

Hydrogen Atom

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Now we turn to our ultimate goal: the hydrogen atom. Quantum mechanically, this is described by the kinetic energies of the proton, the electron, and the Coulomb force between them,

$$H = \frac{p_p^2}{2m_p} + \frac{p_e^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0|\vec{x}_e - \vec{x}_p|}$$

This generally looks like a complicated Hamiltonian involving two coordinates, but as you will show on the problem set, in the center of mass frame of the hydrogen atom this reduces to a problem that depends only on the relative position $\vec{r} = \vec{x}_e - \vec{x}_p$ and the reduced mass $\mu \equiv \frac{m_e m_p}{m_e + m_p} \approx m_e$. In terms of these variables, the time-independent Schrödinger equation takes the form

$$-\frac{\hbar^2}{2\mu}\nabla_r^2\psi_r - \frac{e^2}{4\pi\epsilon_0 r}\psi_r = E_r\psi_r$$

where E_r is the energy associated with the relative separation (the rest being associated with the center of mass kinetic energy); we will henceforth drop the subscript r . Since the $V \rightarrow 0$ as $r \rightarrow \infty$, there are both bound state solutions with $E < 0$ and scattering states with $E \geq 0$. Here we will be interested in the bound states.

Solutions to this equation with $E < 0$ – the bound energy eigenstates – will be of the general form $\psi_{n,\ell,m}(r, \theta, \phi)$. Since the potential is central, we can use our existing solution to the angular part in terms of spherical harmonics $Y_\ell^m(\theta, \phi)$, and reduce the problem to finding the radial wavefunctions $R_\ell(r)$. As we saw last lecture, solving the problem amounts to finding $R_\ell(r)$ satisfying

$$H_\ell R_\ell(r) = E R_\ell(r)$$

where now the effective radial Hamiltonian is

$$H_\ell = \frac{p_r^2}{2\mu} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{e^2}{4\pi\epsilon_0 r}$$

It is helpful to organize the problem in terms of the length scale

$$a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

which is known as the *Bohr radius*. Then we have

$$H_\ell = \frac{p_r^2}{2\mu} + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2} - \frac{\hbar^2}{\mu a_0 r}$$

At this point, we will attempt exactly what we already did with the harmonic oscillator: to factorize the Hamiltonian into the product of two operators, up to a constant. In this case, consider the lowering operator

$$a_\ell \equiv \frac{a_0}{\hbar\sqrt{2}} \left(ip_r - \frac{(\ell+1)\hbar}{r} + \frac{\hbar}{(\ell+1)a_0} \right)$$

Much as with the 3d harmonic oscillator, the commutator of a_ℓ and the raising operator a_ℓ^\dagger can be written as

$$[a_\ell, a_\ell^\dagger] = \frac{a_0^2}{2\hbar^2} (-i\hbar(\ell+1)[p_r, 1/r]) = \frac{(\ell+1)a_0^2}{2r^2} = \frac{a_0^2\mu}{\hbar^2} (H_{\ell+1} - H_\ell)$$

As you can check, we can write the radial Hamiltonian as

$$H_\ell = \frac{\hbar^2}{\mu a_0^2} \left(a_\ell^\dagger a_\ell - \frac{1}{2(\ell+1)^2} \right)$$

Just as with the harmonic oscillator, we can now compute the commutator of a_ℓ with H_ℓ , giving

$$[a_\ell, H_\ell] = \frac{\hbar^2}{\mu a_0^2} [a_\ell, a_\ell^\dagger a_\ell] = \frac{\hbar^2}{\mu a_0^2} [a_\ell, a_\ell^\dagger] a_\ell = (H_{\ell+1} - H_\ell) a_\ell$$

In other words, we have

$$a_\ell H_\ell = H_{\ell+1} a_\ell$$

1 Finding the allowed energies

Now we can proceed to find all of the radial wavefunctions, exactly like we did for the harmonic oscillator. If I give you a solution to

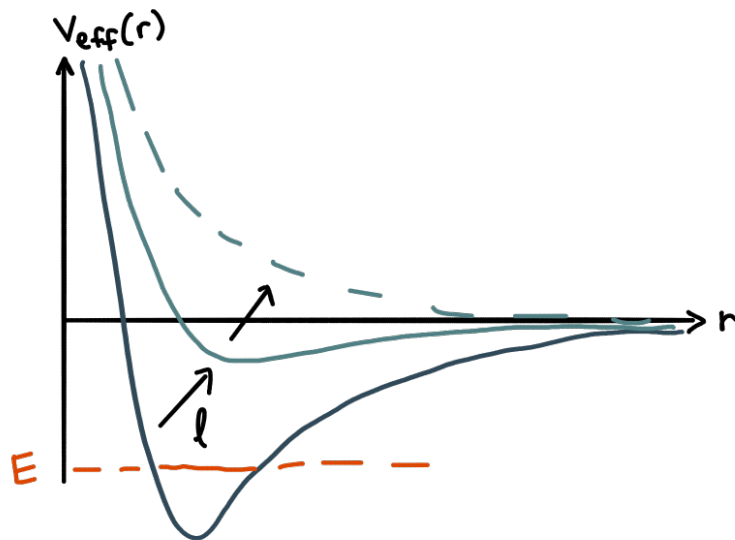
$$H_\ell R_\ell = E_n R_\ell$$

and we act on both sides with a_ℓ , we find

$$E_n a_\ell R_\ell = a_\ell H_\ell R_\ell = H_{\ell+1} a_\ell R_\ell$$

From this we learn that $a_\ell R_\ell$ is an eigenstate of $H_{\ell+1}$ with the same energy E_n . So acting with the lowering operator has given us a new state with the *same* energy but more angular momentum, i.e. larger ℓ . This is slightly different from the harmonic oscillator.

You might think we could make infinitely many solutions by acting suggestively with $a_{\ell+1}, a_{\ell+2}, \dots$, but once again we cannot continue this exercise ad infinitum. Here the argument is a little more subtle, because E is not decreasing. Still, for a fixed value of E , the effective potential has a positive term that goes like $+\ell(\ell+1)/r^2$ and a negative term that goes like $-1/r$. As ℓ increases, the coefficient of the $+1/r^2$ term increases, while the coefficient of the Coulomb term is fixed. For large enough ℓ , E is less than the minimum of the effective potential, and there is no longer a physically allowed bound state, because that would require negative radial kinetic energy.



Thus there must be a maximum value of ℓ , call it \mathcal{L} , for which

$$a_{\mathcal{L}} R_{\mathcal{L}} = 0$$

Just as in the 3d harmonic oscillator, these solutions are circular orbits – they have the largest possible angular momentum for a given energy. The energy of such a solution is

$$H_{\mathcal{L}}R_{\mathcal{L}} = -\frac{\hbar^2}{2\mu a_0^2(\mathcal{L} + 1)^2}$$

Now \mathcal{L} is a non-negative integer, so $\mathcal{L} + 1$ is a positive integer. Let's call it n , with $n = 1, 2, 3, \dots$; this is known as the *principal quantum number*. Thus the allowed energies of circular orbits have the form

$$E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2} = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2}$$

It is conventional to define the Rydberg constant \mathcal{R} as

$$\mathcal{R} \equiv \frac{\hbar^2}{2\mu a_0^2} = 13.6056923 \text{ eV}$$

In terms of this, the allowed energies simply take the form

$$E_n = -\frac{\mathcal{R}}{n^2}$$

Note that the energy increases as n increases, and as $n \rightarrow \infty$ this asymptotes to $E \rightarrow 0$, the limit of the bound states.

Acting on an eigenstate R_{ℓ} of the radial Hamiltonian H_{ℓ} with the lowering operator a_{ℓ} gave us an eigenstate of the radial Hamiltonian $H_{\ell+1}$ with the same energy. Increasing ℓ while keeping the total energy fixed would eventually lead to an unphysical state whose total energy E was less than the minimum of the effective potential V_{eff} . This could be avoided if the ladder instead terminates, i.e., there is some state $R_{\mathcal{L}}$ such that

$$a_{\mathcal{L}}R_{\mathcal{L}} = 0$$

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Although we arrived at the energies for the circular orbits, these are the allowed energies, *period*. We can create less circular orbits by acting with a_ℓ^\dagger , but this just makes states with lower ℓ and the same energy, all the way down to $\ell = 0$. These states are all degenerate with the same E_n . For a given n , the *maximum* allowed value of ℓ is $\mathcal{L} = n - 1$, corresponding to the circular orbit, and lower values of ℓ can be obtained by acting with the lowering operators.

Graphically, the relation between n and ℓ for these solutions is in the Figure in the next page. Thus for a given n , we have a whole host of degenerate states with

$$0 \leq \ell \leq n - 1$$

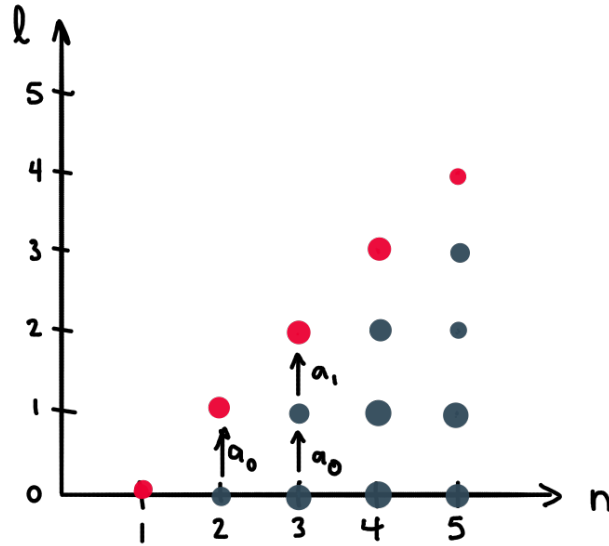
Also recall that for a state of fixed ℓ , the azimuthal quantum number m could run over

$$-\ell \leq m \leq \ell$$

So the degeneracy of a given E_n is

$$\sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} 1 = \sum_{\ell=0}^{n-1} (2\ell + 1) = n^2$$

As you will see in 115C, excited (higher-energy) states of hydrogen may be rendered unstable to decay into lower energy states. When this occurs, the energy is



released in the form of energy, typically electromagnetic radiation. Similarly, lower-energy eigenstates can be induced to transition into higher-energy states by absorbing energy. The amount of energy absorbed or emitted in a transition must be equal to the energy splitting, and thus follows the form

$$E = E_i - E_f = -\mathcal{R} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

This was observed experimentally in the 19th century, and its explanation (and the calculation of \mathcal{R} in terms of fundamental parameters) is one of the great triumphs of quantum mechanics.

It is conventional to label the corresponding radial eigenfunctions by both their principle quantum number n and their value of ℓ , $R_{n,\ell}(r)$. So, putting it all together, our solutions for the energy eigenstates of the hydrogen atom have the form

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

and are separately orthogonal in the quantum numbers n, ℓ , and m .

1.1 Finding the radial functions

We can find the explicit form of the $R_{n,\ell}$ using the same trick as the harmonic oscillator. We know the circular orbits have $\ell = n - 1$, and are annihilated by the corresponding lowering operator,

$$a_{n-1}R_{n,n-1} = 0$$

Recall that lowering operators are just

$$a_{n-1} \equiv \frac{a_0}{\sqrt{2}} \left(\frac{\partial}{\partial r} - \frac{n}{r} + \frac{1}{na_0} \right)$$

where I have written out p_r explicitly. (Please forgive the notation – the a_0 on the RHS is the Bohr radius.) So the circular orbits are solutions to first-order ODEs

$$\left(\frac{d}{dr} - \frac{n}{r} + \frac{1}{na_0} \right) R_{n,n-1}(r) = 0$$

The solutions are of the form

$$R_{n,n-1}(r) = Cr^{n-1}e^{-r/na_0}$$

where C is a normalization constant. These have the form of a fixed power of r multiplying a falling exponential. Normalizing these wavefunctions gives

$$R_{n,n-1}(r) = \frac{1}{\sqrt{(2n)!}} \left(\frac{2}{na_0} \right)^{3/2} \left(\frac{2r}{na_0} \right)^{n-1} e^{-r/na_0}$$

The ground state corresponds to $n = 1$, and tacking on the spherical harmonic part gives the full ground state wavefunction

$$\psi_{1,0,0} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

We have found all of the circular orbits, but now we can get more eccentric orbits (with lower ℓ) by acting on the circular orbits with raising operators. For example, up to normalization

$$R_{n,n-2} = a_{n-2}^\dagger R_{n,n-1} \propto \left(\frac{\partial}{\partial r} + \frac{n-1}{r} + \frac{1}{(n-1)a_0} \right) R_{n,n-1}$$

which you can work out explicitly. As with the harmonic oscillator, acting with raising operators increases the number of wiggles or nodes in the wavefunction, increasing the radial kinetic energy. The radial wavefunctions turn out to be a class of special functions known as *Laguerre polynomials*, whose explicit form is not particularly interesting for us – if you need it, you can look it up.