

Answers to Homework Set 4

From lecture 13: Consider a 2-dimensional so-called planar rigid rotator—a quantum mechanical compact disc, if you will. In this system, rotation is confined to a plane, so all of the angular momentum is along a single axis. The Schrödinger equation for this system is thus

$$\frac{L_z^2}{2I} \Psi = E\Psi$$

If the moment of inertia  $I$  is taken to be  $1/2$ , what are the eigenfunctions and eigenvalues for this system (use spherical polar coordinates)? Looking at the Schrödinger equation for the free particle may be helpful, but this case is quantized, while that for the free particle is not—why is there a difference? What are the lowest 3 possible energies? What degeneracies are associated with these energies?

We have the restricted Schrödinger equation

$$\frac{L_z^2}{2I} \Psi = E\Psi$$

or, noting that  $I = 1/2$  and using eq. 12-8 for  $L_z$

$$-\hbar^2 \frac{d^2}{d\phi^2} \Psi(\phi) = E\Psi(\phi)$$

where  $\phi$  is the variable describing rotation of the disk from 0 to  $2\pi$ . This equation can be rearranged to

$$\left( \frac{d^2}{d\phi^2} + \frac{E}{\hbar^2} \right) \Psi(\phi) = 0$$

which looks almost identical to the free particle wave function but with different constants, and has the solutions (eigenfunctions)

$$\Psi(\phi) = C e^{i\sqrt{E}\phi/\hbar}$$

For the free particle, all values of  $x$  (which replaces  $\phi$  as the variable) are allowed. But, for the rotating disk, the wave function must be identical for  $\phi' = \phi + 2\pi$  since this will represent a complete revolution. Recalling that

$$e^{in\phi} = \cos n\phi + i \sin n\phi$$

it should be clear that

$$\cos n\phi + i \sin n\phi = \cos n(\phi + 2\pi) + i \sin n(\phi + 2\pi)$$

if and only if  $n$  is an integer, i.e.,  $0, \pm 1, \pm 2, \dots$ . So, periodicity requires that

$$\frac{\sqrt{E}}{\hbar} = n$$

or, solving for  $E$  (the eigenvalues)

$$E = n^2 \hbar^2$$

For the  $n = 0$  level, the total energy is zero (stationary disk). This is the lowest level and it is not degenerate. The next higher level has energy  $\hbar^2$ , but this can be achieved for either  $n = 1$  or  $n = -1$  (the disk has the same kinetic energy whether it is rotating clockwise or counterclockwise). The next higher level still has energy  $4\hbar^2$  and is again doubly degenerate.

To complete the earlier part of the problem, we only need to determine the normalization of the eigenfunctions. If we use our above value for  $E$  in the general equation for  $\Psi$  above, we have

$$\Psi(\phi) = C e^{in\phi}$$

so the normalization constant  $C$  is determined as  $\langle e^{in\phi} | e^{in\phi} \rangle^{-1/2}$ . Thus we evaluate

$$\begin{aligned} \int_0^{2\pi} e^{-in\phi} e^{in\phi} d\phi &= \int_0^{2\pi} d\phi \\ &= \phi \Big|_0^{2\pi} \\ &= 2\pi \end{aligned}$$

So, the final eigenfunctions are

$$\Psi_n(\phi) = \frac{1}{\sqrt{2\pi}} e^{in\phi}$$

where  $n = 0, \pm 1, \pm 2, \dots$

From lecture 14: What is the error introduced in the ionization potential of the H atom if the mass of the electron is used in place of the reduced mass of the H atom?

The ionization potential depends linearly on the mass term, so for the ratio of the ionization potentials we need only compute

$$\begin{aligned}
 f &= \frac{m_e}{\mu} \\
 &= \frac{m_e}{\left(\frac{m_e m_p}{m_e + m_p}\right)} \\
 &= \frac{m_e^2 + m_e m_p}{m_e m_p} \\
 &= 1 + \frac{m_e}{m_p} \\
 &= 1 + \frac{9.109 \times 10^{-31} \text{ kg}}{1.673 \times 10^{-27} \text{ kg}} \\
 &= 1.0005
 \end{aligned}$$

So, the error is about five one-hundredths of a percent. Thus, instead of an ionization potential of  $-13.6$  eV, one would compute  $-13.6$  eV (the error does not appear with only 3 significant digits). It takes an excruciatingly sensitive instrument to measure the difference (although the measurement has indeed been made, and one needs to use the reduced mass to achieve perfect accuracy).

From lecture 15: If you were to measure the distance of a 2s electron from the nucleus in a  $\text{He}^+$  atom, what would be the average value, in  $\text{\AA}$ , that you would obtain after a very, very large number of measurements? (Hint: if you've no idea where to start on this problem, think about what operator gives the distance of the electron from the nucleus.) (Caveat: be very careful about using proper limits and volume elements in any integrals you might try to solve—perhaps with the help of an integral table...) Will the value for  $\text{Li}^{2+}$  be the same, or different? Why?

The operator that provides the distance of the electron from the nucleus in the spherical polar coordinate system used for an atom is simply  $r$ . An average from many measurements is the expectation value,  $\langle r \rangle$ . Since our 2s wave function is normalized, we have in general

$$\begin{aligned}
 \langle r \rangle_{2s} &= \langle \Psi_{200} | r | \Psi_{200} \rangle \\
 &= \frac{Z^3}{32\pi} \int_0^\infty \int_0^\pi \int_0^{2\pi} (2-Zr)e^{-Zr/2} r (2-Zr)e^{-Zr/2} r^2 \sin\theta dr d\theta d\phi \\
 &= \frac{Z^3}{32\pi} \int_0^\infty (2-Zr)e^{-Zr/2} r (2-Zr)e^{-Zr/2} r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \\
 &= \frac{Z^3}{8} \int_0^\infty (4r^3 - 4Zr^4 + Z^2r^5) e^{-Zr} dr \\
 &= \frac{Z^3}{2} \int_0^\infty r^3 e^{-Zr} dr - \frac{Z^4}{2} \int_0^\infty r^4 e^{-Zr} dr + \frac{Z^5}{8} \int_0^\infty r^5 e^{-Zr} dr
 \end{aligned}$$

Note that the angular parts of the expectation value simply integrate to  $4\pi$ . To solve the final integrals, we need simply to look up that

$$\int_0^\infty r^n e^{-Zr} dr = \frac{n!}{Z^{n+1}}$$

which then gives for  $\text{He}^+$ , where  $Z = 2$ ,

$$\begin{aligned}
 \langle r \rangle_{2s} &= \frac{2^3}{2} \frac{3!}{2^4} - \frac{2^4}{2} \frac{4!}{2^5} + \frac{2^5}{8} \frac{5!}{2^6} \\
 &= \frac{3}{2} - 6 + \frac{15}{2} \\
 &= 3
 \end{aligned}$$

Since we've used atomic units in the wave function, the expectation value is also in a.u. (recall that the atomic unit of distance is the bohr). The conversion factor tabulated in lecture 15 is  $1 \text{ bohr} = 0.529 \text{ \AA}$ , so our average measurement would be  $1.587 \text{ \AA}$ .

The value for  $\text{Li}^{2+}$  would be smaller, since the more highly charged nucleus of Li will hold the 2s electron more tightly than the less charged nucleus of He. If one carries out the calculation, one obtains an average distance of 2 bohr, or  $1.058 \text{ \AA}$ .