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Lecture notes, 2013
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1 Lecture 7: Bohr atom, Heisenberg microscope, double slit experiment

http://www.youtube.com/watch?v=hUJfjRoxCbk
http://en.wikipedia.org/wiki/Heisenberg%27s_microscope
http://spiff.rit.edu/classes/phys314/lectures/heis/heis.html

2 Lecture 8: problems in three dimensions

Liboff 10.1-10.5

2.1 3d coordinate systems

Generalizing the one-dimensional quantum physics from the previous course to three dimensions is a very straight forward task. Consider the Hamiltonian of a single particle of mass m in a one-dimensional potential $V(x)$

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

In three dimensions this will become

$$H_{\mathrm{3D}} = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right) + V(x,y,z) = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}), \tag{2}$$

where $\nabla = (d/dx, d/dy, d/dz)$ and $\mathbf{r} = (x,y,z)$ are vector operators. In the case of a spherically symmetrix potential, the potential simplifies as $V(\mathbf{r}) = V(r)$, where $r = \sqrt{x^2+y^2+z^2}$ is the distance (say, distance from the nucleus of an atom, the center of the quantum dot or what ever).

2.2 Cartesian coordinates

The simplest case is obtained when the external potential vanishes $V(r) \equiv 0$. Now the Hamiltonian can be written as

$$H = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right) = \sum_{\sigma\in\{x,y,z\}} H_\sigma, \tag{3}$$

where $H_{\mathrm{x}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ and similarly for all $\sigma \in \{x,y,z\}$.

Notice that the Hamiltonian commutes with momentum operators, for example $[H, p_x] = [H, -i\hbar\frac{d}{dx}] = 0$. Thus the eigenstates of the Hamiltonian H are also eigenstates of momentum operators p_σ. These are known to be the plane-waves, for example the eigenstates of p_x are

$$X_{k_x}(x) = \mathcal{N}e^{ik_x x}, \tag{4}$$

where k_x is the corresponding eigenvalue (momentum). The eigenstate of H is thus now necessarily of the form

$$\psi(x, y, z) = X_{k_x}(x)\psi'(y, z). \tag{5}$$

The same reasoning can be repeated in y and z directions yielding the full set of eigenstates

$$\psi_{\mathbf{k}}(x, y, z) = X_{k_x}(x)Y_{k_y}(y)Z_{k_z}(z) = Ae^{i\mathbf{k}\cdot\mathbf{r}}. \tag{6}$$

Thus, not surprisingly, the eigenstates are 3d plane waves. It is a very straightforward task to check that this is indeed an eigenstate of H. Solving the eigenequation

$$H\psi_{\mathbf{k}}(x, y, z) = E\psi_{\mathbf{k}}(x, y, z), \tag{7}$$

yields the corresponding eigenvalue $E_k = \frac{\hbar^2 k^2}{2m}$. These 3d plane wave states behave exactly as their one-dimensional counterparts.

2.3 Example: charged particle in a magnetic field

Before going deeper into three dimensional systems, let us consider one very simple example, namely a charged particle in a uniform magnetic field $\mathbf{B}$. Such system is described by the Hamiltonian (I will not derive this Hamiltonian here, it comes from the classical electrodynamics by simply replacing classical variables by quantized operators)

$$H = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2, \tag{8}$$

where the momentum operator $\mathbf{p} = i\hbar\nabla$, and $\mathbf{A}$ is called vector potential. The vector potential is related to the magnetic field as $\mathbf{B} = \nabla \times \mathbf{A}$. In particular, a uniform magnetic field in the z-direction $\mathbf{B} = (0, 0, B)$ is realized by a vector potential $\mathbf{A} = (-yB, 0, 0)$. Notice that there are actually several possible choices of $\mathbf{A}$ that all produce the same magnetic field, so one has some freedom in choosing which one to use (they are all just as fine). A standard choice for $\mathbf{A}$ is called Coulomb gauge, and it is defined as the choice of vector potential for which $\nabla \cdot \mathbf{A} = 0$. Obviously, here $\nabla \cdot \mathbf{A} = \frac{d}{dx}yB = 0$.

Thus, satisfied that our $\mathbf{A}$ describes a uniform magnetic field $\mathbf{B}$, we can substitute this into the Hamiltonian and obtain

$$H = \frac{1}{2m}\left(p_x + \frac{eyB}{c}\right)^2 + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}. \tag{9}$$

This Hamiltonian commutes with operators p_x and p_z, and hence the eigenstates of H are also eigenstates of these components of the momentum operator. These in turn are well known to be the plane waves $e^{ik_x x}$ and $e^{ik_z z}$. Thus we know that the eigenstates of H are of the form

$$\varphi_{k_x,k_z}(x, y, z) = e^{ik_x x + ik_z z} f(y). \tag{10}$$

The eigenequation $H\varphi = E\varphi$ reads now

$$\left[\frac{1}{2m}\left(p_x + \frac{eyB}{c}\right)^2 + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}\right] e^{ik_x x + ik_z z} f(y) = E e^{ik_x x + ik_z z} f(y), \tag{11}$$

which upon evaluation yields (remember, $p_z = i\hbar d/dz$ and hence $p_z^2 e^{ik_z z} = -\hbar^2 k_z^2$)

$$\left[\frac{1}{2m}\left(\hbar k_x + \frac{eyB}{c}\right)^2 + \frac{p_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m}\right] f(y) = Ef(y). \tag{12}$$

The operator on the left hand side can be written as

$$H' = \frac{p_y^2}{2m} + \frac{1}{2}m\Omega^2 \left(y - y_0\right)^2 + \frac{\hbar^2 k_z^2}{2m}, \tag{13}$$

where $y_0 = -\frac{c\hbar k_x}{eB}$ and $\Omega^2 = \left(\frac{eB}{mc}\right)^2$. This operator is identical to the Hamiltonian of a one-dimensional harmonic oscillator, in which the origo is shifted by y_0 along the y-axis. The last term $\frac{\hbar^2 k_z^2}{2m}$ is simply a constant energy shift (constant in the sense that it is not an operator. Different plane-waves with different k_z of course have different 'constants'.)

The eigenenergies of the one-dimensional harmonic oscillator are known to be $\hbar\Omega(n + 1/2)$, where $n = 0, 1, 2, \ldots$. Taking into account that the energies of our present system are shifted by $\hbar^2 k_z^2/2m$, we obtain the eigenenergies of Hamiltonian H

$$E_{k_z,n_y} = \hbar\Omega\left(n_y + \frac{1}{2}\right) + \frac{\hbar^2 k_z^2}{2m}. \tag{14}$$

Notice that there is no k_x dependence and hence there is a high degree of degeneracy. This form for the eigenenergy does fit the classical picture of a charged particle in a uniform magnetic field: the z-component of the motion is unaffected by a magnetic field in the same direction and hence the z-part enters the energy and the eigenstate unaffected. The first part of the energy describes periodic motion (compare with rotation in classical case) in the xy-plane. The corresponding eigenstates are products of the harmonic oscillator eigenstates in the y-direction (shifted by y_0) and plane-waves in the x and z directions

$$\varphi_{k_x,k_z,n_y}(x,y,z) = A_{n_y}\mathcal{H}_{n_y}\left[\sqrt{\frac{m\Omega}{\hbar}}(y - y_0)\right]^2 \exp\left[-\frac{1}{2}\frac{m\Omega}{\hbar}(y-y_0)^2 + ik_x x + ik_z z\right], \tag{15}$$

where $H_n(x)$ is the nth-order Hermite polynomial and A_n is a normalization constant.

This example of a charged particle in a uniform magnetic field shows the key concepts required when considering more complicated systems. Namely the utilization of symmetries and how they enter commutation relations (H commuted with p_x and p_z) and wavefunctions (product from $e^{ik_x x}e^{ik_z z}f(y)$), and how the resulting eigenproblem is simplified (mapped onto a one-dimensional harmonic oscillator). However, these symmetries are often most easily utilized by writing Hamiltonian using suitably symmetrized operators.

2.4 Spherical coordinates

If the Hamiltonian H is spherically symmetric, one should express operators in spherical coordinates instead of cartesian. For this end, we would like to write the Laplacian operator ∇^2 in spherical coordinates as

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right), \tag{16}$$

yielding the Hamiltonian in spherical coordinates (no external potential $V(r)$ here, we will add it later)

$$H = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\hbar^2}{2mr^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right). \tag{17}$$

Recalling the expression for the angular momentum operator from the previous course, we notice that the operator in the brackets is equal to $-L^2$ allowing us to write the above Hamiltonian simply as

$$H = -\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{L^2}{2mr^2}. \tag{18}$$

2.5 Separation of variables, radial and angular parts

Adding a spherically symmetric external potential $V(r)$ to the Hamiltonian does not affect the subsequent calculation. Therefore, lets include it in order to make the discussion more general. The Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{L^2}{2mr^2} + V(r), \tag{19}$$

commutes with the angular momentum operator L^2 and thus they share common eigenstates. Eigenstates of the angular momentum operator are the spherical harmonics $Y_l^m(\theta,\phi)$ which do not depend on radius r and thus it is a good idea to try a trial wavefunction of the form

$$\varphi(\vec{r}) = R(r)Y(\theta,\phi), \tag{20}$$

where $R(r)$ and $Y(\theta,\phi)$ are referred to as the radial and angular parts of the eigenstate. Substituting this trial wavefunction into the eigenequation $H\varphi(\vec{r}) = E\varphi(\vec{r})$, we obtain

$$-\frac{\hbar^2}{2m}\left[\frac{Y(\theta,\phi)}{r}\frac{d^2}{dr^2}\left(rR(r)\right) - \frac{R(r)}{r^2\hbar^2}L^2Y(\theta,\phi)\right] + V(r)R(r)Y(\theta,\phi) = ER(r)Y(\theta,\phi). \tag{21}$$

Notice that L^2 acts only on the angular part of the wavefunction as it does not have any r-dependence. Multiplying this equation by $2mr^2/\left(R(r)Y(\theta,\phi)\right)$ we obtain

$$-\left\{\frac{\hbar^2 r}{R(r)}\frac{d^2}{dr^2}\left(rR(r)\right) - 2mr^2\left[V(r)-E\right]\right\} + \left\{\frac{1}{Y(\theta,\phi)}L^2Y(\theta,\phi)\right\} = 0. \tag{22}$$

In the equation above, the first term depends only on radius r whereas the latter term depends only on angles θ and ϕ. Since the equation holds for any value of r,θ and ϕ, the two terms must be constants, equal in magnitude, and have opposite signs. That is, we have

$$\frac{\hbar^2 r}{R(r)}\frac{d^2}{dr^2}\left(rR(r)\right) - 2mr^2\left[V(r)-E\right] = C_l, \tag{23}$$

and

$$\frac{1}{Y(\theta,\phi)}L^2Y(\theta,\phi) = C_l, \tag{24}$$

where C_l is some constant (to be determined below).

The second equation is known from the previous course. It was encountered when solving the eigenstates and eigenvalues of the angular momentum operator L^2. Multiplying it by $Y(\theta, \phi)$ yields the standard form of an eigenequation

$$L^2 Y(\theta, \phi) = C_l Y(\theta, \phi). \tag{25}$$

The eigenstates were called spherical harmonics and denoted by $Y_l^m(\theta, \phi)$ with l being integer and the m quantum numbers were allowed to run from $-l, -l+1, \ldots, l-1, l$. The corresponding eigenvalue was $C_l = \hbar^2 l(l+1)$.

Now we have solved the angular part of the eigenstate, what is left is the radial part. From Eq. (22) we have now (multiplying by $R(r)/2mr^2$)

$$\frac{\hbar^2}{2mr}\frac{d^2}{dr^2}\left(rR(r)\right) - R(r)\left[V(r) - E\right] = \frac{\hbar^2}{2mr^2} l(l+1) R(r). \tag{26}$$

Rearranging terms a bit yields

$$-\frac{\hbar^2}{2mr}\frac{d^2}{dr^2}\left(rR(r)\right) + \left[V(r) + \frac{\hbar^2}{2mr^2} l(l+1)\right] R(r) = ER(r). \tag{27}$$

2.6 Radial wavefunction

As is evident from the above discussion, for a spherically symmetric potential, the angular part of the eigenproblem is independent of the actual shape of the potential $V(r)$. The radial part, however, does depend on the potential. On the other hand, the equation (26) is one-dimensional. Thus, for a spherically symmetric potential, the three-dimensional problem is reduced to a one-dimensional radial problem.

The standard approach for solving the radial equation starts from making change of variable $R(r) = u(r)/r$. We get

$$-\frac{\hbar^2}{2mr}\frac{d^2}{dr^2} u(r) + \left[V(r) + \frac{\hbar^2}{2mr^2} l(l+1)\right] u(r)/r = Eu(r)/r. \tag{28}$$

Multiplying this by r we obtain

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} u_l(r) + \left[V(r) + \frac{\hbar^2}{2mr^2} l(l+1)\right] u_l(r) = Eu_l(r). \tag{29}$$

This is exactly like a one-dimensional Schrödinger equation for an effective potential

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}. \tag{30}$$

The second term on the right hand side is called centrifugal term, and it resembles the classical centrifugal force, by keeping a particle with nonzero angular momentum l away from the origin (for $l \neq 0$ it produces a $1/r^2$ diverging potential wall at origin). Notice that I added the subscript l in the function $u_l(r)$ since the radial eigenstate depends on the angular quantum number (i.e. each l has its own set of radial eigenstates). In order to get better understanding to this centrifugal term, let us first reconsider the case where the external potential vanishes $V(r) \equiv 0$ for all r.

3 Lecture 9: solving radial equation, special functions and bound states

3.1 Free particle in spherical coordinates

Liboff 10.3,10.6

We have already solved the free particle in three dimensions using Cartesian coordinates. It is very instructive to do it again using spherical coordinates and then compare the results obtained from the two pictures.

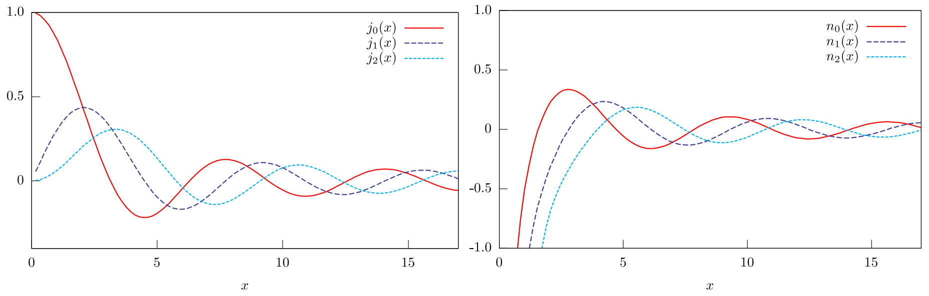

Figure 1: Spherical Bessel $j_l(x)$ and Neumann $n_l(x)$ functions for $l = 0, 1, 2$. Notice that only the Bessel functions are regular at the origin.

In absence of an external potential, the radial eigenequation reads

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u_l(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}u_l(r) = Eu_l(r). \tag{31}$$

The radial eigenstates are given by the spherical Bessel $j_l(r)$ and Neumann $n_l(r)$ functions shown in Fig. 1. The full 3d eigenstates of the free particle Hamiltonian can be written as (remember $R(r) = u(r)/r$)

$$\varphi_{klm}(\mathbf{r}) = j_l(kr)Y_l^m(\theta, \phi), \tag{32}$$

and

$$\varphi'_{klm}(\mathbf{r}) = n_l(kr)Y_l^m(\theta, \phi). \tag{33}$$

The quantum number k, which specifies the set of different radial eigenstates, is analogous to momentum. However, here it must be understood as somekind of 'radial momentum'. The correspondence will become more clear when we discuss scattering problems. Both sets of eigenstates (for Bessel and Neumann functions) have corresponding eigenenergies $E_k = \frac{\hbar^2 k^2}{2m}$. However, only Bessel functions are regular at origin, as the Neumann functions diverge at least as $1/r$. Following Liboff, we will consider only the regular Bessel functions.

These states and energies should be compared with the eigenstates obtained in Cartesian coordinates $Ae^{i\mathbf{k}\cdot\mathbf{r}}$. The energy of such state is also $E_k = \frac{\hbar^2 k^2}{2m}$ but otherwise the states look very different. The reason for this apparent discrepancy is in the degeneracy of the states, for the energy E_k does not depend on the direction (spherically symmetric!). Thus one can combine different plane waves with same magnitude for k but different directions and still obtain an eigenstate of the Hamiltonian. The same can be done for any eigenstate but let us not go there here.

Thus, satisfied that we are seeing the same physics in both coordinate systems, what can we say about the centrifugal term in the Hamiltonian? We know that classically the trajectory of a particle in the Cartesian coordinates is just a straight line (there are no forces acting on it), and the quantum version of this result is that the plane-waves are eigenstates of the Hamiltonian. The point is that the transformation into the spherical coordinate system produces the centrifugal (pseudo-)force, just like moving into a rotating coordinate system. The trajectory is still the straight line but it just does not look like it in the new coordinate system since the plane waves do not arise from the calculation naturally. However, ultimately this is exactly the same thing as seen in classical mechanics when using rotating coordinate system.

The free space eigenstates and the Bessel and Neumann functions will prove useful later on when considering scattering problem in 3d. But let us first consider bound states in presence of a 3d spherically symmetric potential.

3.2 Bound states in spherically harmonic potentials

Most external potentials will yield two kinds of states: bound states, which decay (at least) exponentially in the $r \to \infty$ asymptote and scattering states which do not decay. We will first consider bound states in a few example potentials.

3.2.1 Hydrogen atom

Consider an electron in the vicinity of a massive point like positive charge (such as the nucleus of an hydrogen atom, we want it to be massive so that we can assume that the nucleus does not move), the external potential felt by the electron is given by the Coulomb interaction

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}. \tag{34}$$

We would now like to solve the eigenstates given by the equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u_l(r) + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u_l(r) = E_l u_l(r). \tag{35}$$

I will not go through the full derivation of the radial eigenstates, but rather point out the physically interesting points in the calculation. For more details see Liboff 10.6. The standard derivation starts by observing the asymptotic values of the wavefunction in the limits $r \to \infty$ and $r \to 0$. In the first limit both the centrifugal and the Coulomb interaction terms vanish since they decay as $1/r^2$ and $1/r$, respectively. Thus we have the asymptotic equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u_l(r) \sim E u_l(r), \tag{36}$$

with solutions

$$u_l(r) \sim Ae^{-\alpha r} + Be^{\alpha r}, \tag{37}$$

where $\alpha = \sqrt{-2mE/\hbar^2}$. First of all, if the energy E is positive, the solution $u_l(r)$ consists of two plane waves that extend to infinity. These are called scattering states and such states will be discussed later on. Here we are interested in negative energies $E < 0$. Solutions of these states are called bound states since they describe states where the electron is 'bound' more or less to the vicinity of the nucleus, with the radial wavefunction decaying faster than $1/r$ (remember, the real radial wavefunction $R_l(r)$ is connected to our $u_l(r)$ by $R_l(r) = u_l(r)/r$).

However, for negative energies $E < 0$, the above asymptotic solution for $u_l(r)$ has two parts: one increasing exponentially and one decaying. The exponentially increasing wavefunction is not normalizable and as such not physically possible. Thus we conclude that $B = 0$ and the asymptotic form of the radial eigenstate will become

$$u_l(r) \sim Ae^{-\alpha r}. \tag{38}$$

In the opposite limit $r \to 0$ the centrifugal term will dominate and the asymptotic limit of the eigenequation will be

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u_l(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}u_l(r) = 0, \tag{39}$$

which can be written as

$$\frac{d^2}{dr^2}u_l(r) = \frac{l(l+1)}{r^2}u_l(r) \tag{40}$$

which has the solution $u_l(r) = Cr^{l+1} + Dr^{-l}$. Again, the solution has an unphysically diverging term unless $D = 0$ (except when $l = 0$, but even then the constant term D in $u_0(r)$ would become nonregular D/r for $R(r)$). Thus we have the asymptotic form in the limit $r \to 0$ as

$$u_l(r) \sim Cr^{l+1}. \tag{41}$$

Thus it looks like it would be a good idea to use a trial eigenstate of the form

$$u_l(r) = r^{l+1}e^{-\alpha r}v_l(r). \tag{42}$$

Indeed, continuing the derivation, this turns out to be a good ansatz, with the final result for the radial eigenstates being

$$u_{nl}(r) \sim r^{l+1}e^{-\frac{r}{na_0}}L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right), \tag{43}$$

where $a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$ is called the Bohr radius. The function $L_{n-l-1}^{2l+1}(x)$ is generalized (or associated as called in Liboff) Laguerre polynomial, and the quantum number n (called the *principal quantum number* due to historic reasons) is used to list the discrete set of radial eigenstates. From the derivation we can also obtain the constraint $n \geq l + 1$ which is sometimes written the other way around as $l \leq n - 1$. The corresponding energy of the $u_{nl}(r)$ state is

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}. \tag{44}$$

Notice the high level of degeneracy as the energy does not depend on angular quantum numbers l and m (don't mix quantum number m with mass m). The degeneracy with respect to different values of quantum number m arises from the spherical symmetry and it holds also for more general (spherically symmetric) potentials. The l degeneracy, however, is pure coincidence and a property of the $1/r$ scaling of the Coulomb potential. On the other hand, even in the case of hydrogen atom, the l and m degeneracies will be lifted when one includes interactions due to the spins of the electron and the nucleus (called spin-orbit and spin-spin couplings). That, however, goes beyond our current needs although we will briefly consider those effects later on in the course.

3.2.2 Harmonic trap

Another important 3d potential is the spherically symmetric harmonic potential $V(r)=\frac{1}{2}m\omega^2r^2$. Thus we would like to solve the eigenstates given by the equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u_l(r)+\left[\frac{1}{2}m\omega^2r^2+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u_l(r)=E_lu_l(r). \tag{45}$$

The solutions are (obtained using $R_{nl}(r)=u_{nl}(r)/r$):

$$R_{nl}(r)=\sqrt{2}r_0^{-3/2}\sqrt{\frac{n!}{(n+l+1/2)!}}e^{-\frac{\tilde{r}^2}{2}}\tilde{r}^lL_n^{l+1/2}\left(\tilde{r}^2\right), \tag{46}$$

where the dimensionless distance $\tilde{r}=r/r_0$ and $r_0=\sqrt{\hbar/m\omega}$. The corresponding eigenenergies are $E_{nl}=\hbar\omega\,(2n+l+3/2)$. Notice that the eigenenergies depend on the orbital angular momentum quantum number l. Indeed, the l degeneracy in the case of Coulomb potential was simply a coincidence.

Just like in the case of 3d free space, the spherically symmetric harmonic potential can also be solved easily in Cartesian coordinates. In these coordinates, the Hamiltonian is

$$H=-\frac{\hbar^2}{2m}\nabla^2+\frac{1}{2}m\omega^2r^2=\sum_{\sigma\in\{x,y,z\}}H_\sigma, \tag{47}$$

where for example $H_x=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2x^2$, and similarly for other $\sigma\in\{x,y,z\}$. The reason why this is so easy to solve is that different components H_σ commute with the full Hamiltonian H, i.e $[H,H_\sigma]=0$, for all $\sigma\in\{x,y,z\}$. Thus, just like in the case of free space, the eigenstates can be written as

$$\psi_{n_x,n_y,n_z}(x,y,z)=\phi_{n_x}(x)\phi_{n_y}(y)\phi_{n_z}(z),$$

where the 1d-wavefunctions $\phi_n(x)$ are just the solutions of 1d harmonic oscillators. The energy of this eigenstate is $E_{n_x,n_y,n_z}=\hbar\omega\,(n_x+n_y+n_z+3/2)$. While it is not immediately obvious that the energy spectrum is the same as the one obtained using spherical coordinates ($E_{nl}=\hbar\omega\,(2n+l+3/2)$), they are. This can be seen by counting the degeneracies of different levels. For example degeneracy of the energy $E=\hbar\omega(1+3/2)=\hbar\omega\frac{5}{2}$ is 3: in Cartesian coordinates one has $(n_x,n_y,n_z)=(1,0,0)$, $(0,1,0)$, or $(0,0,1)$. In spherical coordinates one has only $n=0,l=1$; however, the $l=1$ state is three-fold degenerate, since the allowed m quantum numbers are -1,0, and 1. One can generalize this simple observation to arbitrary energy levels, showing that the energy spectrum is the same in both coordinate systems (as it should, as the physics must be unchanged and the energy levels are well defined physical quantities). Of course, we should also show that the corresponding eigenstates can be written as linear combinations.

Harmonic potential has one very unphysical property namely that it becomes infinite at the $r\to\infty$ asymptote. Thus there are not scattering states but instead all states are bound. While the potential itself may be unphysical when taken to extreme, it is often a very good approximation for real physical potentials. The physical setting will then give an upper bound in energy beyond which the harmonic approximation may not hold any more.

This concludes our description of bound states in spherically symmetric 3d potentials. Next we will study the other half of the 3d work, namely the unbound or scattering states.

4 Lecture 10: scattering in 3d

Liboff 10.5, 14
The basic scattering theory in quantum mechanics is treated in different ways in different books. Ultimately they all boil down to the same, but because of non-standardized notation (Liboff, Schwabl and Griffiths define for example differential scattering cross section in different ways) the approaches appear incompatible. I am hoping that I can clarify the somewhat messy scattering calculation. Since Liboff neglects quite a few details in the derivation, I will follow Schwabl. The main result, however, is the same for Liboff and Schwabl.

The scattering problem describes the wavefunction of a particle that approaches the potential $V(r)$ as a plane-wave e^{ikz}, but scatters in all directions. The scattering amplitude $f(\theta)$ describes the probability (amplitude) of scattering in the direction θ.

4.1 Scattering theory in Liboff & Schwabl way

The discussion in the previous lecture regarding 3d spherically symmetric potentials with radial and angular parts for the wavefunction apply equally well to *stationary* scattering states. The stationary states are eigenstates of the Hamiltonian, and satisfy the radial equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u_l(r)+\left[V(r)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u_l(r)=Eu_l(r). \tag{48}$$

However, the difference to the bound states described earlier is that the scattering states states are not bound, and at asymptote $r\to\infty$ they have a plane-wave like form (neglecting normalization)

$$\varphi_k(r,\theta)=e^{ikz}+f_k(\theta)\frac{e^{ikr}}{r}. \tag{49}$$

The first term on the right describes the incoming plane-wave (and also outgoing, but unscattered, plane-wave as part of the plane-wave will necessarily go past the potential unaffected). The second term describes the scattered part, in which the scattering amplitude $f(\theta)$ gives the probability amplitude for scattering to direction θ, e^{ikr} describes a plane-wave propagating out from the scattering potential and the factor $1/r$ ensures proper normalization. [1] Notice that the scattered wave has the same magnitude for the momentum as the incoming wave. This is an assumption that holds for *elastic collisions* (kinetic energy is conserved). The whole scattering problem now boils down to determining the scattering amplitude $f_k(\theta)$. The scattering amplitude $f_k(\theta)$ is of utmost importance, because it is a quantity (or its magnitude) that can be measured in an experiment. The actual interparticle

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[1] Notice that even if the potential $V(r)$ is spherically symmetric, the full scattering state is not. The reason is that the incoming wave e^{ikz} breaks the spherical symmetry by providing a specific direction (direction of the propagation). This is of course a very important point that is worth remembering when considering any symmetries: even if the Hamiltonian has some symmetry, the actual states are not obliged to obey the same symmetries. However, the symmetry of the Hamiltonion does tell us what kind of states are coupled. In the case of spherically symmetric Hamiltonian, the angular momentum is conserved and thus states with different angular momenta are uncoupled. If the state is a linear combination of different angular momenta, then each component can be treated independently. This is of course precisely the same thing as when we express some state in the eigenbasis of the Hamiltonian and follow each eigenstate separately. Symmetries just allow us to do the same thing even if we do not know the full eigenstates of the Hamiltonian.

interaction potentials $V(r)$ cannot generally be directly measured, only its effect on the trajectories of the particles. Thus, one often uses scattering phase shifts and especially scattering amplitudes as input parameters for a theory. However, it is important to understand the processes that go into these phenomenological parameters in order to avoid possible inconsistencies in the theory.

The wavefunction ansatz (49) must be understood as the $r \to \infty$ limit. Assuming that the potential is sufficiently short ranged, we can neglect the potential $V(r)$ at large r. Thus, the asymptotic radial equation simplifies into

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u_l(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}u_l(r) = Eu_l(r). \tag{50}$$

The solutions to this equation are already known and the corresponding radial eigenstates (remember again $R_{kl}(r) = u_{kl}(r)/r$) are the Bessel $j_l(kr)$ and Neumann functions $n_l(kr)$. Following Liboff, I neglect the non-regular Neumann functions (one could also keep them, but the end result will be unaffected. If interested, have a look at what Griffiths does.) The angular momentum is conserved in scattering from a spherically symmetric potential (the radial functions for different l are not coupled), and hence we can limit ourselves to studying scattering with a fixed l.

Let us consider for a minute a case in which there is no scattering at all, i.e. set $V(r) = 0$ and hence also $f_k(\theta) \equiv 0$. Expressing the plane-wave using Bessel functions (for describing the radial part of the wavefunction) and Legendre polynomials (for describing the angular part) yields

$$e^{ikz} = \sum_l (2l+1)i^l j_l(kr)P_l(\cos\theta), \tag{51}$$

and expressing also the full wavefunction in this basis

$$\varphi_k^0(r,\theta) = \sum_l C_l^0 j_l(kr)P_l(\cos\theta) \tag{52}$$

(the superscripts 0 referring to the initial assumption that there is no scattering at all) gives

$$\sum_l C_l^0 j_l(kr)P_l(\cos\theta) = \sum_l (2l+1)i^l j_l(kr)P_l(\cos\theta). \tag{53}$$

The equation must hold for all l, so we have

$$C_l^0 = (2l+1)i^l. \tag{54}$$

Next we will add the effect of scattering. However, the full wavefunction $\varphi_k(r,\theta)$ includes contributions from both incoming and outgoing waves, and the scattering potential cannot affect the ingoing part (otherwise we would need some rebounding from some walls at infinity). The separation into ingoing and outgoing waves can be made explicit in the large r asymptote by writing the Bessel function as

$$j_l(kr) \approx \frac{1}{2ikr}\left[(-i)^l e^{ikr} - i^l e^{-ikr}\right]. \tag{55}$$

The first term on the right describes outgoing spherical wave and the second term describes ingoing wave. Now the ingoing wave must remain unaffected when we introduce the scattering term $f_k(\theta)e^{ikr}/r$ but the outgoing wave can be affected.

However, the scattering term cannot affect the magnitude of the factor C_l (since the probability must be conserved and there are no transitions between different l components due to spherical symmetry), but it can induce a phase shift $2\delta_{kl}$ (factor two is for convenience as it yields the same final equation as Liboff). Thus, the full wavefunction will be of the form

$$\varphi_k(r) = \sum_l C_l^0 \frac{e^{i2\delta_{kl}}(-i)^l e^{ikr} - i^l e^{-ikr}}{2ikr} P_l(\cos\theta). \tag{56}$$

By the way, notice that this wavefunction ansatz is the same as used in Liboff but you will need to rewrite it as

$$\begin{aligned} \varphi_k(r) &= \sum_l C_l^0 e^{i\delta_{kl}} \frac{e^{i\delta_{kl}}(-i)^l e^{ikr} - i^l e^{-ikr} e^{-i\delta_{kl}}}{2ikr} P_l(\cos\theta) \\ &= \sum_l C_l^0 e^{i\delta_{kl}} \frac{\sin(kr - \pi/2l + \delta_{kl})}{kr} P_l(\cos\theta). \end{aligned} \tag{57}$$

Thus we have now

$$\sum_l C_l^0 \frac{e^{i2\delta_{kl}}(-i)^l e^{ikr} - i^l e^{-ikr}}{2ikr} P_l(\cos\theta) = \sum_l (2l+1) i^l j_{kl}(r) P_l(\cos\theta) + f_k(\theta)\frac{e^{ikr}}{r}. \tag{58}$$

Expressing the scattering amplitude $f_k(\theta)$ using Legende polynomials $P_l(\cos\theta)$ as

$$f_k(\theta) = \sum_l (2l+1) a_{kl} P_l(\cos\theta), \tag{59}$$

yields for each l an equation

$$C_l^0 \frac{e^{i2\delta_{kl}}(-i)^l e^{ikr} - i^l e^{-ikr}}{2ikr} = (2l+1) i^l \frac{(-i)^l e^{ikr} - i^l e^{-ikr}}{2ikr} + (2l+1) a_{kl} \frac{e^{ikr}}{r}. \tag{60}$$

Solving for a_{kl} yields (and using $C_l^0 = (2l+1)i^l$)

$$a_{kl} = \frac{e^{i2\delta_{kl}} - 1}{2ik} = \frac{1}{k} e^{i\delta_l} \sin\delta_l. \tag{61}$$

In particular, we obtain the scattering amplitude

$$f_k(\theta) = \frac{1}{k} \sum_l (2l+1) e^{i\delta_{kl}} \sin\delta_{kl} P_l(\cos\theta). \tag{62}$$

And an especially important quantity is the S-wave scattering amplitude which describes low energy scatterings (i.e. scatterings which have so low energy that they cannot exceed the centrifugal barrier of $l = 1$ scatterings). This is obtained by taking only the $l = 0$ contribution (notice that it is also direction independent since $P_0(\cos\theta) = 1$)

$$f_k^S = \frac{1}{k} e^{i\delta_{k0}} \sin\delta_{k0} \tag{63}$$

This is the final equation for the scattering amplitude. However, the question of course remains, what is the phase shift δ_{kl}? Despite all the calculations we did above, we are still no closer to solving the scattering problem, unless one is fortunate enough to have a problem in which the phase shifts can be calculated analytically (or numerically). In the following we will calculate the phase shifts for a few special cases, and you will do more in the exercises. If the potential is too complicated as to deny a proper solution of the scattering problem, one can resort to perturbation theory, which will be studied later.

4.1.1 Spherical square well

Let us assume scattering potential of the form

$$V(r) = \begin{cases} V_0 & \text{for } r < a \\ 0 & \text{for } r > a. \end{cases} \tag{64}$$

This potential is very useful because of its simplicity. Usually we are not interested in the details of the potential, especially when considering dilute (interparticle distance is much larger than range of the potential a) and cold (momenta of the scattering particles are small $k \ll 1/a$) systems such as ultracold atomic gases. Despite short range of the potential, the particles can still be strongly interacting as will be seen.

Solving for the radial eigenstates consists of two parts, one for $r < a$ (denoted by $u_1(r)$) and the other for $r > a$ ($u_2(r)$). Limiting ourselves to S-wave scattering, we will set $l = 0$. For $r < a$ the solution is described by the equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u_1(r) + V_0 u_1(r) = E u_1(r), \tag{65}$$

yielding

$$u_2(r) = A\sin(k_1 r) + B\cos(k_1 r), \tag{66}$$

where $k_1 = \sqrt{2m(E - V_0)/\hbar^2}$, and A and B are constants to be determined. However, the latter term is not regular at origin (remember, the full radial function is again given by $u(r)/r$) and we set $B = 0$.

For $r > a$ the solution is described by the equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u_2(r) = E u_2(r), \tag{67}$$

which yields

$$u_2(r) = \tilde{C}\sin(kr) + \tilde{D}\cos(kr) = C\sin(kr + \delta_{k0}), \tag{68}$$

where $k = \sqrt{2mE/\hbar^2}$ and the constants C and δ_{k0} are to be determined. Notice that I have written the solution in two different ways. The latter form is more useful for present purposes, but they are both completely valid and equal as one can easily check.

Wavefunction must be continuous, and thus we require $u_1(a) = u_2(a)$, yielding

$$A\sin(k_1 a) = C\sin(ka + \delta_{k0}). \tag{69}$$

For a finite potential wall/well, also the first derivative of the wavefunction will be continuous, and thus we have also

$$Ak_1\cos(k_1 a) = Ck\cos(ka + \delta_{k0}). \tag{70}$$

Dividing the two equations yields

$$k_1 \cot(k_1 a) = k \cot(ka + \delta_{k0}). \tag{71}$$

One could of course solve for the phase shift δ_{k0} already here, but when we consider cold (low energy) systems and short ranged potentials, we can do some simplifying approximations. Considering low energy scatterings we have $k \ll k_1$, assuming that the depth of the potential well is not vanishingly small (and hence k_1 is not small). Thus, the left side of the equation is not small whereas the right hand side is multiplied by the small factor k. Therefore $\cot(ka + \delta_{k0})$ must be large. This, however, can be large only if $\sin(ka + \delta_{k0})$ is small ($\cot(x) = \cos(x)/\sin(x)$ and $\cos(x)$ is of course bounded from above). Thus we have $ka + \delta_{k0} \approx n\pi$, where $n = 0, 1, 2, \ldots$. Let us first consider the case $ka + \delta_{k0} \approx 0$ yielding

$$\cot(ka + \delta_{k0}) \approx \frac{1}{\sin(ka + \delta_{k0})} \approx \frac{1}{ka + \delta_{k0}}, \tag{72}$$

finally yielding

$$k_1 \cot(k_1 a) \approx \frac{k}{ka + \delta_{k0}}. \tag{73}$$

Solving for δ_{k0} we obtain

$$\delta_{k0} \approx ka \left(\frac{\tan k_1 a}{k_1 a} - 1 \right), \tag{74}$$

and the S-wave scattering amplitude is thus

$$f_k^S = e^{i\delta_{k0}} a \left(\frac{\tan k_1 a}{k_1 a} - 1 \right). \tag{75}$$

Since δ_{k0} is real, the phase factor $e^{i\delta_{k0}}$ is precisely that, namely just a phase factor. When considering experimentally measurable observables, such as scattering probabilities, the phase factor of course becomes irrelevant.

The interesting part thus is the magnitude

$$a \left(\frac{\tan k_1 a}{k_1 a} - 1 \right). \tag{76}$$

Two observations regarding the magnitude of the scattering amplitude: there are maxima at values $k_1 a = n\frac{\pi}{2}$ for odd n and zeroes for $\tan k_1 a = k_1 a$. Consider for a second a potential where a (the range of the potential) is fixed but somehow we could change the depth (ultimately k_1). Starting from $k_1 = 0$ and increasing, the scattering amplitude (and hence probability) will increase until it reaches a maximum at $k_1 = \frac{\pi}{2a}$. Making the well even deeper, the scattering amplitude will start decreasing until it becomes zero. At this point, the particles stop interacting completely, as the potential becomes effectively transparent. Such resonance transparency is called the *Ramsauer effect*.

A word of warning though, the above equation for the scattering amplitude does not describe correctly the maximum around $k_1 a = n\frac{\pi}{2}$. Looking at Eq. (71), for $k_1 a = n\frac{\pi}{2}$ we obtain

$$0 = k \cot(ka + \delta_0), \tag{77}$$

yielding

$$\delta_0 = n'\frac{\pi}{2} - ka \rightarrow_{k\rightarrow 0} n'\frac{\pi}{2}, \tag{78}$$

for odd n'. Thus the scattering amplitude becomes

$$f_k^S = \frac{1}{k}e^{i\delta_{k0}}\sin\delta_{k0} = \frac{1}{k}e^{i\delta_{k0}}, \tag{79}$$

the magnitude of which is simply $1/k$. Low energy scattering amplitude thus diverges, and despite the short range of the potential, the effect of the scattering potential in the total wavefunction in Eq. (49) is profound.

Increasing the depth of the potential even further, while keeping a fixed, will yield more and more resonances and zeroes. Each resonance in the scattering amplitude corresponds to a depth of the potential such that a new bound state is created inside the well. The scattering properties and the bound states of a potential are thus intimitely intertwined, and this phenomenon is of immense use for example in the studies of ultracold atomic gases. In those systems, one can tune the energy of *bound molecular states* formed of two atoms, and thus change the *scattering properties* of the atoms. In sufficiently short time-scales, the molecular formation can often be neglected, and thus one can study the scattering of two atoms with tunable interparticle interaction strengths.

4.1.2 Two-particle problem

While the above discussion considered a particle in vicinity of some fixed external potential, most of the time the potential may actually be moving and responding to the particle. For example in the case of the hydrogen atom, the nucleus will feel a recoil from the electron. We neglected this effect because the nucleus is so much more massive than the electron but in more general case this may not be the case. Like in classical physics, these problems should be treated in the center of mass coordinate system.

Thus, lets consider two particles of masses m_1 and m_2 interacting through interaction $V(\vec{r})$ where $\vec{r}$ is the interparticle separation. Lets also assume that the interaction potential depends only on the distance of the two particles, i.e. we assume that it is spherically symmetric $V(\vec{r}) = V(r)$. For example, for a hydrogen atom we would have the Coulomb interaction potential $V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$. The corresponding two-particle Hamiltonian is now

$$H = \frac{\vec{p}_1^2}{2m_1} + \frac{\hat{\vec{p}}_2^2}{2m_2} + V(\left|\hat{\vec{r}}_1 - \hat{\vec{r}}_2\right|), \tag{80}$$

where $\hat{\vec{r}}_\sigma$ and $\hat{\vec{p}}_\sigma$ give the position and momentum of particle $\sigma \in \{1,2\}$.

Doing the coordinate transformation into the center of mass coordinates $\hat{\vec{r}} = \hat{\vec{r}}_1 - \hat{\vec{r}}_2$, $\hat{\vec{R}} = \frac{m_1\hat{\vec{r}}_1 + m_2\hat{\vec{r}}_2}{m_1+m_2}$, $\hat{\vec{p}} = \frac{m_1\hat{\vec{p}}_2 - m_2\hat{\vec{p}}_1}{m_1+m_2}$, and $\hat{\vec{P}} = \hat{\vec{p}}_1 + \hat{\vec{p}}_2$, we obtain

$$H = \frac{\hat{\vec{P}}^2}{2M} + \frac{\hat{\vec{p}}^2}{2\mu} + V(\left|\hat{\vec{r}}\right|) \equiv H_{\mathrm{CM}} + H_{\mathrm{rel}}, \tag{81}$$

where $M = m_1 + m_2$, $\mu = \frac{m_1 m_2}{m_1+m_2}$, and $H_{\mathrm{CM}} = \frac{\hat{\vec{P}}^2}{2M}$.

From the above Hamiltonian it is apparent that the center of mass (CM) motion of the two atoms decouples from the relative motion (rel). However, I would suggest checking the commutation relations for the new momentum and position operators $\hat{\vec{p}}$, $\hat{\vec{P}}$, $\hat{\vec{r}}$, $\hat{\vec{R}}$, and to see that indeed these new operators satisfy

$$\begin{aligned} [\hat{r}_i, \hat{p}_i] &= i\hbar \\ \left[\hat{R}_i, \hat{P}_i\right] &= i\hbar, \end{aligned} \tag{82}$$

for all $i \in \{x, y, z\}$ and that all other commutators are zero. Once that has been confirmed, it becomes clear that the first term in the Hamiltonian describing the center-of-mass motion (CM) commutes with the second term (rel). In such case, the eigenstates of the two-particle Schrödinger equation become product states

$$\phi(\vec{r}_1, \vec{r}_2) = \phi_{\mathrm{CM}}(\vec{R})\phi_{\mathrm{rel}}(\vec{r}). \tag{83}$$

The center-of-mass eigenstates are trivial (since it has only the kinetic energy in the Hamiltonian)

$$\phi_{\mathrm{CM}}^{\vec{K}}(\vec{R}) = \mathcal{A}e^{i\vec{K}\vec{R}}, \tag{84}$$

with eigenenergy $E_{\mathrm{CM}} = \frac{\hbar^2 K^2}{2M}$.

The relative eigenstate is determined by the corresponding relative Hamiltonian

$$H_{\mathrm{rel}} = \frac{\hat{\vec{p}}^2}{2\mu} + V(\left|\hat{\vec{r}}\right|). \tag{85}$$

This is exactly like a Hamiltonian for a single particle of mass μ in a spherically symmetric potential $V(r)$ and we can then use the results obtained above.

For a hydrogen atom, if we consider the nucleus as a single proton with mass $m_1 = 1.6726215810^{-27}$ kg and the second particle is the electron with mass $m_2 = 9.1093818810^{-31}$ kg, the nucleus frame of reference and the center of mass frame of reference become effectively the same.

5 Lecture 11: introduction to relativistic quantum mechanics

Liboff 15

In the following sections I will study key concepts of relativistic quantum mechanics. While this topic has usually been left to the end of the course (just like Liboff considers it in the end of the book), there is really no reason for it as the whole theory is based on ordinary Schrödinger mechanics and does not require knowledge of the other stuff considered in this course. Except the extension to 3d quantum mechanics, which we have already covered.

I am assuming that the reader is familiar with the (classical) special relativity theory and here I will give an outline on how the quantum mechanics need to be generalized in order to include relativistic effects as well.

The key question is thus: how does the quantum mechanics change if we consider particles moving at velocities close to the speed of light? The relativistic effects thus are expected to play a role at high energies. Also, when considering very precise measurements, the relativistic effects may be visible at low energies as well. Indeed, relativistic corrections can be shown to explain certain energy shifts in the excitation spectra of atoms (hydrogen in particular). And perhaps the most