Sec. 6.3.

\(^{15}\) It was predicted in 1949 by F. London and experimentally discovered (independently and virtually simultaneously) in 1961 by two experimental groups: B. Deaver and W. Fairbank, and R. Doll and M. Näbauer.

\(^{16}\) A brief review of these effects, and recommendations for further reading may be found in EM Sec. 6.4.
According to the second of Eqs. (21), this imposes the following restriction on the choice of vector-potential:

$$\mathcal{B} = \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}, \quad (3.43)$$

but the gauge transformations still give us a lot of freedom in its choice. The “natural” axially-symmetric form, $A = n_\rho \rho \mathcal{B}/2$, where $\rho = (x^2 + y^2)^{1/2}$ is the distance from some $z$-axis, leads to a cumbersome math. In 1930, L. Landau realized that the energy spectrum of Eq. (41) may be obtained by making a very simple choice

$$A_x = 0, \quad A_y = \mathcal{B}(x - x_0), \quad (3.44)$$

(with arbitrary $x_0$), which evidently satisfies Eq. (43), though it ignores the physical equivalence of the $x$ and $y$ directions. Now, expanding the eigenfunction into the Fourier integral in direction $y$:

$$\psi(x, y) = \int X_k(x)e^{i(ky - y_0)}dk, \quad (3.45)$$

we see that for each component of this integral, Eq. (41) yields a specific equation

$$-\frac{\hbar^2}{2m} \left[ n_s \frac{d}{dx} + in \left( k - \frac{q}{\hbar} \mathcal{B}(x - x_0) \right) \right]^2 X_k = EX_k. \quad (3.46)$$

Since the vectors inside the square brackets are mutually perpendicular, its square has no crossterms, so that Eq. (46) may be rewritten as

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} X_k + \frac{\hbar^2}{2m} \left[ \frac{q}{\hbar} \mathcal{B}(x - x_0') \right]^2 X_k = EX_k, \quad \text{where} \quad x_0' = x_0 + \frac{\hbar k}{q \mathcal{B}}. \quad (3.47)$$

But this 1D Schrödinger equation is identical to Eq. (2.268) for the 1D harmonic oscillator, but with the center at point $x_0'$, and frequency $\omega_0$ equal to

$$\omega_c = \frac{|q| \mathcal{B}}{m}. \quad (3.48)$$

In this expression, it is easy to recognize the classical cyclotron frequency of particle’s motion in the magnetic field. (It may be readily obtained using the 2nd Newton law for a circular orbit of radius $r$,

$$m \frac{v^2}{r} = F_q = qv \mathcal{B}, \quad (3.49)$$

and noting that the resulting ratio $v/r = q \mathcal{B}/m$ is just the radius-independent angular velocity $\omega_c$ of particle’s rotation.) Hence, the energy spectrum for each Fourier component of integral (45) is the same:

$$E_n = \hbar \omega_c \left( n + \frac{1}{2} \right), \quad (3.50)$$

and does not depend on either $x_0$, or $y_0$, or $k$.

This is an example of a highly degenerate system: for each eigenvalue $E_n$, there are many different eigenfunctions that differ by the positions $\{x_0, y_0\}$ of their center on axis $x$, and the rate $k$ of
their phase change along axis $y$. They may be used to assemble a large variety of linear combinations, including 2D wave packets whose centers move along classical circular orbits with some radius $r$ determined by initial conditions. Note, however, that such radius cannot be smaller than the so-called Landau radius,

$$ r_L \equiv \left( \frac{\hbar}{q B} \right)^{1/2}, $$

which characterizes the minimum radius of the wave packet itself, and results from Eq. (2.271) after replacement (48). This radius is remarkably independent on particle’s mass, and may be interpreted in the following way: the scale $B A_{\text{min}}$ of the applied magnetic field’s flux through the effective area $A_{\text{min}} = 2\pi r_L^2$ of the smallest wave packet is just one normal flux quantum $\Phi_0’ = 2\pi\hbar/q$.

A detailed analysis of such wave packets (for which we would not have time in this course) shows that magnetic field does not change the average density $dN_2/dE$ of different 2D states on the energy scale, but just “assembles” them on the Landau levels (see Fig. 5a), so that the number of states on each Landau area (per unit area) is

$$ n_L \equiv \frac{N_2}{A} = \frac{1}{A} \frac{dN_2}{dE} \bigg|_{E=0} \Delta E = \frac{1}{A} \frac{dN_2}{dE} \bigg|_{E=0} \Delta E = \frac{m}{2\pi\hbar^2} \hbar \omega_c = \frac{qB}{2\pi\hbar} = \frac{qB}{\hbar}. \quad (3.52) $$

This expression may again be interpreted in terms of magnetic flux quanta: $n_L \Phi_0’ = B$, i.e. there is one particular state on each Landau level per each flux quantum.

The most famous application of the Landau levels concept is the explanation of the quantum Hall effect\(^{17}\). Generally, the Hall effect\(^{18}\) is observed in the geometry sketched in Fig. 6, where electric current $I$ is passed through a thin rectangular conducting sample (frequently called the Hall bar) placed into a magnetic field $B$ perpendicular to the sample plane. The classical analysis of the effect is based on the notion of the Lorentz force (14). This force the deviates charge carriers (say, electrons) from their straight motion from one external electrode to another, bending them to the isolated edges of the bar (in Fig. 6, parallel to axis $x$). Here the carriers accumulate, generating a gradually increasing electric field $E$, until its force (16) exactly balances the Lorentz force (14):

\(^{17}\) It was first observed in 1980 by K. von Klitzing and coworkers.

\(^{18}\) Discovered in 1879 by E. Hall.
where $v_x$ is the drift velocity of the electrons along the bar (Fig. 6), providing the sustained balance condition $\mathcal{E}_y/v_x = B_z$ at each point of the 2D sample.

With $n_2$ carriers per unit area, in a sample of width $W$, this condition yields the following classical expression for the so-called Hall resistance $R_H$:

$$R_H \equiv \frac{V_y}{I_x} = \frac{\mathcal{E}_y W}{qn_2 v_x W} = \frac{B}{qn_2}.$$  \hspace{1cm} (3.54)

This formula is broadly used in practice for the measurement of the carrier density $n_2$, and (in semiconductors) the carrier type – negative electrons or positive holes.

However, in experiments with high-quality (low-defect) 2D quantum wells at very low, sub-kelvin temperatures\(^{19}\) and high magnetic fields, the linear growth of $R_H$ with $B$, described by Eq. (54), is interrupted by virtually horizontal plateaus (Fig. 7) with constant values

$$R_H = \frac{1}{i} R_K,$$  \hspace{1cm} (3.55)

where $i$ (only in this context, following tradition!) is an integer, and value

$$R_K \approx 25.812807557 \text{ k}\Omega$$  \hspace{1cm} (3.56)

is reproduced with extremely high accuracy ($\sim 10^{-9}$) from experiment to experiment and from sample to sample. Such stability is a very rare exception in solid state physics were most results are noticeably dependent on the particular material and particular sample under study.

Let us apply the Landau level picture. The 2D sample is typically in a weak contact with 3D electrodes whose conductivity electrons form a Fermi sea with certain Fermi energy $E_F$, so that at low temperatures all states with $E < E_F$ are filled with electrons – see Fig. 5b. As $B$ is increased, spacing $\hbar \omega_k$ between the Landau levels increases, so that fewer and fewer of these levels are below $E_F$ and are filled, and within broad ranges of field variation, the number $i$ of filled levels is constant. (In Fig. 5b, $i = 2$.) So, plugging $n_2 = in_L$ and $q = \pm e$ into Eq. (54), we get

$$R_H = \frac{1}{i} \frac{B}{qn_L} = \frac{1}{i} \frac{2\pi \hbar}{e^2} = \frac{1}{i} \frac{h}{e^2},$$  \hspace{1cm} (3.57)

\(^{19}\) Recently, the quantum Hall effect was observed at room temperature in the graphene (a virtually perfect 2D sheet of carbon atoms, see Sec. 4 below) – see K. Novoselov et al., Science 315, 1379 (2007).
i.e. exactly the experimental result (55), with

\[
R_k = \frac{h}{e^2} = 4\frac{\pi h}{2e^2}. \quad (3.58)
\]

This constant, exactly 4 times the quantum unit of resistance \(R_Q\) given by Eq. (2.259), is in an excellent agreement with experimental value (56), and is sometimes called the Klitzing constant.

However, this oversimplified explanation of the quantum Hall effect does not take into account several important factors, including:

(i) the role of nonuniformity of the quantum well bottom potential \(U(x, y)\), and of the localized states this nonuniformity produces, and the surprisingly small effect of these factors on the extraordinary accuracy of Eq. (55);\(^{20}\) and

(ii) the mutual Coulomb interaction of the electrons, in high-quality samples leading to the formation of \(R_H\) plateaus with not only integer, but also fractional values of \(i\) (1/3, 2/5, 3/7, etc.).\(^{21}\)

Unfortunately, a thorough discussion of these interesting features is well beyond the framework of this course.\(^{22}\)

### 3.3. Scattering and diffraction

The second class of quantum effects that become more rich in multi-dimensional space is typically referred to as either *diffraction* or *scattering* - depending on the context. (Diffraction is essentially the interference, but of waves emitted by several many coherent sources.) Just as in the two –

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\(^{20}\) The explanation of this paradox may be obtained in terms of the so-called *quantum edge channels* – the quasi-1D regions of width (51), along the lines were the Landau levels cross the Fermi surface. Particle motion along these channels, which is responsible for electron transfer, is effectively one-dimensional and thus cannot be affected by modest uniformities of the potential distribution \(U(x, y)\).

\(^{21}\) This *fractional quantum Hall effect* was discovered in 1982 by D. Tsui, H. Stormer, and A. Gossard. In contrast, the effect described by Eq. (55) with integer \(i\) (Fig. 7) is now called the *integer quantum Hall effect*.

slits in the Young-type experiment (Fig. 1), these sources are most frequently the elementary re-emitters of some initial wave from a single source. More generally, such re-emitting is called scattering; this term is also applied to particles – even if their quantum properties may be ignored.\(^{23}\)

Figure 8 shows the general scattering situation. Most commonly, the detector of scattered particles (in the quantum case, read de Broglie waves) is located at a large distance \(r \gg a\) from the scatterer.\(^{24}\) In this case, the main observable independent of \(r\) is the flux (number of particles per unit time) of particles scattered in a certain direction, i.e. their flux per unit solid angle. Since such flux is proportional to the incident flux of particles per unit area, the ability of the scatterer to re-emit in a particular direction may be characterized by the ratio of these two fluxes. This ratio has the dimensionality of area per unit angle, and is called the \textit{differential cross-section} of the scatterer:

\[
\frac{d\sigma}{d\Omega} = \frac{\text{flux of scattered particles per unit solid angle}}{\text{flux of incident particles per unit area}}. \tag{3.58}
\]

Such name and notation stem from the fact that the integral of \(d\sigma/d\Omega\) over all scattering angles, (also with the dimensionality of area), has a simple interpretation as the \textit{full cross-section} of scattering. For the simplest case when a macroscopic solid object scatters all classical particles hitting its surface, but does not affect the particles flying by it, \(\sigma\) is just the geometrical cross-section of the object, as visible from the direction of incoming particles.

In classical mechanics,\(^{25}\) we first calculate the particle scattering angle as a function of the \textit{impact parameter} \(b\), and then average the result over all values of \(b\), considered random. In this sense the calculations in wave mechanics are simpler, because a parallel beam of incident particles of fixed energy \(E\) may be fairly presented by a plane de Broglie wave

\[
\psi_0 = a_0 e^{ik_0 \cdot r}, \tag{3.60}
\]

\(^{23}\) See, e.g., CM Sec. 3.7.

\(^{24}\) In optics, this limit is called the \textit{Fraunhofer diffraction} – see, e.g., EM Secs. (8.6) and (8.8).

\(^{25}\) For example, in the simplest task of derivation of the so-called \textit{Rutherford formula} for scattering of a charged non-relativistic particle by a point fixed charge, due to their Coulomb interaction – see, e.g., CM Sec. 3.7.
with the free-space wave number \( k_0 = (2mE)^{1/2}/\hbar \) and constant probability current density (1.49):

\[
\mathbf{j}_0 = |a_0|^2 \frac{\hbar}{m} \mathbf{k}_0. \tag{3.61}
\]

This current density is exactly the flux of incident particles per unit area that is used in the denominator of definition (58), so the “only” remaining thing to do is to calculate the nominator of that fraction.

To do this, let us write the Schrödinger equation for the scattering problem (now in the whole space including the scatterer) in the form

\[
(E - \hat{H}_0)\psi = U(\mathbf{r})\psi, \tag{3.62}
\]

where

\[
\hat{H}_0 \equiv -\frac{\hbar^2}{2m}\nabla^2, \quad \text{and} \quad E = \frac{\hbar^2 k_0^2}{2m} = \frac{\hbar^2 k^2}{2m}. \tag{3.63}
\]

the potential energy \( U(\mathbf{r}) \) describes the effect of scatterer. Looking for the solution of Eq. (62) in the natural form

\[
\psi = \psi_0 + \psi_s, \tag{3.64}
\]

where \( \psi_0 \) is the incident wave (60), and \( \psi_s \) has the sense of the scattered wave, and taking into account that former wave satisfies the free-space equation

\[
\hat{H}_0\psi_0 = E\psi_0, \tag{3.65}
\]

we may reduce Eq. (62) to

\[
(E - \hat{H}_0)\psi_s = U(\mathbf{r})(\psi_0 + \psi_s). \tag{3.66}
\]

The most straightforward (and common) simplification of this problem is possible if the scattering potential \( U(\mathbf{r}) \) is in some sense weak. (We will derive the exact condition of this smallness below.) Then since at \( U(\mathbf{r}) = 0 \) the scattering wave \( \psi_s \) disappears, we may expect that at small but nonvanishing \( U(\mathbf{r}) \), the main part of \( \psi_s \) is proportional to its scale \( U_0 \). Then all terms in Eq. (66) are proportional to \( U_0 \), besides the product \( U\psi_s \), which is proportional to \( U_0^2 \). Hence, in the first approximation in \( U_0 \), that term may be ignored, and Eq. (66) reduces to the famous equation of the Born approximation:26

\[
(E - \hat{H}_0)\psi_s = U(\mathbf{r})\psi_0. \tag{3.67a}
\]

This simplification changes the situation drastically, because the linear superposition principle allows finding an explicit solution of this equation (in the form of an integral) for an arbitrary function \( U(\mathbf{r}) \). Indeed, after rewriting Eq. (67a) as

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26 Named after M. Born, who was the first one to apply this approximation in quantum mechanics. However, the basic idea of this approach had been developed much earlier (in 1881) by Lord Rayleigh in the context of electromagnetic wave scattering – see, e.g., EM Sec. 8.3. Note that the contents of that section repeats much of our current discussion – regrettably but unavoidably so, because the Born approximation is a centerpiece of scattering theory for both electromagnetic and de Broglie waves.
we may notice that $\psi_s$ is just a response of a linear system to a certain “excitation” (represented by the right-hand part) that is fixed, i.e. does not depend on the solution. Hence we can present $\psi_s$ as a sum of responses to elementary excitations from elementary volumes $d^3r'$:

$$\psi_s(r) = \frac{2m}{\hbar^2} \int U(r')\psi_0(r')G(r,r')d^3r'. \quad (3.68)$$

Here $G(r, r')$ is the spatial Green’s function, defined as such an elementary response of the free-space Schrödinger equation to a point excitation, i.e. the solution of the following equation

$$\left(\nabla^2 + k^2\right) G = \delta(r - r'). \quad (3.69)$$

But we already know the physically-relevant spherically-symmetric solution of this equation – see Eq. (7) and its discussion:

$$G(r, r') = \frac{f_+}{R} e^{ikR}, \quad (3.70)$$

so that we need just to calculate the coefficient $f_+$ for Eq. (67). This can be done in several ways, for example by noticing that at $r << k^{-1}$, the second term in Eq. (70) is negligible, and it is reduced to the well-known Poisson equation with delta-functional right-hand part, which describes, for example, the electrostatic potential generated by a point electric charge. Either recalling the Coulomb law, or applying the Gauss theorem, we readily get the asymptote

$$G \to -\frac{1}{4\pi R}, \quad \text{at } kr << 1, \quad (3.71)$$

which is compatible with Eq. (70) only if $f_+ = -1/4\pi$, i.e. if

$$G(r, r') = -\frac{1}{4\pi R} e^{ikR}. \quad (3.72)$$

Plugging this result into Eq. (68), we get the final solution of Eq. (67):

$$\psi_s(r) = -\frac{m}{2\hbar^2} \int U(r')\frac{\psi_0(r')}{R} e^{ikR} d^3r'. \quad (3.73)$$

Note that if function $U(r)$ is smooth, the singularity in the denominator is integrable (i.e. not dangerous); indeed, the contribution of a sphere of radius $R \to 0$, with the center in point $r' = 0$, scales as

$$\int_{R<\tilde{R}} \frac{d^3R}{R} = 4\pi \int_{0}^{\tilde{R}} \frac{R^2 dR}{R} = 4\pi \int_{0}^{\tilde{R}} RdR = 2\pi\tilde{R}^2 \to 0. \quad (3.74)$$

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27 Please notice both the similarity and difference between this Green’s function and the propagator discussed in Sec. 2.1. In both cases, we use the linear superposition principle to solve wave equations, but while Eq. (68) gives the solution of the inhomogeneous equation (67), Eq. (2.44) does that for a homogeneous Schrödinger equation in which the wave sources are presented by initial conditions rather than by equation’s right-hand part.

28 See, e.g., EM Sec. 1.2.
Actually, Eq. (73) gives us more than we wanted: it evaluates the scattered wave at any point, including those within of the scattering object, while our goal was to find the wave far from the scatterer – please revisit Fig. 8 if you need. However, before going to that limit, we can use the general formula to find the quantitative criterion of the Born approximation’s validity. Indeed, let us estimate the magnitude of the right hand part of this equation, for a scatterer of linear size ~a, and the potential magnitude scale $U_0$, in two limits:

(i) If $ka \ll 1$, then inside the scatterer (i.e., at distances $r' \sim a$), both $\psi_0 \sim \exp\{ikr\}$ and the second exponent under the integral change slowly, so that a crude estimate of the solution is

$$|\psi_s| \sim \frac{m}{2\pi \hbar^2} U_0 |\psi_0| a^2. \tag{3.75}$$

(ii) In the opposite limit $ka \gg 1$, the integration along one of the dimensions (that of the wave propagation) is cut out on distances of the order of the de Broglie wavelength $k^{-1}$, so that the integral is correspondingly smaller:

$$|\psi_s| \sim \frac{m}{2\pi \hbar^2} U_0 |\psi_0| \frac{a^2}{ka}. \tag{3.76}$$

Since the reduction of Eq. (66) to Eq. (67) requires $|\psi_s| << |\psi_0|$ everywhere within the scatterer, we may now formulate the conditions of this requirement as

$$U_0 << \frac{\hbar^2}{ma^2} \max[ka, 1]. \tag{3.77}$$

In the first factor of the right-hand part, we may readily recognize the scale of the kinetic (quantum-confinement) energy $E_a$ of the particle inside a quantum well of size ~a, so that the Born approximation is valid essentially if the potential energy of particle’s interaction with the scatterer is smaller than $E_a$. Note, however, that estimates (75) and (76) are not valid in special situations when the effects of scattering accumulate in some direction. This is frequently the case for small scattering angles in extended objects (when $ka \gg 1$ but $ka\theta < 1$), and especially in 1D (or quasi-1D) scatterers oriented along the incident particle beam.

Now let us proceed to large distances $r >> r' \sim a$, and simplify Eq. (73) using an approximation similar to the dipole expansion in electrodynamics. In denominator’s $R$, we can merely ignore $r'$ in comparison with $r$, but the exponent requires more care, because even if $r' \sim a << r$, the product $kr' \sim ka$ may still be larger than 1. In the first approximation in $r'$, we can take (Fig. 9a):

$$29 \text{ See, e.g., EM Sec. 8.2.}$$
and since the directions of vectors $k$ and $r$ coincide, i.e. $k = kn_r$, 

\[ kR \approx kr - k \cdot r', \quad \text{and} \quad e^{ikR} \approx e^{ikr} e^{-ik \cdot r'}, \]  

With this replacement, and the incident wave in form (60), the Born approximation yields 

\[ \psi_s(r) = -\frac{m}{2\pi\hbar^2} \frac{a_0}{r} e^{ikr} \int U(r') e^{-i(k-k_0) \cdot r'} d^3 r'. \]  

This relation may be presented in a general form

\[ \psi_s = a_0 \frac{f(k, k_0)}{r} e^{ikr}, \]  

where $f(k, k_0)$ is called the scattering function. Its physical sense becomes clear from the calculation of the corresponding probability current density $j$. For that, generally we need to use Eq. (1.47) with the gradient operator having all spherical-coordinate components. However, at $kr >> 1$ the main contribution to $\nabla \psi_s$, proportional to $k >> 1/r$, is provided by the term $\exp\{ikr\}$ which changes fast in the common direction of vectors $r$ and $k$, so that

\[ \nabla \psi_s \approx n_r \frac{\partial}{\partial r} \psi_s \approx k \psi_s, \quad \text{at} \quad kr >> 1. \]  

so that Eq. (1.47) yields

\[ j_s(\theta) \approx \frac{\hbar}{m} |a_0|^2 \frac{|f(k, k_0)|^2}{r^2} k. \]  

Since this vector is parallel to $k$ and hence to $r$, the flux in the nominator of Eq. (58), i.e. the probability current per unit solid angle, is just $r^2 j_s$. Hence, the differential cross-section is simply

\[ \frac{d\sigma}{d\Omega} = \frac{j_s r^2}{j_0} = |f(k, k_0)|^2, \]  

and the total cross-section is

\[ \sigma = \int |f(k, k_0)|^2 d\Omega, \]  

so that the scattering function $f(k, k_0)$ gives us everything we need (and in fact more, because the function also contains information about the phase of the scattered wave).

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30 It is easy to prove that this form is an asymptotic form of any solution $\psi_s$ of the scattering problem (even that beyond the Born approximation) at sufficiently large distances $r >> a, k^{-1}$.

31 Note that function $f$ has the dimension of length, and does not account for the incident wave. This is why sometimes a dimensionless function, $S = 1 + 2ikf$, is used instead. This function $S$ is called the scattering matrix, because it may be considered as a natural generalization of the 1D matrix $S$, defined by Eq. (2.133), to higher dimensionality.

32 See, e.g., MA Eq. (10.8).
According to Eq. (80), in the Born approximation the scattering function may be presented as the Born integral
\[ f(k,k_0) = -\frac{m}{2\pi \hbar^2} \int U(r) e^{-i q \cdot r} d^3r, \] (3.86)
where for the notation simplicity I have replaced \( r' \) with \( r \), and also introduced the scattering vector
\[ q = k - k_0, \] (3.87)
with length \( q = 2k \sin(\theta/2) \), where \( \theta \) is the scattering angle between vectors \( k \) and \( k_0 \) – see Fig. 9b. For the differential cross-section, Eq. (86) yields
\[ \frac{d\sigma}{d\Omega} = \left( \frac{m}{2\pi \hbar^2} \right)^2 \left| \int U(r) e^{-i q \cdot r} d^3r \right|^2, \] (3.88)
and the total cross-section may be now readily calculated from the first of Eqs. (59).33

This is the main result of this section; it may be further simplified for spherically-symmetric scatterers, with
\[ U(r) = U(r). \] (3.89)
Here, it is convenient to present the exponent in the Born integral as \( \exp\{-i q \cdot r \cos \chi \} \), where \( \chi \) is the angle between vectors \( k \) (i.e. the direction \( n \), toward the detector) and \( q \) (rather than the incident wave vector \( k_0 \!) \) – see Fig. 9b. Now, for fixed \( q \), we can take this vector’s direction as the polar axis of a spherical coordinate system, and reduce Eq. (86) to a 1D integral:
\[ f(k,k_0) = -\frac{m}{2\pi \hbar^2} \int r^2 dr U(r) \int_0^{2\pi} \int_0^\pi \sin \chi d\chi \exp\{-i q r \cos \chi \} \]
\[ = -\frac{m}{2\pi \hbar^2} \int r^2 dr U(r) 2\pi \frac{2\sin qr}{qr} = -\frac{2m}{\hbar^2 q} \int U(r) \sin(qr) rdr. \] (3.90)

As a simple example, let us use the Born approximation to analyze scattering on the following spherically-symmetric potential:
\[ U(r) = U_0 \exp\left\{ -\frac{r^2}{2a^2} \right\}. \] (3.91)

In this particular case, it is better to avoid the temptation to exploit the spherical symmetry by using Eq. (90), and instead use the generic Eq. (88), because it falls apart into a product of three similar Cartesian factors:
\[ f(k,k_0) = -\frac{mU_0}{2\pi \hbar^2} I_x I_y I_z, \] (3.92)

with

33 Note that according to Eq. (88), in the Born approximation the scattering intensity does not depend on the sign of potential \( U \), and also that scattering in a certain direction is completely determined by a specific Fourier harmonic of function \( U(r) \), namely by the harmonic with the wave vector equal to the scattering vector \( q \).
\[ I_x = \int_{-\infty}^{\infty} \exp \left\{ -\left( \frac{x^2}{2a^2} + i q_x x \right) \right\} dx, \]  

Equation (3.93)

and similar integrals for \( I_y \) and \( I_z \). From Chapter 2, we already know that Gaussian integrals like \( I_x \) may be readily worked out by complementing the exponent to the full square, in our current case giving

\[ I_x = (2\pi)^{1/2} a \exp \left\{ -\frac{q_x^2 a^2}{2} \right\}, \text{ etc.,} \]

Equation (3.94)

so that, finally,

\[ \frac{d\sigma}{d\Omega} = \left| f(k, k_0) \right|^2 = \left( \frac{mU_0}{2\pi\hbar^2} I_x I_x I_z \right)^2 = 2\pi a^2 \left( \frac{mU_0 a^2}{\hbar^2} \right)^2 e^{-q^2 a^2}. \]

Equation (3.95)

Now, the total cross-section \( \sigma \) is an integral of \( d\sigma/d\Omega \) over all directions of vector \( k \). Since in our case the scattering intensity does not depend on the azimuthal angle \( \varphi \), the integration is reduced to that over the scattering angle \( \theta \) (Fig. 9b):

\[
\sigma = \frac{1}{2\pi} \int_0^{2\pi} \frac{d\sigma}{d\Omega} \sin \theta d\theta = 4\pi^2 a^2 \left( \frac{mU_0 a^2}{\hbar^2} \right)^2 \int_0^{2\pi} \sin \theta d\theta \exp \left\{ -\left( \frac{2k \sin \frac{\theta}{2}}{a} \right)^2 \right\} \\
= 4\pi^2 a^2 \left( \frac{mU_0 a^2}{\hbar^2} \right)^2 \int_0^{\pi} \exp \left\{ -2k^2 a^2 (1 - \cos \theta) \right\} d(1 - \cos \theta) = \frac{2\pi^2}{k^2} \left( \frac{mU_0 a^2}{\hbar^2} \right)^2 \left[ 1 - e^{-4k^2 a^2} \right].
\]

Equation (3.96)

Let us analyze these formulas. In the low-energy limit, \( ka \ll 1 \) (and hence \( qa \ll 1 \) for any scattering angle), the scattered wave is virtually isotropic: \( d\sigma/d\Omega \approx \text{const} \) – a very typical feature of scattering by small objects, in any approximation. Notice that in this limit, the Born expression for \( \sigma \),

\[ \sigma \approx 8\pi^2 a^2 \left( \frac{mU_0 a^2}{\hbar^2} \right)^2, \]

Equation (3.97)

is only valid if \( \sigma \) is much smaller than the scale \( a^2 \) of the physical cross-section of the scatterer.

In the opposite, high-energy limit \( ka \gg 1 \), the scattering is dominated by small angles \( \theta \approx q/k \sim 1/ka \sim \lambda/a \):

\[ \frac{d\sigma}{d\Omega} \approx 2\pi a^2 \left( \frac{mU_0 a^2}{\hbar^2} \right)^2 \exp \left\{ -k^2 a^2 \frac{\theta^2}{2} \right\}. \]

Equation (3.98)

This is, again, very typical for diffraction. Notice, however, that due to the smooth character of the Gaussian potential (91), the diffraction pattern exhibits no oscillations; such oscillations of \( d\sigma/d\Omega \) as function of angle naturally appear for potentials with sharp borders – see, e.g., Problems 2 and 3.

The Born approximation, while being very simple and used more often than any other scattering theory, is not without substantial shortcomings, as is clear from the following example. It is not too difficult to prove the following general optical theorem, valid for an arbitrary scatterer:
However, Eq. (86) shows that in the Born approximation, function $f$ is purely real at $q = 0$ (i.e. $k = k_0$), and hence cannot satisfy the optical theorem. Even more evidently, it cannot describe such a simple effect as a dark shadow ($\psi \approx 0$) cast by an opaque object (say, with $U_0 >> E$).

There are several ways to improve the Born approximation, while still holding the general idea of approximate treatment of $U$.

(i) Instead of the main assumption $\psi_s \propto U_0$, we can use a complete perturbation series:

$$\psi = \psi_1 + \psi_2 + \ldots$$

with $\psi_n \propto U_0^n$, and find successive approximations $\psi_n$ one by one. In the 1st approximation we of course return to the Born formula, but already the 2nd approximation yields

$$\text{Im} f_2(k_0, k_0) = \frac{k}{4\pi} \sigma_1,$$

where $\sigma_1$ is the full cross-section calculated in the 1st approximation, so that the optical theorem (99) is “almost” satisfied. 34

(ii) As was mentioned above, the Born approximation does not work very well for small-angle scattering by extended objects. This deficiency may be corrected by the so-called eikonal approximation (from Greek word $\varepsilon\iota\kappa\omicron\nu$, meaning “icon”) that replaces the plane wave exponent $\exp\{ik_0x\}$ representation of the incident wave by a WKB-like exponent, though still in the first nonvanishing approximation in $U \rightarrow 0$:

$$e^{ikx} \rightarrow \exp\left\{i \int_0^x k(x')dx'\right\} = \exp\left\{i \left[\frac{2m[E-U(x')]}{\hbar} \right]^{1/2} \right\} \approx e^{ikx} - \frac{m}{\hbar^2 k} \int_0^x U(x')dx'. $$

This approximation’s results satisfy the optical theorem (99) already in the 1st approximation in $U$.

### 3.4. Energy bands in higher dimensions

In Sec. 2.5, we have discussed the 1D band theory for potential profiles $U(x)$ that obey the periodicity condition (2.192). For what follows, let us notice that that condition may be rewritten as

$$U(x + X) = U(x),$$

This is one of forms of the Lipmann-Schwinger equation that is exactly equivalent to the differential Schrödinger equation (66) but is more convenient for some applications, in particular for the calculation of higher approximations $\psi_n$. Unfortunately, I will have not time to discuss this approach in detail and have to refer the reader, for example, to either Chapter 9 of the textbook by L. Schiff, Quantum Mechanics, 3rd ed., McGraw-Hill, 1968, or (for even more details) to monograph by J. Taylor, Scattering Theory, Dover, 2006.
where \( X = \tau a \), with \( \tau \) being an arbitrary integer. One can say that the set of points \( X \) forms a periodic 1D lattice in the direct (x-) space. We have also seen that each Bloch state (i.e., each eigenstate of the Schrödinger equation for such periodic potential) is characterized by the quasi-momentum \( \hbar q \) and its energy does not change if \( q \) is changed by a multiple of \( 2\pi a \). Hence if we form, in the reciprocal (k-) space, a 1D lattice of points \( Q = lb \), with \( b = 2\pi a \) and integer \( l \), any pair of points from these two mutually reciprocal lattices satisfies the following rule:

\[
\exp[iQX] = \exp\left(\frac{\pi l}{a} \tau \right) = e^{\frac{2\pi l \tau}{a}} = 1.
\]

In this form, the results of Sec. 2.5 may be readily extended to \( d \)-dimensional periodic potentials whose translational symmetry obeys the following generalization of Eq. (103):

\[
U(r + R) = U(r),
\]

where points \( R \), which may be numbered by \( d \) integers \( \tau_j \), form the so-called Bravais lattice\(^{35}\) of points

\[
R = \sum_{j=1}^{d} \tau_j a_j,
\]

with \( d \) primitive vectors \( a_j \). The simplest example of a 3D Bravais lattice are given by the simple cubic lattice (Fig. 10a), which may be described by the system of mutually perpendicular primitive vectors \( a_j \) of equal length. However, not in any lattice these vectors are perpendicular; for example Figs. 10b and 10c show possible sets of the primitive vectors describing the face-centered cubic lattice (fcc) and body-centered cubic lattice (bcc). In 3D, the science of crystallography, based on the group theory, distinguishes, by their symmetry properties, 14 Bravais lattices grouped into 7 different lattice systems\(^{36}\).

Fig. 3.10. The simplest (and most common) 3D Bravais lattices: (a) simple cubic, (b) face-centered cubic (fcc), and (c) body-centered cubic (bcc), and possible choices of their primitive vector sets (blue arrows).

Note, however, not all highly symmetric sets of points form Bravais lattices. As probably the most striking example, nodes of the very simple 2D honeycomb lattice (Fig. 11a) cannot be described by

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\(^{35}\) Named after A. Bravais, the crystallographer who introduced this notion in 1850.

\(^{36}\) The strongest motivation for the band theory is provided by properties of solid crystals. Thus it is not surprising that perhaps the most clear, well illustrated introduction to the Bravais lattices may be found in Chapters 4 and 7 of the famous textbook by N. Ashcroft and N. Mermin, *Solid State Physics*, Saunders College, 1976.
a Bravais lattice - while the 2D hexagonal lattice, shown in Fig. 11b, cannot. The most prominent 3D case of such a lattice is the diamond structure (Fig. 11c), which describes, in particular, atoms of world’s most important crystal – silicon.\textsuperscript{37} In cases like these, the band theory is much facilitated by the fact that the Bravais lattices using some point assemblies (called \textit{primitive unit cells}) may describe these point systems. For example, Fig. 11a shows the possible choice of primitive vectors for the honeycomb structure,\textsuperscript{38} with the primitive unit cell formed by any two adjacent points of the original lattice (say, within the dashed ellipses in Fig. 11a). Similarly, the diamond lattice may be described as the fcc Bravais lattice with two-point primitive unit cell.\textsuperscript{39}

Now we are ready for the following generalization of the 1D Bloch theorem, given by Eqs. (2.193) and (2.210), to higher dimensions. Any eigenfunction of the Schrödinger equation describing particle’s motion in the periodic potential (105) may be presented either as

\[
\psi (r + R) = \psi (r) e^{i \mathbf{q} \cdot \mathbf{R}},
\]

or as

\[
\psi (r) = u (r) e^{i \mathbf{q} \cdot \mathbf{r}}, \quad \text{with} \quad u (r + R) = u (r),
\]

where the quasi-momentum \( \mathbf{q} \) is again a constant of motion, but now is a vector.

\[\text{Fig. 3.11. Some important periodic structures that require two-point primitive cells for their Bravais lattice presentation: (a) 2D honeycomb lattice and their primitive vectors and (c) 3D diamond lattice. For a contrast, panel (b) shows the 2D hexagonal structure which forms a Bravais lattice with a single-point primitive cell.}\]

The key notion of the band theory is the \textit{reciprocal lattice} in the wavevector space, formed as

\[
\mathbf{Q} = \sum_{j=1}^{d} l_j \mathbf{b}_j,
\]

\textsuperscript{37} It may be best understood as the sum of two fcc lattices of side \( a \), mutually shifted by vector \( \{1, 1, 1\}a/4 \), so that the distances between each point of the combined lattice and its 4 nearest neighbors (see the thick gray lines in Fig. 11c) are all equal.

\textsuperscript{38} This structure is presently very popular due to the recent discovery of \textit{graphene} – isolated monolayer sheets of carbon atoms arranged in a honeycomb lattice with the interatomic distance of 0.142 nm.

\textsuperscript{39} A harder case is presented by \textit{quasicrystals} (whose idea may be traced down to medieval Islamic tilings, but was discovered in natural crystals, by D. Shechtman \textit{et al.}, only in 1984), which obey high (say, 5-fold) rotational symmetry, but cannot be described by a Bravais lattice with any finite primitive unit cell. For a popular review of quasicrystals see, for example, P. Stephens and A. Goldman, \textit{Sci. Amer.} 264, #4, 24 (1991).
with integer $l_j$, and vectors $b_j$ selected in such way that the following generalization of Eq. (104) is valid for any pair of points of the direct and reciprocal lattices:

$$e^{iQ \cdot R} = 1. \quad (3.110)$$

The importance of lattice $Q$ is immediately clear from the first formulation of the Bloch theorem, given by Eq. (107): if we add to $q$ any vector $Q$ of the reciprocal lattice, the wavefunction does not change. This means that all information about the system is contained in just one elementary cell of the reciprocal space $q$. Its most frequent choice, called the 1st Brillouin zone, is the set of all points $q$ that are closer to the origin than to any other point of lattice $Q$.

It is easy to see that primitive vectors $b_j$ of the reciprocal 3D lattice\(^{40}\) may be constructed from those of the initial, direct lattice as

$$b_1 = 2\pi \frac{a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)}, \quad b_2 = 2\pi \frac{a_3 \times a_1}{a_2 \cdot (a_2 \times a_3)}, \quad b_3 = 2\pi \frac{a_1 \times a_2}{a_3 \cdot (a_2 \times a_3)}. \quad (3.111)$$

Indeed, from the “operand rotation rule” of the vector algebra\(^{41}\) it is evident that $a_j \cdot b_{j'} = 2\pi \delta_{jj'}$. Hence, the exponent in the left-hand part of Eq. (110) is reduced to

$$e^{iQ \cdot R} = \exp\{2\pi i (l_1 \tau_1 + l_2 \tau_2 + l_3 \tau_3)\}. \quad (3.112)$$

Since all $l_j$ and $\tau_j$ are integers, the expression in the parentheses is also an integer, so the exponent indeed equals 1, thus satisfying the definition of the reciprocal lattice given by Eq. (110).

As the simplest example, let us return to the simple cubic lattice of period $a$ (Fig. 10a), oriented in space so that

$$a_1 = an_x, \quad a_2 = an_y, \quad a_3 = an_z. \quad (3.113)$$

According to Eq. (111), its reciprocal lattice is (of course) also cubic:

$$Q = \frac{2\pi}{a} (l_x n_x + l_y n_y + l_z n_z), \quad (3.114)$$

so that the 1st Brillouin zone is a cube with side $b = 2\pi/a$. Almost similarly simple calculations show that the reciprocal lattice of fcc is bcc, and vice versa. Figure 12 shows the resulting 1st Brillouin zone of the fcc lattice.

The notion of the reciprocal lattice\(^{42}\) makes the multi-dimensional band theory not much more complex than that in 1D, especially for numerical calculations, at least for the single-point Bravais lattices. Indeed, repeating all the steps that have led to Eq. (2.218), but now with a $d$-dimensional Fourier expansion of functions $U(r)$ and $u(d)$, we readily get its generalization:

$$\sum_{l \neq 0} U_{l-l} u_l = (E - E_l) u_l, \quad (3.115)$$

\(^{40}\) For the 2D case ($j = 1, 2$), one may use, for example, the first two formulas of Eq. (111) with $a_3 = a_1 \times a_2$.

\(^{41}\) See, e.g., MA Eq. (7.6).

\(^{42}\) This notion is also the main starting point of X-ray diffraction studies of crystals, because it allows rewriting the well-known Bragg condition for diffraction peaks in an extremely simple form of the momentum conservation law: $k = k_0 + Q$, where $k_0$ and $k$ are the wave vectors of the, respectively, incident and diffracted photon.
where \( \mathbf{l} \) is now a \( d \)-dimensional vector of integer indices \( l_j \). The summation in Eq. (115) should be carried over all (essential) components of this vector (i.e. over all relevant nodes of the reciprocal lattice), so writing a corresponding computer code requires a bit more care than in 1D; however, this is just a homogeneous system of linear equations, and numerous routines of finding its eigenvalues \( E \) are readily available from both public sources and commercial software packages.\(^{43}\)

What is indeed more complex than in 1D is the presentation (and hence the comprehension :-) of the calculation results and experimental data. Typically, the presentation is limited to plotting the Bloch state eigenenergy as a function of components of vector \( \mathbf{q} \) along certain special directions the reciprocal space of quasi-momentum (see, e.g., the lines shown in Fig. 12), typically plotted on single panel. Figure 12 shows perhaps the most famous (and certainly the most practically important) of such plots, the band structure of silicon. The dashed horizontal lines mark the “indirect” gap of width 1.12 eV between the “valence” and “conduction” energy bands, which is the playground of virtually all silicon-based electronics.

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\(^{43}\) See, e.g., MA Sec. 16 (iv).
In order to understand the reason of this band structure presentation complexity, let us see how we would start to develop the weak-potential approximation for the simplest case of a 2D square lattice (which is a subset of the cubic lattice, with \( \tau_3 = 0 \)). Its 1st Brillouin zone is of course also a square, of area \( (2\pi a)^2 \). Let us draw the lines of constant energy of a free particle \((U = 0)\) in this zone. Repeating the arguments of Sec. 2.7 (see especially Fig. 2.28 and its discussion), we should conclude that Eq. (2.216) should now be generalized as follows,

\[
E = E_1 = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left[ \left( q_x - \frac{2\pi \tau_x}{a} \right)^2 + \left( q_y - \frac{2\pi \tau_y}{a} \right)^2 \right],
\]

(3.116)

with all possible integers \( l_x \) and \( l_y \). Considering the result only within the 1st Brillouin zone, we see that as energy \( E \) grows, the lines of equal energy evolve as shown in Fig. 14. Just like in 1D, the weak-potential effects are only important at the Brillouin zone boundaries, and may be crudely considered as the appearance of narrow energy gaps, but one can see that the band structure in \( \mathbf{q} \)-space is complex enough even without these effects.

![Fig. 3.14. Lines of constant energy \( E \) of a free particle, within the 1st Brillouin zone of a square Bravais lattice, for: (a) \( E/E_1 \approx 0.95 \), (b) \( E/E_1 \approx 1.05 \); and (c) \( E/E_1 \approx 2.05 \), where \( E_1 = \pi^2 \hbar^2/2ma^2 \).](image)

The tight-binding approximation is usually easier to follow. For example, for the same square 2D lattice, we may repeat the arguments that have led us to Eq. (2.203), to write 44

\[
\frac{\hbar^2}{2m} \frac{da_{0,0}}{dt} = -\delta_n \left( a_{-1,0} + a_{+1,0} + a_{0,+1} + a_{0,-1} \right),
\]

(3.117)

where indices correspond to the deviations of integers \( \tau_x \) and \( \tau_y \) from an arbitrarily selected minimum of the potential energy - and hence wavefunction’s “hump” quasi-localized at this minimum. Now, looking for the stationary solution of these equations, that corresponds to the Bloch theorem (107), instead of Eq. (2.206) we get

\[
E = E_n + \varepsilon_n = E_n - \delta_n \left( e^{iq_x a} + e^{-iq_x a} + e^{iq_y a} + e^{-iq_y a} \right) = E_n - 2\delta_n \left( \cos q_x a + \cos q_y a \right)
\]

(3.118)

Figure 15 shows this result, within the 1st Brillouin zone, in two forms: as the color-coded lines of equal energy and as a 3D plot (also enhanced by color).

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44 Actually, using the same values of \( \delta \), in both directions implies some sort of symmetry of the quasi-localized states. For example, \( s \)-states of axially-symmetric potentials (see the next section) always have such a symmetry.
It is evident that the plots of this function along different lines on the $q$-plane, for example along one of axes (say, $q_x$) and along a diagonal of the $1$st Brillouin zone (say, $q_x = q_y$) give different curves, qualitatively similar to those of silicon (Fig. 13). The latter structure is complicated by the fact that the primitive cell of their Bravais lattices contains more than 2 atoms – see Fig. 11c and its discussion. In this case, even the tight-binding picture becomes more complex. Indeed, even if the atoms in the different positions of the primitive unit cell are similar (as they are, for example, in both graphene and silicon), and hence the potential well shape near those points and the corresponding local wavefunctions $u(r)$ are similar as well, the Bloch theorem (which only pertains to Bravais lattices!) does not forbid them to have different complex amplitudes $a(t)$ whose time evolution should be described by a specific differential equation.

For example, in order to describe the honeycomb lattice shown in Fig. 11a, we have to prescribe different amplitudes to the “top” and “bottom” points of its primitive cell - say, $\alpha$ and $\beta$, correspondingly. Since each of these points is surrounded (and hence weakly interacts) with 3 neighbors of the opposite type, instead of Eq. (117) we have to write two equations

$$i\hbar \frac{d\alpha}{dt} = -\delta_n \sum_{j=1}^{3} \beta_j, \quad i\hbar \frac{d\beta}{dt} = -\delta_n \sum_{j'=1}^{3} \alpha_{j'};$$

(3.119)

where each summation is over 3 next-neighbor points. (I am using different summation indices just to emphasize that these directions are different for the “top” and “bottom” points of the primitive cell – see Fig. 11a.) Now using the Bloch theorem (107) in the form similar to Eq. (2.205), we get two coupled systems of linear algebraic equations:

$$(E - E_n)\alpha = -\delta_n \beta \sum_{j=1}^{3} e^{i\mathbf{q}\cdot\mathbf{r}_j}, \quad (E - E_n)\beta = -\delta_n \alpha \sum_{j'=1}^{3} e^{i\mathbf{q}\cdot\mathbf{r}'_{j'}};$$

(3.120)

where $\mathbf{r}_j$ and $\mathbf{r}'_{j'}$ are the next-neighbor positions, as seen from the top and bottom points, respectively. Writing the condition of consistency of this system, we get two equal and opposite values for energy correction for each value of $\mathbf{q}$:

$$E_\pm = E_n \pm \delta_n \Sigma^{1/2}, \quad \text{where } \Sigma \equiv \sum_{j,j'=1}^{3} e^{i\mathbf{q}(\mathbf{r}_j + \mathbf{r}'_{j'})}.$$

(3.121)
According to Eq. (120), these two energy bands correspond to the phase shifts (on the top of the regular Bloch shift $\mathbf{q} \cdot \Delta \mathbf{r}$) of either 0 or $\pi$ between the adjacent quasi-localized wavefunctions $u(\mathbf{r})$.

The most interesting corollary of such energy symmetry, augmented by the honeycomb lattice symmetry, is that for certain values $\mathbf{q}_D$ of vector $\mathbf{q}$ (that turn out to be in each of 6 corners of the honeycomb-shaped 1st Brillouin zone), the double sum $\Sigma$ vanishes, i.e. the two band surfaces $E_{\pm}(\mathbf{q})$ touch each other. As a result, in vicinities of these Dirac points the dispersion relation is linear:

$$E_{\pm} |_{ \mathbf{q} = \mathbf{q}_D } \approx E_n \pm \hbar v_n | \tilde{\mathbf{q}} | \quad \text{where} \quad \tilde{\mathbf{q}} \equiv \mathbf{q} - \mathbf{q}_D,$$

(3.122)

with $v_n \propto \delta_n$ being a constant with the dimension of velocity (for graphene, close to $10^6$ m/s). Such a linear dispersion relation ensures several interesting transport properties of graphene. For their discussion, I have to refer the reader to special literature.

3.5. Axially-symmetric systems

I cannot conclude this chapter (and hence our review of wave mechanics) without addressing the issue of eigenstates and eigenvalues at full confinement in multi-dimensional potentials $U(\mathbf{r})$. For an arbitrary potential, the stationary Schrödinger equation does not have an analytical solution, but a substantial symmetry of function $U(\mathbf{r})$ may make such solution possible. This pertains, in particular, to the axial symmetry in 2D problems and the spherical symmetry in 3D problems, which are typical for several important situations (or their reasonable models), especially in atomic and nuclear physics.

In rare cases such symmetry may be exploited by the separation of variables in Cartesian coordinates. The most famous example is the $d$-dimensional harmonic oscillator, i.e. a particle moving inside the potential

$$U = \frac{m \omega_0^2}{2} \sum_{j=1}^{d} r_j^2.$$

(3.123)

Separating the variables exactly as we did for the rectangular quantum well (see Sec. 1.5), for each degree of freedom we get the Schrödinger equation (2.268) of a 1D oscillator, whose eigenfunctions are given by Eq. (2.278), and the energy spectrum is described by Eq. (2.114). As a result, the total energy spectrum may be indexed by a vector $\mathbf{n} = \{n_1, n_2, \ldots, n_d\}$ of $d$ independent integers (quantum numbers):

$$E_n = \hbar \omega_0 \left( \sum_{j=1}^{d} n_j + \frac{d}{2} \right),$$

(3.124)

---

45 This term is based on a (pretty loose) analogy with the Dirac theory of relativistic quantum mechanics, to be discussed in Chapter 9 below. Namely, in the vicinity of a Dirac point (122), Schrödinger equations (119), and hence the dispersion relation (122), may be obtained from the effective Hamiltonian $\hat{H}_n = \hbar v_n \hat{\sigma} \cdot \tilde{\mathbf{q}}$. (Since vector $\tilde{\mathbf{q}}$ is two-dimensional, this Hamiltonian employs only two of three Pauli matrices.) This expression reminds the first term of Dirac’s Hamiltonian (9.97), which is defined, however, in a different Hilbert space.

46 See, e.g., a recent review by A. Castro Neto et al., Rev. Mod. Phys. 81, 109 (2009). Note that transport properties of graphene are determined by coupling of $2p_z$ electron states of carbon atoms, whose wavefunctions are proportional to $\exp\{\pm i \varphi\}$ rather than are axially-symmetric as implied by Eqs. (120). However, due to the lattice symmetry this fact does not affect the dispersion relation $E(\mathbf{q})$. 
all of them ranging from 0 to \( \infty \). Note that every energy level of this system, with the only exception of the ground state,

\[
\psi_g = \prod_{j=1}^{d} \psi_0(r_j) = \frac{1}{\pi^{d/4} x_0^{d/2}} \exp \left\{ -\frac{1}{2x_0^2} \sum_{j=1}^{d} r_j^2 \right\},
\]

(3.125)
is degenerate: several different wavefunctions, each with its own different set of quantum numbers \( n_j \), but the same value of their sum, have the same energy.

However, the harmonic oscillator problem is an exception: for other central- and spherically-symmetric problems the solution is made easier by using more appropriate coordinates. Let us start with the simplest axially-symmetric problem: the so-called planar rigid rotator (or “rotor”), i.e. a particle constrained (confined) to move along a plane, round circle of radius \( R \) (Fig. 15).47

\[
\text{Fig. 3.16. Planar rigid rotator.}
\]

The planar rotator has just one degree of freedom, say the displacement arc \( l = R\phi \). So, its classical energy (and Hamiltonian function) is \( H = p_l^2/2m \), \( p_l = mv = m(dl/dt) \). This function is similar to that of a free 1D particle (with the replacement \( x \rightarrow l \)), and hence rotator’s quantum properties may be described by a similar Hamiltonian operator:

\[
\hat{H} = \frac{\hat{p}_l^2}{2m}, \quad \text{with} \quad \hat{p}_l = -i\hbar \frac{\partial}{\partial l},
\]

(3.126)

and its eigenfunctions have a similar structure:

\[
\psi = Ce^{ikl}.
\]

(3.127)

The “only” new feature is that in the rotator, all observables should be \( 2\pi R \)-periodic functions of \( l \), and hence, as we have already discussed in the context of the magnetic flux quantization (see Fig. 4 and its discussion), as the particle makes one turn about the center, its wavefunction’s phase \( kl \) may only change by \( 2\pi n \), with an arbitrary integer \( n \) (from \( -\infty \) to \( +\infty \)),:

\[
\psi_n(l + 2\pi R) = \psi_n(l)e^{2\pi in}.
\]

(3.128)

With eigenfunctions (127), this immediately gives condition gives \( k \ 2\pi R = 2\pi n \). Thus, wavenumber \( k \) can take only quantized values \( k_n = n/R \), so that the eigenfunctions should be indexed by \( n \):

\[
\psi_n = C_n \exp \left\{ in \frac{l}{R} \right\},
\]

(3.129)

47 This is a reasonable model for the confinement of light atoms, notably hydrogen, in some organic compounds.
and the energy spectrum is discrete:

\[
E_n = \frac{p_n^2}{2m} = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2}{2mR^2}.
\] (3.130)

So, while the free translation motion of a quantum particle is continuous, in the sense that its momentum has a continuous spectrum, its rotation is quantized – the most important fact, which has so many implications (including the existence of atoms, molecules, and hence us humans, and hence science including this course :-).

This simple model allows an exact analysis of external magnetic field effects on a quantum-confined motion of an electrically charged particle. Indeed, if this field is uniform and directed perpendicular to rotator’s plane, it does not violate the axial symmetry of the system. According to Eq. (26), in this case we have to generalize Eq. (126) as

\[
\hat{H} = \frac{1}{2m} \left( -i\hbar \frac{\partial}{\partial \varphi} - qA \right)^2.
\] (3.131)

Here, in contrast to the gauge choice (44), which was so instrumental in the Landau level problem, it is now clearly beneficial to take the vector-potential in a manifestly axially-symmetric form \( A = A(\rho) n_{\varphi} \), where \( \rho \equiv \{x, y\} \) is the 2D radius-vector. Using the well-known expression for curl in cylindrical coordinates, we can readily check that the requirement \( \mathbf{\nabla} \times \mathbf{A} = \mathbf{B} e_\varphi \), with \( \mathbf{B} = \text{const} \), is satisfied by the following function:

\[
A = n_{\varphi} \frac{B \rho}{2}.
\] (3.132)

For the planar rotator, \( \rho = R = \text{const} \), so that the stationary Schrödinger equation becomes

\[
\frac{1}{2m} \left( -i\hbar \frac{\partial}{\partial \varphi} - q\frac{B R}{2} \right)^2 \psi_n = E_n \psi_n.
\] (3.133)

A little bit surprisingly, this equation is still satisfied with the sine-wave eigenfunctions (127). Moreover, since the periodicity condition (128) is also unaffected by the applied magnetic field, we return to field-independent eigenfunctions (129). However, the field does affect the system’s energy:

\[
E_n = \frac{1}{2m} \left( \frac{\hbar n}{R} - q\frac{B R}{2} \right)^2 = \frac{\hbar^2}{2mR^2} \left( n - \frac{\Phi}{\Phi_0'} \right)^2,
\] (3.134)

where \( \Phi \equiv \pi R^2 B \) is the magnetic flux through the area limited by the particle’s trajectory, and \( \Phi_0' \equiv 2\pi\hbar/q \) is the “normal” magnetic flux quantum we have already met in the AB effect context – see Eq. (34) and its discussion. The field also changes the electric current of the particle in \( n \)-th state:

\[
I_n = q \frac{\hbar}{2m} \left[ \psi^*_n \left( \frac{\partial}{\partial \varphi} - i\frac{qB}{2\hbar} \right) \psi_n - \text{c.c.} \right] = q \frac{\hbar}{mR} \left| C_n \right|^2 \left( n - \frac{\Phi}{\Phi_0'} \right).
\] (3.135)

Normalizing wavefunction (129) to have \( W_n = 1 \), we get \( |C_n|^2 = 1/2\pi R \), so that Eq. (135) becomes

---

48 See, e.g., MA Eq. (10.5).
\[ I_n = I_0 \left( n - \frac{\Phi}{\Phi_0'} \right), \quad \text{with} \quad I_0 \equiv \frac{\hbar q}{2\pi m R^2}. \] (3.136)

Functions \( E_n(\Phi) \) and \( I_n(\Phi) \) are shown in Fig. 17. Note that since \( \Phi_0' \propto 1/q \), for any sign of the particle’s charge, \( dI_n/d\Phi < 0 \). It is easy to check that this means that the current is diamagnetic;\(^{49}\) i.e. corresponds to the Lenz rule of the Faraday’s electromagnetic induction: the field-induced current flows in such direction that its own magnetic field tries to compensate the external magnetic flux applied to the loop.

![Fig. 3.17. Effect of magnetic field on a charged planar rotator. Dashed lines show possible inelastic transitions between metastable and ground states, due to weak interaction with environment, as the magnetic field is being increased.](image)

This result may be interpreted as a different implementation of the AB effect.\(^{50}\) In contrast to the two-slit interference experiment that was discussed in Sec. 1, in the situation shown in Fig. 17 the particle is not absorbed by the detector, but travels around the ring continuously. As a result, its wavefunction is rigid: due to the boundary condition (128), the topological quantum number \( n \) is discrete, and magnetic field cannot change the wavefunction gradually. In this sense, the system is similar to a superconducting loop - see Fig. 4 and its discussion. The difference between these systems is two-fold:

(i) For a single charged particle, in a macroscopic systems with practicable values of \( q, R, \) and \( m \), the current scale \( I_0 \) is very small. For example, for \( m = m_e, q = -e, \) and \( R = 1 \text{ \mu m} \), Eq. (136) yields \( I_0 \approx 3 \text{ pA}.^{51} \) The contribution \( LI \sim \mu_0 R I_0 \approx 10^{-24} \text{ Wb} \) of the current so small into the net magnetic flux is

\(^{49}\) This effect, whose qualitative features remain the same for all 2D or 3D localized states (see Chapter 6 below), is frequently referred to as the orbital diamagnetism. In magnetic materials consisting of particles with uncompensated spins, this effect competes with another effect, spin paramagnetism - see, e.g., EM Sec. 5.5.

\(^{50}\) It is straightforward to check that Eqs. (133) and hence (135) remain valid even if the magnetic field lines do not touch the particle’s trajectory, and the field is localized well inside rotator’s ring.

\(^{51}\) Such persistent, macroscopic diamagnetic currents in non-superconducting systems may be experimentally observed, for example, by measuring the weak magnetic field generated by electrons in a system of a large number (~10^7) of similar conducting rings – see, e.g., L. Lévy et al., Phys. Rev. Lett. 64, 2074 (1990). Due to the
negligible in comparison with $\Phi_0' \sim 10^{-15}$ Wb, so that the quantization of $n$ does not lead to the magnetic flux quantization.

(ii) As soon as the magnetic field raises the eigenstate energy $E_n$ above that of another eigenstate $E_n'$, the former state becomes metastable, and weak interactions of the system with its environment (which are neglected in our simple model) may induce a quantum transition of the system to the lower-energy state, thus reducing the diamagnetic current’s magnitude – see the dashed lines in Fig. 17. The flux quantization in superconductors is much more robust to such perturbations.\(^{52}\)

Now let us return, for one more time, to Eq. (129), and see what do they give for one more observable, particle’s angular momentum

$$L \equiv \mathbf{r} \times \mathbf{p}, \quad (3.137)$$

In our current problem, vector $L$ has just one component perpendicular to the rotator plane,

$$L_z = Rp. \quad (3.138)$$

In classical mechanics, $L_z$ of the rotator should be conserved (due to the absence of external torque), but can take arbitrary values. In quantum mechanics the situation changes: with $p = \hbar k$, our result $k_n = n/R$ may be rewritten as

$$L_z = (L_z)_n = R\hbar k_n = \hbar n. \quad (3.139)$$

Thus, the angular momentum is quantized: it may be only a multiple of the Planck constant $\hbar$ - confirming Bohr’s guess – see Eq. (1.10). As we will see in Chapter 5, this result is very general (though may be modified by spin effects) and that wavefunctions (129) may be interpreted as eigenfunctions of the angular momentum operator.

In order to implement the planar rotator in our 3D world, we needed to provide rigid confinement of the particle both in the motion plane, and along radius $\rho$. Let us proceed to the more general problem when only the former confinement is strict, i.e. to a 2D particle moving in an arbitrary centrally-symmetric potential

$$U(\rho) = U(\rho). \quad (3.140)$$

Using the well-known expression for the 2D Laplace operator in polar coordinates,\(^{53}\) we may present the 2D stationary Schrödinger equation in the form

$$-\frac{\hbar^2}{2m} \left[ \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right] \psi + U(\rho)\psi = E\psi. \quad (3.141)$$

Separating the radial and angular variables as\(^{54}\)
\[ \psi = R(\rho)F(\varphi), \quad (3.142) \]

we get, after the division by \( \psi \) and multiplication by \( \rho^2 \), the following equation:

\[ \frac{-\hbar^2}{2m} \left[ \frac{\rho}{R} \frac{dR}{d\rho} \left( \rho^2 \frac{d^2 F}{d\rho^2} \right) + \frac{1}{F} \frac{d^2 F}{d\varphi^2} \right] + \rho^2 U(\rho) = \rho^2 E. \quad (3.143) \]

It is clear that the fraction \( (d^2 F/d\varphi^2)/F \) should be a constant (because all other terms of the equation may be only functions of \( \rho \) alone), so that we get for function \( F(\varphi) \) an ordinary differential equation,

\[ \frac{d^2 F}{d\varphi^2} + \nu^2 F = 0, \quad (3.144) \]

where \( \nu^2 \) is the variable separation constant. The fundamental solution of Eq. (144) is evidently \( F \propto \exp\{\pm i \nu \varphi \} \). Now requiring, as we did for the planar rotator, the \( 2\pi \) periodicity of any observable, i.e.

\[ F(\varphi + 2\pi) = F(\varphi)e^{2\pi i n}, \quad (3.145) \]

so that constant \( \nu \) has to be integer (say, \( n \)), and we can write:55

\[ F_n = C_n e^{in\varphi}, \quad (3.146) \]

Plugging the resulting relation \( (d^2 F/d\varphi^2)/F = -n^2 \) into Eq. (143), we may rewrite is as

\[ \frac{-\hbar^2}{2m} \left[ \frac{1}{\rho R} \frac{dR}{d\rho} \left( \rho^2 \frac{dR}{d\rho} \right) - \frac{n^2}{\rho^2} \right] + U(\rho) = E. \quad (3.147) \]

The physical interpretation of this equation is that the full energy is a sum,

\[ E = E_\rho + E_\varphi, \quad (3.148) \]

of the radial-motion part

\[ E_\rho = -\frac{\hbar^2}{2m} \frac{1}{\rho} \frac{d}{d\rho} \left( \rho \frac{dR}{d\rho} \right) + U(\rho). \quad (3.149) \]

and the angular-motion part

\[ E_\varphi = \frac{\hbar^2 n^2}{2m \rho^2}. \quad (3.150) \]

Now let us notice that a similar separation exists in classical mechanics,56 because the total energy of a particle moving in a central field may be presented, within the plane of motion, as

\[ E = \frac{m}{2} \nu^2 + U(\rho) = \frac{m}{2} \left( \rho^2 + \rho \dot{\varphi}^2 \right) + U(\rho) = E_\rho + E_\varphi, \quad (3.151) \]

where

55 Noting that for the planar rotator (Fig. 16) \( l/R = \varphi \), we can present Eq. (129) in a similar form. This is natural, because the rotator is just a particular case of our current problem - with a rigid confinement along axis \( \rho \).

56 See, e.g., CM Sec. 3.5.
\[
E_p = \frac{p_p^2}{2m} + U(p), \quad E_\rho = \frac{L_z^2}{2m\rho^2}.
\] (3.152)

The comparison of the latter relation with Eqs. (139) and (150) gives us grounds to suspect that the quantization rule \( L_z = n\hbar \) may be valid for this problem as well, and may be in other cases as well. In Sec. 5.6, we will see that this is indeed the case.

Returning to Eq. (147), on the basis of our experience with 1D wave mechanics we may expect that this ordinary, linear, second-order differential equation should have (for a motion confined to a certain final region of its argument \( \rho \)), for any fixed \( n \), a discrete energy spectrum described by some other integer quantum number (say, \( l \)). This means that eigenfunctions (142), and corresponding eigenenergies (148) should be indexed by two quantum numbers. Note, however, that since the radial function obeys equation (147), which already depends on \( n \), function \( \mathcal{R}(\rho) \) should carry both indices, so the variable separation is not so “clean” as it was for the rectangular quantum well. Normalizing the angular function to the full circle, \( \Delta \varphi = 2\pi \), we may rewrite Eq. (142) as

\[
\psi_{n,l} = \mathcal{R}_{n,l}(\rho)F_n(\varphi) = \frac{1}{(2\pi)^{1/2}}\mathcal{R}_{n,l}(\rho)e^{in\varphi}.
\] (3.153)

A good (and important) example of a solvable problem of this type is a free 2D particle whose motion is rigidly confined to a disk of radius \( R \):

\[
U(\rho) = \begin{cases} 
0, & \text{for } 0 \leq \rho < R, \\
+\infty, & \text{for } R < \rho.
\end{cases}
\] (3.154)

In this case, the solutions \( \mathcal{R}_{n,l}(\rho) \) of Eq. (147) are proportional to the first-order Bessel functions \( J_n(k\rho) \),\(^{57}\) and the spectrum of possible values of parameter \( k \) should found the boundary condition \( \mathcal{R}_{n,l}(R) = 0 \). Let me leave the detailed solution and analysis of this problem for reader’s exercise.

3.6. Spherically-symmetric systems: Brute force approach

Now let us address the (mathematically more involved) case of 3D motion, with spherically-symmetric potential

\[
U(\mathbf{r}) = U(r).
\] (3.155)

Let me start, again, with a rigid rotator - now a spherical rotator, i.e. a particle confined to move on the surface of a sphere of radius \( R \). It has 2 degrees of freedom, because any position on the spherical surface is completely described by two coordinates – say, the polar angle \( \theta \) and the azimuthal angle \( \phi \). In this case, the kinetic energy we need to consider is limited to its angular part, so that in the Laplace operator in spherical coordinates\(^{58}\) we may keep only those parts, with fixed \( r = R \). Then the stationary Schrödinger equation becomes

---

\(^{57}\) A short summary of properties of these function, plus a few plots and a useful table of values, may be found in EM Sec. 2.4. For more on of Bessel functions, see the literature recommended in MA Sec. 16(ii).

\(^{58}\) See, e.g., MA Eq. (10.9).
\[
- \frac{\hbar^2}{2mR^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi = E \psi .
\]

(Again, I abstain from attaching any indices to \( \psi \) and \( E \) for the time being.) With the usual variable separation assumption,

\[
\psi = \Theta(\theta) F(\varphi),
\]

Eq. (156), with all terms multiplied by \( \sin^2 \theta \Theta F \), yields

\[
- \frac{\hbar^2}{2mR^2} \left[ \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \frac{\sin \theta}{\Theta} \frac{d\Theta}{d\theta} \right) + \frac{1}{F} \frac{d^2 F}{d\varphi^2} \right] = E \sin^2 \theta .
\]

Just as in Eq. (143), fraction \( \frac{d^2 F}{dx^2}/F \) may be a function of \( \varphi \) only, and hence has to be constant, giving for it an equation similar to Eq. (144). So, the azimuthal functions are just the sine waves (146) again, and we can use the same periodicity condition (145) to write them in the normalized form\(^{59}\)

\[
F_m(\varphi) = \frac{1}{(2\pi)^{1/2}} e^{im\varphi} .
\]

With that, fraction \( \frac{d^2 F}{dx^2}/F \) equals \((-m^2)\), and Eq. (158), after multiplication by \( \Theta/\sin^2 \theta \), is reduced to the following ordinary, linear differential equation for function \( \Theta(\theta) \):

\[
- \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{m^2}{\sin^2 \theta} \Theta = \varepsilon \Theta, \quad \text{with} \quad \varepsilon \equiv E/\left( \frac{\hbar^2}{2mR^2} \right).
\]

It is convenient to recast it into an equation for a new variable \( P(\xi) \equiv \Theta(\theta) \), with \( \xi \equiv \cos \theta \):

\[
\frac{d}{d\xi} \left[ (1-\xi^2) \frac{dP}{d\xi} \right] + \left[ l(l+1) - \frac{m^2}{1-\xi^2} \right] P = 0 ,
\]

where a new notation for the normalized energy is introduced: \( l(l+1) \equiv \varepsilon \). The motivation for such notation is that, according to a mathematical analysis,\(^{60}\) Eq. (161) with integer \( m \), has solutions only if parameter \( l \) is integer: \( l = 0, 1, 2, \ldots \), and only if that integer is not smaller than \( |m| \), i.e. if

\[
-l \leq m \leq +l .
\]

This immediately gives the following energy spectrum of the spherical rotator:

\[
E_l = \frac{\hbar^2 l(l+1)}{2mR^2} ,
\]

\(^{59}\) Here, rather regrettably, I had to replace the notation of the integer from \( n \) to \( m \), in order to comply with the generally accepted convention for this so-called \textit{magnetic quantum number}. Let me hope that the difference between this integer and particle’s mass is absolutely clear from the context.

\(^{60}\) It was carried out by A.-M. Legendre (1752-1833). Just as a historic note: besides many original mathematical results, Dr. Legendre has authored the famous textbook \textit{Éléments de Géométrie} which dominated teaching geometry through the 19th century.
so that the only effect of the magnetic quantum number \( m \) here is imposing the restriction (162) on the orbital quantum number \( l \). This means, in particular, that each of energy level (163) corresponds to \((2l + 1)\) different values of \( m \), i.e. is \((2l + 1)\)-degenerate.

To understand the physics of this degeneracy, we need to explore the corresponding eigenfunctions of Eq. (161). They are naturally numbered by two integers, \( m \) and \( l \), and are called the associated Legendre functions \( P_l^m \). For the particular, simplest case \( m = 0 \), these functions are just (Legendre) polynomials \( P_l(\xi) \equiv P_l^0(\xi) \), which may be either defined as the solutions of the Legendre equation following from Eq. (161) at \( m = 0 \):

\[
\frac{d}{d\xi} \left( (1 - \xi^2) \frac{d}{d\xi} P \right) + l(l + 1)P = 0,
\]

or calculated explicitly from the following Rodrigues formula:\(^{61}\)

\[
P_l(\xi) = \frac{1}{2^l l!} \frac{d^l}{d\xi^l} (\xi^2 - 1)^l, \quad l = 0, 1, 2, \ldots
\]

Using this formula, it easy to spell out a few lowest Legendre polynomials:

\[
P_0(\xi) = 1, \quad P_1(\xi) = \xi, \quad P_2(\xi) = \frac{1}{2} (3\xi^2 - 1), \quad P_3(\xi) = \frac{1}{2} (5\xi^3 - 3\xi), \ldots
\]

though such expressions become more and more bulky as \( l \) is increased. As Fig. 18 shows, as argument \( \xi \) is decreased, all these functions start in one point, \( P_l(1) = 1 \), and end up either in the same point or in the opposite point: \( P_l(-1) = (-1)^l \). On the way between these two end points, the \( l^{th} \) polynomial crosses the horizontal axis exactly \( l \) times, i.e. has \( l \) roots.\(^{62}\) It may be shown that on the segment \([-1,+1]\), the Lagrange polynomials form a full orthogonal set of functions, with the following normalization rule:

\[
\int_{-1}^{+1} P_l(\xi)P_m(\xi) d\xi = \frac{2}{2l + 1} \delta_{ll},
\]


\(^{62}\) In this behavior, we readily recognize the standing wave pattern typical for all 1D eigenproblems – cf. Fig. 1.7. The quantitative deviation from the sinusoidal waveform is due to the different metric of the sphere.

---

\( \xi = \cos \theta \)
For \( m > 0 \), the associated Legendre functions may be expressed via the Legendre polynomials (165) using the following formula, which reminds Eq. (165):

\[
P_l^m(\xi) = (-1)^m (1 - \xi^2)^{m/2} \frac{d^m}{d\xi^m} P_l(\xi),
\]

while if the index \( m \) is negative, the following simple relation may be used:

\[
P_l^{-m}(\xi) = (-1)^m (l-m)! \frac{(l+m)!}{(l-m)!} P_l^m(\xi).
\]

On the segment \( \xi = [-1, +1] \), each set of the associated Legendre functions with fixed index \( m \) forms a full orthogonal set, with the normalization relation,

\[
\int_{-1}^{+1} P_l^m(\xi) P_l^n(\xi) d\xi = \frac{2}{2l+1} \frac{(l+m)!}{(l-m)!} \delta_{ll},
\]

which is evidently a generalization of Eq. (167) for arbitrary \( m \).

Since the difference between angles \( \theta \) and \( \phi \) is to some extent artificial (caused by the arbitrary direction of the polar axis), physicists prefer to use not the functions \( \Theta(\theta) \propto P_l^m(\cos \theta) \) and \( F_m(\phi) \propto \exp\{im\phi\} \) separately, but their products (157), which are called spherical harmonics:

\[
Y_{lm}(\theta, \phi) \equiv \left[ \frac{(2l+1)(l-m)!}{4\pi (l+m)!} \right]^{1/2} P_l^m(\cos \theta) e^{im\phi}.
\]

The specific coefficient in Eq. (171) is chosen in a way to simplify the following two relations: the equation for negative \( m \),

\[
Y_l^{-m}(\theta, \phi) = (-1)^m \left[ Y_l^m(\theta, \phi) \right]^*,
\]

and the normalization relation

\[
\oint Y_l^m(\theta, \phi) Y_l^m(\theta, \phi)^* d\Omega = \delta_{ll'} \delta_{mm'},
\]

with integration over the whole solid angle \( 4\pi \). The last relation shows that the spherical harmonics form an orthonormal set of functions. This set is also full, so that any function defined on a sphere may be uniquely presented as a linear combination of \( Y_{lm} \).

Despite a somewhat intimidating formulas given above, they yield rather simple expressions for the lowest spherical harmonics:

\[
l = 0: \quad Y_0^0 = \left(1/4\pi\right)^{1/2},
\]

\[
l = 1:
\[
\begin{cases}
Y_1^1 = -(3/8\pi)^{1/2} \sin \theta e^{i\phi}, \\
Y_0^0 = (3/4\pi)^{1/2} \cos \theta, \\
Y_{-1}^{-1} = +(3/8\pi)^{1/2} \sin \theta e^{-i\phi},
\end{cases}
\]

\[
Y_1^0 = (3/4\pi)^{1/2} \cos \theta.
\]
It is important to understand the symmetry of these functions. Since spherical functions with \( m \neq 0 \) are complex, the most popular way of their graphical representation is first to form their real combinations corresponding to two opposite values of \( m \),

\[
Y_{lm} \equiv \frac{1}{\sqrt{2}} \left[ |Y_l^m| + \text{sgn}(m)(-1)^m Y_l^{-m} \right] \propto \begin{cases} 
\cos m \varphi, & \text{for } m > 0, \\
\sin m \varphi, & \text{for } m < 0,
\end{cases}
\]  

(3.177)

(for \( m = 0 \), \( Y_{l0} \equiv Y_l^0 \)), and then plot the magnitude of these combinations in spherical coordinates as the distance from the origin, while using two colors to show their sign – see Fig. 19.

---

\[ 63 \text{ Such real functions } Y_{lm}, \text{ which also form the full set of orthonormal eigenfunctions and are frequently called the real spherical harmonics, are more convenient than the complex functions } Y_l^m \text{ for several applications, especially when the variables of interest are real by definition.} \]
Let us starting from the simplest case \( l = 0 \). According to Eq. (162), there could be only one such \( s \) state,\(^{64}\) with \( m = 0 \). The spherical harmonic corresponding to that state is just a constant, so that the wavefunction is uniformly distributed over the sphere. Since the functions does not have gradient in any direction, the kinetic energy (163) of the particle equals is zero.

For \( l = 1 \), there could be 3 different \( p \) states, with \( m = -1, 0, \) and \(+1\). As the second row in Fig. 19 shows, these states are essentially identical in structure, and are just differently oriented in space, thus explaining the 3-fold degeneracy of the kinetic energy – see Eq. (163). This is not quite true for 5 different \( d \) states (\( l = 2 \)), shown in the bottom row of Fig. 19, as well as states with higher \( l \): despite their equal energies, they differ not only by their special orientation. The states with \( m = 0 \) have gradient only in the \( \theta \) direction, while the states with the ultimate values of \( m (m = \pm l) \) change only gradually (as \( \sin \theta \)) in the polar direction, while oscillating in the azimuthal direction. The states with intermediate values of \( m \) provide a crossover between these two extremes, oscillating in both directions, stronger and stronger in the direction of \( \phi \) as \(|m|\) is increased. Still, the magnetic quantum number, surprisingly, does not affect the energy for any \( l \). Another surprising feature of the spherical harmonics follows from the comparison of Eq. (163) with the second of classical relations (152). These expressions coincide if we interpret constant

\[
L^2 = \hbar^2 l(l + 1),
\]

as the value of the full angular momentum squared \( L^2 = |L|^2 \) (including its both \( \theta \) and \( \phi \) components) in the eigenstate with eigenfunction \( Y_l^m \). On the other hand, the structure of the azimuthal component \( F(\phi) \) of the wavefunction is exactly the same as in 2D axially-symmetric problems, suggesting that Eq. (139) still gives correct values (in our new notation, \( L_z = m \hbar \)) for the \( z \)-component of the angular momentum. If this is so, why for any state with \( l > 0 \), \((L_z)^2 = m^2 \hbar^2 \leq \hbar^2 \) is less than \( L^2 = l(l + 1)\hbar^2 \)? In other words, what prevents the angular momentum vector to be fully aligned with axis \( z \)?

Besides that issue, though the above analysis of the spherical rotator is formally (mathematically) complete, it is as unsatisfactory on the physics level as the harmonic oscillator analysis in Sec. 2.6. In particular, it does not explain the meaning of the extremely simple relations for eigenvalues of energy and angular momentum on the backdrop of rather complicated wavefunctions.

We will obtain natural answers to all these questions and concerns in Sec. 5.6, but now let us complete our survey of wave mechanics by extending it to 3D motion in an arbitrary spherically-symmetric potential (155). In this case we have to use the full form of the Laplace operator in spherical coordinates. The variable separation procedure is an evident generalization of what we have done before, with the particular solution

\[
\psi = R(\rho)\Theta(\theta)F(\phi),
\]

whose substitution into the stationary Schrödinger equation yields

\[
-\frac{\hbar^2}{2mr^2} \left[ \frac{1}{\rho} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\sin^2 \theta} \frac{d^2F}{d\phi^2} \right] + U(r) = E. \tag{3.180}
\]

\(^{64}\) The letter names for states with different values of \( l \) stem from the history of optical spectroscopy - for example, letter “\( s \)”, used for \( l = 0 \), originally denoted the “sharp” optical line series, etc. The sequence of the letters is as follows: \( s, p, d, f, g, h \), and further in the alphabetical order.
It is evident that the angular part (the two last terms in square brackets) separates from the radial part, and for the former part we get Eq. (156) again, with the only change, \( R \to r \). This change does not affect the fact that the eigenfunctions of that equation are the spherical harmonics (171), and the angular eigenenergy is given by Eq. (163), again with the replacement \( R \to r \). This means that for the radial function, Eq. (180) gives the following equation,

\[
- \frac{\hbar^2}{2mr^2} \left[ \frac{1}{\mathcal{R}} \frac{d}{dr} \left( r^2 \frac{d\mathcal{R}}{dr} \right) - l(l+1) \right] + U(r) = E. \tag{3.181}
\]

Note that no information about the magnetic quantum number \( m \) has not crept into the radial equation (besides establishing the limitation (162) for possible values of \( l \)), so that this equation depends only on the latter quantum number.

The radial equation becomes rather simple for \( U(r) = 0 \), and may be used, for example, to solve the eigenproblem for the free 3D motion of a particle inside the sphere of radius \( R \). Leaving that problem for the reader’s exercise, I will proceed to the most important Bohr atom problem, i.e. of motion in the so-called attractive Coulomb potential,\(^{65}\)

\[
U(r) = -\frac{C}{r}, \quad \text{with } C > 0. \tag{3.182}
\]

The natural scales of \( r \) and \( E \) are, respectively,\(^{66}\)

\[
r_0 \equiv \frac{\hbar^2}{mc} \quad \text{and} \quad E_0 \equiv \frac{\hbar^2}{m^2 r_0^2} \equiv m \left( \frac{C}{\hbar} \right)^2.
\tag{3.183}
\]

In the normalized units \( \varepsilon \equiv E/E_0 \) and \( \xi \equiv r/r_0 \), Eq. (181) looks simpler,

\[
\frac{d^2\mathcal{R}}{d\xi^2} + 2 \frac{d\mathcal{R}}{d\xi} \left( \xi + \frac{1}{\xi} \right) \mathcal{R} = 0,
\tag{3.184}
\]

but unfortunately its eigenfunctions may be called elementary only in the most generous meaning of the word. With the adequate normalization,

\[
\int_0^{\infty} \mathcal{R}_{\nu,l} \mathcal{R}_{\nu',l'} \, r^2 \, dr = \delta_{\nu\nu'},
\tag{3.185}
\]

these (mutually orthogonal) functions may be presented as

\(^{65}\) Historically, the solution of this problem in 1928, that reproduced the main result (1.8)-(1.9) of the “old” quantum theory developed by N. Bohr in 1912, without its restrictive assumptions, was the decisive step for the general acceptance of Schrödinger’s wave mechanics.

\(^{66}\) These two scales are obtained from relations \( E_0 \equiv \hbar^2/mr_0^2 = C/r_0 \), i.e. from the equality of the natural scales of the potential and kinetic energies, dropping all numerical coefficients. For the most important case of the hydrogen atom, \( C = e^2/4\pi\varepsilon_0 \), these scales are reduced, respectively, to the Bohr radius \( r_B \) (1.13) and the Hartree energy \( E_H \) (1.9). Note also that for a hydrogen-like atom (or rather ion), with \( C = Z(e^2/4\pi\varepsilon_0) \), these two key parameters are rescaled as \( r_0 = r_B/Z \), \( E_0 = Z^2E_H \).
Here \( L_p^q (\xi) \) are the so-called associated Laguerre polynomials, which may be calculated as

\[
L_p^q (\xi) = (-1)^q \frac{d^q}{d\xi^q} L_{p+q}^0 (\xi).
\]  \hspace{1cm} (3.187)

from simple Laguerre polynomials \( L_p^0 (\xi) \). In turn, the easiest way to obtain \( L_p^q (\xi) \) is to use the following Rodrigues formula:68

\[
L_p (\xi) = e^{\xi} \frac{d^p}{d\xi^p} \left( \xi^p e^{-\xi} \right).
\]  \hspace{1cm} (3.188)

Notice that in contrast with the associated Legendre functions \( P_l^m \) participating in spherical harmonics, \( L_p^q \) are just polynomials, and those with small indices \( p \) and \( q \) are indeed simple.

Returning to Eq. (186), we see that the natural quantization of the radial equation (184) has brought us a new quantum number (integer) \( n \). In order to understand its range, we should notice that according to Eq. (188), the highest power of terms in polynomial \( L_{p+q} \) is \( (p + q) \), and hence, according to Eq. (187), that of \( L_p^q \) is \( p \), so that of the highest power in the polynomial participating in Eq. (186) is \( (n - l - 1) \). Since the power cannot be negative (to avoid the unphysical divergence of wavefunctions at \( r \to 0 \)), the radial quantum number \( n \) has to obey the restriction \( n \geq l + 1 \). Since \( l \), as we already know, may take values \( l = 0, 1, 2, \ldots \), we may conclude that \( n \) may only take values

\[
n = 1, 2, \ldots \hspace{1cm} (3.189)
\]

What makes this relation important is the following, most surprising result of the theory: the eigenenergies corresponding to wavefunctions (179), which are indexed with 3 quantum numbers:

\[
\psi_{n,l,m} = \mathcal{R}_{n,l}(r) Y_l^m (\theta, \varphi),
\]  \hspace{1cm} (3.190)

depend only on \( n \) and agree with Bohr’s formula (1.8):

\[
E_n = -\frac{E_0}{2n^2} = -\frac{1}{2n^2} m \left( \frac{C}{\hbar} \right)^2.
\]  \hspace{1cm} (3.191)

Because of this reason, \( n \) is usually called the principal quantum number, and the above relation between it and “more subordinate” \( l \) is rewritten as

\[
l \leq n - 1.
\]  \hspace{1cm} (3.192)

Together with inequality (162), this gives us the most important hierarchy of the 3 quantum numbers involved in the problem:

\[
1 \leq n \leq \infty \Rightarrow 0 \leq l \leq n - 1 \Rightarrow -l \leq m \leq +l,
\]  \hspace{1cm} (3.193)

---

67 In Eqs. (187)-(188), \( p \) and \( q \) are non-negative integers, with no relation whatsoever to particle’s momentum or electric charge. Sorry for this notation, but it is absolutely common, and can hardly result in any confusion.

68 Named after the same B. O. Rodrigues, and belonging to the same class as his another key result, Eq. (165).
Taking into account the \((2l + 1)\)-degeneracy related to the magnetic number \(m\), and using the well-known formula for the arithmetic progression,\(^{69}\) we see that each energy level \((191)\) has the following orbital degeneracy:

\[
g = \sum_{l=0}^{n-1} (2l + 1) = 2 \sum_{l=0}^{n-1} l - \sum_{l=0}^{n-1} 1 = 2 \frac{n(n-1)}{2} - n = n^2. \tag{3.194}
\]

Due to its importance for applications, let us spell out the quantum number hierarchy of a few lowest-energy states, using the traditional notation in which the value of \(n\) is followed by the letter that denotes the value of \(l\):

- \(n = 1: \) \(l = 0\) (one 1s state) \(m = 0\). \tag{3.195}
- \(n = 2: \) \(l = 0\) (one 2s state) \(m = 0\), \(l = 1\) (three 2p states) \(m = 0, \pm 1\). \tag{3.196}
- \(n = 3: \) \(l = 0\) (one 3s state) \(m = 0\), \(l = 1\) (three 3p states) \(m = 0, \pm 1\), \(l = 2\) (five 3d states) \(m = 0, \pm 1, \pm 2\). \tag{3.197}

Figure 20 shows plots of the radial functions \((186)\) of the listed states. The most important of them is of course the ground (1s) state with \(n = 1\) and hence \(E = - E_0/2\), whose radial function \((186)\) is just

\[
R_{1,0}(r) = \frac{2}{r_0^{3/2}} e^{-r/r_0}, \tag{3.198}
\]

and the angular distribution is uniform - see Eq. (174). The gap between the ground energy and the energy \(E = - E_0/8\) of the lowest excited states (with \(n = 2\)) in a hydrogen atom (in which \(E_0 = E_H \approx 27.2\) eV) is as large as \(~ 10\) eV, so that their thermal excitation requires temperatures as high as \(~10^5\) K, and the overwhelming part of all hydrogen atoms in the visible Universe are in their ground state. Since atomic hydrogen makes up about 75% of the “normal” matter, we are very fortunate that such simple formulas as Eqs. (174) and (198) describe the atomic states most frequently met in Mother Nature!\(^{70}\)

The radial functions of the next states, 2s and 2p, are also not too complex:

\[
R_{2,0}(r) = \frac{1}{(2r_0)^{3/2}} \left(2 - \frac{r}{r_0}\right) e^{-r/2r_0}, \quad R_{2,1}(r) = \frac{1}{(2r_0)^{3/2}} \frac{r}{3^{1/2}r_0} e^{-r/2r_0}. \tag{3.199}
\]

(Note again that the former of these states (2s) can only have a uniform angular distribution, while three 2p states have different values of \(m = 0, \pm 1\), and hence have different angular distributions – see Eq. (175) and the second row of Fig. 19.) The most important trend here is a larger radius of decay of the exponent \((2r_0\) for \(n = 2\) instead of \(r_0\) for \(n = 1\)), and hence the radial extension of the states. This trend is confirmed by the following general formula:\(^{71}\)

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\(^{69}\) See, e.g., MA Eq. (2.5a).

\(^{70}\) Forgetting for a minute about such new “dark clouds” on the horizon of the modern physics as the hypothetical dark matter and dark energy.

\(^{71}\) Note that even at the largest value of \(l\), equal to \((n - 1)\), term \(l(l + 1)\) in Eq. (200) cannot compensate term \(3n^2\).
The second important trend is that at fixed $n$, the orbital quantum number $l$ determines how fast does the wavefunction change with $r$ near the origin, and how much it oscillates in the radial direction at larger $r$. For example, the $2s$ eigenfunction $R_{2,0}(r)$ is nonvanishing at $r = 0$, and makes one “wiggle” (has one root) in the radial direction, while eigenfunctions $2p$ equal zero at $r = 0$, and do not oscillate at all in the radial direction. Instead, those wavefunctions always oscillate as functions of some angle – see the second row of Fig. 19. The same trend is clearly visible for $n = 3$ (see Fig. 20), and continues for the higher values of $n$.

![Graphs of $R_{n,l}(r)$ for different $n$ and $l$](image)

Fig. 3.20. The lowest radial functions of the Bohr atom problem.

The interpretation of these results is that the states with $l = l_{\text{max}} = n - 1$ may be viewed as analogs of the circular motion of a particle in a plane whose orientation defines the quantum number $m$, with an almost fixed radius $r \approx r_0 (n^2 \pm n)$. On the other hand, the best classical image of an $s$-state ($l = 0$) is the purely radial motion of the particle to and from the attracting center. (The latter image is especially imperfect, because the motion would need to happen simultaneously in all radial directions.) The classical language becomes reasonable only for the so-called Rydberg states, with $n \gg 1$, whose linear superpositions may be used to compose wave packets closely following the classical, circular or elliptic trajectories of the particle – just as was discussed in Sec. 2.2 for the free 1D motion.
Besides Eq. (200), mathematics gives us several other simple relations for the radial functions $R_{n,l}$ (and, since the spherical harmonics are normalized to 1, for the eigenfunctions as the whole), including those that we will use later in the course:\(^72\)

$$\left(\frac{1}{r}\right)_{n,l} = \frac{1}{n^2 r_0}, \quad \left(\frac{1}{r^2}\right)_{n,l} = \frac{1}{n^2 (l+1/2) r_0^2}, \quad \left(\frac{1}{r^3}\right)_{n,l} = \frac{1}{n^3 l(l+1/2) (l+1) r_0^3}. \quad (3.201)$$

In particular, the first of them means that for any eigenfunction $\psi_{n,l,m}$, with all its complicated radial and angular dependencies, there is a simple relation between the potential and full energies:

$$\langle U \rangle_{n,l} = -C \left(\frac{1}{r}\right)_{n,l} = -\frac{C}{n^2 r_0} = -\frac{E_0}{n^2} = 2E_n, \quad (3.202)$$

so that the average kinetic energy of the particle, $\langle T \rangle_{n,l} = E_n - \langle U \rangle_{n,l}$, is equal to $|E_n| > 0$.

These simple results are in a sharp contrast with the rather complicated expressions for the eigenfunctions, and motivate a search for more general methods of quantum mechanics, which would replace or at least complement our brute-force (wave-mechanics) approach, to reveal their real nature. Such an approach will be the main topic of the next chapter.

### 3.7. Atoms

Before proceeding to that chapter, let me show that, rather strikingly, the classification of quantum numbers in the simple potential well (182), carried out in the last section, together with very modest borrowings from the further theory, allows an semi-quantitative explanation of the whole system of chemical elements. The “only” two additions we need are the following facts:

(i) due to interaction with relatively low-temperature environments, atoms tend to relax into their lowest-energy state, and

(ii) due to the Pauli principle (valid for electrons as Fermi particles), each orbital eigenstate discussed above can be occupied with 2 electrons with opposite spins.

Of course, atomic electrons do interact, so that their quantitative description requires quantum mechanics of multiparticle systems, which is rather complex. (Its main concepts will be discussed in Chapter 8.) However, the lion’s share of this interaction reduces to simple electrostatic screening, i.e. the partial compensation of the electric charge of the atomic nucleus, as felt by a particular electron, by other electrons of the atom. This screening changes the qualitative results (such as the energy scale) dramatically; however, the quantum number hierarchy, and hence their classification, is not affected.

The system of atoms is most often presented as the famous periodic table of chemical elements,\(^73\) whose simple version is shown in Fig. 21, while Fig. 22 presents a sequential list of the elements with their electron configurations. The numbers in table’s cells (and the first column in the list) are the

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\(^72\) The first of these relations may be also readily proved using the Heller-Feynman theorem (see Chapter 1); this proof is left for reader’s exercise. Note also that the last of the expressions diverges at $l = 0$, in particular in the ground state of the system (with $n = 1, l = 0$).

\(^73\) Also called the Mendeleev table, after D. Mendeleev who put forward the concept of the periodicity of chemical element properties as functions of $Z$ phenomenologically in 1869. (The explanation of the periodicity had to wait for 60 more years until the quantum mechanics formulation in the late 1920s.)
atomic numbers \( Z \), which physically are the numbers of protons in the atomic nucleus, and hence the numbers of electrons in the electrically neutral atom. The electron configuration in Fig. 22 follows the convention already used in Eqs. (195)-(197), with the additional upper index showing the number of electrons with the indicated values of quantum numbers \( n \) and \( l \).

The lightest atom, with \( Z = 1 \), is hydrogen (chemical symbol H) – the only atom for each the theory discussed in Sec. 6 is quantitatively correct.\(^{74}\) According to Eq. (191), the 1s ground state of its only electron corresponds to quantum numbers \( n = 1, l = 0 \), and \( m = 0 \) – see Eq. (196). In most versions of the periodic table, the cell of H is placed in the top left corner. In the next atom, helium (He, \( Z = 2 \), the same orbital quantum state (1s) is filled with two electrons with different spins.\(^{75}\) Note that due to the twice higher electric charge of the nucleus, i.e. the twice higher value of constant \( C \) in Eq. (182), resulting in a 4-fold increase of constant \( E_0 \) (183), the binding energy of each electron is crudely 4 times higher than that of the hydrogen atom - though the electron interaction decreases it by about 25% - see Sec. 7.2. This is why taking one electron away (i.e. form a negative ion) either. As a result, helium, and all other elements with fully completed electron shells (sets of states with eigenenergies well separated from higher energy levels) is a chemically inert noble gas, thus starting the whole right-most column of the periodic table, committed to such elements.

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>He</td>
</tr>
<tr>
<td>Li</td>
<td>Be</td>
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<tr>
<td>Na</td>
<td>Mg</td>
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<tr>
<td>K</td>
<td>Ca</td>
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<td>Rb</td>
<td>Sr</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
</tr>
<tr>
<td>Fr</td>
<td>Ra</td>
</tr>
</tbody>
</table>

Property legend:

alkali metals
alkali-earth metals
rare-earth metals
transition metals
other metals
metals metals
halogens
noble gases
metalloids

table of elements, showing their atomic numbers, as well as their basic physical/chemical properties at the so-called ambient (meaning usual laboratory) conditions.

\(^{74}\) Besides very small “fine-structure” corrections – to be discussed in Chapters 6 and 9.

\(^{75}\) As will be discussed in detail in Chapter 8, electrons of the same atom are actually indistinguishable, and their quantum states are not independent, and frequently entangled. These factors are important for several properties of helium atoms (and heavier elements as well), especially for their response to external fields. However, for the atom classification purposes, they are not crucial.
Fig. 3.22. Atomic electron configurations. The upper index shows the number of electrons in states with the indicated quantum numbers $n$ (the first digit) and $l$ (letter-coded as listed above).
The situation changes dramatically as we move to the next element, lithium (Li), with \( Z = 3 \) electrons. Two of them are still accommodated by the inner shell \( n = 1 \) (listed in Fig. 22 as the helium shell [He]), but the third one has to reside in the next shell with \( n = 2 \) and \( l = 0 \), i.e. in the 2\( s \) state. According to Eq. (191), the binding energy of this electron is much lower, especially if we take into account that according to Eq. (200), the 1\( s \) electrons of the [He] shell are much closer to the nucleus and almost completely compensate two thirds of its electric charge +3\( e \). As a result, the 2\( s \) electron is reasonably well described by Eq. (199), with binding energy of just 5.39 eV, so that a lithium atom can give out that electron rather easily – to either atoms of other elements to form chemical compounds, or into the common conduction band of solid state lithium - and as a result it is a typical alkali metal. The similarity of chemical properties of lithium and hydrogen, with the chemical valence of one,76 places Li as the starting element of the second period (row), with the first period limited to only H and He.

In the next element, beryllium (\( Z = 4 \)), the 2\( s \) state (\( n = 2, l = 0 \)) picks up one more electron, with the opposite spin. Due to the higher electric charge of the nucleus, \( Q = 4e \), with only half of it compensated by 1\( s \) electrons of the [He] shell, the binding energy of the 2\( s \) electrons is higher than in lithium, so that the ionization energy increases to 9.32 eV. As a result, beryllium is also chemically active but not as active as lithium, with the valence of two, and is also is metallic in its solid state phase, but does not conduct electric current as well as lithium.

Moving in this way along the second row of the periodic table (from \( Z = 3 \) to \( Z = 10 \)), we see the gradual filling of all 4 different orbital states of the \( n = 2 \) shell, by 2 electrons each, with gradually growing ionization potential (up to 21.6 eV in Ne with \( Z = 10 \)), i.e. the growing reluctance to have metallic conductance or form positive ions. However, the final elements of the row, such as oxygen (O, with \( Z = 8 \)) and especially fluorine (F, with \( Z = 9 \)) can readily pick up extra electrons to fill their 2\( p \) states, i.e. form negative ions. As a result, these elements are chemically active, with the double valence for oxygen and single valence for fluorine. However, the final element of this row, neon, has its \( n = 2 \) shell full, and cannot form a stable negative ion. This is why it is a noble gas, like helium. Traditionally, in the periodic table it is placed right under helium (Fig. 21), to emphasize the similarity of their chemical and physical properties. But this necessitates making an at least 6-cell gap in the 1\(^{st} \) row. (Actually, the gap is often made larger, to accommodate next rows – keep reading.)

Period 3, i.e. the 3\(^{rd} \) row of the table starts exactly like period 2, with sodium (Na, with \( Z = 11 \)), also a chemically active alkali metal whose atom features 10 electrons filling shells with \( n = 1 \) and \( n = 2 \) (in Fig. 22 collectively called the neon shell, [Ne]), plus one electron in a 3\( s \) state (\( n = 3, l = 0, m = 0 \)), which may be reasonably well described by the hydrogen atom theory – see, e.g., the red trace on the last panel of Fig. 20. Naively we could expect that, according to Eq. (194), and with the account of double spin degeneracy, this period of the table should have \( 2n^2 = 2\times3^2 = 18 \) elements, with gradual filling of two 3\( s \) states, six 3\( p \) states, and ten 3\( d \) states. However, here we run into a big surprise: after argon (Ar, with \( Z = 18 \)), a relatively inert element with ionization energy of 15.7 eV due to the fully filled 3\( s \) and 3\( p \) states, the next element, potassium (K, with \( Z = 19 \)) is an alkali metal again!

The reason for that is the difference of the actual electron energies from those of the hydrogen atom, which is due mostly to inter-electron interactions and gradually accumulates with the growth of \( Z \). It may be semi-quantitatively understood from the results of Sec. 6. In hydrogen-like atoms, electron state energies do not depend on the quantum number \( l \) (as well as \( m \)) – see Eq. (191). However, the

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76 Chemical valence is a relatively vague term describing the number of atom’s electrons involved in chemical reactions. For the same atom, the number may depend on the chemical compound formed.
orbital quantum number does affect the wavefunction of an electron. As Fig. 20 shows, the larger \( n \) the less the probability for an electron to be close to the nucleus, where its positive charge is less compensated by other electrons. As a result of this effect (and also the relativistic corrections to be discussed in Sec. 6.3), electron’s energy grows with \( l \). Actually, this effect was visible even in period 2: it manifests itself in the filling order \( (p \text{ states after } s \text{ states}) \). However, for potassium (K, with \( Z = 19 \)) and calcium (Ca, with \( Z = 20 \)), energies of \( 3d \) states become so high that energies of two \( 4s \) states (with opposite spins) are lower, and they are filled first. As described by factor 3 in the square brackets of Eq. (200), and also by Eq. (201), the effect of the principal number \( n \) on the distance from the nucleus is stronger than that of \( l < n \), so that \( 4s \) wavefunctions of K and Ca are relatively far from the nucleus, and determine the chemical valence (equal to 1 and 2, correspondingly) of these elements. The next atoms, from Sc \((Z = 21)\) to Zn \((Z = 30)\), with the gradually filled “internal” \( 3d \) states, are the so-called *transition metals* whose (comparable) ionization energies and chemical properties are determined by \( 4s \) electrons.

This fact is the origin of the difference between various forms of the “periodic” table. In its most popular option, shown in Fig. 21, K is used to start the next, period 4, and then a new period is started each time and only when the first electron with the next principal quantum number \( (n) \) appears.\(^{77}\) This topology provides a very clear mapping on the chemical properties of the first element of each period (an alkali metal), as well as its last element (a noble gas). This also automatically means making gaps in all previous rows. Usually, this gap is made between the atoms with completely filled \( s \) states and with the first electron in a \( p \) state, because here the properties of the elements make a somewhat larger step. (For example, the step from Be to B makes the material an insulator, but it is not large enough to make a similar difference between Mg to Al.) As a result, elements of the same column have *approximately* similar chemical valence and physical properties.

However, to accommodate longer lowest rows, such presentation is inconvenient, because the whole table would be too broad. This is why the so-called *rare earths*, including lanthanides (with \( Z \) from 57 to 70, of the 6\(^{th}\) row, with gradual filling of \( 4f \) and \( 5d \) states) and actinides (\( Z \) from 89 to 103, of the 7\(^{th}\) row, with gradual filling of \( 5f \) and \( 6d \) states), are presented as outlet lines (Fig. 21). This is quite acceptable for the purposes of standard chemistry, because chemical properties of elements within each group are rather close.

To summarize, the “periodic table of elements” is not periodic in the strict sense of the word. Nevertheless, it has had an enormous historic significance for chemistry, as well as atomic and solid state physics, and is still very convenient for many purposes. For our course, the most important aspect of its discussion is the surprising possibility to describe, at least for classification purposes, such a complex multi-electron system as an atom as a set of quasi-independent electrons in certain quantum states indexed with the same quantum numbers \( n, l, \) and \( m \) as those of the hydrogen atom. This fact enables the use of various *perturbation theories*, which give more quantitative description of atomic properties. Some of these techniques will be reviewed in Chapters 6 and 8 of this course.\(^{78}\)

\(^{77}\) Another option is to return to the first column as soon an atom has one electron in \( s \) state (like it is in Cu, Ag, and Au, in addition to the alkali metals).

\(^{78}\) For a bit more detailed (but still very succinct) discussion of valence and other chemical aspects of atomic structure, I can recommend Chapter 5 of the classical text by L. Pauling, *General Chemistry*, Dover, 1988.
3.8. Exercise problems

3.1. A particle of energy $E$ is incident (in Fig. on the right, within the plane of drawing) on a sharp potential step:

$$U(r) = \begin{cases} 0, & \text{for } x < 0, \\ U_0, & \text{for } 0 < x. \end{cases}$$

Find the particle reflection probability $R$ as a function of the incidence angle $\theta$; sketch and discuss the function, for different magnitudes and signs of $U_0$.

3.2. Use the finite difference method with step $h = a/2$ to calculate as many eigenenergies as possible, for a free particle confined to the interior of:

(i) a square with side $a$;
(ii) a cube with side $a$.

For the square, repeat the calculations, using a finer step: $h = a/3$. Compare the results for different $h$, with the exact formula.

*Hint:* It is advisable to first solve (or review the solution of :) the similar 1D problem in Chapter 1, or start from reading about the finite difference method.\(^{79}\) Also, try to exploit problem’s symmetry.

3.3. Use the variational method to estimate the ground state energy of a particle of mass $m$, moving in a spherically-symmetric potential

$$U(r) = ar^4.$$

3.4. In the classical version of the Landau level problem discussed in Sec. 2, the center of particle’s orbit is an integral of motion, determined by initial conditions. Calculate the commutation relations between the quantum-mechanical operators corresponding to the Cartesian coordinates of the center, and to the sum of their squares.

3.5.\(^*\) Analyze how are the Landau levels (3.50) modified by an additional constant electric field $E$, directed along the particle plane. Contemplate the physical meaning of your result, and its implications for the quantum Hall effect in a gate-defined Hall bar. (The area $L \times W$ area of such a bar [see Fig. 3.6 of the lecture notes] is defined by metallic gate electrodes parallel to the 2D electron gas plane - see Fig. on the right. The negative voltage $V_g$, applied to the gates, chases the electrons gas out of the confinement plane at the remaining sample area.)

3.6. Analyze how are the Landau levels (50) modified if a 2D particle is confined in an additional 1D potential well $U(x) = m\omega_0^2x^2/2$

\(^{79}\) See, e.g., CM Sec. 8.5 or EM Sec. 2.8.
3.7. Find the eigenfunctions of a spinless, charged 3D particle moving in “crossed” (perpendicular), uniform electric and magnetic fields. For each eigenfunction, calculate the expectation value of particle’s velocity in the direction perpendicular to both fields, and compare the result with the solution of the corresponding classical problem.

*Hint:* Generalize Landau’s solution for 2D particles, discussed in Sec. 2.

3.8. Use the Born approximation to calculate the angular dependence and the full cross-section of scattering of an incident plane wave, propagating along axis $x$, by the following pair of point inhomogeneities:

$$U(r) = W \left[ \delta \left( r - \mathbf{n} \frac{a}{2} \right) + \delta \left( r + \mathbf{n} \frac{a}{2} \right) \right].$$

Analyze the results in detail. Derive the condition of the Born approximation’s validity for such delta-functional scatterers.

3.9. Use the Born approximation to calculate the differential and full cross-sections of a spherical scatterer:

$$U(r) = \begin{cases} U_0, & \text{for } r < R, \\ 0, & \text{otherwise.} \end{cases}$$

Analyze both results, especially the angular dependence of $d\sigma/d\Omega$, in detail, for $kR \ll 1$ and $kR \gg 1$.

3.10. Use the Born approximation to calculate differential and full cross-sections of electron scattering by a screened Coulomb field of a point charge $Ze$, with electrostatic potential

$$\phi(r) = \frac{Ze}{4\pi\epsilon_0 r} e^{-\lambda r},$$

neglecting the spin interaction effects, and analyzed their dependence on the screening parameter $\lambda$. Compare the results with those given by the classical (“Rutherford”) formula$^{80}$ for the unscreened Coulomb potential ($\lambda \to 0$), and formulate the condition of Born approximation’s validity in this limit.

3.11. A quantum particle of mass $m$ with electric charge $Q$ is scattered by a localized distributed charge with a spherically-symmetric density $\rho(r)$ and zero total charge. Use the Born approximation to calculate the differential cross-section of forward scattering (with scattering angle $\theta = 0$), and evaluate it for scattering of electrons by a hydrogen atom in its ground state.

3.12. Reformulate the Born approximation for the 1D case. Use the result to find the scattering and transfer matrices of a “rectangular” scatterer

$$U(x) = \begin{cases} U_0, & \text{for } |x| < d / 2, \\ 0, & \text{otherwise.} \end{cases}$$

$^{80}$ See, e.g., CM Sec. 3.7, in particular Eq. (3.72).
Compare the results with the those of the exact calculations carried out earlier in the course.

3.13. Use Eq. (88) to show that the Bragg rule for the diffraction wave maxima, \( k = k_0 + Q \), where \( Q \) is any vector of the reciprocal lattice defined by Eq. (110), is valid not only for electromagnetic waves, but also for non-relativistic quantum particle scattering by a periodic (Bravais) lattice.

3.14. In the tight-binding approximation, calculate the eigenstates and eigenvalues of three similar, weakly coupled quantum wells located in the vertices of an equilateral triangle.

3.15. Figure on the right shows a fragment of a periodic 2D lattice, with open and solid points showing the location of different local potentials – say, different atoms.

(i) Find the reciprocal lattice and the 1st Brillouin zone;
(ii) Find wave number \( k \) of the monochromatic radiation incident along axis \( x \), at which the lattice creates the first-order diffraction peak within the \([x, y] \) plane, and the direction towards this peak.
(iii) Semi-qualitatively, describe the evolution of the intensity of the peak if the local potentials represented by the open and solid points tend to each other.

3.16. For the 2D hexagonal lattice (Fig. 11b):

(i) find the reciprocal lattice \( Q \) and the 1st Brillouin zone;
(ii) use the tight-binding approximation to calculate the dispersion relation \( E(q) \) for a 2D particle moving in a potential with such periodicity, close to the eigenenergy of an axially-symmetric state quasi-localized at the potential minima;
(iii) analyze and sketch (or plot) the resulting dispersion relation \( E(q) \) inside the 1st Brillouin zone.

3.17. Complete the tight-binding approximation calculation of band structure of the honeycomb lattice, started in the end of Sec. 4. Analyze the results. Prove that the Dirac points \( q_D \) are located in the corners of the 1st Brillouin zone, and express the velocity \( v_n \), participating in Eq. (122), in terms of the coupling energy \( \delta_n \). Show that the final results do not change if the quasi-localized wavefunctions are not axially-symmetric, but are proportional to \( \exp\{i \phi \} \) - as they are, with \( n = 1 \), for the 2pz electrons of carbon atoms in graphene, which are responsible for its transport properties.

3.18. Examine basic properties of the so-called Wannier functions defined as

\[
\phi_R(r) = \text{const} \times \int_{BZ} \psi_q(r)e^{-i\mathbf{q} \cdot \mathbf{R}} d^3q,
\]

where \( \psi_q(r) \) is the Bloch wavefunction (3.108), \( \mathbf{R} \) is any vector of the Bravais lattice, and the integration over quasi-momentum \( q \) is extended over any (e.g., the first) Brillouin zone.

3.19. Evaluate the long-range electrostatic interaction (the so-called London dispersion force) between two similar, electrically-neutral but polarizable molecules, modeling them as isotropic 3D harmonic oscillators.
Hint: Using the classical expression for the interaction between two electric dipoles, try to present the total Hamiltonian of the system as a sum of Hamiltonians of several independent harmonic oscillators, and calculate their ground-state energy as a function of distance between the molecules.

3.20. Use the variable separation method to find expressions for the eigenfunctions and the corresponding eigenenergies of a free 2D particle confined inside a thin round disk of radius $R$:

$$U = \begin{cases} 0, & \text{for } 0 \leq \rho < R, \\ + \infty, & \text{for } R < \rho, \end{cases}$$

where $\rho \equiv \{x, y, 0\}$. What is the level degeneracy? Calculate 5 lowest energy levels with accuracy better than 1%.

3.21. Calculate the ground-state energy of a 2D particle localized in a shallow flat-bottom potential well

$$U(\rho) = \begin{cases} -U_0, & \text{for } \rho < R \\ 0, & \text{for } \rho > R \end{cases},$$

with $0 < U_0 \ll \frac{\hbar^2}{mR^2}$.

3.22. Spell out the explicit form of spherical harmonics $Y_4^0(\theta, \phi)$ and $Y_4^4(\theta, \phi)$.

3.23. Calculate $\langle x \rangle$ and $\langle x^2 \rangle$ in the ground state of the planar and spherical rotators of radius $R$. What can you say about averages $\langle p_x \rangle$ and $\langle p_x^2 \rangle$?

3.24. According to the discussion in the beginning of Sec. 5, eigenfunctions of a 3D harmonic oscillator may be calculated as products of three 1D “Cartesian oscillators” - see, in particular Eq. (124), with $d = 3$. However, according to the discussion in Sec. 3.6, wavefunctions of the type (190), proportional to spherical harmonics $Y_l^m$, are also eigenstates of this spherically-symmetric system. Represent:

(i) the ground state of the oscillator, and
(ii) each of its lowest excited states,

taken in the form (190), as linear combinations of products of 1D oscillator wavefunctions. Also, calculate the degeneracy of $n^{th}$ energy level of the oscillator.

3.25. A spherical rotator (with $r \equiv (x^2 + y^2 + z^2)^{1/2} = R = \text{const}$) of mass $m$ is in the state with wavefunction

$$\psi = \text{const} \times \left( \frac{1}{3} + \sin^2 \theta \right).$$

Calculate the system’s energy.

3.26.* Calculate the eigenfunctions and the energy spectrum of a 3D particle free to move inside a sphere of radius $R$:

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81 See, e.g., EM Sec. 3.1.


\[ U = \begin{cases} 0, & \text{for } 0 \leq r < R, \\ +\infty, & \text{for } R < r. \end{cases} \]

Calculate 5 lowest energy levels with a 1% accuracy, and indicate the degeneracy of each level.

*Hint:* The solution of this problem requires the so-called spherical Bessel functions \( j_\ell(\xi) \), whose description is available in most math handbooks.82

3.27. Find the smallest value of depth \( U_0 \) for that the spherical quantum well

\[ U = \begin{cases} -U_0, & \text{for } r < R, \\ 0, & \text{for } R < r, \end{cases} \]

has a bound (localized) eigenstate. Does such a state exist for a very narrow and deep well \( U = -\mathcal{W}\delta(r) \), with a positive and finite \( \mathcal{W} \)?

3.28. Calculate the smallest value of depth \( U_0 \) for that the following spherically-symmetric quantum well,

\[ U(r) = -U_0e^{-r/R}, \quad \text{with } U_0, R > 0, \]

has a bound (localized) eigenstate.

*Hint:* Try to introduce the following new variables: \( f \equiv rR \) and \( \xi \equiv Ce^{-r/2R} \), with an appropriate choice of constant \( C \).

3.29. Calculate the lifetime of the lowest metastable state in the spherical-shell potential

\[ U(r) = \mathcal{W}\delta(r - R), \quad \text{with } \mathcal{W} > 0, \]

in the limit of large \( \mathcal{W} \). Specify the limit of validity of your result.

3.30. Calculate the condition at which a particle of mass \( m \), moving in the field of a very thin spherically-symmetric shell, with

\[ U(r) = -\mathcal{W}\delta(r - R), \quad \text{with } \mathcal{W} > 0, \]

has at least one localized (“bound”) stationary state. Compare the result with that for potential

\[ U_0(r) = -\mathcal{W}_0\delta(r), \quad \text{with } \mathcal{W}_0 > 0. \]

*Hint:* Note that the first delta-function is one-dimensional, while the second one is three-dimensional, so that parameters \( \mathcal{W} \) and \( \mathcal{W}_0 \) have different dimensionalities.

3.31. A particle, moving in a central potential \( U(r) \), with \( U(r) \to 0 \) at \( r \to \infty \), has a stationary state with the following wavefunction:

\[ \psi = Cr^\alpha e^{-\beta r} \cos \theta, \]

where \( C, \alpha, \) and \( \beta \) are constants. Calculate:

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82 See, e.g., any of the handbooks recommended in MA Sec. 16(ii).
(i) probabilities of all possible values of quantum numbers $m$ and $l$,
(ii) the confining potential, and
(iii) state’s energy.

3.32. Calculate the energy spectrum of a particle moving in a monotonic, but otherwise arbitrary attractive central potential $U(r)$, in the approximation of large orbital quantum numbers $l$. Formulate the quantitative condition(s) of validity of your theory. Check that for the Coulomb potential $U(r) = -C/r$, your result agrees with Eq. (191).

3.33. An electron had been in the ground state of a hydrogen-like atom/ion with nuclear charge $Ze$, when the charge suddenly changed to $(Z + 1)e$. Calculate the probabilities for the electron of the changed system to be:

(i) in the ground state, and
(ii) in the lowest excited state.

Evaluate these probabilities for the particular case of the beta decay of tritium, with the formation of a single-positive ion of $^{3}{\text{He}}$.

3.34. Calculate $\langle x^2 \rangle$ and $\langle p_x^2 \rangle$ in the ground state of a hydrogen-like atom. Compare the results with Heisenberg’s uncertainty relation. What do these results tell about electron’s velocity in the atom?

3.35. Apply to Eq. (181) the Hellmann-Feynman theorem (see Problem 1.4) to prove:

(i) the first of Eqs. (3.201), and
(ii) the fact that for a spinless particle in an arbitrary spherically-symmetric attractive potential $U(r)$, the ground state is always an $s$-state (with the orbital quantum number $l = 0$).

3.36. For the ground state of a hydrogen atom, calculate the expectation values of $E$ and $E^2$, where $E$ is the electric field created by the atom at distance $r \gg r_0$ from its nucleus. Interpret the resulting relation between $\langle E^2 \rangle$ and $\langle E^2 \rangle$ (at the same observation point).

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83 Such a fast change happens, for example, at the beta-decay, when one of nucleus’ neurons suddenly becomes a proton, emitting a high-energy electron and a neutrino which leave the system very fast (instantly on the atomic time scale), and do not participate in the atom transition’s dynamics.
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