Tutorial
Atomic physics

Week 1: Quantum refreshment, the hydrogen atom

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Exercise 1 *A gentle warm-up*

An atom is in the state

$$|\psi\rangle = 0.5|a\rangle + 0.4|b\rangle + 0.7|c\rangle$$

where states $|a\rangle, |b\rangle$, and $|c\rangle$ are orthonormal.

1. Normalise the above wavefunction.
2. What is the probability of measuring the atom in state $|b\rangle$?
3. Consider the operator

$$\hat{O} = 2|a\rangle\langle a| + 3|b\rangle\langle b| + 4|c\rangle\langle c|$$

What is the expectation value for this operator for the state $|\psi\rangle$?

Solution 1

An atom is in the state

$$|\psi\rangle = 0.5|a\rangle + 0.4|b\rangle + 0.7|c\rangle$$

where states $|a\rangle, |b\rangle$, and $|c\rangle$ are orthonormal.

1. Normalise the above wavefunction.
   To normalise the faction, we must ensure $\langle\psi|\psi\rangle = 1$, which gives

$$\begin{aligned}\langle\psi|\psi\rangle &= (0.5\ \langle a| + 0.4\ \langle b| + 0.7\ \langle c|)\,(0.5\ |a\rangle + 0.4\ |b\rangle + 0.7\ |c\rangle)\\ &= 0.5^2\ \langle a|a\rangle + 0.4^2\ \langle b|b\rangle + 0.7^2\ \langle c|c\rangle\\ &= 0.9\end{aligned}$$

   as our basis states are orthonormal. So our normalised wavefunction will be

$$\begin{aligned}|\psi\rangle &= \sqrt{\frac{10}{9}}\,(0.5|a\rangle + 0.4|b\rangle + 0.7|c\rangle)\\ &\approx 0.527|a\rangle + 0.421|b\rangle + 0.738|c\rangle\end{aligned}$$

2. What is the probability of measuring the atom in state $|b\rangle$?
   The probability of measuring the system in state be is given by

$$\begin{aligned}\mathscr{P}(|b\rangle) &= |\langle b|\psi\rangle|^2\\ &= |\langle b|(0.527|a\rangle + 0.421|b\rangle + 0.738|c\rangle)|^2\\ &= |0.527\langle b|a\rangle + 0.421\langle b|b\rangle + 0.738\langle b|c\rangle|^2\\ &= |0.421|^2\\ &= 0.177\end{aligned}$$

3. Consider the operator

$$\hat{O} = 2|a\rangle\langle a| + 3|b\rangle\langle b| + 4|c\rangle\langle c|$$

What is the expectation value for this operator for the state $|\psi\rangle$?

This is slightly tedious. We need to compute

$$\begin{aligned}\langle\psi|\hat{O}|\psi\rangle &= (0.527\langle a| + 0.421\langle b| + 0.738\langle c|)\,(2|a\rangle\langle a| + 3|b\rangle\langle b| + 4|c\rangle\langle c|) \\ &\quad (0.527|a\rangle + 0.421|b\rangle + 0.738|c\rangle) \\ &= 0.527^2 \times 2\langle a|a\rangle + 0.421^2 \times 3\langle b|b\rangle + 0.738^2 \times 4\langle c|c\rangle \\ &\approx 0.56 + 0.53 + 2.18 \\ &= 3.27\end{aligned}$$

Exercise 2 *Rydberg atoms*

1. Show that the energy of the transitions between two shells with principal quantum numbers n and $n = n+1$ is proportional to $1/n^3$ for large n.
2. Calculate the frequency of the transition between the $n = 51$ and $n = 50$ shells of a neutral atom.
3. What is the size of an atom in these Rydberg states? Express your answer both in atomic units and SI units.

Solution 2

1. Show that the energy of the transitions between two shells with principal quantum numbers n and $n = n+1$ is proportional to $1/n^3$ for large n.

   We have the energy given by

   $$E = -\frac{Ze^2/4\pi\epsilon_0}{2a_0}\frac{1}{n^2} \propto Z^2$$

   and so

   $$\frac{dE}{dn} = -\frac{Ze^2/4\pi\epsilon_0}{2a_0}\frac{-2}{n^3} = \frac{Ry}{n^3}$$

2. Calculate the frequency of the transition between the $n = 51$ and $n = 50$ shells of a neutral atom.

   The energy between states is given by:

   $$\begin{aligned}\Delta E &= \mathrm{Ry}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right) \\ &= 13.6\left(\frac{1}{50^2} - \frac{1}{51'^2}\right) \\ &= 13.6\left(4\times10^{-4} - 3.85\times10^{-4}\right) \\ &= 13.6 \times 0.15 \times 10^{-4} = 2.04\times10^{-4}\,\mathrm{eV}\end{aligned}$$

   which we convert to frequency by multiplying by a factor of e/h, or $f = 49\,\mathrm{GHz}$

3. What is the size of an atom in these Rydberg states? Express your answer both in atomic units and SI units.

   To compute the size, one can use the formula $r_n \approx a_0 n^2$ where a_0 is the Bohr radius. The origin of this relation is the Bohr model of the atom, where the force on the electron due to the Coulomb potential must balance the centripetal force

$$\frac{m_e v^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}.$$

The other postulate of the Bohr model is that angular momentum is quantised in units of $\hbar$, or

$$m_e v r = n\hbar,$$

which when combined, these yield the results that

$$r = \frac{4\pi\epsilon_0 n^2 \hbar^2}{m_e e^2} \equiv a_0 n^2$$

For $n = 50$, the radius of the atom would be 2500 a.u. or 1.32×10^{-7} m(*HUGE*!)

Exercise 3 *Inside the nucleus!?*

Calculate the probability that the electron in the ground state of a hydrogenic atom of nuclear charge Z is measured to be inside the nucleus. A nucleus with A nucleons (Z protons and A-Z neutrons) has an approximate radius of $r \approx (1.2 \times 10^{-15}) \times A^{1/3}$[m]. Calculate the probabilities for hydrogen and uranium-238.

Solution 3

Calculate the probability that the electron in the ground state of a hydrogenic atom of nuclear charge Z is measured to be inside the nucleus. A nucleus with A nucleons (Z protons and A-Z neutrons) has an approximate radius of $r \approx (1.2 \times 10^{-15}) \times A^{1/3}$[m]. Calculate the probabilities for hydrogen and uranium-238.

The probability that the electron resides within the nucleus is

$$\mathscr{P}_{inside} = \int_{nucleus} \mathscr{P}(r,\theta,\phi) = \int_0^{r_n} \int_0^{2\pi} \int_0^{\pi} |R_{nl}(r) Y_l^m(\theta,\phi)|^2 r^2 \sin(\theta) d\theta d\phi dr$$

By normalisation of the spherical harmonics, the angular integral evaluates to 1. For the $1s$ state, we get

$$\begin{aligned}
\mathscr{P}_{inside} &= \int_0^{r_n} r^2 dr = |R_{nl}(r)|^2 \, 4\left(\frac{Z}{a_0}\right)^3 \int_0^{r} r^2 e^{-2Zr/a_0} dr \\
&= 4\left(\frac{Z}{a_0}\right)^3 \left(\frac{a_0}{2Z}\right)^3 \int_0^{2Zr_n/a_0} x^2 e^{-x} dr \\
&= 4\left(\frac{Z}{a_0}\right)^3 \left(\frac{a_0}{2Z}\right)^3 \left[-x^2 e^{-x} - 2xe^{-x} - 2e^{-x}\right]_0^{2Zr_n/a_0} \\
&= \frac{1}{2}\left[-\left(\frac{2Zr_n}{a_0}\right)^2 e^{-2Zr_n/a_0} - 2\left(\frac{2Zr_n}{a_0}\right) e^{-2Zr_n/a_0} - 2e^{-2Zr_n/a_0} + 2\right] \\
&= 1 - e^{-\beta} - \beta e^{-\beta} - \frac{1}{2}\beta^2 e^{-\beta}
\end{aligned}$$

where $\beta = 2Zr_n/a_0$. The value for r_n is given as approximately $(1.2 \times 10^{-15}) \times A^{1/3}$, which means $\beta = 4.54 \times 10^{-5} Z A^{1/3}$.
For hydrogen, $A = Z = 1 \Rightarrow \beta = 4.54 \times 10^-5$ and so

$$\mathscr{P}_{inside} \approx 1.6 \times 10^{-14}$$

For uranium, $Z = 92$ and $A = 238 \Rightarrow \beta = 2.59 \times 10^-2$ and so

$$\mathscr{P}_{inside} \approx 2.8 \times 10^{-6}$$

Exercise 4 *Super superpositions*

A hydrogen atom is initially in the superposition state

$$|\psi(0)\rangle = \frac{1}{\sqrt{14}}|211\rangle - \frac{2}{\sqrt{14}}|32,-1\rangle + \frac{3i}{\sqrt{14}}|422\rangle$$

1. What are the possible results of a measurement of the energy and with what probabilities would they occur? Calculate the expectation value of the energy.
2. What are the possible results of a measurement of the angular momentum operator $\mathbf{L}^2$ and with what probabilities would they occur? Calculate the expectation value of $\mathbf{L}^2$.
3. What are the possible results of a measurement of the angular momentum component operator L_z and with what probabilities would they occur? Calculate the expectation value of L_z.
4. How do the above answers depend upon time?

Solution 4

A hydrogen atom is initially in the superposition state

$$|\psi(0)\rangle = \frac{1}{\sqrt{14}}|211\rangle - \frac{2}{\sqrt{14}}|32,-1\rangle + \frac{3i}{\sqrt{14}}|422\rangle$$

1. What are the possible results of a measurement of the energy and with what probabilities would they occur? Calculate the expectation value of the energy.

   The possible values of the energy are E_2, E_3, and E_4 where the values $E_n = -\mathrm{Ry}/n^2$.

   The probabilities are

$$\mathscr{P}(E = E_n) = \sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{\ell} |\langle n\ell m|\psi\rangle|^2$$

   For each of the energies, we have

$$\mathscr{P}(E = E_2) = \sum_{\ell=0}^{1}\sum_{m=-\ell}^{\ell} \left|\left\langle 2\ell m \middle| \frac{1}{\sqrt{14}}|211\rangle - \frac{2}{\sqrt{14}}|32,-1\rangle + \frac{3i}{\sqrt{14}}|422\rangle\right\rangle\right|^2 = \frac{1}{14}$$
$$\mathscr{P}(E = E_3) = \sum_{\ell=0}^{2}\sum_{m=-\ell}^{\ell} \left|\left\langle 3\ell m \middle| \frac{1}{\sqrt{14}}|211\rangle - \frac{2}{\sqrt{14}}|32,-1\rangle + \frac{3i}{\sqrt{14}}|422\rangle\right\rangle\right|^2 = \frac{4}{14}$$
$$\mathscr{P}(E = E_4) = \sum_{\ell=0}^{3}\sum_{m=-\ell}^{\ell} \left|\left\langle 4\ell m \middle| \frac{1}{\sqrt{14}}|211\rangle - \frac{2}{\sqrt{14}}|32,-1\rangle + \frac{3i}{\sqrt{14}}|422\rangle\right\rangle\right|^2 = \frac{9}{14}$$

   The expectation value of the energy is

$$
\begin{aligned}
\langle E\rangle = \langle\psi|H|\psi\rangle = \sum_{n=1}^{\infty} E_n \mathscr{P}(E=E_n) &= -\mathrm{Ry}\sum_{n=1}^{\infty}\mathscr{P}(E=E_n)/n^2 \\
&= -\mathrm{Ry}\left(\frac{1}{4}\mathscr{P}(E=E_2)+\frac{1}{9}\mathscr{P}(E=E_3)+\frac{1}{16}\mathscr{P}(E=E_4)\right) \\
&= -\mathrm{Ry}\left(\frac{181}{2016}\right) = -1.221\,\mathrm{eV}
\end{aligned}
$$

2. What are the possible results of a measurement of the angular momentum operator $\mathbf{L}^2$ and with what probabilities would they occur? Calculate the expectation value of $\mathbf{L}^2$.

   The allowed values of $\mathbf{L}^2$ are $\ell(\ell+1)\hbar$, and the probabilities are

$$
\begin{aligned}
\mathscr{P}_\ell &= \sum_{n=\ell+1}^{\infty}\sum_{m=-\ell}^{\ell}|\langle n\ell m|\psi\rangle|^2 \\
\mathscr{P}(\ell=1) &= \sum_{n=2}^{\infty}\sum_{m=-1}^{1}\left|\left\langle n1m\middle|\frac{1}{\sqrt{14}}|211\rangle-\frac{2}{\sqrt{14}}|32,-1\rangle+\frac{3i}{\sqrt{14}}|422\rangle\right\rangle\right|^2 = \frac{1}{14} \\
\mathscr{P}(\ell=2) &= \sum_{n=3}^{\infty}\sum_{m=-2}^{2}\left|\left\langle n2m\middle|\frac{1}{\sqrt{14}}|211\rangle-\frac{2}{\sqrt{14}}|32,-1\rangle+\frac{3i}{\sqrt{14}}|422\rangle\right\rangle\right|^2 = \frac{4}{14}+\frac{9}{14}=\frac{13}{14}
\end{aligned}
$$

   The expectation value of $\mathbf{L}^2$ is

$$
\begin{aligned}
\langle\mathbf{L}^2\rangle = \langle\psi|\mathbf{L}^2|\psi\rangle &= \sum_{l=0}^{\infty}\ell(\ell+1)\hbar^2\mathscr{P}_\ell \\
&= \hbar^2(2\mathscr{P}(\ell=1)+6\mathscr{P}(\ell=2)) \\
&= \frac{40}{7}\hbar^2
\end{aligned}
$$

3. What are the possible results of a measurement of the angular momentum component operator L_z and with what probabilities would they occur? Calculate the expectation value of L_z.

   The allowed values of L_z are $m\hbar$, and the probabilities for measurement are

$$
\begin{aligned}
\mathscr{P}_m &= \sum_{n=|m|+1}^{\infty}\sum_{l=|m|}^{n-1}|\langle n\ell m|\psi\rangle|^2 \\
\mathscr{P}(m=-1) &= \sum_{n=2}^{\infty}\sum_{l=1}^{n-1}\left|\left\langle n\ell,-1\middle|\frac{1}{\sqrt{14}}|211\rangle-\frac{2}{\sqrt{14}}|32,-1\rangle+\frac{3i}{\sqrt{14}}|422\rangle\right\rangle\right|^2 = \frac{4}{14} \\
\mathscr{P}(m=1) &= \sum_{n=2}^{\infty}\sum_{l=1}^{n-1}\left|\left\langle n\ell 1\middle|\frac{1}{\sqrt{14}}|211\rangle-\frac{2}{\sqrt{14}}|32,-1\rangle+\frac{3i}{\sqrt{14}}|422\rangle\right\rangle\right|^2 = \frac{1}{14} \\
\mathscr{P}(m=2) &= \sum_{n=3}^{\infty}\sum_{l=2}^{n-1}\left|\left\langle n\ell 2\middle|\frac{1}{\sqrt{14}}|211\rangle-\frac{2}{\sqrt{14}}|32,-1\rangle+\frac{3i}{\sqrt{14}}|422\rangle\right\rangle\right|^2 = \frac{9}{14}
\end{aligned}
$$

   The expectation value of L_z is

$$
\begin{aligned}
\langle L_z \rangle = \langle \psi | L_z | \psi \rangle &= \sum_{m=-\infty}^{\infty} m\hbar \mathscr{P}_m \\
&= (-1\hbar)\mathscr{P}(m=-1) + (1\hbar)\mathscr{P}(m=1)) + (2\hbar)\mathscr{P}(m=2)) \\
&= \frac{15}{14}\hbar
\end{aligned}
$$

4. How do the above answers depend upon time?

   All answers are time-independent because the operators all commute with the Hamiltonian. The explicit time dependence of the state vector is

$$
|\psi(t)\rangle = \frac{1}{\sqrt{14}} e^{-iE_2 t/\hbar} |211\rangle - \frac{2}{\sqrt{14}} e^{-iE_3 t/\hbar} |32,-1\rangle + \frac{3i}{\sqrt{14}} e^{-iE_4 t/\hbar} |422\rangle
$$

   and hopefully it is clear that in all probability calculations, the time dependence will vanish upon multiplication with the conjugate.

Exercise 5 *Wavefunctions do the darnedest things*

At the time $t = 0$, the a system is described by the wavefunction

$$
\psi(\mathbf{r}, 0) = \frac{1}{\sqrt{10}} \left(2\psi_{100} + \psi_{210} + \sqrt{2}\psi_{211} + \sqrt{3}\psi_{21,-1} \right).
$$

1. What is the expectation value for the energy of the above system?
2. What is the probability of finding the system with $\ell = 1$ and $m = +1$ as a function of time?
3. What is the probability of finding an electron within 10^{-10} cm of the proton at $t = 0$? Feel free to Taylor expand any pesky exponential terms to first-order to make the evaluation of integrals easier.
4. How does the wave function evolve in time?
5. Suppose a measurement is performed on the above system, yielding values of $L = 1$ and $L_z = +1$. What is the wavefunction immediately following the measurement, expressed in terms of the ψ_{nlm} used above?

Solution 5

At the time $t = 0$, the a system is described by the wavefunction

$$
\psi(\mathbf{r}, 0) = \frac{1}{\sqrt{10}} \left(2\psi_{100} + \psi_{210} + \sqrt{2}\psi_{211} + \sqrt{3}\psi_{21,-1} \right).
$$

1. (a) What is the expectation value for the energy of the above system?

   We calculate the expectation value via

$$
\begin{aligned}
E = \langle \psi | H | \psi \rangle = \frac{1}{10} \langle 2\psi_{100} + \psi_{210} + \sqrt{2}\psi_{211} + \sqrt{3}\psi_{21,-1} | 2E_1\psi_{100} \\
+ E_2\psi_{210} + E_2\sqrt{2}\psi_{211} + E_2\sqrt{3}\psi_{21,-1} \rangle \\
= \frac{1}{10}(4E_1 + E_2 + 2E_2 + 3E_2) = \frac{1}{10}(4E_1 + 6E_2)
\end{aligned}
$$

and since $E_2 = E_1/4$,

$$\begin{aligned}\langle E \rangle &= \frac{E_1}{10}(4 + 3/2) \\ &= 0.55E_1 = 0.55 \times -13.6 = -7.47\,\text{eV}\end{aligned}$$

2. (b) What is the probability of finding the system with $\ell = 1$ and $m = +1$ as a function of time?

   The time evolution of the state is given by

$$|\psi(t)\rangle = \exp\left(-\frac{iHt}{\hbar}\right)|\psi(0)\rangle$$

   and so for a state with $\ell = 1$ and $m = +1$, we have

$$\begin{aligned}\langle n11|\psi(t)\rangle &= \delta_{n2}\left\langle 211 \left| \exp\left(-\frac{iHt}{\hbar}\right)\right| |\psi(0)\rangle \right\rangle \\ &= \delta_{n2}\sqrt{\frac{1}{5}}\exp\left(-\frac{iE_2 t}{\hbar}\right)\end{aligned}$$

   and therefore the probability is given by $|\langle n11|\psi(t)\rangle|^2 = \delta_{n2}/5$, meaning that if $n = 2$, $\mathscr{P} = 1/5$ and $\mathscr{P} = 0$ otherwise.

3. (c) What is the probability of finding an electron within 10^{-10} cm of the proton at $t = 0$? Feel free to Taylor expand any pesky exponential terms to first-order to make the evaluation of integrals easier.

   Let's define $\alpha = 10^{-10}$ cm, so then we have

$$\begin{aligned}\mathcal{P} &= \int_0^\alpha \psi^* \psi r^2 dr d\Omega \\ &= \int_0^\alpha \frac{1}{10}\left(4|R_{10}|^2 + 6|R_{21}|^2\right) r^2 dr.\end{aligned}$$

   Looking explicitly at the radial wavefunctions for Hydrogen, we have

$$\begin{aligned}|R_{10}|^2 &= \frac{4}{a_0^3}e^{-2r/a_0} \\ |R_{21}|^2 &= \frac{r^2}{25a_0^5}e^{-r/2a_0}\end{aligned}$$

   and so given 5.29×10^{-11} m and we are looking at $r \leq \alpha \ll a_0$, we can make use of the approximation

$$e^{-x} \approx 1 - x$$

   to get the probability

$$\begin{aligned}\mathcal{P} &= \frac{4}{10}\int_0^{\frac{4}{a_0^3}}\left(1 - \frac{2r}{a_0}\right) r^2 dr + \frac{6}{10}\int_0^{\frac{r^2}{24a_0^5}}\left(1 - \frac{r}{2a_0}\right) r^2 dr \\ &= \frac{4}{10}\left[\frac{4}{3}\left(\frac{\alpha}{a_0}\right)^3 - 2\left(\frac{\alpha}{a_0}\right)^4\right] + \frac{6}{10}\left[\frac{1}{120}\left(\frac{\alpha}{a_0}\right)^5 - \frac{1}{288}\left(\frac{\alpha}{a_0}\right)^6\right] \\ &\approx \frac{8}{15}\left(\frac{\alpha}{a_0}\right)^3 \approx 3.6 \times 10^{-6}\end{aligned}$$

4. (d) How does the wave function evolve in time?

   The wavefunction at time t is

$$\psi(\mathbf{r}, t) = \exp\left(-\frac{iHt}{\hbar}\right)\psi(\mathbf{r}, 0)$$

   or explicitly

$$\psi(\mathbf{r}, t) = \frac{1}{\sqrt{10}}\left(2e^{-i\omega_1 t}\psi_{100} + e^{-i\omega_2 t}\psi_{210} + \sqrt{2}e^{-i\omega_2 t}\psi_{211} + \sqrt{3}e^{-i\omega_2 t}\psi_{21,-1}\right)$$

   where $\omega_{1,2} = E_{1,2}/\hbar$

5. (e) Suppose a measurement is performed on the above system, yielding values of $L = 1$ and $L_z = +1$. What is the wavefunction immediately following the measurement, expressed in terms of the ψ_{nlm} used above?

   Given $\ell = 1$, in terms of the states given, we must have $n = 2$, and with $L_z = +1$, the state would simply be in the eigenstate $|211\rangle$. An interesting experiment is to once again make measurements of $\mathbf{L}^2$ and L_z, and verify if they still remain the same, and then increase the delay between the original and subsequent measurements... What will happen?