

HYDROGEN ATOM

Consider an arbitrary potential $U(r)$ that only depends on the distance between two particles from the origin. We can write the Hamiltonian simply

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 + U(r)$$

One interesting potential of this type arises for hydrogen-like atoms. In this situation, we picture a nucleus of charge $+Z$ sitting at the origin with a single electron orbiting it. This exemplifies H, He⁺, Li²⁺.... In this case, the only potential is due to the Coulomb attraction between the nucleus and the electron

$$U(r) = \frac{-Ze^2}{4\pi\epsilon_0 r}$$

which depends only on the distance of the electron from the origin. This situation has obvious importance for the description of atoms, so we'll study the potential in detail. Note that if the nucleus was infinitely more massive than the electron (which is nearly true), then, $\mu = m_e$. In practice, we will make this infinite mass approximation for convenience.

Atomic units and their SI equivalents		
Quantity	Natural unit	SI equivalent
Electron mass	$m = 1$	9.11×10^{-31} kg
Charge	$ e = 1$	1.06×10^{-19} C
Angular momentum	$\hbar = 1$	1.05×10^{-34} J · s
Permittivity	$\kappa_0 = 4\pi\epsilon_0 = 1$	1.11×10^{-10} C ² · J ⁻¹ · m ⁻¹
Length	$\kappa_0 \hbar^2 / me^2 = a_0 = 1$ (bohr) (Bohr radius)	5.29×10^{-11} m
Energy	$me^4 / \kappa_0^2 \hbar^2 = e^2 / \kappa_0 a_0 = 1$ (hartree) (twice the ionization energy of H)	4.36×10^{-18} J = 27.2 eV
Time	$\kappa_0^2 \hbar^3 / me^4 = 1$ (period of an electron in the first Bohr orbit)	2.42×10^{-17} s
Speed	$e^2 / \kappa_0 \hbar = 1$ (speed of an electron in the first Bohr orbit)	2.19×10^8 m/s
Electric potential	$me^3 / \kappa_0^2 \hbar^2 = e^2 / \kappa_0 a_0 = 1$ (potential energy of an electron in the first Bohr orbit)	27.21 V
Magnetic dipole moment	$e\hbar / m = 1$ (twice a Bohr magneton)	1.85×10^{-23} J · T ⁻¹

First, we can simplify our equations by choosing our units in a clever way. Typically, one chooses a unit of length (say a meter) and a unit of mass (kilogram) and time (second) based on a convenient convention. These choices determine the dimensions of all computed quantities. Thus, in meter-kilogram-second units, the unit of energy is the Joule. We could instead of length and unit of mass to be something else. In **atomic units**, one chooses the units of length, mass and time so that $\hbar = m = e = 1$. Choosing our units in this way, the relatively unimportant factors of \hbar and m disappear from our equations, making the algebra much simpler to follow. In the end, once we have calculated an observable (such as the position) we will need to convert the result to a set of standard units (such as meters). The table above includes the atomic units for every conceivable observable.

Thus, in atomic units:

$$H = -\frac{\nabla^2}{2} + U(r) = \frac{-1}{2r^2} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + U(r)$$

where the second equality just reinforces the gory details wrapped up in the Laplacian operator. At this point we notice that \mathbf{L}^2 plays a conspicuous role in the Hamiltonian:

$$H = \frac{-1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\mathbf{L}^2}{2r^2} + U(r)$$

Hence, **all** of the angular dependence of H is contained in \mathbf{L}^2 and we immediately conclude that:

$$[H, \mathbf{L}^2] = 0 \quad [H, L_z] = 0$$

which means that the eigenfunctions of H are also angular momentum eigenfunctions! That is, for any fixed r ,

$$\psi_i(r, \theta, \phi) \propto Y_l^m(\theta, \phi)$$

Noting that the proportionality constant can depend on r , as well as the quantum numbers l and m , we can write

$$\psi_i(r, \theta, \phi) = R_l^m(r) Y_l^m(\theta, \phi)$$

The radial function - ($R_l^m(r)$) - will depend on the form of $U(r)$, but the angular parts are **universal** - they are just the spherical harmonics. Combining our expression for the spherical harmonics with the previous results, we find that the eigenfunctions for any central potential can be written

$$\psi_i(r, \theta, \phi) = R_l^m(r) P_l^m(\theta) e^{im\phi}$$

that is, the three dimensional wavefunction is **separable** into a product of three one dimensional wavefunctions. This is not generally the case, and is one of the particularly nice properties of spherically symmetric potentials. The radial

function will generally depend on the form of the potential, but it will obey the equation:

$$\left(\frac{-1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} + U(r) \right) R_l^m(r) = E_l R_l^m(r)$$

This equation can be solved exactly for only a few cases (the harmonic oscillator and the Coulomb potential are the most notable). Notice that the eigenvalue equation depends on the value of l , the quantum number for \hat{L}^2 , but not m , which indicates the projection of the angular momentum along the z axis. Hence the R_l^m 's do not actually depend on m . Further, we anticipate the appearance of another quantum number (call it n) that indexes the solutions to this radial equation. Hence, we replace $R_l^m(r) \rightarrow R_{nl}(r)$ in what follows.

For the Hydrogen-like atom, then, we want the solutions of:

$$\left(\frac{-1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) R_{nl}(r) = E_{nl} R_{nl}(r)$$

Like most of the differential equations in this course, the solutions of the above equation were worked out centuries ago and are associated with the name Laguerre. The derivation is quite lengthy and can be found in many textbooks (e.g. Sakurai's *Modern Quantum Mechanics*) We will not reproduce it here. Instead, we will focus on *analyzing* the results. The general solution for the Hydrogen atom radial functions is ($\sigma = 2Zr/n$)

$$R_{nl}(r) = \sqrt{\frac{(n-l-1)! 4Z^3}{((n+l)!)^3 n^4}} e^{-\frac{\sigma}{2}} \sigma^l \frac{d^{2l+1}}{d\sigma^{2l+1}} e^{\sigma} \frac{d^{n+l}}{d\sigma^{n+l}} e^{-\sigma} \sigma^{n+l}$$

As defined, these functions are normalized so that (don't forget the r^2 volume element!)

$$\int_0^\infty dr r^2 R_{nl}^*(r) R_{nl}(r) = 1$$

The lowest few radial wavefunctions are explicitly given by:

$$\begin{aligned} R_{10}(r) &= 2Z^{3/2} e^{-Zr} \\ R_{20}(r) &= \left(\frac{Z}{2}\right)^{3/2} (Zr - 2) e^{-Zr/2} \\ R_{21}(r) &= \left(\frac{1}{24}\right)^{1/2} Z^{5/2} r e^{-Zr/2} \end{aligned}$$

We note that, in general, the radial functions decay exponentially far from the nucleus. This makes sense because the electron is attracted to the nucleus, so that the probability of finding the electron very far away should decay quickly. Second, we note that as we increase the **radial quantum number**, n , the degree of the polynomial in front of the exponential increases by 1. As we will see, this

leads to the expected result that for $n=1$ we have zero radial nodes, $n=2$ we have one

Several other Interesting Facts:

1) One finds that solutions only exist if $l < n$. Hence, while a Hydrogenic atom can only have any integer angular momentum, these values are further restricted for fixed n . We typically denote the l states as 's', 'p', 'd', 'f', 'g', 'h' ... orbitals, for $l=0,1,2,3,4,5,\dots$. Hence, we have 1s, 2s, 2p, 3s, 3p, 3d, etc orbitals, but not 1d orbitals or 3f orbitals. These designations are familiar to us from freshman chemistry. Here we see that these seemingly arbitrary rules fall out of the Schrodinger equation: there simply **are no solutions** with $l \geq n$. This situation is analogous to what we have seen before: for the Harmonic oscillator, we couldn't have $n < 0$; for angular momentum, we couldn't have $m > l$. These simply mathematical restrictions clearly have profound impacts on chemistry.

2) The energies of the Hydrogenic atom are $E_n = -\frac{1}{2} \frac{Z^2}{n^2}$, which were known experimentally long before Schrödinger ever came along. The interesting thing here is that the energies *do not depend on l*! This is a feature peculiar to Hydrogenic potentials and is related to an additional symmetry possessed by the Coulomb potential. This is termed an "accidental" degeneracy of the levels. The number of degeneracy, g_n , of a given level increases with n as $g_n = \sum_{l < n} 2l + 1 = n^2$.

SHAPES AND SYMMETRIES OF THE ORBITALS

As of the present writing, there is a wonderful java applet for viewing hydrogen orbitals available on the web (<http://www.falstad.com/qmatom/>). This viewer allows you to plot orbitals for various values of n, l, m , and rotate, zoom, change colors.... Feel free to visit this site and toy around with some orbitals

The one thing that falls out from this analysis is that the p orbitals do not look like you might expect. In freshman chemistry, we taught you that there are $2p_x$, $2p_y$ and $2p_z$ orbitals that all look like dumbbells oriented along the appropriate axis. ψ_{210} looks just like the $2p_z$ orbital we expect, but $\psi_{21\pm 1}$ look wrong. They are both donut-shaped in the xy -plane. Further, these orbitals are complex (because of the $e^{\pm i\phi}$ term)! In order to get the $2p_x$ and $2p_y$ orbitals, we have to take the real and imaginary parts of $\psi_{21\pm 1}$. Because these orbitals are

complex conjugates of one another, this is easily done by taking the + and - combinations:

$$\psi_{2px} = \frac{1}{\sqrt{2}}(\psi_{21-1} - \psi_{211}) = \frac{1}{4\sqrt{2}\pi} Z^{5/2} r e^{-Zr/2} \sin\theta \cos\phi$$

$$\psi_{2py} = \frac{i}{\sqrt{2}}(\psi_{21-1} + \psi_{211}) = \frac{1}{4\sqrt{2}\pi} Z^{5/2} r e^{-Zr/2} \sin\theta \sin\phi$$

This gives us some orbitals that are easier to visualize. A similar transformation needs to be done to the d orbitals to render them real. In the common parlance, the nlm solutions are termed spherical harmonics, while the linear combinations that give real functions are termed solid harmonics.

It is important to note that the $2p_x$ and $2p_y$ are eigenfunctions of the hydrogen atom, just like $\psi_{21\pm 1}$. To see this, note that for $2p_x$

$$H\psi_{2px} = H \frac{1}{\sqrt{2}}(\psi_{21-1} - \psi_{211}) = \frac{1}{\sqrt{2}}(H\psi_{21-1} - H\psi_{211})$$

$$= \frac{1}{\sqrt{2}} \left(\frac{-Z^2}{8} \psi_{21-1} - \frac{-Z^2}{8} \psi_{211} \right) = \frac{-Z^2}{8} \frac{1}{\sqrt{2}}(\psi_{21-1} - \psi_{211}) = \frac{-Z^2}{8} \psi_{2px}$$

with an analogous result for $2p_y$. Thus, $2p_x$ and $2p_y$ are *eigenfunctions with the same eigenvalue* as $\psi_{21\pm 1}$ ($-Z^2/8$). Note that the same would not have been true if we had taken + and - combinations of ψ_{211} and ψ_{100} [try it and see!] because those two orbitals are not degenerate. These findings illustrate a general point: **if we make a linear combination of two degenerate eigenfunctions, we obtain a new eigenfunction with the same eigenvalue.**

As a consequence, one is free to say that the hydrogen eigenstates with $n=2$ and $l=1$ are either $2p_x$, $2p_y$ and $2p_z$ or ψ_{211} , ψ_{210} and ψ_{21-1} . The two sets of orbitals contain the same information.

SUMMARY: TOTAL HYDROGEN ATOM WAVEFUNCTIONS

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$

principle quantum number	$n = 1, 2, 3, \dots$
angular momentum quantum number	$l = 0, 1, 2, \dots, n-1$
magnetic quantum number	$m = 0, \pm 1, \pm 2, \dots, \pm l$

ENERGY depends on n :

$$E_n = -\frac{1}{2} \frac{Z^2}{n^2} = \frac{-Z^2 e^2}{8\pi\epsilon_0 a_0 n^2}$$

Total H atom wavefunctions are normalized and orthogonal:

$$\int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^2 dr \psi_{nlm}^*(r, \theta, \phi) \psi_{n'l'm'}(r, \theta, \phi) = \delta_{nn'} \delta_{ll'} \delta_{mm'}$$

Lowest few total H atom wavefunctions, for $n = 1$ and 2 (with $\sigma = Zr/a_0$):

$$n = 1 \quad l = 0 \quad m = 0 \quad \psi_{100} \equiv \psi_{1s} = \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Zr}$$

$$n = 2 \quad l = 0 \quad m = 0 \quad \psi_{200} \equiv \psi_{2s} = \frac{1}{4\sqrt{2\pi}} Z^{3/2} (2 - Zr) e^{-Zr/2}$$

$$n = 2 \quad l = 1 \quad m = 0 \quad \psi_{210} \equiv \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} Z^{5/2} r e^{-Zr/2} \cos\theta$$

$$n = 2 \quad l = 1 \quad m = \pm 1 \quad \psi_{21\pm 1} = \frac{\mp 1}{8\sqrt{\pi}} Z^{5/2} r e^{-Zr/2} \sin\theta e^{\pm i\phi}$$

or, using the solid harmonics, the last two p-orbitals can be written

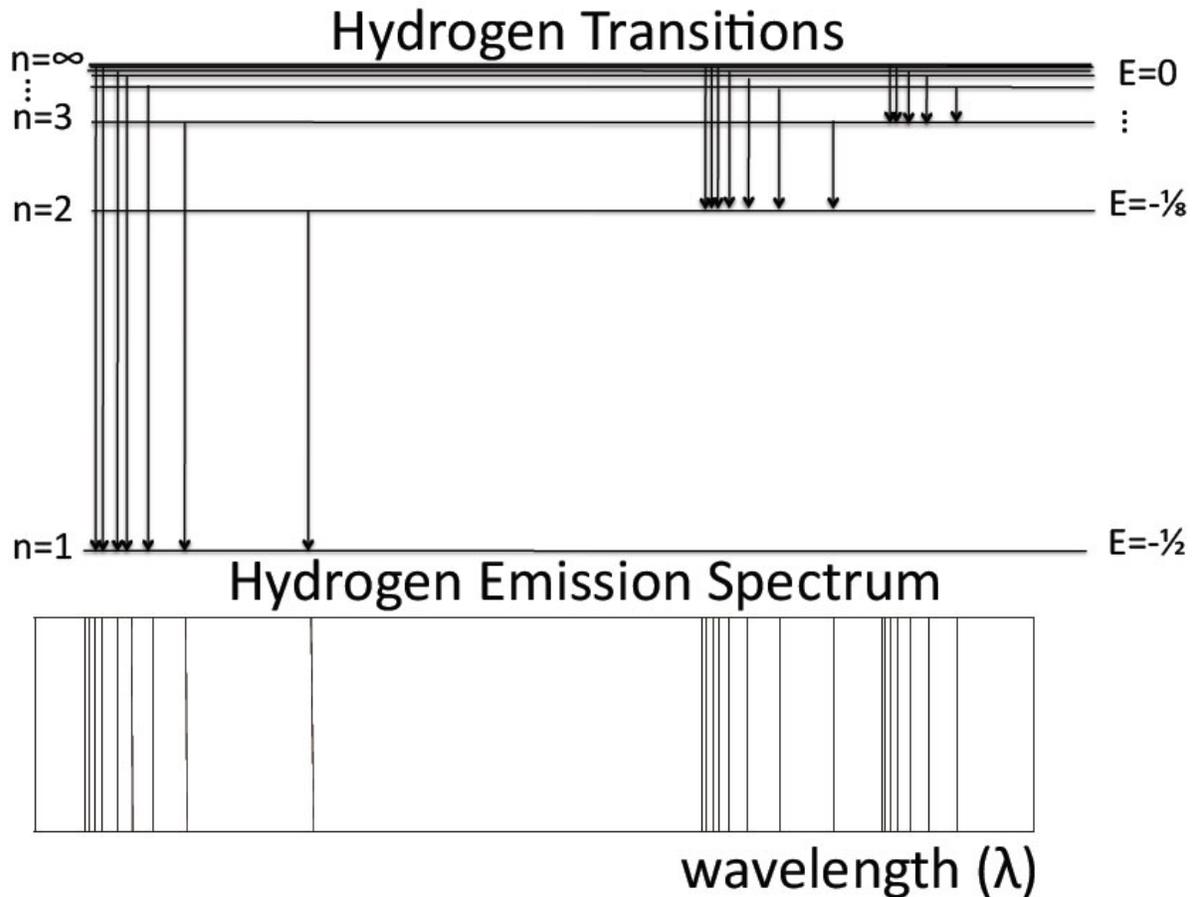
$$\psi_{2px} \equiv \frac{1}{\sqrt{2}} (\psi_{21-1} - \psi_{211}) = \frac{1}{4\sqrt{2\pi}} Z^{5/2} r e^{-Zr/2} \sin\theta \cos\phi$$

$$\psi_{2py} \equiv \frac{i}{\sqrt{2}} (\psi_{21-1} + \psi_{211}) = \frac{1}{4\sqrt{2\pi}} Z^{5/2} r e^{-Zr/2} \sin\theta \sin\phi$$

HYDROGEN ATOM SPECTROSCOPY

One of the most satisfying things about the hydrogen atom energies we obtained above is that they are essentially **exactly** right. We know this because we can obtain the spectrum of an isolated H atom in vacuum and compare the frequencies of the spectroscopic transitions to differences in the H atom energy levels above. Indeed, spectra of this type predate quantum mechanics, and provided immediate validation of the quantum viewpoint in the early days.

The H atom has some relatively complicated **selection rules**. For the 1D harmonic oscillator and the rigid rotor, we learned that spectroscopic transitions only occurred between adjacent energy levels. Thus, for the Harmonic oscillator we got only one transition frequency, while for the rigid rotor, we got a series of equally spaced transitions. For the Hydrogen atom, it turns out that one can have **transitions between any two values of n** , without restriction. This results in a fairly complicated spectrum that is illustrated below.



First, we recognize that the hydrogen atom energies get closer and closer to one another as n gets larger. In the spectrum, we see several distinct **series** depending on the final state ($n=1, n=2, n=3, \dots$). These series are each associated with a name (Lyman, Balmer, Paschen...) based on the person who first observed the relevant series. Within a given series, we see the same bunching of lines as the initial value of n gets larger. The precise positions of the experimental hydrogen spectral lines fit extremely well to $\Delta E = 1/n_1^2 - 1/n_2^2$.

Non-Lecture sketch of hydrogen atom selection rules. It is a good exercise to work out the selection rules for the hydrogen atom. If nothing else this gives us some practice working with the hydrogen atom wave functions and computing selection rules. But there also may be a bit of insight here for us. Recall that for **any** new problem, the first step in deriving selection rules is the same: we do integrals of the dipole moment operator between two different eigenstates of the Hamiltonian and try to decide when these integrals are zero (forbidden transitions) or nonzero (allowed transitions). Thus, we need two ingredients: 1)

the eigenstates and 2) the dipole moment operator. We've just worked out the eigenstates of the hydrogen atom:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$

Meanwhile, the dipole moment in hydrogen arises because there are two charges (the proton and the electron) of charge $|e|$ separated by a distance r . Thus, the dipole moment operator is just $\mu = er$. Thus, a given $n'l'm' \rightarrow nlm$ transition will be allowed if the integral

$$\int_0^\infty \int_0^{2\pi} \int_0^\pi \psi_{nlm}^*(r, \theta, \phi) e \vec{r} \psi_{n'l'm'}(r, \theta, \phi) \sin \theta d\theta d\phi r^2 dr$$

Is non-zero. Now, since the dipole moment is a vector, this is technically three different integrals (x, y and z components). It is tedious to do all three integrals. We can simplify the algebra a bit if we assume our light is polarized. Going back to our derivation of Fermi's golden rule, we find that the intensity is actually proportional to $\mathbf{k} \cdot \boldsymbol{\mu}$, where \mathbf{k} is the vector that determines the polarization of our light. So if we assume our light is z-polarized (for simplicity) then only the z-component of r is important above and the selection rules hinge on:

$$\begin{aligned} \int_0^\infty \int_0^{2\pi} \int_0^\pi \psi_{nlm}^*(r, \theta, \phi) e \vec{r} \psi_{n'l'm'}(r, \theta, \phi) \sin \theta d\theta d\phi r^2 dr = \\ e \int_0^\infty \int_0^{2\pi} \int_0^\pi R_{nl}(r) Y_l^{m*}(\theta, \phi) r \cos \theta R_{n'l'}(r) Y_{l'}^{m'}(\theta, \phi) \sin \theta d\theta d\phi r^2 dr \end{aligned}$$

where on the second line we have re-written z in spherical polar coordinates. Now, the integrand is the product of some terms that depend only on r and some terms that depend only on θ, ϕ . We can thus rearrange terms to write the integral as a product of an r -dependent bit and a θ, ϕ -dependent bit:

$$e \int_0^\infty \int_0^{2\pi} Y_l^{m*}(\theta, \phi) \cos \theta Y_{l'}^{m'}(\theta, \phi) \sin \theta d\theta d\phi \int_0^\pi R_{nl}(r) r R_{n'l'}(r) r^2 dr \neq 0$$

The integral will be zero if the θ, ϕ integral is zero or the r integral is zero. Thus, a transition is allowed only if *both* of these integrals are non-zero.

The θ, ϕ integral is the same one we encountered looking at selection rules for the rigid rotor. There, we found that this integral is only non zero if:

$$\Delta l = \pm 1 \quad \text{and} \quad \Delta m = 0 \quad (\text{z-polarized light})$$

Thus, the hydrogen atom inherits these same selection rules. They don't have any effect on the spectrum because the different l, m levels are all degenerate. But they are still there. We expect to see a $2p \rightarrow 1s$ transition, but not a $2s \rightarrow 1s$ transition, and this is precisely what is seen: as it turns out, $2s$ and $2p$ have ever

so slightly different energies due to relativistic effects (the so-called Lamb shift) and the $2p \rightarrow 1s$ transition is many orders of magnitude more intense than the $2s \rightarrow 1s$ transition. Also, note that if we had not assumed our light was z-polarized we would have found that x- or y-polarized light produces selection rules:

$$\Delta l = \pm 1 \quad \text{and} \quad \Delta m = \pm 1 \quad (\text{x or y-polarized light})$$

Thus, in the case where one does not have polarized light, one will also sometimes see the selection rules for hydrogen written as:

$$\Delta l = \pm 1 \quad \text{and} \quad \Delta m = \pm 1, 0 \quad (\text{unpolarized light})$$

One can rationalize these selection rules by realizing that a photon has one unit of angular momentum - thus in absorbing or emitting a photon the total angular momentum (l) must change by 1. Meanwhile, the z-projection of the photon angular momentum is governed by the polarization. Thus, if the photons are z-polarized, they don't change the z-projection of the system angular momentum, so $\Delta m = 0$. Meanwhile x- or y-polarized photons have ± 1 units of angular momentum along z, so they change m by ± 1 . We won't nitpick about which set of selection rules you assume in answering problems for 5.61 as long as you are consistent within the problem.

For the radial part, we need the integral

$$\int_0^{\pi} R_{nl}(r) r R_{n'l'}(r) r^2 dr$$

to be nonzero. This is a complicated integral and there are no symmetries (even/odd, etc.) or raising and lowering operators we can use to simplify it. Thus, we have no way to argue this integral should be zero. As a result, we will default to assuming it is always non-zero - which turns out to be the case. Thus, the selection rules for the hydrogen atom are:

$$\begin{array}{llll} \Delta n = \text{Anything} & \Delta l = \pm 1 & \text{and} & \Delta m = 0 & (\text{polarized light}) \\ \Delta n = \text{Anything} & \Delta l = \pm 1 & \text{and} & \Delta m = \pm 1, 0 & (\text{unpolarized light}) \end{array}$$

MAGNETIC FIELD EFFECTS

Now, even though there are many transitions that are easily visible in the H atom spectrum above, not every state is distinguishable, because each value of n actually corresponds to many, many states (due to degeneracy). It turns out this degeneracy can be largely lifted by the application of a magnetic field. Note that the electron has orbital angular momentum and is therefore a circulating charge. According to classical mechanics this leads to a magnetic moment (in atomic units)

$$\vec{\mu} = -\frac{e}{2m}\mathbf{L} = -\frac{1}{2}\mathbf{L}$$

If we apply a magnetic field \mathbf{B} applied along the z axis, we obtain an additional term in our Hamiltonian:

$$-\vec{\mu} \cdot \mathbf{B} = -\mu_z B_z = \frac{1}{2} B_z L_z$$

We can easily add this term to our hydrogen Hamiltonian operator:

$$H = H_{atom} + \frac{1}{2} B_z L_z$$

Now, as we showed above, the H atom wavefunctions are eigenfunctions of both \hat{H}_0 and \hat{L}_z operators (assuming we choose the nlm functions, as discussed above)

Thus, the original hydrogen orbitals are also eigenfunctions of new \hat{H} operator!

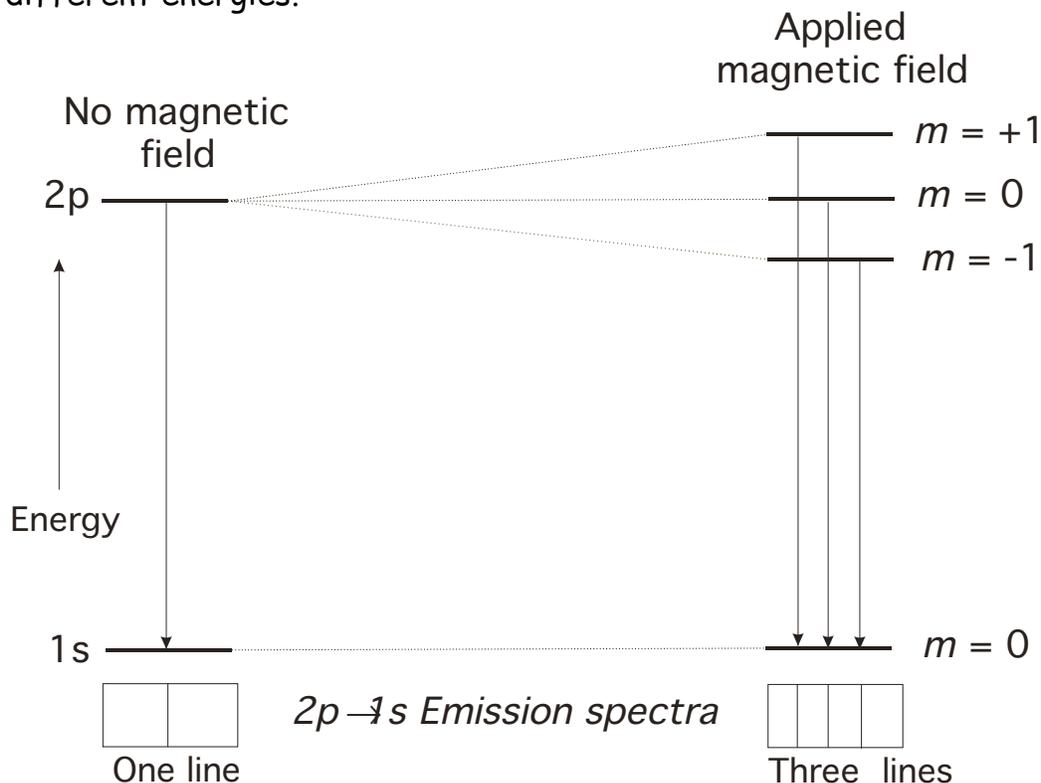
The only thing that has changed are the eigenvalues:

$$H\psi_{nlm} = \left(H_{atom} + \frac{1}{2} B_z L_z \right) \psi_{nlm} = \left(-\frac{Z^2}{2n^2} + \frac{1}{2} B_z m \right) \psi_{nlm}$$

Whereas the unperturbed hydrogen atom energies for different values of m were degenerate, the new Hamiltonian has energies that depend on m :

$$E_{nm} = \frac{-Z^2}{2n^2} + \frac{m}{2} B_z$$

Thus, for example, in a magnetic field the 2p orbitals with $m = -1, 0, +1$ will have different energies.



As illustrated in the figure, this will **split the degeneracy** in the spectrum. Whereas without a magnetic field all three p orbitals had the same transition energy to the ground state, in the presence of the field, we will see three different lines corresponding to the three different m values. Finally, we note that the splitting is proportional to the strength of the applied field, B_z , so that we can tune the splitting between these lines by changing the field strength.

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