10 Angular Momentum II

10.1 Central force and pseudopotential

Our goal is now to solve the Hydrogen atom completely at the nonrelativistic level (& for an infinitely massive proton, an assumption we will soon relax), where the Hamiltonian is

\[ H = -\frac{\hbar^2 \nabla^2}{2m} - \frac{e^2}{4\pi \epsilon_0 r} \]

Griffiths follows a mathematical strategy in Ch. 4, using the technique of separation of variables. He separates the variables by assuming \( \psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \), and then after substituting in finds that the Schrödinger equation can be written in the form above Eq. (4.16) in his book. The angular momentum is then introduced purely mathematically, as a separation constant \( \ell(\ell + 1) \) which he pulls out of a hat, in (Eqs. 4.16-4.17). I would like to pursue a more physical strategy based on the angular momentum results we obtained last week.

The idea is, after exploring properties of \( \hat{L} \), we now want to express \( H \) in terms of \( \hat{L} \) in order to explicitly classify eigenfunctions by angular momentum eigenvalues. I will skip tedious calculation (however, it’s good for cultural background— you can read about it in Peebles, Quantum Mechanics, p. 141.). Remember what you are trying to do is express \( \hat{L}^2 \) in terms of \( \nabla^2 \), but \( \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \), and

\[
\begin{align*}
\hat{L}_x &= y\hat{p}_z - z\hat{p}_y \\
\hat{L}_y &= z\hat{p}_x - x\hat{p}_z \\
\hat{L}_z &= x\hat{p}_y - y\hat{p}_x,
\end{align*}
\]

(1) (2)
so in principle you can work it out. The final result is

\[ \nabla^2 = \frac{-\hat{L}^2}{\hbar^2 r^2} + \frac{1}{r} \frac{\partial^2}{\partial r^2} \]  \tag{3} \]

(Note meaning of 2nd term—\(-r^{-1}(\partial^2/\partial r^2)\psi = r^{-1}(\partial^2/\partial r^2)(r\psi)\)).

So kinetic energy operator in Hamiltonian is

\[ -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hat{L}^2}{2mr^2} \]  \tag{4} \]

and full Hamiltonian for central force problem is

\[
H = -\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hat{L}^2}{2mr^2} + V(r). \tag{5}
\]

1st want to solve t-ind. S.-eqn. \(H \psi = E\psi\), have already argued should be able to find simultaneous e’fctns. of \(H, \hat{L}^2, \hat{L}_z\). Label as \(\psi_{n\ell m}\) with

\[
H\psi_{n\ell m} = E_n\psi_{n\ell m}, \hspace{1cm} \hat{L}^2\psi_{n\ell m} = \hbar^2 \ell (\ell + 1)\psi_{n\ell m} \hspace{1cm} \hat{L}_z\psi_{n\ell m} = m\hbar\psi_{n\ell m}
\]

S. eqn. is then (using fact that \(\psi_{n\ell m}\) are e’fctns of \(\hat{L}^2\))

\[
-\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} r\psi_{n\ell m} + \frac{\hbar^2 \ell (\ell + 1)}{2mr^2} \psi_{n\ell m} + V(r)\psi_{n\ell m} = E_n\psi_{n\ell m} \tag{6}
\]

Convenient to multiply (4) by \(r\), introduce radial wave fctn. \(u_{n\ell m} \equiv r\psi_{n\ell m}\). Then eqn. reads

\[
-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} u_{n\ell m} + \left[ \frac{\hbar^2 \ell (\ell + 1)}{2mr^2} + V(r) \right] u_{n\ell m} = E_n u_{n\ell m} \tag{7}
\]

which looks like a 1D problem in the radial variable \(r\) for a particle moving in an effective potential depending on \(\ell\).
Reminder: similar equation found in classical mechanics in polar coordinates (example in 2D for illustration):

\[
H = \frac{1}{2}mv^2 + V(r) = \frac{m}{2}(r^2 + r^2\dot{\theta}^2) + V = \frac{1}{2}mr^2 + \left[ \frac{\hat{L}^2}{2mr^2} + V \right]
\]

10.2 H-atom bound states

Electron sees potential \( V = e^2/r \) from nucleus:

\[
-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} u + \left[ \frac{\hbar^2 \ell (\ell + 1)}{2mr^2} - \frac{e^2}{r} \right] u = Eu = -E u \tag{8}
\]

with \( E = -\mathcal{E} \) the binding energy of the electron as usual. Rewrite as

\[
\frac{\partial^2 u}{\partial r^2} - \frac{\ell (\ell + 1)}{r^2} u + \frac{2me^2}{\hbar^2 r} u = \frac{2m\mathcal{E}}{\hbar^2} u \tag{9}
\]

This is just “radial S.-eqn.” we wrote down before assuming spherically symmetric solutions (Eq. 4-15 et seq.) only now including \( \ell (\ell + 1) \) term! Recall trick leading to solution back then was to write

\[
u(r) = f(r)e^{-r\sqrt{2m\mathcal{E}/\hbar^2}} \tag{10}\]

which we guessed because 1) we wanted solns. localized around the origin, and 2) could get some terms to cancel...

Substitute, find

\[
\frac{\partial^2 f}{\partial r^2} - \frac{\ell (\ell + 1)}{r^2} f + \frac{2me^2}{\hbar^2 r} f - 2\sqrt{\frac{2m\mathcal{E} df}{\hbar^2 dr}} = 0 \tag{11}
\]

Now look for series soln.:

\[
f = \sum_p A_p r^p \tag{12}\]
Substitute, require coefficient of each power of $r$ vanish, find

$$[p(p + 1) - \ell(\ell + 1)]A_{p+1} = \left[\frac{2p\sqrt{2m\mathcal{E}}}{\hbar} - \frac{2me^2}{\hbar^2}\right] A_p \quad (13)$$

$A_\ell$ is zero, since factor on lhs vanishes and $[\ ]$ on right is nonzero. Then all $A_p$ are zero for $p \leq \ell$. (Take $p + 1 = \ell$, then you find $A_{\ell-1} = 0$, iterate again...)

If series does not terminate, asymptotic value of ratio

$$\frac{A_{p+1}}{A_p} \sim \frac{2\sqrt{2m\mathcal{E}}}{\hbar} \frac{1}{p} \quad (14)$$

which has soln. $A_{p+1} \sim (2\sqrt{2m\mathcal{E}/\hbar})^p / p!$, meaning

$$f \sim \sum_p A_p r^p \sim e^{\frac{2\sqrt{2m\mathcal{E}}}{\hbar} r} \quad (15)$$

which is no good since $u \equiv f e^{-\sqrt{2m\mathcal{E}/\hbar} r}$ blows up at $r \to \infty$.

But can escape this conundrum by assuming termination if for some integer $n > \ell$

$$\frac{2n\sqrt{2m\mathcal{E}}}{\hbar} = \frac{2me^2}{\hbar^2} \quad (16)$$

(Then all $A_p$ with $p > n$ will vanish due to (11).) This gives energy eigenvalues as before:

$$E_n = -\mathcal{E} = \frac{e^4 m}{2\hbar^2 n^2}, \quad n = 1, 2, 3, \ldots > \ell \quad (17)$$

and eigenfunctions (neglect angular part for now!)

$$\psi_{n\ell m} \sim \frac{u_{n\ell m}}{r} = [A_{\ell+1} r^\ell + \cdots A_n r^{n-1}] e^{-\frac{\sqrt{2m|E_n|}}{\hbar} r} \quad (18)$$

related to Laguerre polynomial

$$\text{Radial part of eigenfunction } R_{n\ell}(r) \text{ different for each } \ell!$$
Now for each \( \ell \) there are \( 2\ell + 1 \) degenerate orthogonal eigenfctns. corresponding to different \( m \)'s, i.e. \( \propto e^{im\phi} \). Examples:

\[
\begin{align*}
\psi_{100} & \sim e^{-r/a_0} \\
\psi_{200} & \sim (1 - r/2a_0)e^{-r/2a_0} \\
\psi_{211} & \sim r \sin \theta e^{i\phi} e^{-r/2a_0} \\
\psi_{210} & \sim r \cos \theta e^{-r/2a_0} \\
\psi_{21-1} & \sim r \sin \theta e^{-i\phi} e^{-r/2a_0}
\end{align*}
\] (20)

**Remarks:**

1. Eigenfunctions of \( \hat{L}^2 \) are **Legendre functions** (sometimes called associated Leg. polynomials) \( P_{\ell m}(\cos \theta) \). For \( m = 0 \), reduce to familiar Legendre polynomials \( P_\ell(\cos \theta) \). Won’t belabor definitions now, can look up anywhere.

2. Recall e’fctns of \( \hat{L}_z \) are \( \sim e^{im\phi} \).

3. Simultaneous e’fctns of both \( \hat{L}^2 \) and \( \hat{L}_z \) easy to construct, just multiply two together, get **spherical harmonics** \( Y_{\ell m} \equiv P_{\ell m}(\cos \theta)e^{im\phi} \). Note orthonormality:

\[
\int d\Omega \ Y_{\ell m}^*(\theta, \phi)Y_{\ell' m'}(\theta, \phi) = \delta_{\ell\ell'}\delta_{m,m'}
\] (25)

4. 1st few:

\[
Y_{00} = \frac{1}{\sqrt{4\pi}}
\]

\[
Y_{1,-1} = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}, \quad Y_{1,0} = -\sqrt{\frac{3}{4\pi}} \cos \theta, \quad Y_{1,1} = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}
\]

\[
Y_{22} = \sqrt{\frac{15}{32\pi}} e^{2i\phi} \sin^2 \theta, \quad Y_{21} = -\sqrt{\frac{15}{8\pi}} e^{i\phi} \sin \theta \cos \theta,
\]

\[
Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1), \quad \ldots
\]
5. Full normalized e’fctns $\psi_{n\ell m}$ for $H$-atom problem are radial fctns. (see Eq. 17) times spherical harmonics,

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi)$$

Recap: nonrelativistic hydrogen energy levels

• **1s. (Ground state)** \(n=1, \ell=0, E=-13.6\ eV\)
  spectroscopic notation: (s=“sharp”)

• **2s. (1st excited state)** \(n=2, \ell = 0, E=13.6\ eV/(2^2)\)

• **2p.** \(n=2, \ell = 1.\) Degeneracy = 2\ell+1 = 3.

• **3s.** \(n=3, \ell = 0\)
  spectroscopic notation: (p=“principal”)

• **3p.** \(n=3, \ell = 1\) Degeneracy =3.

• **3d.** \(n=3, \ell = 2\) Degeneracy =5.
  spectroscopic notation: (d=“diffuse”).
10.3 Two body problem

Need to ask what happens if proton allowed to have finite mass, also consider other 2– or more–particle systems where masses are similar. For now stick to 2 particles, think of electron and proton in $H$ atom.

Write down single wave function to describe entire two-particle system, fctn of electron position $\mathbf{r}_e$ and proton position $\mathbf{r}_p$:

$$\psi = \psi(\mathbf{r}_e, \mathbf{r}_p, t)$$  \hspace{1cm} (27)

related to joint probability of finding the electron in $d^3r_e$ at $\mathbf{r}_e$ simultaneously with proton in $d^3r_p$ at $\mathbf{r}_p$:

$$dP = |\psi(\mathbf{r}_e, \mathbf{r}_p, t)|^2 d^3r_p d^3r_e$$  \hspace{1cm} (28)

with normalization condition

$$\int |\psi|^2 d^3r_p d^3r_e = 1$$  \hspace{1cm} (29)

which we again write as $(\psi, \psi) = 1$.

**Total momentum:**

$$P = p_e + p_p = -i\hbar \frac{\partial}{\partial \mathbf{r}_e} - i\hbar \frac{\partial}{\partial \mathbf{r}_p}$$  \hspace{1cm} (30)

**Total energy:**

$$H = \frac{\hat{p}_e^2}{2m_e} + \frac{\hat{p}_p^2}{2m_p} - \frac{e^2}{|\mathbf{r}_p - \mathbf{r}_e|}$$  \hspace{1cm} (31)

10.4 Momentum conservation in 2-body system

Check commutators:

- $$[p_e, H] = [p_e, V] = -i\hbar \frac{\partial}{\partial \mathbf{r}_e} V$$
\[ -i\hbar \frac{dV}{dr} \frac{\partial}{\partial r_e} r_e = -i\hbar \frac{dV}{dr} \left( r_e - r_p \right) \]  \hspace{1cm} (32)

and similarly

\[ [p_p, H] = -i\hbar \frac{dV}{dr} \left( r_p - r_e \right) \]  \hspace{1cm} (33)

so total momentum \( P = p_e + p_p \) commutes with \( H \)

\[ [P, H] = 0 \]  \hspace{1cm} (34)

Consequences:

1. Can find complete set of eigenstates of energy and total momentum.
2. Momentum conserved: if \( \psi \) is eigenfctn. of \( P \) at time \( t \), still an eigenstate at later time \( t' \).
3. Total \( p \) is generator of translations in same sense that total ang. mom. was generator of rotations. If \( \psi'(r_e, r_p, t) \) is defined to be the wave function of a system described by \( \psi \) shifted in space by the displacement \( \vec{\delta} \), can show (See Peebles p. 121)

\[ \psi' = U\psi, \quad U = e^{-i\delta \cdot \mathbf{p}/\hbar} \]  \hspace{1cm} (35)

where again operator \( U \) is unitary, the exponentiation of a Hermitian operator

10.5 Reduction from 2-body to 1-body problem.

Define as in classical mechanics:
Total mass \[ M = m_e + m_p \] (36)

Center of mass position \[ \mathbf{R} = \frac{m_e}{M} \mathbf{r}_e + \frac{m_p}{M} \mathbf{r}_p \] (37)

Relative position \[ \mathbf{r} = \mathbf{r}_e - \mathbf{r}_p \] (38)

or invert:

\[ \mathbf{r}_e = \mathbf{R} + \frac{m_p}{M} \mathbf{r} \] (39)

\[ \mathbf{r}_p = \mathbf{R} - \frac{m_e}{M} \mathbf{r} \] (40)

Change variables in S.-eqn. (Hamiltonian Eq. (27)) from \( \mathbf{r}_e, \mathbf{r}_p \) to \( \mathbf{R}, \mathbf{r} \):

\[ \frac{\partial \psi}{\partial \mathbf{R}} \bigg|_\mathbf{r} = \frac{\partial \psi}{\partial \mathbf{r}_e} \frac{\partial \mathbf{r}_e}{\partial \mathbf{R}} \bigg|_\mathbf{r} + \frac{\partial \psi}{\partial \mathbf{r}_p} \frac{\partial \mathbf{r}_p}{\partial \mathbf{R}} \bigg|_\mathbf{r} \] (41)

and note \( \frac{\partial \mathbf{r}_e}{\partial \mathbf{R}} = \frac{\partial \mathbf{r}_p}{\partial \mathbf{R}} = 1 \). So

\[ \frac{\partial \psi}{\partial \mathbf{R}} \bigg|_\mathbf{r} = \frac{\partial \psi}{\partial \mathbf{r}_e} + \frac{\partial \psi}{\partial \mathbf{r}_p} \text{, or} \] (42)

\[ \frac{\partial}{\partial \mathbf{R}} = \frac{\partial}{\partial \mathbf{r}_e} + \frac{\partial}{\partial \mathbf{r}_p} \] (43)

Similarly

\[ \frac{\partial}{\partial \mathbf{r}} = \frac{m_p}{M} \frac{\partial}{\partial \mathbf{r}_e} - \frac{m_e}{M} \frac{\partial}{\partial \mathbf{r}_p} \] (44)

Now put (mostly old definitions):

\[ \mathbf{p}_e = -i\hbar \frac{\partial}{\partial \mathbf{r}_e} \quad \mathbf{p}_p = -i\hbar \frac{\partial}{\partial \mathbf{r}_p} \] (45)

\[ \mathbf{P} = -i\hbar \frac{\partial}{\partial \mathbf{R}} \quad \mathbf{p} = -i\hbar \frac{\partial}{\partial \mathbf{r}} \] (46)
So have same relations as in classical mechanics:

\[ \mathbf{P} = \mathbf{p}_e + \mathbf{p}_p \quad \text{Center of mass momentum} \quad (47) \]
\[ \mathbf{p} = \frac{m_p}{M} \mathbf{p}_e - \frac{m_e}{M} \mathbf{p}_p \quad \text{relative momentum} \quad (48) \]

or inverted

\[ \mathbf{p}_e = \frac{m_e}{M} \mathbf{P} + \mathbf{p} \quad (49) \]
\[ \mathbf{p}_p = \frac{m_p}{M} \mathbf{P} - \mathbf{p} \quad (50) \]

Rewrite kinetic energy operator in terms of center of mass and relative momentum:

\[ \frac{\hat{p}_e^2}{2m_e} + \frac{\hat{p}_p^2}{2m_p} = \frac{\hat{P}^2}{2M} + \frac{1}{2} \left( \frac{1}{m_e} + \frac{1}{m_p} \right) \hat{p}^2 \]
\[ = \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2\mu} \quad (51) \]

where \( \mu \) is the reduced mass

\[ \mu = \frac{m_em_p}{m_e + m_p} \quad (52) \]

Since we normally are not interested in the center of mass motion, discard, and write for 2-body problem (e.g. H-atom with finite proton mass):

\[ H = \frac{\hat{p}^2}{2\mu} + V(r) \quad (53) \]

exactly as in classical mechanics.

### 10.6 Addition of 2 angular momenta.

We now ask the question, if we have two particles with different angular momenta, what are the allowed eigenvalues of the total angular momentum? This situation might arise for two particles with intrinsic angular
momentum (spin), such as the two quarks in a pion, or it might be a question we would ask about two electrons in different angular momentum states of a multielectron atom. In any case, suppose there are two particles, one with angular momentum operator \( \mathbf{L}(1) \) and one with \( \mathbf{L}(2) \). The total angular momentum operator is

\[
\mathbf{L} = \mathbf{L}(1) + \mathbf{L}(2),
\]

and we assume that since particles 1 and 2 are distinct particles, any operator referring to 1 commutes with any operator referring to 2. So for example we have \([L_x(1), L_y(1)] = i\hbar L_z(1)\), but \([L_x(1), L_y(2)] = 0\). Then what are the possible sets of commuting observables we can construct whose eigenvalues we can use to label our states with? One obvious choice is \(L^2(1), L_z(1), L^2(2), L_z(2)\), whose eigenvalues we would call \(\ell_1, m_1, \ell_2, m_2\), as usual. But we can also show that

\[
\begin{align*}
[L^2, L_z] &= 0 \\
[L^2, L^2(\alpha)] &= 0 \\
[L_z, L^2(\alpha)] &= 0 \\
&\text{but} \quad [L^2, L_z(\alpha)] \neq 0,
\end{align*}
\]

\(\alpha = 1, 2\), which suggests that there is another set of four commuting operators we could chose with which to label our states, namely \(L^2, L_z, L^2(1)\) and \(L^2(2)\). Note that the total angular momentum operators for each particle \(L^2(\alpha)\) are members of both sets. For a given pair of quantum numbers \(\ell_1, \ell_2\), however, the two sets differ, because using the first set, the states can be classified in addition by \(m_1, m_2\), and we will write \(|m_1m_2\ell_1\ell_2\rangle\), whereas using the second set, states can be classified according to \(\ell, m\), where \(\ell, m\) are the total angular momentum quantum number and total \(z\)-component quantum number, i.e. the operators \(L^2\) and \(L_z\) have the following effect on the states \(|\ell m\ell_1\ell_2\rangle\):
\[
\begin{align*}
L^2|\ell m\ell_1\ell_2\rangle &= \hbar^2 \ell(\ell + 1)|\ell m\ell_1\ell_2\rangle \\
L_z|\ell m\ell_1\ell_2\rangle &= \hbar m|\ell m\ell_1\ell_2\rangle,
\end{align*}
\]
and of course still
\[
\begin{align*}
L^2(1)|\ell m\ell_1\ell_2\rangle &= \hbar^2 \ell_1(\ell_1 + 1)|\ell m\ell_1\ell_2\rangle \\
L^2(2)|\ell m\ell_1\ell_2\rangle &= \hbar^2 \ell_2(\ell_2 + 1)|\ell m\ell_1\ell_2\rangle.
\end{align*}
\]
Note however that \(|\ell m\ell_1\ell_2\rangle\) is not an eigenstate of \(L_z(\alpha)\), because \(L^2\) doesn’t commute with it.

We have two different ways of labelling the eigenstates of angular momentum, neither of which is preferred. How are the “new” quantum numbers \(\ell, m\) related to \(\ell_1, \ell_2, m_1, m_2\)? Well we have \(L_z = L_z(1) + L_z(2)\), so certainly \(m = m_1 + m_2\). The relation between \(\ell\) and \(\ell_1\) and \(\ell_2\) is not so simple, but the answer is contained in what is sometimes called the triangle rule:

\[|\ell_1 - \ell_2| \leq \ell \leq \ell_1 + \ell_2.\]

I will not derive this here, but you will derive it in part in the homework.

Since both the \(|\ell m\ell_1\ell_2\rangle\) and the \(|m_1m_2\ell_1\ell_2\rangle\) represent a complete set of states, it must be that we can always express any given state in either representation in terms of linear combinations of the other. For example, we can write

\[
|m_1m_2\ell_1\ell_2\rangle = \sum_{\ell=|\ell_1-\ell_2|}^{\ell_1+\ell_2} \langle \ell m_1 + m_2\ell_1\ell_2 | \ell m_1 + m_2\ell_1\ell_2 \rangle |\ell m\ell_1\ell_2\rangle
\]

or

\[
|\ell m\ell_1\ell_2\rangle = \sum_{m_1+m_2=m} \langle m_1m_2\ell_1\ell_2 | \ell m\ell_1\ell_2 \rangle |m_1m_2\ell_1\ell_2\rangle.
\]

The amplitudes (just numbers) \(\langle m_1m_2\ell_1\ell_2 | \ell m\ell_1\ell_2 \rangle\) are called Clebsch-Gordon coefficients, and are tabulated in Griffiths on p. 188. A concrete example is for \(\ell_1 = 2, \ell_2 = 1,\)
\[
|3 0 2 1\rangle = \frac{1}{\sqrt{5}}|1 - 1 2 1\rangle + \sqrt{\frac{3}{5}}|0 0 2 1\rangle + \frac{1}{\sqrt{5}}| - 1 1 2 1\rangle,
\]
where (careful!) the left side of the equation is written in \(lml_1l_2\) notation, whereas the kets on the right are in the \(m_1m_2l_1l_2\) notation. Compare directly with Griifiths’ Eq. below (4.185). It’s the same equation in different notation. A third notation is given to you in the homework! Choose whichever seems most natural to you.