

1. Concepts in quantum mechanics

This is mainly a review of ideas that you've already encountered in the 2nd year Quantum Mechanics course. These ideas are important for the rest of the course.

1.1. Eigenvalues and eigenfunctions

We wish to find the quantum state, ψ , of some system, let's say an atom or a molecule. The internal interactions (i.e. the electric and magnetic interactions between all the particles that make up the system) are described by a Hamiltonian \hat{H} , and the state of the system is given by the Schrödinger equation

$$i \hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi. \quad (1.1)$$

There will be a set of states, $\psi_n = \phi_n e^{-i \omega_n t}$, that are special. They are special because their entire time-dependence is contained in the factor $e^{-i \omega_n t}$. The functions ϕ_n do not depend on time and they are called the eigenfunctions of the system. We often refer to them as *stationary states* to emphasize the fact that there is no time-dependence other than the $e^{-i \omega_n t}$ factor - the probability distribution is unchanging in time. If we substitute one of our special states - $\psi_n = \phi_n e^{-i \omega_n t}$ - into the Schrödinger equation we obtain

$$i \hbar (-i \omega_n) \phi_n e^{-i \omega_n t} = \hat{H} \phi_n e^{-i \omega_n t}.$$

The $e^{-i \omega_n t}$ factor cancels out and we are left with an equation which is independent of time:

$$\hat{H} \phi_n = E_n \phi_n \quad (1.2)$$

or in Dirac notation

$$\hat{H} |n\rangle = E_n |n\rangle \quad (1.3)$$

This is the time-independent Schrödinger equation. We have introduced the quantity $E_n = \hbar \omega_n$, which is the *energy eigenvalue* corresponding to the *eigenfunction* ϕ_n . Our first aim is to find these eigenvalues and eigenfunctions.

In the case of the hydrogen atom, we can solve the time-independent Schrödinger equation directly to find the eigenvalues and eigenfunctions. This will be our starting point, and it forms the foundation for much of the rest of the course. For atoms or molecules with more than one electron, the Schrödinger equation cannot be solved exactly. Nevertheless, it is possible to calculate the energy levels to a high degree of precision using approximate methods.

1.2. Degeneracy, commuting operators and simultaneous eigenfunctions

When two or more eigenfunctions have the same eigenvalue, they are *degenerate*. We encounter degeneracy all of the time. Suppose we have two states - we'll label them $|1\rangle$ and $|2\rangle$ for now - that are both eigenstates of our Hamiltonian with the same energy: $\hat{H} |1\rangle = E_n |1\rangle$, $\hat{H} |2\rangle = E_n |2\rangle$. The labelling (1 and 2) is arbitrary and not helpful in telling us about the properties of the states. What's more, when $|1\rangle$ and $|2\rangle$ are both eigenstates with the same eigenvalue, so too is any linear combination of them: $\hat{H}(\alpha |1\rangle + \beta |2\rangle) = E_n(\alpha |1\rangle + \beta |2\rangle)$, for any arbitrary α and β . So we have an infinity of possible eigenfunctions, none apparently any more special than any other.

What we like to do when we have such a degeneracy is to find a physically meaningful operator which commutes with the Hamiltonian - let's just call it \hat{X} for now - $[\hat{X}, \hat{H}] = 0$. Because \hat{X} commutes with the Hamiltonian we can find states that are *simultaneous eigenfunctions* of both \hat{H} and \hat{X} . This procedure identifies special linear combinations of $|1\rangle$ and $|2\rangle$ - special because these particular combinations are eigenfunctions of \hat{X} as well as being eigenfunctions of \hat{H} . These states are obviously still degenerate with respect to \hat{H} , but are not necessarily degenerate with respect to \hat{X} . Let's assume that they're not for the moment. Then, we can label these states according to their eigenvalues of \hat{H} and \hat{X} - we'll call them $|n, a\rangle$ and $|n, b\rangle$. They have the following properties:

$$\hat{H} |n, a\rangle = E_n |n, a\rangle,$$

$$\hat{H} |n, b\rangle = E_n |n, b\rangle,$$

$$\hat{X} |n, a\rangle = a |n, a\rangle,$$

$$\hat{X} |n, b\rangle = b |n, b\rangle.$$

You see that we have distinguished the states according to their eigenvalues - the states are just lists that specify the eigenvalues of the two commuting operators (in an order that has to be understood). This is a much more helpful and physically meaningful way of labelling states - we instantly know the properties of the states we are talking about.

Now it could be that our two states are also degenerate with respect to \hat{X} (i.e. $a = b$). Then, we can't distinguish the states according to the eigenvalues of \hat{H} and \hat{X} alone. When this happens, we look for a third operator, \hat{Y} , that commutes with the other two, and we find the states

that are simultaneous eigenfunctions of \hat{H} , \hat{X} and \hat{Y} , labelling them (say) $|n, a, p\rangle$ and $|n, a, q\rangle$ where p and q are the eigenvalues of \hat{Y} . If it happens that $p = q$, then we continue with the procedure, finding a fourth commuting observable, and so on until we've found unique states. It's always possible to do this. Though we've illustrated the procedure using just two states, it clearly generalizes to an arbitrary number of degenerate states.

1.3. Constants of the motion

We often describe dynamical systems with the help of quantities that stay constant. If you throw a ball, for example, it travels in a parabola, which you can resolve into a horizontal and vertical motion. The horizontal momentum is a constant of the motion (if there's no resistance). If the ball is spinning, this angular momentum is also a constant of the motion. The same ideas are important in quantum mechanics. Here, we have operators corresponding to observables. An important result in quantum mechanics is that when an operator commutes with the Hamiltonian the corresponding observable does not change in time. This means that if we make a measurement of the observable, the possible outcomes and their probabilities do not change in time. So when $[\hat{X}, \hat{H}] = 0$ we say that \hat{X} is a constant of the motion. We also know that when $[\hat{X}, \hat{H}] = 0$ we can find states that are simultaneous eigenfunctions of both \hat{H} and \hat{X} , and that we label these states with their eigenvalues. All we are doing when we specify the eigenstate in this way is to list the quantum numbers that correspond to the constants of the motion, the properties that do not change in time. We often call these the "good quantum numbers".

To take an example, consider the energy eigenstates of the hydrogen atom, which we can write as $|n, l, s, m_l, m_s\rangle$. These quantum numbers label (respectively) the energy, the orbital angular momentum, the spin angular momentum, the projection of the orbital angular momentum onto the z-axis, and the projection of the spin angular momentum onto the z-axis. All these quantities are constants of the motion (because of the conservation of energy and the conservation of angular momentum).

1.4. Perturbation theory

The energy levels of atoms and molecules can be determined to very high precision, both experimentally and theoretically. Very precise theoretical calculations are possible even though there are no exact solutions for atoms with more than one electron. The solution proceeds through a series of approximations. An important approximation method is perturbation theory. We want to find the eigenvalues of the Hamiltonian \hat{H} but we cannot do it exactly. So we divide \hat{H} up into a part that we can solve, \hat{H}_0 , plus a much smaller additional part \hat{H}' : $\hat{H} = \hat{H}_0 + \hat{H}'$. We solve for \hat{H}_0 and find the eigenfunctions and eigenvalues

$$\hat{H}_0 \phi_n = E_n^0 \phi_n \quad (1.4)$$

or, in Dirac notation,

$$\hat{H}_0 |n\rangle = E_n^0 |n\rangle. \quad (1.5)$$

The perturbation \hat{H}' shifts the energy eigenvalues, so that the new eigenvalues are $E_n^1 = E_n^0 + \Delta E_n$. The result of first-order perturbation theory is that the energy shift is the expectation value of the perturbation, evaluated using the zeroth-order eigenstates:

$$\Delta E_n = \langle \hat{H}' \rangle = \langle n | \hat{H}' | n \rangle = \int \phi_n^* \hat{H}' \phi_n dV \quad (1.6)$$

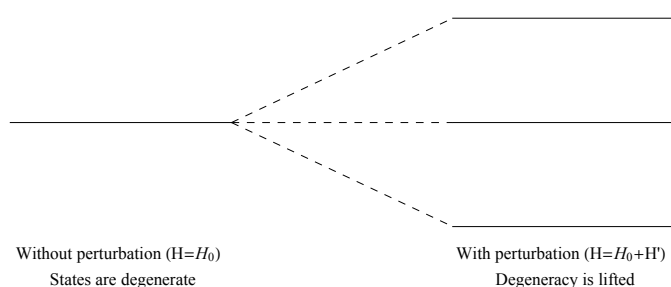
Here, as a reminder, I've written down the result using both Dirac notation and the explicit integral form. We will use Dirac notation much of the time, and you should be familiar with what it means. In the second form above ($\langle \hat{H}' \rangle$), the expectation value is simply indicated by the angle brackets, and we have to remember to use the zeroth-order eigenstates.

First-order perturbation theory also tells us that the perturbation changes the eigenstates. The corrected eigenstates are given by

$$|n'\rangle = |n\rangle + \sum_{k \neq n} \frac{\langle k | \hat{H}' | n \rangle}{E_n^0 - E_k^0} |k\rangle \quad \left[\text{Equivalently, } \phi_n' = \phi_n + \sum_{k \neq n} \frac{\int \phi_k^* \hat{H}' \phi_n dV}{E_n^0 - E_k^0} \phi_k \right]. \quad (1.7)$$

1.5. Perturbation theory with degeneracy

The above results apply to non-degenerate states. Often though, we are dealing with states that are degenerate, so we need to know how to handle this. States that have the same energy in the absence of the perturbation usually have slightly different energies in the presence of the perturbation. We say that the perturbation removes or 'lifts' the degeneracy. To give a simple example, think of a single electron in an atom with an orbital angular momentum $l = 1$. The projection of this angular momentum onto the z-axis can take three possible values with quantum numbers $m = -1, 0, +1$. If there are no external fields applied there is nothing special about the z-axis, and so the energy cannot depend on the value of m . We say that the state is 3-fold degenerate. Let's apply, as a small perturbation, a magnetic field in the z-direction. The electron in its orbit is a little current loop with an associated magnetic moment, the value of m tells us which way this magnetic moment is pointing, and the energy depends on the relative orientation of the magnetic moment and the applied magnetic field. So now the energy does depend on m - the perturbation has lifted the degeneracy.



When there's degeneracy, we can still use the perturbation results given above, but we have to be careful. You can immediately see this from equation (1.7): when there's degeneracy, $E_n^0 = E_k^0$ for some k - then there are terms in the sum where the denominator is zero, and the result seems to be infinite. The problem arises because, as discussed above, all linear combinations $\alpha |1\rangle + \beta |2\rangle$ are eigenfunctions when $|1\rangle$ and $|2\rangle$ are degenerate. Suppose we try to calculate the energy shift using equation (1.6) when two of the zeroth-order eigenfunctions are degenerate. We have a choice about which linear combination of these eigenfunctions to use (i.e. the values of α and β), and the result of the calculation depends on this choice (the choice of "basis" or "representation"). So how do we know which choice is the correct one?

Answer: choose the linear combinations such that $\langle k | \hat{H}' | n \rangle = 0$ for all cases where $E_n^0 = E_k^0$. When $\langle k | \hat{H}' | n \rangle = 0$ we say that the perturbation \hat{H}' does not connect states $|n\rangle$ and $|k\rangle$.

Provided we do this, we can just use standard perturbation theory (i.e. the above results) in the usual way. How do we find the linear combinations of degenerate states that satisfy the above requirement? The formal method is as follows: calculate all the matrix elements $\langle k | \hat{H}' | n \rangle$ in whatever representation you like, arrange these matrix elements in a matrix, then diagonalize it. The diagonalization procedure picks out the correct linear combinations and gives us the perturbed set of eigenstates and eigenvalues. We won't use this method. Instead, we'll use a method that is easier and brings a lot more physical insight. It is based on identifying the constants of the motion. Here are the steps:

1. Identify an observable, \hat{X} , that is a constant of the motion for both the unperturbed and perturbed system. This means that \hat{X} commutes both with \hat{H}_0 and $\hat{H}_0 + \hat{H}'$. There is usually a physical argument that helps to identify the things that remain constant - for example, if the perturbation doesn't apply any torque, the angular momentum is still a constant of the motion.
2. Find the set of states that are simultaneous eigenfunctions of \hat{H}_0 and \hat{X} . It can be shown that the perturbation does not connect these states, i.e. $\langle n, a | \hat{H}' | n, b \rangle = 0$ if a and b are two different eigenvalues of \hat{X} , both with the same zeroth-order energy E_n .
3. Using these states, apply the standard results of perturbation theory (as above).

Don't worry if this all seems a bit abstract at this point - the examples we'll meet along the way will make it clearer.

Proof

You don't need to know the proof of the above result, but here it is for interest. Since \hat{X} commutes with both \hat{H}_0 and $\hat{H}_0 + \hat{H}'$, it must also commute with \hat{H}' , i.e. $\hat{X} \hat{H}' = \hat{H}' \hat{X}$. So

$$\begin{aligned} \langle n, a | \hat{X} \hat{H}' | n, b \rangle - \langle n, a | \hat{H}' \hat{X} | n, b \rangle &= 0 \\ \therefore (a - b) \langle n, a | \hat{H}' | n, b \rangle &= 0. \end{aligned}$$

In the second step, we've used the fact that the states are eigenstates of \hat{X} with eigenvalues a and b , and also the fact that \hat{X} is a Hermitian operator (it corresponds to an observable). From the above, we immediately see that $\langle n, a | \hat{H}' | n, b \rangle = 0$ when $a \neq b$.

1.6. Energy level structure through a hierarchy of approximations

We find the energy level structure of complicated atoms and molecules by making a series of approximations. In fact, even for the simplest atom - hydrogen - we need to make this series of approximations to fully describe the energy level structure. A consideration of the hydrogen atom is a nice introduction to the various interactions and splittings that we'll encounter.

First we solve the Schrödinger equation for a single electron moving in the Coulomb potential of the nucleus. This gives us a set of energy levels which we call the gross energy level structure. The spacing between the low-lying energy levels is in the 1-10eV range. Expressed as a wavelength it is in the range from 100-1000nm. So transitions between these levels produce spectral lines in the uv, visible or near-ir.

This is not the end of the story for hydrogen, because there are interactions that we haven't yet included. Most important are effects due to relativity. The electron moves at about 1% the speed of light, so relativistic effects are small, but not completely negligible. Because the effects are small, we can treat them using perturbation theory. The electron is moving through the electric field of the nucleus, but motion through an electric field produces a magnetic field, and so the electron sees this motional magnetic field. The electron also possesses an intrinsic magnetic dipole moment - the magnetic moment associated with its intrinsic spin. There is an interaction between this magnetic moment and the motional magnetic field which causes the energy levels to shift and to split up into components, according to the value of the angular momentum. This splitting is called the fine structure. In hydrogen, the fine-structure splitting is about $10^{-4} - 10^{-5}$ eV. The effects of relativity are stronger in heavier atoms, and the fine-structure splitting in heavy atoms can be as large as 10^{-1} eV.

This is still not the end of the story, because we still have to consider interactions of the electron with properties of the nucleus other than its

charge. In particular, the nucleus has a spin, and a magnetic moment associated with this spin. There is an interaction between the nuclear and electron magnetic moments which splits the energy levels up even further. This is called the hyperfine structure, and it too can be calculated to high accuracy using perturbation theory. The splittings are typically about 10^{-5} eV.

1.7. Summary of the main points

- When the Hamiltonian is not changing in time, we can identify a set of special states, $\psi_n = \phi_n e^{-i\omega_n t}$, where the ϕ_n are time-independent. They are the eigenfunctions and they satisfy the time-independent Schrödinger equation.
- Energy eigenstates are often degenerate. We use additional quantum numbers (e.g. angular momentum quantum numbers) to distinguish degenerate states. These additional quantum numbers identify constants of the motion for the system.
- For a one-electron atom, we can solve the Schrödinger equation to find the eigenvalues and eigenfunctions.
- For many electron atoms, we use approximate methods (in this course: first-order perturbation theory).
- We find all the details of the energy-level structure through a hierarchy of approximations.

1.8. To do

- Do question 1 from problem set 1. If necessary, use the notes from the 2nd year Quantum Mechanics lecture course to help you, or a book on quantum mechanics.
- Make sure you are comfortable with Dirac notation, and the concepts of degeneracy, commuting operators and simultaneous eigenfunctions. Useful reading are the notes from the 2nd year quantum mechanics course.

2. Angular momentum

2.1. Properties of angular momentum

You have already met the two types of angular momentum - orbital angular momentum and spin angular momentum. The eigenstates of orbital angular momentum can be represented by spherical harmonics. The spin eigenstates cannot be represented using spatial functions - spin is just different. Nevertheless, both kinds of angular momentum can be represented and handled using exactly the same mathematics - this is the quantum mechanics of angular momentum in general.

An angular momentum operator $\hbar \hat{\mathbf{J}}$ is a vector operator that satisfies the following commutation relations:

$$[\hat{J}_x, \hat{J}_y] = i \hat{J}_z, \quad [\hat{J}_y, \hat{J}_z] = i \hat{J}_x, \quad [\hat{J}_z, \hat{J}_x] = i \hat{J}_y. \quad (2.1)$$

Since the components of $\hat{\mathbf{J}}$ do not commute, we cannot have states that are simultaneous eigenstates of more than one component. However, each of the components commutes with the operator $\hat{\mathbf{J}}^2$:

$$[\hat{J}_x, \hat{\mathbf{J}}^2] = [\hat{J}_y, \hat{\mathbf{J}}^2] = [\hat{J}_z, \hat{\mathbf{J}}^2] = 0. \quad (2.2)$$

This means that we can form states that are simultaneous eigenstates of $\hat{\mathbf{J}}^2$ and one of the components of $\hat{\mathbf{J}}$, chosen by convention to be \hat{J}_z . These correspond to quantum mechanical constants of the motion, which we denote using the quantum numbers j and m . We label the eigenstates using these quantum numbers, so they are written as $|j, m\rangle$ and have the following properties:

$$\hat{\mathbf{J}}^2 |j, m\rangle = j(j+1) |j, m\rangle \quad (2.3)$$

$$\hat{J}_z |j, m\rangle = m |j, m\rangle. \quad (2.4)$$

The quantum number j is called the *angular momentum quantum number*, but you should be careful to remember that j is not itself the eigenvalue - the important operator is $\hat{\mathbf{J}}^2$ whose eigenvalue is $j(j+1)$. The quantum number m is often called the *magnetic quantum number* because of the role it plays when a magnetic field is applied to an atom (see later). It can only have the values

$$m = -j, -j+1, \dots, j-1, j. \quad (2.5)$$

So for any value of j there are always $2j+1$ possible values of m . For example, when $j = 1/2$, there are only two possible values of m , namely $-1/2$ and $1/2$. When $j = 1$, m can have three possible values $m = -1, 0, 1$.

Electrons have spin-1/2. Electrons in atoms can have orbital angular momentum - integer values from zero upwards. Photons have spin-1.

We often make use of the angular momentum raising and lowering operators, defined by

$$\hat{J}_{\pm} = \hat{J}_x \pm i \hat{J}_y \quad (2.6)$$

Recall (from your quantum mechanics lectures) that these operators increase/decrease the value of m by one unit without changing the value of j :

$$\hat{J}_+ |j, m\rangle = \sqrt{(j-m)(j+m+1)} |j, m+1\rangle, \quad (2.7)$$

$$\hat{J}_- |j, m\rangle = \sqrt{(j+m)(j-m+1)} |j, m-1\rangle. \quad (2.8)$$

Notation

Note that I have defined the angular momentum operator as $\hbar \hat{\mathbf{J}}$. This means that $\hat{\mathbf{J}}$ is dimensionless, and has dimensionless eigenvalues. These multiply \hbar to give the actual angular momentum in SI units. Be careful about this when reading the text books - some authors use this same notation, but some have $\hat{\mathbf{J}}$ itself be the angular momentum operator. This can cause confusion over the \hbar 's, so be aware of that.

2.2. The vector model for angular momentum

As emphasized above, the components of an angular momentum operator do not commute with one another. We can still calculate the expectation values of each component however. It should be obvious that

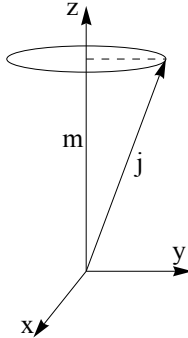
$$\langle j, m | \hat{J}_z | j, m \rangle = m.$$

The easiest way to calculate the expectation values of \hat{J}_x and \hat{J}_y is to use the raising and lowering operators, equation (2.6). From these, we see that $\hat{J}_x = \frac{1}{2}(\hat{J}_+ + \hat{J}_-)$ and $\hat{J}_y = \frac{1}{2i}(\hat{J}_+ - \hat{J}_-)$. Since \hat{J}_{\pm} change the value of m , and states of different m are orthogonal, we immediately arrive at the result

$$\langle j, m | \hat{J}_x | j, m \rangle = \langle j, m | \hat{J}_y | j, m \rangle = 0. \quad (2.9)$$

These expectation values motivate a semiclassical model of angular momentum known as the *vector model*. The model is drawn below. We picture the angular momentum as a vector precessing around the z-axis, in much the same way as the spin of a spinning top or gyroscope precesses about a vertical axis. The vector itself is labelled by j . This is just a label so that, when we are dealing with more than one angular

momentum, we know which one we are talking about - we have to always remember that the expectation value of \hat{J}^2 is *not* j^2 but $j(j+1)$. Because the precession is a precession *about the z-axis* the z-component of the angular momentum has a constant value - we say that it is a *constant of the motion* and we label it as m to remind ourselves that the expectation value of \hat{J}_z is m . The x and y components of the angular momentum are not constants - they change in time as the angular momentum precesses. This expresses the quantum mechanical idea that, once the z -component is fixed, the x and y components are uncertain. The time-average of the x -component is zero, as is the time-average of the y -component. So we see that the classical time-averages behave just like the quantum mechanical expectation values.



It is important to appreciate that this vector model is a picture that helps us to understand angular momentum in quantum mechanics. It is a very helpful picture which provides a lot of insight, especially when we have more than one angular momentum to consider. It can also be used as an aid to calculations in quantum mechanics, but this has to be done carefully, since its applicability is limited.

2.3. Adding angular momenta

We need to know the proper way to add up angular momenta. We already need this for a one-electron atom because the electron can have both orbital and spin angular momentum, and we might need to add these up to make a total angular momentum. For many-electron atoms we'll need to add up the angular momenta of the individual electrons to make a total.

Suppose we have two angular momentum operators (again, spin or orbital, it doesn't matter), \hat{J}_1 and \hat{J}_2 . We can add them up to give the total angular momentum

$$\hat{J} = \hat{J}_1 + \hat{J}_2. \quad (2.10)$$

Since \hat{J}_1 and \hat{J}_2 are angular momentum operators, so too is \hat{J} . We can prove this explicitly by showing that \hat{J} satisfies the commutation relations for angular momentum. For example:

$$[\hat{J}_x, \hat{J}_y] = [\hat{J}_{1x} + \hat{J}_{2x}, \hat{J}_{1y} + \hat{J}_{2y}] = [\hat{J}_{1x}, \hat{J}_{1y}] + [\hat{J}_{2x}, \hat{J}_{2y}] + [\hat{J}_{1x}, \hat{J}_{2y}] + [\hat{J}_{2x}, \hat{J}_{1y}] = i\hat{J}_{1z} + i\hat{J}_{2z} + 0 + 0 = i\hat{J}_z.$$

Here, we have used the commutation relations for \hat{J}_1 and \hat{J}_2 and we've used the fact that all components of \hat{J}_1 commute with all those of \hat{J}_2 since these are two different angular momenta.

\hat{J}^2 has eigenvalues $j(j+1)$ where the possible values of j are

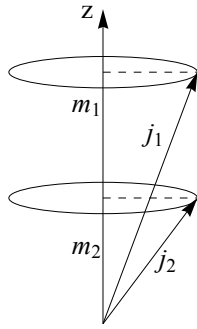
$$j = |j_1 - j_2|, |j_1 - j_2| + 1, \dots, j_1 + j_2 - 1, j_1 + j_2. \quad (2.11)$$

This makes sense when you think about adding together the two vectors. The largest total angular momentum you can make is when the two are lined up (going around in the same direction) and then you just get the sum of the two. The smallest you can make is when the two are going around in opposite directions - then you get the larger minus the smaller. For example, if we add together $j_1 = 2$ with $j_1 = 1/2$ the possible values of j are $3/2$ and $5/2$. Or if we add $j_1 = 2$ with $j_1 = 1$, the possible values of j are $1, 2$ and 3 .

How shall we write down the total state of the system? Let's consider an important example, namely that of adding two spin-1/2 angular momenta, $j_1 = 1/2$, $j_2 = 1/2$. Since each spin-1/2 can have two possible values of m ($\pm 1/2$), there must be 4 possible states of the combined system. We could write these out explicitly using the notation $|j_1, m_1; j_2, m_2\rangle$. In fact, since we know that j_1 and j_2 are both $1/2$, we can use the simpler shorthand $|m_1; m_2\rangle$. Then, the four possible states are $|1/2; 1/2\rangle$, $|1/2; -1/2\rangle$, $|-1/2; 1/2\rangle$, $|-1/2; -1/2\rangle$. An even nicer shorthand than this is to use an up arrow for $1/2$ and a down arrow for $-1/2$, always with m_1 written first and m_2 second. This nicely represents whether each spin is up or down relative to the z -axis. In this notation, the states are

$$|m_1 m_2\rangle = |\uparrow \uparrow\rangle, |\uparrow \downarrow\rangle, |\downarrow \uparrow\rangle, |\downarrow \downarrow\rangle. \quad (2.12)$$

In the vector model, we just draw two separate vectors for \hat{J}_1 and \hat{J}_2 , like the picture below. Here, m_1 and m_2 are the projections of j_1 and j_2 onto the z -axis. j_1 , j_2 , m_1 and m_2 are all constants of the motion. This is a picture where there is no coupling between the two angular momenta - each angular momentum does its own thing and we treat the two completely independently. You can think of this like two independent gyroscopes.

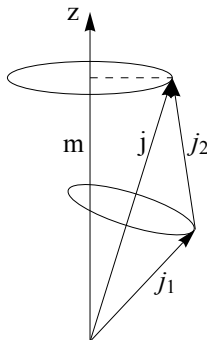


There is a second way of writing down these same states. We specify them by the quantum numbers j_1, j_2, j, m , using the notation $|j_1; j_2; j, m\rangle$. For the case where j_1 and j_2 are both $1/2$, we can drop j_1 and j_2 from the notation to keep it a bit simpler - so we just specify $|j, m\rangle$. Now, when $j_1 = j_2 = 1/2$, the possible values of j are 0 and 1. So the allowed states are

$$|j, m\rangle = |1, 1\rangle, |1, 0\rangle, |1, -1\rangle, |0, 0\rangle. \quad (2.13)$$

Notice that, whichever way we choose to write them, we always get 4 states. That's good - the number of states is a physical thing and shouldn't depend on how they are represented. We can choose to write the states in either of the two representations, but it is often more convenient to use a representation that best matches the physical situation - i.e. whether the angular momenta are independent or are coupled together.

There is often some interaction that couples together two angular momenta. We will encounter several interactions of this kind, e.g. the spin-orbit interaction which introduces a coupling between the orbital angular momentum of the electron and its spin. Before introducing this interaction the two angular momenta are independent, but afterwards they are not independent - they are coupled together. You can think of the two gyroscopes again, but now there is an interaction between them. For example, the gyroscopes might be connected by a weak spring. Because of the interaction, each gyroscope exerts a torque on the other, and each starts precessing. In this complicated situation, there is one thing that we can be sure of - there is no external torque acting on the system as a whole, and so the total angular momentum of the whole system is a constant. What's more, the precession of the individual angular momenta is a precession about their resultant (the total angular momentum). In the vector model, the coupled angular momenta are represented like this:



In this picture, j_1 and j_2 precess together about their resultant j . j_1 and j_2 are constants of the motion, but their projections onto the z-axis are not constants. The picture makes this clear - the projection of j_1 onto the z-axis changes as j_1 precesses around j (and the same is true for j_2). j is a constant of the motion, and so too is its projection onto the z-axis, which is m . If we make the interaction that is coupling j_1 and j_2 stronger, the precession about the resultant is faster. The rate of precession is proportional to the strength of the interaction.

2.4. Relation of coupled and uncoupled representations

Now we come to an important point. There has to be a way of linking the two representations, i.e. of writing the state in one representation in terms of the states in the other representation. We often do this in quantum mechanics - writing down a quantum state as a linear superposition of some basis states. For our example of two spin- $1/2$ particles, the relationship is:

$$|1, 1\rangle = |\uparrow\uparrow\rangle, \quad (2.14)$$

$$|1, 0\rangle = \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}, \quad (2.15)$$

$$|1, -1\rangle = |\downarrow\downarrow\rangle, \quad (2.16)$$

$$|0, 0\rangle = \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}. \quad (2.17)$$

Proof

It should be obvious that the only way to make the state $|1, 1\rangle$ (total angular momentum 1 and projection 1) is to have the two spin- $1/2$'s both pointing upwards. Formally this is obtained using the relation $\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$ (which follows from equation (2.10)), which tells us that

$m = m_1 + m_2$. Similarly, to get the state $|1, -1\rangle$ we must have the two spin-1/2's pointing downwards. This explains (2.14) and (2.16). Now apply \hat{J}_- , the lowering operator, to equation (2.14), and we immediately obtain result (2.15). A second application of \hat{J}_- will give us (2.16), though we already had this. Finally, we find the expression for the state $|0, 0\rangle$ by requiring it to be orthogonal to all the others.

Generalization

When we add together two angular momenta, we can always represent the state in two different, equally valid ways.

Option 1. Because \hat{J}_1 and \hat{J}_2 are different angular momenta, all components of \hat{J}_1 commute with all components of \hat{J}_2 . So we can write the state as a simultaneous eigenstate of \hat{J}_1^2 , \hat{J}_2^2 , \hat{J}_{1z} and \hat{J}_{2z} , with eigenvalues $j_1(j_1 + 1)$, $j_2(j_2 + 1)$, m_1 and m_2 . The state is written $|j_1, m_1; j_2, m_2\rangle$. This is called the uncoupled representation.

Option 2. Since \hat{J}_1^2 , \hat{J}_2^2 , \hat{J}^2 and \hat{J}_z all commute we can write the state in terms of their eigenvalues, $j_1(j_1 + 1)$, $j_2(j_2 + 1)$, $j(j + 1)$ and m . The state is written $|j_1, j_2, j, m\rangle$. This is called the coupled representation.

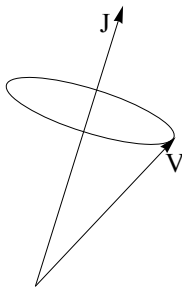
It is always possible to transform from one representation to another. The coefficients that define this transformation are found using the raising and lowering operators. You don't need to know how to do this, but it is helpful to know that it can be done.

2.5. The projection theorem

Suppose we have some system with total angular momentum operator \hat{J} , such that $\hat{J}^2 |j, m\rangle = j(j + 1) |j, m\rangle$. Then it is possible to show that for any vector operator \hat{V} ,

$$\langle j, m | \hat{V}_k | j, m \rangle = \frac{\langle j, m | \hat{V} \cdot \hat{J} | j, m \rangle}{j(j + 1)} \langle j, m | \hat{J}_k | j, m \rangle. \quad (2.18)$$

Here, \hat{V}_k is any of the three components of the vector. This important result is called the *projection theorem*. It tells us that the expectation value of a component of \hat{V} is proportional to the expectation value of the same component of the total angular momentum \hat{J} . The formal proof is beyond the scope of the course, but we can use the vector model to see how it comes about, as shown below. Since the system has angular momentum, any vector in the system must be precessing about the direction of that angular momentum, i.e. V is precessing about J . Let j be a unit vector in the direction of J , i.e. $J = Jj$. The component of V perpendicular to j time-averages to zero, so the time-average is in the direction of j . The magnitude of this parallel component is the projection of V onto j , i.e. $V \cdot j$. So we see that the time average is $\langle V \rangle = (V \cdot j) j = (V \cdot J) J / J^2$. Translating time-averages into quantum-mechanical expectation values, we get result (2.18).



2.6. Summary of the main points

- There are two types of angular momentum - orbital and spin. Mathematically, they can be handled in exactly the same way.
- Every component of \hat{J} commutes with \hat{J}^2 .
- The components of \hat{J} do not commute with one another.
- $|j, m\rangle$ is a simultaneous eigenfunction of \hat{J}^2 [with eigenvalue $j(j + 1)$] and of \hat{J}_z [with eigenvalue m]. It is not an eigenstate of \hat{J}_x or \hat{J}_y .
- For a given j there are $2j + 1$ allowed values for m : They are $m = -j, -j + 1, \dots, j - 1, j$.
- Angular momenta can be added together: $\hat{J} = \hat{J}_1 + \hat{J}_2$. Then, we have two possible ways of representing the total state of the system. We can use the “uncoupled representation” $|j_1, m_1; j_2, m_2\rangle$, or we can use the “coupled representation” $|j_1, j_2, j, m\rangle$. In the coupled representation $\hat{J}^2 |j_1, j_2, j, m\rangle = j(j + 1) |j_1, j_2, j, m\rangle$ where j can take values between $j_1 + j_2$ and $|j_1 - j_2|$.
- When we add together two spin-1/2's there are 4 possible states - three with total angular momentum $j = 1$ ($m = -1, 0, +1$), and one with total angular momentum $j = 0$.
- We often use the vector model as a picture of how angular momenta are coupled together, and to help us calculate expectation values.

2.7. To do

- Revise the material in this handout. Useful reading: lecture notes from 2nd year Quantum Mechanics, chapter 4 of Rae (‘Quantum Mechanics’), section 1.5 of Softley, or appendix C of Woodgate.
- Do questions 2 and 3 from problem set 1.

3. Gross structure of one electron atoms

This is revision of material you have already covered in the 2nd year Atomic, Nuclear & Particle course, so we will just bring out the important points here.

3.1. Bohr model and orders of magnitude

You will have encountered the Bohr model of the hydrogen atom before. Although the Bohr model is an ad hoc model, it gives many of the correct results for the hydrogen atom (as we'll see later), and it is a useful starting point for understanding the orders of magnitudes of various atomic properties. In the Bohr model, an electron of mass m_e and charge $-e$ moves in a circular orbit around a much heavier nucleus of charge $+e$, and the angular momentum is quantized in integer units of \hbar . To keep the electron in orbit with radius r and speed v , the centrifugal and electrostatic forces must balance:

$$\frac{m_e v^2}{r} = \frac{e^2}{4 \pi \epsilon_0 r^2}. \quad (3.1)$$

The quantization of angular momentum (L) is expressed simply as

$$L = m_e v r = n \hbar, \quad (3.2)$$

where n is an integer.

The size of an atom and the Bohr radius

From these two equations we find the orbital radius as:

$$r = n^2 \frac{4 \pi \epsilon_0 \hbar^2}{m_e e^2} = n^2 a_0, \quad (3.3)$$

where we've defined the quantity

$$a_0 = \frac{4 \pi \epsilon_0 \hbar^2}{m_e e^2}, \quad (3.4)$$

which is known as the *Bohr radius*. It depends only on fundamental constants and has the value $5.292 \times 10^{-11} \text{m}$. This is (roughly speaking) the size of hydrogen in its ground state. For many-electron atoms the greater Coulomb attraction to the nucleus is largely offset by the electron-electron repulsion, and so other atoms are roughly the same size as this.

The speed of the electron and the fine-structure constant

From the same equations, we get the speed of the electron as

$$v = \frac{1}{n} \frac{e^2}{4 \pi \epsilon_0 \hbar c} c = \frac{1}{n} \alpha c, \quad (3.5)$$

where we've defined the dimensionless quantity

$$\alpha = \frac{e^2}{4 \pi \epsilon_0 \hbar c}, \quad (3.6)$$

which is known as the *fine structure constant*. It is a fundamental constant and has the approximate value $1/137$. We see that the speed of the electron in the ground state is $\alpha c \approx c/137$. Because the speed is a small fraction of the speed of light, we can use non-relativistic quantum mechanics to a fairly good approximation. However, to understand the finer details of atomic structure we will need to consider relativistic effects.

The energy levels and the Rydberg constant

Adding together the kinetic energy, $\frac{1}{2} m_e v^2$, and the potential energy, $e^2/(4 \pi \epsilon_0 r)$, and using the above formulae for v and r , we get the total energy to be

$$E_n = -\frac{1}{2 n^2} \alpha^2 m_e c^2. \quad (3.7)$$

The factor $1/2 \alpha^2 m_e c^2$ is known as the Rydberg energy and, in electron-volts, has the value 13.6eV. After dividing the Rydberg energy by $\hbar c$, we get the *Rydberg constant*, which is usually given the symbol R_∞ . It is the most precisely measured quantity in physics. Also note that the kinetic energy T , and the potential energy V are related by $T = -1/2 V$, which is an example of the *virial theorem*.

The magnetic moment and the Bohr magneton

The orbiting electron is a current loop, and associated with this current loop is a magnetic dipole moment. Recall from electromagnetism that the magnetic moment of a current loop where the current I encloses an area A is simply $\mu = I A$. The current is $I = \frac{dq}{dt}$. In the ground state, the time taken for the electron to complete an orbit is $t = 2 \pi a_0/v$, so the current in the loop is $I = e \alpha c / (2 \pi a_0)$. The area of the current loop is πa_0^2 , and so the magnetic moment is

$$\mu = \frac{1}{2} e a_0 \alpha c = \frac{e \hbar}{2 m_e} = \mu_B, \quad (3.8)$$

where we've defined

$$\mu_B = \frac{e \hbar}{2 m_e}, \quad (3.9)$$

which is known as the *Bohr magneton*. It sets the scale for atomic magnetic moments and has the value $9.274 \times 10^{-24} \text{ J T}^{-1}$.

3.2. Schrödinger equation for a one-electron atom

Our task is to calculate the energy levels and wavefunctions of a single electron of charge $-e$ and mass m_e moving in the field of a nucleus of charge Ze and mass M . We will usually be talking about the hydrogen atom, in which case the nucleus is a proton and $Z = 1$, but our treatment will also apply to other one-electron systems such as the He^+ ion ($Z = 2$) or more exotic one-electron atoms (see later). For now, we approximate the nucleus as a point particle.

The time-independent Schrödinger equation for the relative motion is

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) \psi = E \psi, \quad (3.10)$$

where the potential $V(r)$ is the Coulomb potential,

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}, \quad (3.11)$$

and m is the reduced mass of the electron-nucleus system

$$m = \frac{m_e M}{m_e + M}. \quad (3.12)$$

The electron is much lighter than the nucleus, and so it does most of the moving. But we are interested in obtaining precise results and so we have *not* assumed that the nucleus is stationary. Our equation describes the *relative motion* of the two particles, which is why it is the reduced mass that appears and not the electron mass. Since $M \gg m_e$ the reduced mass is close to the mass of an electron, $m \approx m_e$.

3.3. Angular part

We will solve equation (3.10) in spherical polar coordinates, (r, θ, ϕ) , but the potential depends only on the distance between the electron and the nucleus, i.e. only on the coordinate r and not on the angles θ and ϕ . We call it a *central potential*. This is a crucial point. We can discover a great deal about the atom without needing to know the actual form of the potential (equation (3.11)) - we just have to know that it depends only on r . This idea becomes particularly important when, later, we come to many-electron atoms. In spherical polar coordinates equation (3.10) is

$$\left(-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hbar^2 \hat{L}^2}{2m r^2} + V(r) \right) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi), \quad (3.13)$$

where $\hbar \mathbf{L}$ is the angular momentum operator, defined by $\hbar \mathbf{L} = \mathbf{r} \times \mathbf{p}$. Note carefully the way we have defined \mathbf{L} - it is a dimensionless operator equal to the angular momentum operator divided by \hbar (some text books use \mathbf{L} itself as the angular momentum operator, so be aware of this possible difference). In spherical polar coordinates the squared angular momentum operator is

$$\hbar^2 \hat{L}^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right), \quad (3.14)$$

and the z-component of the angular momentum operator is

$$\hbar \hat{L}_z = -i \hbar \frac{\partial}{\partial \phi}. \quad (3.15)$$

Because $V(r)$ depends only on r , the wavefunction separates into a product of a radial part and an angular part and there are a complete set of solutions of the form

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi). \quad (3.16)$$

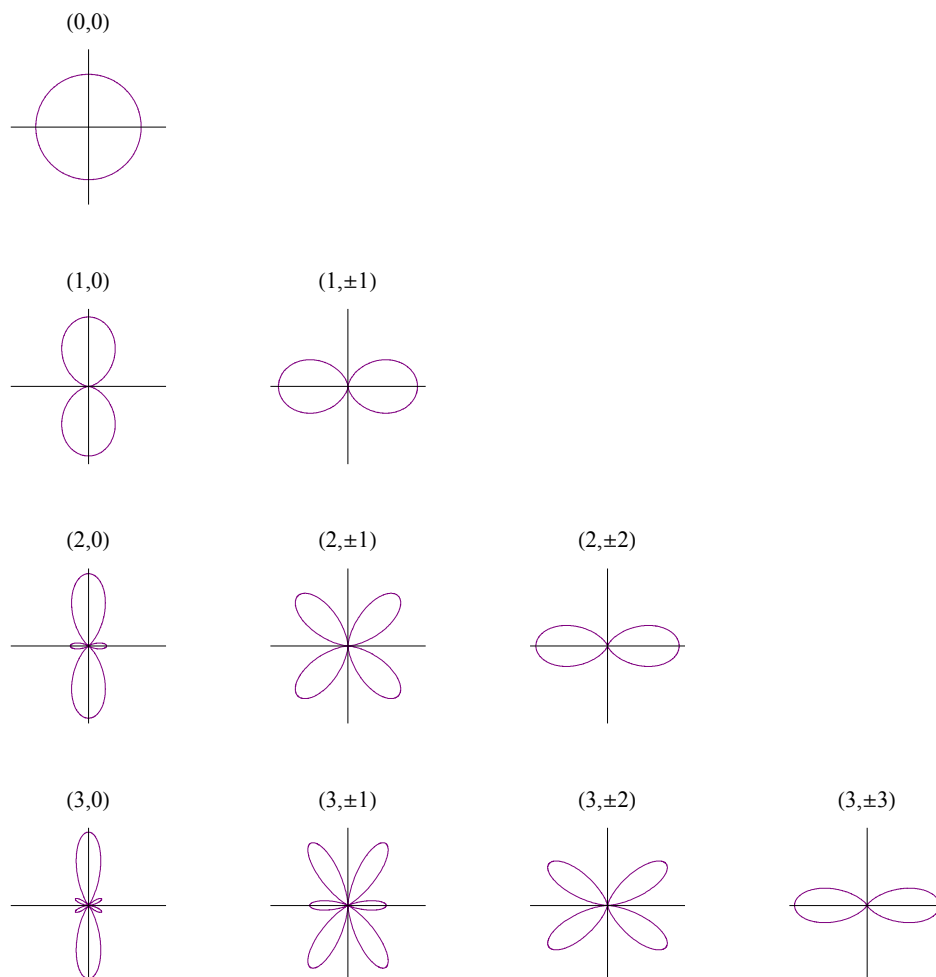
The angular part, $Y(\theta, \phi)$, should be familiar to you. It is an eigenfunction of the operator \hat{L}^2 with eigenvalues $l(l+1)$ and l having integer values. It is also an eigenfunction of \hat{L}_z with eigenvalues m , an integer in the range $-l \leq m \leq l$. The l and m appear as formal constants in the separation of variables and the constraints on their values are a consequence of requiring the wavefunction to be single-valued and finite everywhere. More important is their physical meaning: l is the quantum number that specifies the value of the angular momentum, while m is the quantum number that specifies the projection of the angular momentum onto the z-axis. Note that we have a set of functions $Y(\theta, \phi)$, one function for each eigenstate specified by the quantum numbers l and m , and so we label them using subscripts - $Y_{l,m}(\theta, \phi)$. To

summarize

$$\hat{L}^2 Y_{l,m}(\theta, \phi) = l(l+1) Y_{l,m}(\theta, \phi), \quad (3.17)$$

$$\hat{L}_z Y_{l,m}(\theta, \phi) = m Y_{l,m}(\theta, \phi). \quad (3.18)$$

You can look up the mathematical forms for the $Y_{l,m}$ functions in a text book. The ϕ dependence is simply $e^{im\phi}$, while the θ dependence is given by the associated Legendre polynomials, $P_{l,m}(\theta)$. Below are polar plots showing the angular probability distributions $|Y_{l,m}(\theta, \phi)|^2$ for a range of values of (l, m) . Note that (because we have taken the modulus squared) these distributions do not depend on ϕ . In the polar plots, θ is measured from the vertical axis and the distance from the origin of a point on the curve is proportional to the value of the function in that direction.



For any given value of l there are $2l+1$ possible values of m . When we sum the $|Y_{l,m}(\theta, \phi)|^2$ over all the values of m for a given l , the result is independent of θ and ϕ , and so is spherically symmetric:

$$\sum_{m=-l}^l |Y_{l,m}(\theta, \phi)|^2 \text{ is independent of } \theta \text{ and } \phi.$$

Notation

We use a letter to indicate the electron's state of orbital angular momentum. For historical reasons the letters are

$l=0$	$l=1$	$l=2$	$l=3$	$l=4$	$l=5$
s	p	d	f	g	h

with higher values of l then following alphabetically.

3.4. Radial part

The radial part of the problem is found by solving the radial equation which is

$$\left(-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hbar^2 l(l+1)}{2m r^2} + V(r) \right) R(r) = E R(r). \quad (3.19)$$

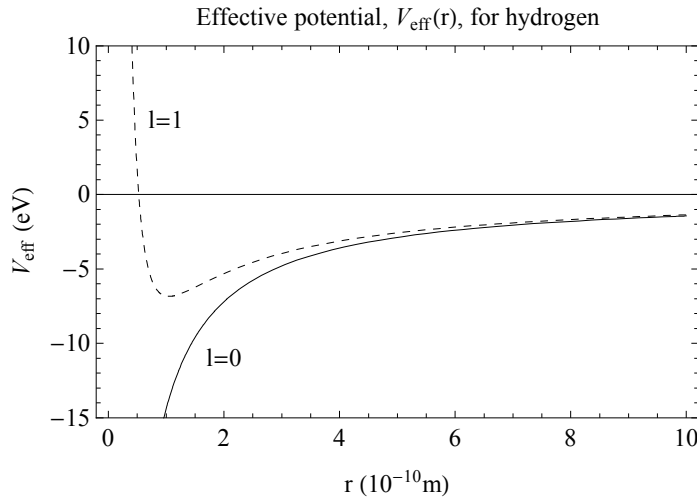
It is usual to cast this in a slightly simpler form using the substitution $P(r) = r R(r)$, which gives us

$$-\frac{\hbar^2}{2m} \frac{d^2 P}{dr^2} + \left(\frac{\hbar^2 l(l+1)}{2m r^2} + V(r) \right) P = E P. \quad (3.20)$$

The formal solution can be found in most quantum mechanics text books, but we can learn a lot just by looking at the above equation. The first term on the left hand side is the radial kinetic energy. We can consider the bracketed term as an effective potential for the motion:

$$V_{\text{eff}}(r) = \frac{\hbar^2 l(l+1)}{2m r^2} + V(r). \quad (3.21)$$

In this effective potential, the first term is a centrifugal barrier proportional to $l(l+1)$ while the second term is the Coulomb potential, equation (3.11). The effective potential for hydrogen is plotted below for both $l = 0$ (solid line) and $l = 1$ (dashed line). The two terms in the effective potential have opposite signs - the Coulomb potential pulls the electron towards the nucleus while the centrifugal barrier keeps the electron away from the nucleus. At small enough distances, the centrifugal barrier (scaling as $1/r^2$) overwhelms the Coulomb attraction (scaling only as $1/r$) and the electron cannot reach the nucleus. States with zero angular momentum, $l = 0$, are the exception to this - for them the centrifugal barrier vanishes and they can reach the nucleus. So for states with $l \neq 0$, we can expect the wavefunction to go to zero at the origin, whereas for states with $l = 0$ we expect the wavefunction to have a maximum at the origin.



At large distances, as $r \rightarrow \infty$, the potential energy terms fall off and the radial kinetic energy dominates. For the bound states that we are interested in (negative values of E) the wavefunctions must then fall off exponentially as $\exp(-\kappa r)$, where $\kappa^2 = -2mE/\hbar^2$.

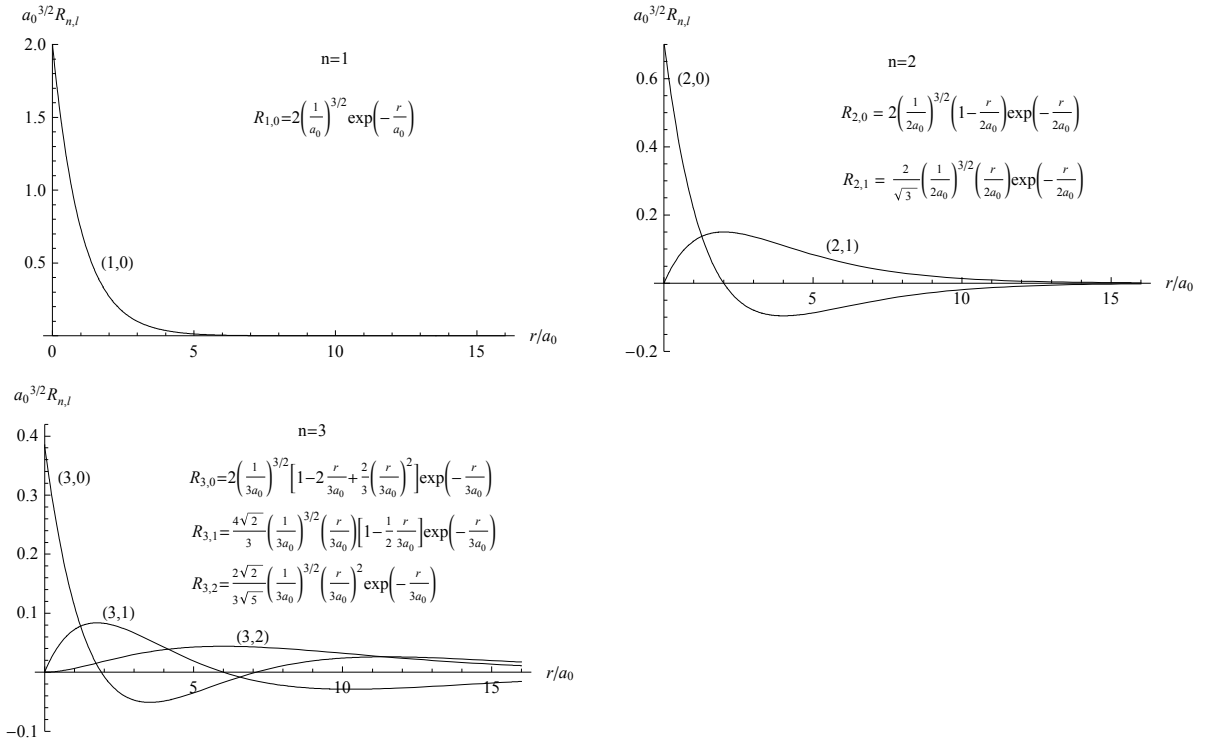
The solution of the radial equation introduces a new integer from the requirement that the wavefunction behaves correctly as $r \rightarrow 0$ and as $r \rightarrow \infty$ - this is the principal quantum number n which can take all integer values greater than the value of l . The solutions are labelled by the two quantum numbers n and l and we write $R_{n,l}(r)$. The first six radial functions for hydrogen ($Z = 1$) are plotted in the figure below as a function of position r . For reference (don't try to remember them!), the equations for these radial functions are also given.

Important things to note about these radial functions:

- ◆ The radial coordinate r is scaled by the quantity a_0 . This is the “Bohr radius”. We see from the plots (or the formulae) that it tells us the approximate size of the radial wavefunctions. It has the value $5.292 \times 10^{-11} \text{ m}$, and is given by

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}. \quad (3.22)$$

- ◆ At large distances, all the wavefunctions fall off exponentially, with the scale for the exponential decay being $n a_0$. The wavefunction extends further for larger values of the principal quantum number n . In fact, the expectation value of r scales as n^2 (you can check this yourself).
- ◆ The plots and formulae above are for $Z = 1$. For other values of Z , simply replace a_0 by a_0/Z everywhere. This makes sense: increasing the nuclear charge pulls the electron in closer to the nucleus.
- ◆ The wavefunctions for $l = 0$ are largest at the nucleus (i.e. at the origin), whereas those for $l \neq 0$ are zero at the nucleus. This will be important later when we come to consider the small effects due to the properties of the nucleus.
- ◆ The number of nodes in the radial wavefunction is equal to $n - l - 1$.



3.5. Energy levels

The same procedure that gives us the radial functions also gives us the energy eigenvalues. These are

$$E_n = -\frac{Z^2 e^4 m}{2 (4\pi\epsilon_0)^2 \hbar^2 n^2} \quad (3.23)$$

This is an important result, but it is not easy to remember in this form. We can rewrite it by using the *fine structure constant* given by equation (3.6):

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c}.$$

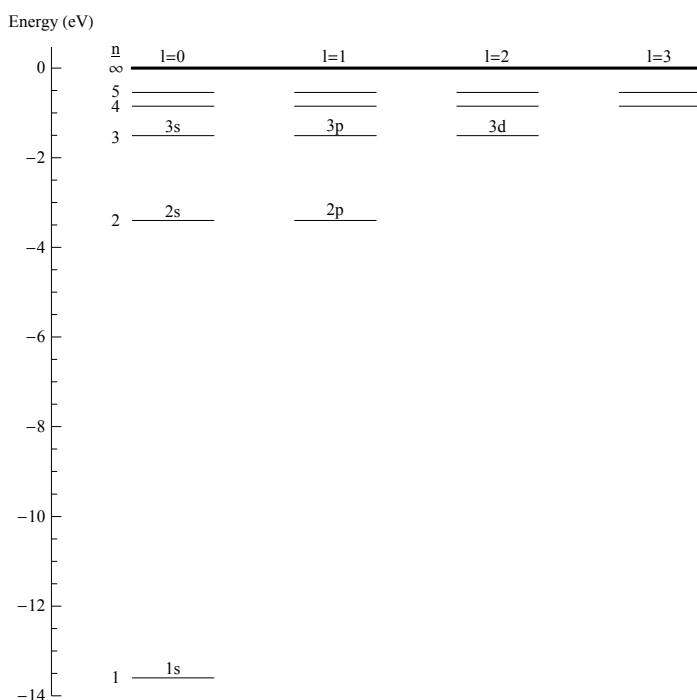
In terms of α , the energy levels are

$$E_n = -\frac{1}{2} \frac{Z^2 \alpha^2}{n^2} m c^2. \quad (3.24)$$

Consider what this means for the ground-state of the hydrogen atom ($Z = 1$, $n = 1$, $m \approx m_e$). $m_e c^2$ is the rest mass of the electron and the equation tells us that (in the ground state) the binding energy to the proton is simply $1/2 \alpha^2$ times this rest mass. The energy $\frac{1}{2} m_e \alpha^2 c^2$ is called the *Rydberg energy* and its value is 13.6eV. Note that it is defined in terms of the full electron mass, not the reduced mass. This means that the ionisation energy of hydrogen is slightly smaller than the Rydberg energy, smaller in fact by the ratio m/m_e . After dividing the Rydberg energy by $\hbar c$, we get the *Rydberg constant*, which is usually given the symbol R_∞ . It is the most precisely measured constant in physics, with a relative uncertainty of 5 parts in 10^{12} : $R_\infty = 10,973,731.568539 \pm 0.000055 m^{-1}$.

Note that, although the eigenfunctions of a one-electron atom are specified by three quantum numbers, n , l , m , the energy levels depend only on the quantum number n . This is a special case which has its origin in the $1/r$ form of the Coulomb potential. For all other atoms we will find that the energies depend on both n and l .

The energy levels of hydrogen are plotted in the figure below, labelled by the quantum numbers n and l . It is common to show the energy levels of atoms on a diagram similar to this one. Note once again that for hydrogen, and *only for hydrogen*, states of the same n but different l are degenerate (have the same energy). This is not the case for other atoms.



Notation

We specify the state of the electron using the quantum numbers n and l , but for l we use the letter (see above) instead of the number. Remember that l can only take integer values smaller than n . So the allowed states of hydrogen are 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f etc. These are indicated in the energy level diagram.

3.6. Hydrogen-like systems

As already noted above, our treatment is also valid for other one-electron atoms. Important examples are He^+ , Li^{2+} etc. We see from equation (3.24) that the energies scale as Z^2 - so (for example) the ionization energy of He^+ is 4 times that of hydrogen, the ionization energy of Li^{2+} is 9 times that of hydrogen etc. Another important one-electron atom is deuterium. It has $Z = 1$, but the nuclear mass is twice that of hydrogen so the reduced mass is slightly different. This shifts all the energy levels by a small amount - you can work out the size of this shift yourself. Also interesting and relevant is positronium - a bound state of an electron and a positron. This atom is unstable because the electron and positron annihilate, but it lives for long enough ($\sim 1\mu\text{s}$) to study it. Its reduced mass is simply half the electron mass and so all the energies are halved.

A topical example of a hydrogen-like atom is antihydrogen - a positron bound to an antiproton. Through an amazing research effort, it is now possible to produce and store many thousands of antihydrogen atoms. Researchers are now turning their attention to the study of the energy level structure of antihydrogen to find out whether it is exactly the same as that of hydrogen. They will also test whether it behaves the same under gravity as normal matter. This research tests some of our most basic laws of physics.

3.7. Summary of the main points

- Orders of magnitude: size of atom is order a_0 , speed of electron is order αc , energy levels are order α^2 times the electron rest-mass energy, magnetic moments are order μ_B .
- Because the Coulomb potential is a central potential the solution for the hydrogen atom separates into an angular part and a radial part.
- The angular solutions are the spherical harmonics. They are the eigenfunctions of \hat{L}^2 and \hat{L}_z with eigenvalues $l(l+1)$ and m respectively.
- The characteristic size of the ground-state radial function is a_0 , the Bohr radius. The wavefunction extends to larger distances for higher values of n .
- The eigenfunctions are zero at the origin, except for s-states.
- The energies are proportional to $1/n^2$ and are degenerate with respect to l .
- The energies are proportional to Z^2 and to the reduced mass m .

3.8. To do

- Check that you can derive the results for the Bohr atom written down in this handout.
- Make sure that you've understood all the material in this handout. Revise any parts that are unfamiliar. Useful reading are the lecture notes for 2nd year Quantum Mechanics, chapter 2 of Softley, chapter 2 of Woodgate, or chapter 3 of Rae ('Quantum Mechanics').
- Do questions 3-6 from problem set 1.

4. Many-electron atoms in the central field approximation

Having studied the main structure of one-electron atoms, we now look at atoms with many electrons.

4.1. The central field approximation

The Hamiltonian that describes the electrostatic interactions for N electrons and a nucleus of charge Ze is

$$\hat{H} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (4.1)$$

Here, ∇_i^2 is the Laplacian operator with derivatives taken with respect to the coordinates of the i^{th} electron, r_i is the distance of the i^{th} electron from the nucleus, and r_{ij} is the distance between electrons i and j . In the last sum, we have to sum over all electron pairs: so we sum over all j from 1 to N , and for each j we sum over all i from $j+1$ to N (so that we don't do any double-counting). The Schrödinger equation is $\hat{H}\psi(r_1, r_2 \dots r_N) = E\psi(r_1, r_2 \dots r_N)$, where the wavefunction is a function of the coordinates of every electron.

For an atom with many electrons, the mutual repulsion term is large and we cannot treat it as a perturbation. Instead, we make progress by guessing that the repulsive terms contain a large component which is spherically symmetric. This is the *central field approximation*. In this approximation, each electron moves independently in an effective central potential, $V(r_i)$, which is made up of the attraction to the nucleus plus the central part of the electron-electron repulsion which we write as $\sum_i S(r_i)$. Now we can split up our Hamiltonian into a central part and a residual part:

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \quad (4.2)$$

where our zeroth-order Hamiltonian is

$$\hat{H}_0 = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m_e} \nabla_i^2 + V(r_i) \right), \quad (4.3)$$

and

$$V(r_i) = -\frac{Ze^2}{4\pi\epsilon_0 r_i} + S(r_i). \quad (4.4)$$

The residual part, H_1 , is the part of the electron-repulsion that is not contained in the central potential, i.e.

$$\hat{H}_1 = \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{i=1}^N S(r_i). \quad (4.5)$$

Because the majority (the central part) of the electrostatic repulsion is now included in the zeroth-order Hamiltonian, \hat{H}_1 can now successfully be treated as a small perturbation.

We'll come to the question of how we find the correct $V(r_i)$ later. First, let's examine the effect of applying this central field approximation. Notice that \hat{H}_0 in equation (4.3) is a sum over single-electron Hamiltonians, $\hat{H}_0 = \sum_i \hat{H}_{0i}$. As a result, the wavefunction separates into a product of single particle wavefunctions, and the Schrödinger equation separates into N equations, one for each electron. Writing $\psi(r_1, r_2 \dots r_N) = \psi_1(r_1) \psi_2(r_2) \dots \psi_N(r_N)$, we have for each electron the equation

$$\left(-\frac{\hbar^2}{2m_e} \nabla_i^2 + V(r_i) \right) \psi_{n,l,m_l} = E_{n,l} \psi_{n,l,m_l}. \quad (4.6)$$

This is the equation for a single-electron moving in a central potential. We already know that we can separate this into an angular part and a radial part, with the angular part being the spherical harmonics, $Y_{l,m_l}(\theta, \phi)$, labelled by the orbital angular momentum quantum numbers l and m_l . The solution to the radial part depends on the exact form of $V(r_i)$, but we know that there will be a set of functions labelled by n and l . The energy eigenvalues E_i will also, in general, depend on n and l . This is why (anticipating the result) we have labelled the single-particle wavefunctions with the indices n, l, m_l and the energies with the indices n, l . The total energy is just the sum of the individual energies

$$E = \sum_{i=1}^N E_{n_i, l_i}.$$

When we include the spin of each electron, we see that there's one extra quantum number we need - m_s - to completely define the state of every electron.

Now we can write the complete state of the atom just by writing down the quantum numbers n, l, m_l, m_s for every electron. In doing so, we have to take care to obey the Pauli exclusion principle which tells us that no two electrons can have the same set of quantum numbers. Since the energy does not depend on m_l or m_s , we normally do not write these down, but we remember that for any state n, l there are two possible values of m_s ($\pm 1/2$) and $2l+1$ possible values of m_l - giving $2(2l+1)$ states in total. So, 2 electrons for an s state, 6 electrons for a p state, 10 electrons for a d state, 14 electrons for an f state, and so on.

Notation

We write the state of the atom by listing the occupied energy levels, for example $1s^2 2s^2 2p^6$ for the ground state of neon, and $1s^2 2s^2 2p^6 3s$ for the ground state of sodium. This is called the *configuration*. The electrons that have the same n are said to belong to a *shell*. Electrons that have the same values of n and l belong to the same *sub-shell*. So, for sodium, there are 2 electrons in shell 1, 8 electrons in shell 2 and 1 electron in shell 3. If we talk about sub-shells there are 2 electrons in 1s, 2 in 2s, 6 in 2p and 1 in 3s. We often abbreviate the configuration by replacing the configuration of all the inner shells by the corresponding element symbol - so we can write sodium as [Ne] 3s. The *filled* shells, sometimes called *closed* shells, form the *core*, and the ones outside the closed shells are the *valence* electrons.

4.2. The self-consistent field

To calculate the energy levels and wavefunctions we still have to solve the radial equation, and to do that we need to know $V(r)$. The method that is used is the *self-consistent field method*, sometimes called the *Hartree* method. Here are the steps that make up the method:

1. Make some reasonable guess for $V(r)$.
2. Solve the single-electron Schrödinger equation (equation (4.6)) using this $V(r)$ to obtain all the eigenvalues and eigenstates, $\phi_{n,l}$. This is straightforward to do numerically on a computer.
3. Take the many-electron state to be the product of the N single electron eigenstates of lowest energy, filling up the states according to the exclusion principle.
4. Calculate the charge distribution due to the electrons, i.e. $\rho_e = -e |\phi_{n,l}|^2$. Then calculate the electrostatic potential due to the charge of the nucleus and the charge distribution of the electrons. This is a new potential $V'(r)$ and is probably not the same as the original potential $V(r)$. We take $V'(r)$ to be a better approximation to the true potential than our original $V(r)$.
5. Iterate steps 2-4, until the potential obtained converges. Then we will have a self-consistent field, meaning that the field we assume in solving the Schrödinger equation is exactly the field produced by the nucleus and the electron distribution of our solution.

This procedure proves to be successful in predicting the energy-level structure of many-electron atoms.

4.3. Screening, the alkalis, and the quantum defect

Of all many-electron atoms, the alkalis are the simplest to understand. They all have a single electron outside spherically symmetric closed shells. Here are the electron configurations:

Li	$1s^2 2s$
Na	$1s^2 2s^2 2p^6 3s$
K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s$
Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s$
Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s$

For Li and Na, the shells fill up in the order that you would expect - first the $n = 1$ shell fills, then the $n = 2$ shell and so on. But for K, there is a deviation from the obvious ordering. The 4s sub-shell fills before the 3d sub-shell. It's the same story with Rb, where the 5s sub-shell fills before either the 4d or the 4f sub-shells. We can understand this ordering using the idea of screening.

For a $1/r$ potential, as in hydrogen, we know that the energy levels are ordered according to the principal quantum number n only; there is no dependence on l . For many-electrons, the central potential is not simply $1/r$ and the energies depend on both n and l . We can get a feel for what the central potential must look like from some simple arguments. If we take an electron out to large r , the nuclear charge Ze is almost fully screened by the inner electrons which together have a charge $(Z - 1)e$. So, at large r , the potential just looks like the $e^2/4\pi\epsilon_0 r$ potential of hydrogen. If we take the electron to very small r , the potential will be dominated entirely by the nucleus and will be $Ze^2/4\pi\epsilon_0 r$. At intermediate distances the form of the potential will be intermediate between these two forms.

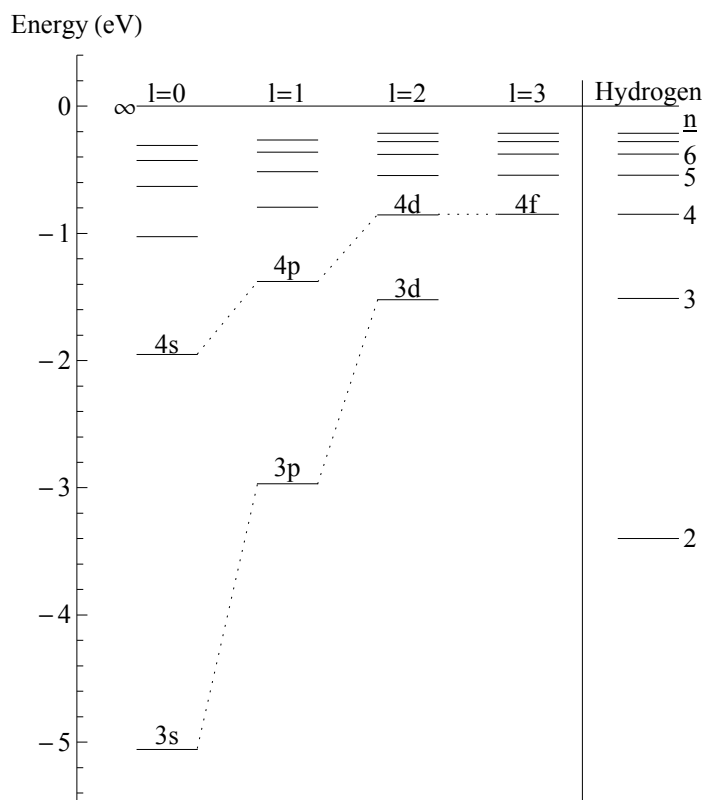
Consider the Na atoms. The states 3s, 3p and 3d are not degenerate (as they are in hydrogen). The large orbital angular momentum of the 3d electron prevents it from reaching small r , so it spends almost all its time outside the closed shell. The inner electrons are very effective at screening the nucleus and so the energy of the 3d state is very close to the $n = 3$ level of hydrogen. For the 3s electron there is no angular momentum barrier and it is able to penetrate the inner core of electrons and see a stronger potential. So its energy is lowered compared to the $n = 3$ level of hydrogen. The 3p level lies somewhere in between. Moving now to K, exactly the same principles apply. We find that the 4s state is shifted down in energy so far that it is below the 3d state, and this is the reason why the 4s state fills up first.

There is a very simple formula that quite accurately describes the energy levels of the alkalis. It is

$$E_{n,l} = -\frac{hcR_\infty}{(n - \delta_l)^2} \quad (4.7)$$

Here, R_∞ is the Rydberg constant ($hcR_\infty \approx 13.6$ eV). The formula is almost the same as the energy level formula for hydrogen, but instead of n^2 in the denominator we have $(n - \delta_l)^2$. The quantity δ_l is called the *quantum defect*. Its value depends on l , and varies from one alkali to another, but it has almost no dependence on n . Moreover, for $l > 2$, δ_l is zero to a good approximation. This is as we would expect from the above arguments which show that for high l the energy levels are hydrogenic. The use of the quantum defect is extremely useful - we can describe the entire energy level structure of an alkali once we know just three numbers, δ_0 , δ_1 and δ_2 (sometimes written δ_s , δ_p and δ_d).

The quantum defects are different from one alkali to another. For sodium, the values are $\delta_0 = 1.36$, $\delta_1 = 0.86$, $\delta_2 = 0.01$. Using these numbers, and equation (4.7), we can draw the complete energy level diagram for sodium.



4.4. Summary of the main points

- A large part of the electron-electron repulsion can be included into a central potential
- In this central potential, the total wavefunction is a product of single-electron wavefunctions, each labelled by the set of quantum numbers (n, l, m_l, m_s) .
- For a given n , the s state has the lowest energy because an s electron penetrates quite deeply into the electron core and so the shielding of the nucleus is incomplete. Next in energy is the p state, then the d state and so on. The levels with high angular momentum are hydrogenic.
- Knowing the ordering of the energy levels, and applying the exclusion principle, the configurations of all the atoms in the periodic table can be understood.
- The energy levels and eigenfunctions can be calculated using the self-consistent field method.
- The energy levels of the alkalis are described by a simple formula involving the quantum defect.

4.5. To do

- Revise the material in this handout. Useful reading: chapter 4 of Softley, chapter 6 of Woodgate, chapter 4 of Foot.
- Do questions 1 and 2 from problem set 2.

5. The residual electron-electron interaction

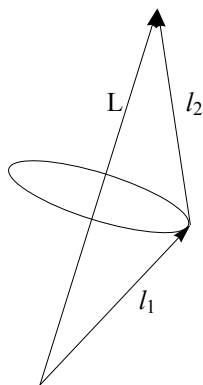
So far, we have looked at the energy level structure in the central field approximation and understood how this leads to electron configurations. We still need to account for the effect of the *residual electrostatic interaction*, given by equation (4.4). This is treated as a perturbation. We will not attempt to calculate the energy shifts and splittings due to this perturbation, but instead understand its effect qualitatively. We take the approach of identifying quantities that remain constants of the motion in the presence of the perturbation (in other words, we look for operators that commute with the zeroth-order Hamiltonian and with the perturbation).

5.1. LS coupling

A force that is directed towards the origin (the nucleus) does not exert any torque about the origin (remember $\tau = \mathbf{F} \times \mathbf{r}$, where τ is the torque, \mathbf{F} the force, and \mathbf{r} the displacement; so $\tau = 0$ when \mathbf{F} is in the direction of \mathbf{r}). Our residual interaction is the part that is *not* directed towards the origin, and so it exerts a torque about the origin. This causes the angular momenta of the individual electrons to precess. However, the interaction is internal to the atom, and so it cannot change the total orbital angular momentum of the atom. So it's a good idea to define the total orbital angular momentum

$$\hat{\mathbf{L}} = \sum_i \hat{\mathbf{l}}_i. \quad (5.1)$$

This is a constant of the motion, and we can be sure that, even in the presence of the perturbation, the energy eigenstates must be eigenstates of $\hat{\mathbf{L}}^2$ (with eigenvalue $L(L+1)$) and of \hat{L}_z (with eigenvalue M_L). Electrons that form closed sub-shells do not contribute to the sum because their total angular momentum is zero. Suppose we have two electrons outside closed sub-shells for example, with orbital angular momenta $\hat{\mathbf{l}}_1$ and $\hat{\mathbf{l}}_2$. In the vector model, the perturbation due to the residual electrostatic interaction causes $\hat{\mathbf{l}}_1$ and $\hat{\mathbf{l}}_2$ to precess about the total orbital angular momentum $\hat{\mathbf{L}}$. This is shown in the picture below. We see that l_1 , l_2 , L and M_L are the constants of the motion, but m_{l_1} and m_{l_2} are not.



The addition of l_1 and l_2 gives several possible values of L , according to the usual rules for adding angular momenta. After applying the perturbation, the energy depends upon the value of L . So the perturbation causes a given configuration to split into a set of *terms*, labelled by the total orbital angular momentum L .

The residual electrostatic interaction has no influence on the spin, but the spin enters into our discussion because of the requirement that the total wavefunction be antisymmetric under exchange of electrons (as explained below). So we also introduce the total spin angular momentum which is the vector sum of all the spins of the individual electrons:

$$\hat{\mathbf{S}} = \sum_i \hat{\mathbf{s}}_i. \quad (5.2)$$

This is also a constant of the motion. The energy eigenstates are also eigenstates of $\hat{\mathbf{S}}^2$ (with eigenvalue $S(S+1)$) and of \hat{S}_z (with eigenvalue M_S). Once again, filled shells do not contribute anything to the total spin, so we only have to sum over the electrons that are outside closed sub-shells. The vector model for the spins is similar to the one drawn above for the orbital angular momenta.

Notation

This coupling scheme, where we add up the individual $\hat{\mathbf{l}}_i$ to make a total $\hat{\mathbf{L}}$, and add up the individual $\hat{\mathbf{s}}_i$ to make a total $\hat{\mathbf{S}}$ is called LS-coupling. In some textbooks, it is referred to as “Russell-Saunders coupling”. A configuration splits up into levels labelled by L and S and called *terms*. These terms are degenerate with respect to M_L and M_S . The notation used to denote a term is

$$^{2S+1}L$$

Just as we use $s, p, d \dots$ to stand for $l = 0, 1, 2 \dots$, we use $S, P, D \dots$ to stand for $L = 0, 1, 2 \dots$. We write the pre-superscript as $2S+1$ to denote the spin *multiplicity*. There is also a naming convention that follows the multiplicity as shown in the table below:

S	multiplicity	name
0	1	singlet
1/2	2	doublet
1	3	triplet
3/2	4	quadruplet

So the term 2S is a doublet-S, while 3P is a triplet-P.

Working out terms

Let's consider some configurations, and work out what terms are allowed.

The configuration $1s^2 2s$. The full $1s^2$ shell does not contribute to the total angular momenta. So L and S are just given by the $2s$ electron. So the only possible term is 2S .

The configuration $1s 2s$. We have $l_1 = l_2 = 0$ and $s_1 = s_2 = 1/2$. So we must have $L = 0$, but we can have $S = 0$ or $S = 1$. So there are two terms - 1S and 3S .

The configuration $2p 3p$. We have $l_1 = l_2 = 1$ and $s_1 = s_2 = 1/2$. So we can have $L = 0, 1, 2$, and $S = 0, 1$. So there are 6 terms - $^1S, ^3S, ^1P, ^3P, ^1D, ^3D$.

This is all straightforward when the electrons are not equivalent (i.e. not in the same subshell). When the electrons are equivalent, it's more complicated because we have to make sure that the total angular momentum state is antisymmetric. This reduces the number of possible terms. In the case of the configuration $2p^2$, it turns out that the only allowed terms are $^1S, ^3P$ and 1D .

5.2. Exchange symmetry

In the central field approximation we write the total wavefunction as a product of single-electron wavefunctions, $\psi(r_1, r_2 \dots r_N) = \prod_i \psi_{n_i l_i m_i}(r_i)$. Each single-electron wavefunction is characterized by the three quantum numbers (n, l, m) , and is a function only of the coordinates of that electron. To keep the notation under control, let's just think of two electrons and write the product wavefunction as

$$\psi = u_a(1) u_b(2), \quad (5.3)$$

where the subscripts a and b label the set of quantum numbers and the 1 and 2 refer to the electron coordinates r_1 and r_2 . Consider the alternative wavefunction

$$\psi' = u_b(1) u_a(2). \quad (5.4)$$

It is exactly the same as wavefunction (5.3), but with the coordinates 1 and 2 swapped. Swapping the two electrons cannot possibly change anything - this is both physically obvious and obvious from inspection of equation (4.1) where swapping coordinates 1 and 2 leaves the equation unchanged. Both ψ and ψ' are eigenfunctions of the Hamiltonian, both with the same energy eigenvalue - there is a degeneracy with respect to the exchange of electrons. What's more, any arbitrary linear combination of these two eigenfunctions, $\alpha u_a(1) u_b(2) + \beta u_b(1) u_a(2)$ is also an eigenfunction. To make sure that the probability distribution is unchanged when we swap electrons, we must have to give equal weight to the two combinations $u_a(1) u_b(2)$ and $u_b(1) u_a(2)$. So we see that there are two wavefunctions that have the right behaviour, one symmetric and the other antisymmetric under exchange:

$$\begin{aligned} \psi^+ &= \frac{1}{\sqrt{2}} [u_a(1) u_b(2) + u_b(1) u_a(2)] = \frac{1}{\sqrt{2}} (u_{ab} + u_{ba}), \\ \psi^- &= \frac{1}{\sqrt{2}} [u_a(1) u_b(2) - u_b(1) u_a(2)] = \frac{1}{\sqrt{2}} (u_{ab} - u_{ba}). \end{aligned}$$

In the final expressions, we've used a further shorthand, simply writing $u_a(1) u_b(2)$ as u_{ab} and writing $u_b(1) u_a(2) = u_{ba}$. The same ideas apply when there are more than two electrons - from the product wavefunction you can form the linear combinations that are either symmetric or antisymmetric under the exchange of any two electrons.

5.3. The effect of the residual electrostatic interaction

Now we return to the residual electrostatic interaction, \hat{H}_1 . We have already seen that it has the effect of splitting a configuration so that states of different L belonging to the same configuration have different energies. Next, we will see that the energy also depends on the exchange symmetry of the wavefunction.

The perturbation is the non-central part of the electrostatic repulsion between the electrons. Because it's a repulsion, its effect is to increase the energy. Clearly, this repulsion gets big when the electrons are close together. So let's look at the behaviour of ψ^+ and ψ^- as we reduce the distance between the two electrons to zero. We see that when $r_1 = r_2$, ψ^- goes to zero - so for the ψ^- state, the probability of the electrons being very close together goes to zero. This is not the case for ψ^+ which remains non-zero when the electrons are close together. So the electrons are more likely to be close together when they are in state ψ^+ than when they are in the state ψ^- . You can think of this as the overlapping parts of the wavefunctions of the two electrons interfering constructively in ψ^+ but destructively in ψ^- . Since the upward energy shift produced by the residual electrostatic repulsion is largest when the electrons are closer together, the energy level corresponding to ψ^+ will be higher than the one corresponding to ψ^- .

To calculate the energy shift, we apply first order perturbation theory.

$$\Delta E^+ = \langle \psi^+ | \hat{H}_1 | \psi^+ \rangle = \frac{1}{2} \langle u_{ab} + u_{ba} | \hat{H}_1 | u_{ab} + u_{ba} \rangle = \langle u_{ab} | \hat{H}_1 | u_{ab} \rangle + \langle u_{ab} | \hat{H}_1 | u_{ba} \rangle, \quad (5.5)$$

$$\Delta E^- = \langle \psi^- | \hat{H}_1 | \psi^- \rangle = \frac{1}{2} \langle u_{ab} - u_{ba} | \hat{H}_1 | u_{ab} - u_{ba} \rangle = \langle u_{ab} | \hat{H}_1 | u_{ab} \rangle - \langle u_{ab} | \hat{H}_1 | u_{ba} \rangle. \quad (5.6)$$

In the last step, we've used the fact that $\langle u_{ba} | \hat{H}_1 | u_{ba} \rangle = \langle u_{ab} | \hat{H}_1 | u_{ab} \rangle$ and $\langle u_{ba} | \hat{H}_1 | u_{ab} \rangle = \langle u_{ab} | \hat{H}_1 | u_{ba} \rangle$ which follows from the fact that nothing changes if we simply swap the electrons. It is usual to give names and symbols to these matrix elements. We define

$$J = \langle u_{ab} | \hat{H}_1 | u_{ab} \rangle, \quad (5.7)$$

and call this the *direct integral*, and define

$$K = \langle u_{ab} | \hat{H}_1 | u_{ba} \rangle. \quad (5.8)$$

which we call the *exchange integral*. Remember that u_a and u_b are the single-electron wavefunctions found in the central-field approximation. Once they have been found the integrals can be calculated.

5.4. Spin

The Hamiltonian for the many-electron atom, equation (4.1), does not couple the spin degree of freedom to the spatial degree of freedom, so the total wavefunction is just a product of a spatial part and a spin part. For two electrons there are 4 possible spin states - as given by equations (2.14) - (2.17). These spin states are reproduced here. Recall that on the left hand side of each equality the spin state is represented using the total spin S , and its projection M , $|S, M\rangle$, while on the right hand side the state is represented by the individual projection quantum numbers $|m_1, m_2\rangle$:

$$\begin{aligned} |1, 1\rangle &= |\uparrow\uparrow\rangle, \\ |1, 0\rangle &= \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}, \\ |1, -1\rangle &= |\downarrow\downarrow\rangle, \\ |0, 0\rangle &= \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}. \end{aligned}$$

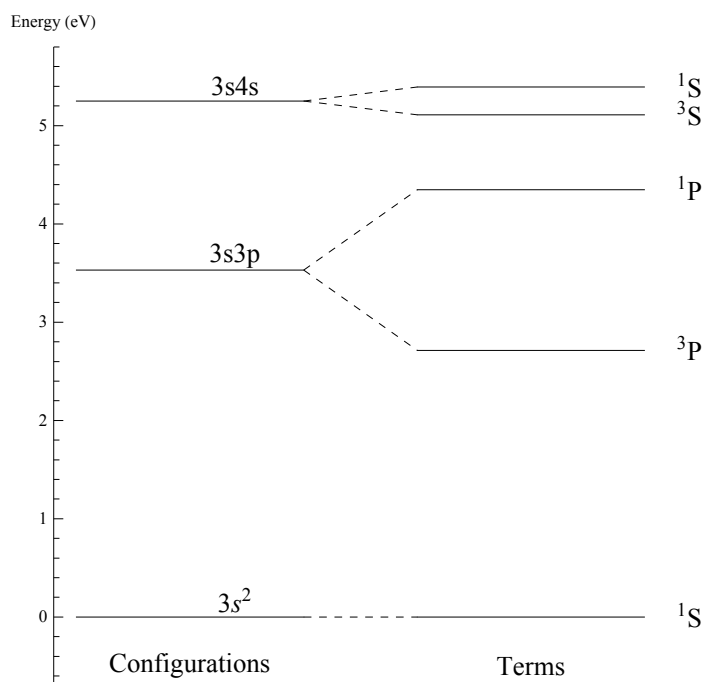
Just as for the spatial wavefunctions, let's consider the symmetry of these states under exchange of particles. It's obvious from the right hand sides that the first three states, the ones with $S = 1$, are symmetric under exchange, while the fourth, with $S = 0$, is antisymmetric.

Since there are four spin states and the two spatial states (ψ^+ , ψ^-) we might imagine that there are now 8 allowed states in total. This is *not the case*. This is because the *total wavefunction for a system of fermions has to be antisymmetric under the exchange of particles*. This means that we are constrained in the way we put together the spatial states and the spin states - for two electrons, the only ones we are allowed are $|\psi^+\rangle|0, 0\rangle$ and $|\psi^-\rangle|1, M\rangle$ (with $M = 0, \pm 1$). So the symmetric spatial state (ψ^+), which is the one of higher energy, goes together with the antisymmetric spin state which is the state of total spin zero. Since there is only one of these states, we call it a singlet. Similarly, the antisymmetric spatial state (ψ^-) which has the lower energy goes together with the symmetric spin states which are the three states with total spin one, $S = 1$. Since there are three of these states, we call it a triplet.

So now we see that the energy depends on both L and S - *each of the possible terms has a different energy*. The energy depends on L , because the residual repulsion between electrons depends on the relative orientation of the angular momenta (i.e. which orbitals the electrons are in). The energy depends on S because of the exchange-antisymmetry requirement and the fact that the repulsion depends on the symmetry of the spatial wavefunction under exchange.

5.5. An example - magnesium

Magnesium has 12 electrons. The electronic configuration of the ground state is $1s^2 2s^2 2p^6 3s^2$. Because the two 3s electrons are in the same sub-shell, the only spatial wavefunction that we can form is the symmetric one ($u_{3s} u_{3s}$); the antisymmetric spatial wavefunction is zero. It follows that, in the ground state, the only possible term is 1S . In the first excited configuration, one of the 3s electrons is excited to a 3p state, so we have the configuration $1s^2 2s^2 2p^6 3s 3p$. The allowed terms are 1P and 3P , with the latter having the lower energy. The next excited configuration is $1s^2 2s^2 2p^6 3s 4s$, and the allowed terms are 1S and 3S . These energy levels are shown below, drawn to scale.



5.6. Summary of the main points

- The central field approximation gives us *configurations* labelled as $n_1, l_1, n_2, l_2 \dots$
- To handle the perturbation due to the residual electrostatic interaction we introduce the total angular momentum quantum number L and total spin quantum number S .
- Spatial wavefunctions, and spin wavefunctions, should be either symmetric or anti-symmetric under exchange of electrons.
- The total wavefunction is the product of spatial and spin wavefunctions and must be anti-symmetric.
- The residual electrostatic interaction, plus the exchange anti-symmetry requirement, splits configurations into *terms* labelled by L and S as ^{2S+1}L .
- When there are just two valence electrons, the terms are singlets and triplets, with the triplets having the lower energy.

5.7. To do

- Revise the material in this handout. Useful reading: chapter 7 of Woodgate, chapter 5 of Foot.
- Do questions 3 and 4 from problem set 2.

6. Fine structure

We found the energy levels of hydrogen by solving the Schrödinger equation. This is a non-relativistic equation, and therefore approximate. Since the equation is approximate, the energy levels are also approximate. As we will see, the approximation is a good one, but we would like to go further and include the effects of relativity. There are two ways we could do that. One way is to solve the correct relativistic equation, which is the Dirac equation. This is beyond the scope of this course, so we will use the second way: we introduce relativistic corrections as perturbations and find the energy shift using first-order perturbation theory. Because the perturbations due to relativity are small, this procedure works well, and it also gives us a great deal of physical insight.

For our present case of the fine structure in hydrogen, the zeroth-order Hamiltonian is

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + V(r) \quad (6.1)$$

and the zeroth-order eigenfunctions and eigenvalues are the ones already worked out (see lecture 3): $\hat{H}_0 |n, l, m\rangle = E_n |n, l, m\rangle$, where

$$E_n = -\frac{1}{2} \frac{Z^2 \alpha^2}{n^2} m c^2. \quad (6.2)$$

When we include relativistic corrections we find that there are three separate perturbations. In this course, we will treat the most important of these, known as the spin-orbit interaction. The other two corrections shift the energy levels but do not result in a splitting (if you are interested, they are discussed in the supplement to this lecture).

6.1. Spin-orbit interaction

The electron is moving through the electric field of the nucleus. Motion at velocity \mathbf{v} in an electric field \mathbf{E} produces a magnetic field

$$\mathbf{B} = -\frac{1}{c^2} \mathbf{v} \times \mathbf{E}. \quad (6.3)$$

This magnetic field interacts with the intrinsic magnetic dipole moment, $\hat{\mu}_s$, of the electron and we get an interaction term

$$\hat{H}_1' = -\hat{\mu}_s \cdot \mathbf{B} \quad (6.4)$$

For any radial electric field, we can write the electric field in terms of the potential energy V as

$$\mathbf{E} = -\frac{1}{e} \frac{dV}{dr} \frac{\mathbf{r}}{r}. \quad (6.5)$$

Thus, our perturbation is

$$\hat{H}_1' = \frac{1}{m_e e c^2} \frac{1}{r} \frac{dV}{dr} \hat{\mu}_s \cdot (\hat{\mathbf{p}} \times \hat{\mathbf{r}}), \quad (6.6)$$

where we have introduced the momentum $\mathbf{p} = m_e \mathbf{v}$. Next we use the relationship between the magnetic moment and the spin, $\hat{\mu}_s = -g_s \left(\frac{e\hbar}{2m_e} \right) \hat{\mathbf{s}}$, and the definition of the orbital angular momentum, $\hbar \hat{\mathbf{l}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$. We'll also use the fact that $g_s = 2$ (to a very good approximation). Finally, we have to introduce an extra factor of 1/2 due to *Thomas precession* which is a further relativistic effect that comes from a careful consideration of the Lorentz transformation in a rotating frame. The derivation of this extra factor is beyond the scope of this course. Using these substitutions, we obtain

$$\hat{H}_1' = \frac{\hbar^2}{2m_e^2 c^2} \frac{dV}{dr} \frac{1}{r} \hat{\mathbf{s}} \cdot \hat{\mathbf{l}} \quad (6.7)$$

For the case of a one-electron atom, we have $V = -Ze^2/(4\pi\epsilon_0 r)$, and so

$$\frac{1}{r} \frac{dV}{dr} = \frac{Ze^2}{4\pi\epsilon_0 r^3}.$$

Thus, for a one-electron atom, the perturbation is

$$\hat{H}_1' = \frac{\hbar^2}{2m_e^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^3} \hat{\mathbf{s}} \cdot \hat{\mathbf{l}} \quad (6.8)$$

To calculate the energy shift we need to calculate the expectation value of $1/r^3$ and of $\hat{\mathbf{s}} \cdot \hat{\mathbf{l}}$. The first is a standard result for a one-electron atom:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l+1/2)(l+1)n^3} \left(\frac{Z}{a_0} \right)^3. \quad (6.9)$$

To calculate the expectation value of $\hat{\mathbf{s}} \cdot \hat{\mathbf{l}}$ we introduce the total angular momentum of the electron $\hat{\mathbf{j}} = \hat{\mathbf{l}} + \hat{\mathbf{s}}$. Squaring, we get $\hat{\mathbf{j}}^2 = \hat{\mathbf{l}}^2 + \hat{\mathbf{s}}^2 + 2\hat{\mathbf{s}} \cdot \hat{\mathbf{l}}$ and so

$$\hat{s} \cdot \hat{l} = \frac{1}{2} (\hat{j}^2 - \hat{l}^2 - \hat{s}^2). \quad (6.10)$$

Our zero-order eigenstates are eigenstates of \hat{l}^2 , \hat{s}^2 and \hat{j}^2 with eigenvalues $l(l+1)$, $s(s+1)$ and $j(j+1)$ respectively. So the expectation value we need is

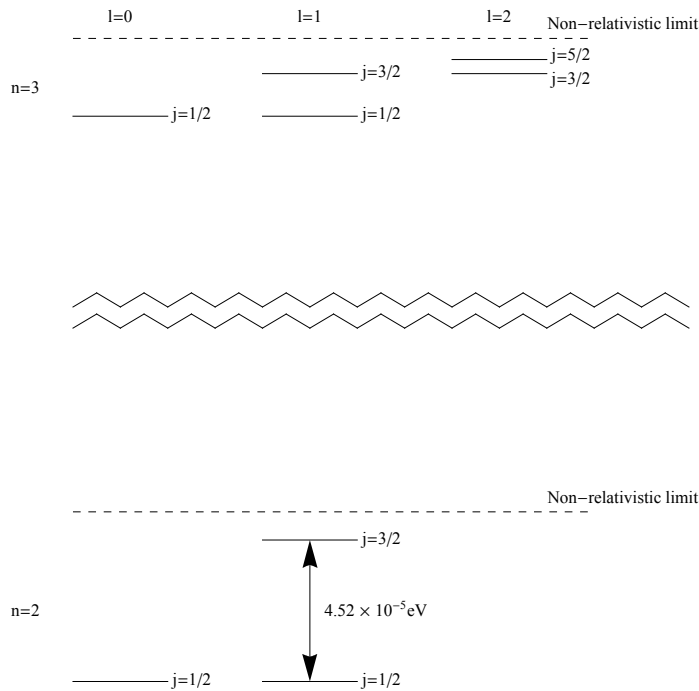
$$\langle \hat{s} \cdot \hat{l} \rangle = \frac{1}{2} [j(j+1) - l(l+1) - s(s+1)]. \quad (6.11)$$

Using these expectation values we obtain the expression for the energy shift:

$$\Delta E_1 = \langle \hat{H}_2 \rangle = -E_n \frac{Z^2 \alpha^2}{n} \frac{[j(j+1) - l(l+1) - s(s+1)]}{2l(l+1/2)(l+1)} \quad (6.12)$$

Note that this shift does not apply when $l = 0$. The quantum number j can take values from $|l - s|$ to $l + s$. For hydrogen, $s = 1/2$, and so each energy level described by the quantum numbers (n, l, s) is split into two *fine structure levels*, one with $j = l + 1/2$ and the other with $j = l - 1/2$. States with $l = 0$ are an exception - they are not split.

The diagram below shows the fine structure splittings for the $n = 2$ and $n = 3$ states of hydrogen. The scale of the fine-structure splitting is indicated. The other fine structure splittings are approximately to scale. The $n = 2$ to $n = 3$ energy difference is not on the same scale (it is vastly larger than the fine structure splittings).



6.2. Spin-orbit interaction for many-electron atoms

We have focussed on hydrogen because we know the wavefunctions and so can calculate everything. The same spin-orbit interaction is also present in many-electron atoms, and causes a splitting of energy levels just like in hydrogen. For many electrons, we add up the spin-orbit interactions of each electron:

$$H_{so} = \sum_i \beta_i \hat{l}_i \cdot \hat{s}_i.$$

Here,

$$\beta_i = \frac{\hbar^2}{2m_e^2 c^2} \frac{dV(r_i)}{dr_i} \frac{1}{r_i},$$

where $V(r_i)$ is the central potential at the position of electron i - the potential that we find when we make the central field approximation. The projection theorem tells us that each individual \hat{l}_i is proportional to the total orbital angular momentum \hat{L} , and each individual \hat{s}_i is proportional to the total orbital spin \hat{S} . The upshot is that the perturbation becomes

$$H_{so} = \beta_{LS} \hat{L} \cdot \hat{S}, \quad (6.13)$$

where β_{LS} is a function only of radial coordinates. Following exactly the same procedure as for hydrogen, we introduce the total angular momentum $\hat{J} = \hat{L} + \hat{S}$. Then we immediately see that the energy shift is

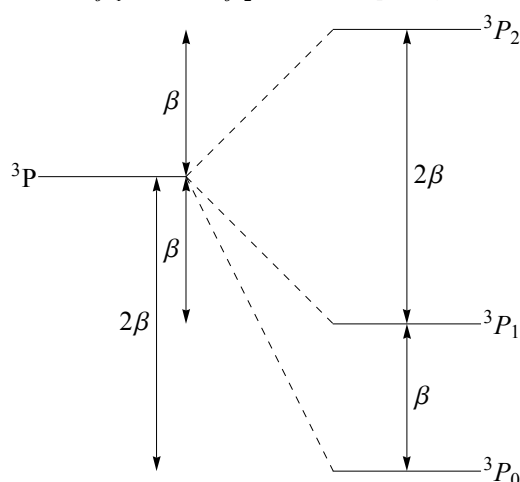
$$\Delta E_J = \frac{\beta}{2} [J(J+1) - L(L+1) - S(S+1)]. \quad (6.14)$$

Here, $\beta = \langle \beta_{LS} \rangle$ is the expectation value of β_{LS} . This can be calculated (numerically) once the wavefunctions and the central potential have been found in the central-field approximation. The main point here is that the *terms* of a many-electron atom are split by the spin-orbit interaction into *levels* according to the value of the quantum number J . To label a particular level, we have to give the values of L , S and J , which we do using the notation

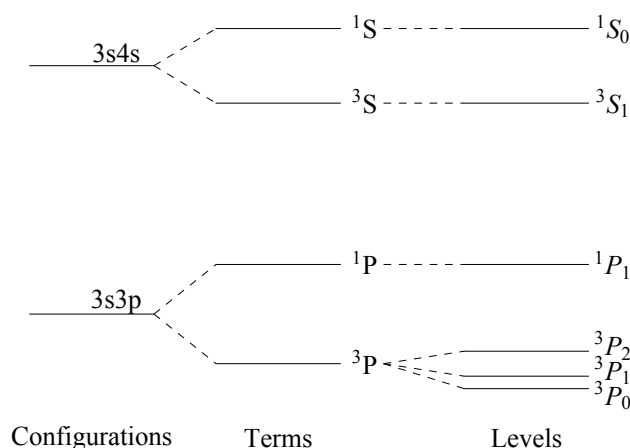
$$^{2S+1}L_J.$$

This is just the same as the notation used to label terms, except that we've added the value of J as a subscript.

As an example, consider a 3P term. This could be in helium, or in another atom with two valence electrons. The term has $S = 1$ and $L = 1$, and the spin-orbit interaction splits this into three levels with total angular momentum $J = 0, 1, 2$. According to equation (6.14), $\Delta E_{J=0} = -2\beta$, $\Delta E_{J=1} = -\beta$, $\Delta E_{J=2} = \beta$. So the splitting into fine-structure levels is as shown below.



In lecture 5 we looked at the energy levels of magnesium and saw how the residual electron-electron interaction split configurations into terms, labelled by the quantum numbers L and S . Now we have completed the picture: when the spin-orbit interaction is included these terms (may) split up into fine-structure levels according to the possible values of J . Here are the terms and levels for the $3s3p$ and $3s4s$ excited configurations of magnesium



6.3. Summary of the main points

- Fine structure is due to relativistic effects.
- The most important of these is the spin-orbit interaction which is due to the interaction of the electron's magnetic moment with the magnetic field it sees as it moves through the electric field of the nucleus.
- The splitting is into levels labelled by the total angular momentum quantum number j .
- The fine structure splitting is of order $Z^2 \alpha^2$ times smaller than the gross energy.
- The fine structure splitting is largest for states of low n .
- For many electron atoms, a term labelled by L and S is split into fine-structure levels labelled by J .

6.4. To do

- Revise the material in this handout. Useful reading: section 2.10 and 2.11 of Softley, chapter 4 of Woodgate or section 2.3 of Foot.
- Do questions 5 and 6 from problem set 2.

Supplement to lecture 6

The material in this supplement is not on the syllabus. It is here for your interest, and to complete the picture of the fine structure of hydrogen. There are two additional perturbations that need to be considered.

6.6. Relativistic correction to the kinetic energy

The relativistic kinetic energy of the electron is

$$\hat{T} = (\hat{p}^2 c^2 + m_e^2 c^4)^{1/2} - m_e c^2 = m_e c^2 \left(1 + \frac{\hat{p}^2}{m_e^2 c^2} \right)^{1/2} - m_e c^2 \approx \frac{\hat{p}^2}{2 m_e} - \frac{\hat{p}^4}{8 m_e^3 c^2}, \quad (6.15)$$

where in the last step we have used a Taylor expansion of the square root to second order in the small quantity $\hat{p}^2 / m_e^2 c^2$. The first term is just the kinetic energy that already appears in the non-relativistic Hamiltonian (i.e. in the Schrödinger equation). The second term is our perturbation, which we'll call \hat{H}_2' :

$$\hat{H}_2' = -\frac{\hat{p}^4}{8 m_e^3 c^2} = -\frac{1}{2 m_e c^2} \left(\frac{\hat{p}^2}{2 m_e} \right)^2 = -\frac{1}{2 m_e c^2} (\hat{H}_0 - V)^2. \quad (6.16)$$

The energy shift is

$$\Delta E_2 = -\frac{1}{2 m_e c^2} \langle (\hat{H}_0 - V)^2 \rangle = -\frac{1}{2 m_e c^2} [E_n^2 - 2 E_n \langle V \rangle + \langle V^2 \rangle], \quad (6.17)$$

where we have used the fact that the expectation value of \hat{H}_0 is simply the zeroth order energy $E_n = -\frac{1}{2} \frac{Z^2 \alpha^2}{n^2} m_e c^2$, as given by equation (3.24). Inserting the Coulomb potential for V , we get

$$\langle V \rangle = -\frac{Z e^2}{4 \pi \epsilon_0} \left\langle \frac{1}{r} \right\rangle = -\frac{Z e^2}{4 \pi \epsilon_0} \frac{Z}{n^2 a_0} = -\frac{Z^2}{n^2} \alpha^2 m_e c^2, \quad (6.18)$$

$$\langle V^2 \rangle = \frac{Z^2 e^4}{(4 \pi \epsilon_0)^2} \left\langle \frac{1}{r^2} \right\rangle = \frac{Z^2 e^4}{(4 \pi \epsilon_0)^2} \frac{1}{(l + 1/2) n^3} \left(\frac{Z}{a_0} \right)^2 = \frac{Z^4}{n^3} \frac{1}{(l + 1/2)} \alpha^4 m_e^2 c^4. \quad (6.19)$$

Here, we have used standard results for the expectation values of $1/r$ and $1/r^2$ for a one-electron atom (you can look them up, or work them out yourself), and we've used the expressions for a_0 and α given by equations (3.4) and (3.6). Adding up the terms and simplifying we reach the result

$$\Delta E_2 = -E_n \frac{Z^2 \alpha^2}{n^2} \left(\frac{3}{4} - \frac{n}{(l + 1/2)} \right). \quad (6.20)$$

6.7. Darwin term for $l = 0$

There is an additional relativistic term that applies to s-states only. It can be obtained from the Dirac equation and it accounts for the breakdown of the non-relativistic approximation as $r \rightarrow 0$ and the potential energy becomes very large. It only applies to s-states because only s-states have a non-vanishing wavefunction at the origin. The energy shift due to this term is found to be

$$\Delta E_3 = -E_n \frac{Z^2 \alpha^2}{n} \quad (l = 0 \text{ only}). \quad (6.21)$$

6.8. Putting it all together

The total energy shift is found by adding up the three individual shifts, $\Delta E_{n,j} = \Delta E_1 + \Delta E_2 + \Delta E_3$, remembering that ΔE_1 only applies when $l \neq 0$ and ΔE_3 only applies when $l = 0$. The result, valid for all l is

$$\Delta E_{n,j} = -E_n \frac{Z^2 \alpha^2}{n^2} \left(\frac{3}{4} - \frac{n}{j + 1/2} \right). \quad (6.22)$$

Important points to note about this result:

- ◆ The fine structure shifts are of order $Z^2 \alpha^2$ smaller than the gross energy. For hydrogen ($Z=1$), this makes them about $1/137^2 = 5 \times 10^{-4}$ times smaller.
- ◆ The fine structure is largest for small n .
- ◆ The energy shift depends on n and j , but not on l . This means that states with the same n and j , but different l , remain degenerate when relativistic effects are included. Consider $n = 2$ for example. The 2s state can only have $j = 1/2$, whereas the 2p state has two components $j = 1/2$ and $j = 3/2$. These latter two have different energies, but the $j = 1/2$ components of the 2s and 2p states are degenerate.
- ◆ $\Delta E_{n,j}$ is always negative (E_n is negative and $n \geq j + 1/2$). So all states are shifted down in energy.

- ◆ It is the spin-orbit interaction that is responsible for the splitting of levels that have different j . The other two terms only result in a shift, not a splitting. For this reason, it is the spin-orbit interaction that is most important in many-electron atoms.

6.9. The Dirac result

It is worth writing down the result obtained by solving the Dirac equation directly:

$$E_{n,j} = m_e c^2 \left(1 + Z^2 \alpha^2 \left(\frac{1}{n - (j + \frac{1}{2}) + \left[(j + \frac{1}{2})^2 - Z^2 \alpha^2 \right]^{1/2}} \right)^2 \right)^{-1/2}. \quad (6.23)$$

This remarkably simple formula is an exact result for the energy levels of a one-electron atom (apart from the effects of QED and hyperfine structure). Again, the energies depend on n and j but not on l . If we expand this formula in powers of $Z \alpha$, we find the following:

- ◆ The first term is simply $m_e c^2$, the rest mass of the electron.
- ◆ The second term is of size $Z^2 \alpha^2$ and is equal to the gross energy E_n (equation (3.24)) that we find from the Schrödinger equation.
- ◆ The third term is of size $Z^4 \alpha^4$ and is exactly equal to the total fine-structure energy shift that we found above using perturbation theory, i.e. equation (6.22).

6.10. The Lamb shift

Even this Dirac result is not exactly correct. Even smaller corrections due to Quantum Electrodynamics (QED) need to be applied. These corrections have their origin in the fluctuations of the vacuum. The fluctuations of the vacuum cause tiny fluctuations in the position of the electron. This smears out the charge a little bit and the mean potential it sees due to the field of the nucleus is slightly different to that seen by a point particle. The QED effect can be calculated to extremely high precision. It is greatest for s states of low n . In $n = 2$ it results in a small splitting between the $2 s_{1/2}$ and $2 p_{1/2}$ states (remember that these are degenerate before the QED effects are included). This splitting is called the Lamb shift, named after W.E. Lamb who, along with R.C. Retherford, was the first to measure this splitting. The splitting is about 10 times smaller than the fine structure splitting. It has now been measured to extremely high precision and is one of the most exact tests that we have of QED.

7. Hyperfine structure

There is one last level of structure that we need to consider, the *hyperfine structure*. It is due to properties of the nucleus other than its charge, most importantly the magnetic moment of the nucleus. There are also other nuclear properties that can make a significant contribution to the hyperfine structure, such as the electric quadrupole moment of the nucleus, but this is beyond the scope of this course. Although the hyperfine structure is very small compared to the other levels of structure, it plays an extremely important role in physics.

7.1. General treatment

Let the nucleus have a spin angular momentum $\hbar \hat{I}$. Associated with this spin, and parallel to it, the nucleus will have a magnetic moment $\hat{\mu}_I$. We usually write

$$\hat{\mu}_I = g_I \mu_N \hat{I}. \quad (7.1)$$

Here, $\mu_N = \frac{e\hbar}{2M_p}$, where M_p is the proton mass. The g factor, g_I , is a constant of proportionality. We might think it would be equal to 2, just like the g factor for an electron, but it isn't because the nucleus has structure - the protons and neutrons - and even they have structure - the quarks. So each nucleus has a different value for g_I (but they are all of order 1).

There is an interaction between this nuclear magnetic moment and the magnetic field produced at the nucleus by the electrons, \mathbf{B}_{el} . The interaction Hamiltonian is

$$\hat{H}_{\text{hfs}} = -\hat{\mu}_I \cdot \mathbf{B}_{\text{el}}. \quad (7.2)$$

The magnetic field produced by the electrons is due both to their orbital angular momentum around the nucleus and their intrinsic magnetic moments proportional to their spins. According to the projection theorem, the total magnetic field is proportional to the total electronic angular momentum \hat{J} . So we can write $\mathbf{B}_{\text{el}} \propto \hat{J}$, and our interaction Hamiltonian has the form

$$\hat{H}_{\text{hfs}} = A_{\text{hfs}} \hat{I} \cdot \hat{J}. \quad (7.3)$$

We find the energy splitting by applying first-order perturbation theory. We proceed in exactly the same way as we did for fine structure. First, we introduce the total angular momentum \hat{F} . It is the sum of the total electronic angular momentum \hat{J} , and the nuclear spin \hat{I} , and is now the true total angular momentum of the atom (there is nothing more we need to include!):

$$\hat{F} = \hat{I} + \hat{J}. \quad (7.4)$$

We can form eigenstates of this total angular momentum, which we write as $|I; J; F, M_F\rangle$, meaning that \hat{I} and \hat{J} are coupled to form a resultant \hat{F} . This state is an eigenstate of \hat{I}^2 , \hat{J}^2 , \hat{F}^2 and \hat{F}_z , with eigenvalues $I(I+1)$, $J(J+1)$, $F(F+1)$ and M_F respectively. It is not an eigenstate of \hat{I}_z or of \hat{J}_z . Since $\hat{F}^2 = \hat{I}^2 + \hat{J}^2 + 2\hat{I} \cdot \hat{J}$, we can write

$$\hat{H}_{\text{hfs}} = \frac{A_{\text{hfs}}}{2} (\hat{F}^2 - \hat{I}^2 - \hat{J}^2). \quad (7.5)$$

Using first-order perturbation theory, and our $|I; J; F, M_F\rangle$ eigenstates, the energy shift is

$$\Delta E_F = \langle I; J; F, M_F | \hat{H}_{\text{hfs}} | I; J; F, M_F \rangle = \frac{A}{2} [F(F+1) - I(I+1) - J(J+1)], \quad (7.6)$$

where, $A = \langle A_{\text{hfs}} \rangle$. The hyperfine interaction causes a splitting of a level into hyperfine components labelled by the total angular momentum F , which can take values between $|J - I|$ and $J + I$.

We can see that the hyperfine interaction will be small - the form of the interaction is similar to the spin-orbit interaction, except with the nuclear magnetic moment $\hat{\mu}_I$ replacing the electron magnetic moment $\hat{\mu}_s$. Since $\mu_I/\mu_s = m_e/M_p \approx \frac{1}{2000}$, the hyperfine structure is expected to be about 3 orders of magnitude smaller than the fine-structure. Note that many nuclei have zero spin, in which case the atom has no hyperfine structure.

This deals with hyperfine structure in general. We gain more insight by looking at some specific and important examples, which is what we do next.

7.2. Hyperfine structure in the ground state of hydrogen

Consider the ground state of hydrogen, $1s$. The electron has no orbital angular momentum, and so the only contribution to \mathbf{B}_{el} comes from the intrinsic magnetic moment $\hat{\mu}_s = -g_s \mu_B \hat{s}$. To find the magnetic field this produces at the nucleus we can use the following result from electromagnetism: the magnetic field inside a uniformly magnetized sphere of magnetization \mathbf{M} is $\frac{2}{3} \mu_0 \mathbf{M}$. The magnetization is the magnetic moment per unit volume, and so the magnetization at position r due to the electron's magnetic moment is the total magnetic moment multiplied by the probability density of finding the electron at position r , which is just $|\psi(r)|^2$. This is not a constant everywhere, but it is very nearly constant over the volume occupied by the nucleus which is what matters to us. So the magnetization at the nucleus is

$$\mathbf{M}(0) = -g_s \mu_B s |\psi_{1s}(0)|^2 \quad (7.7)$$

and the magnetic field this produces is

$$\mathbf{B}_{\text{el}} = -\frac{2}{3} g_s \mu_0 \mu_B \left| \psi_{1s}(0) \right|^2 \hat{\mathbf{s}}. \quad (7.8)$$

Using equation (7.1) for $\hat{\boldsymbol{\mu}}_I$, and equation (7.2) for the hyperfine Hamiltonian, and the fact that for our single s electron in hydrogen $\hat{\mathbf{J}} = \hat{\mathbf{s}}$, we obtain

$$\hat{H}_{\text{hfs}} = \frac{2}{3} g_s g_I \mu_0 \mu_B \mu_N \left| \psi_{1s}(0) \right|^2 \hat{\mathbf{I}} \cdot \hat{\mathbf{J}}, \quad (7.9)$$

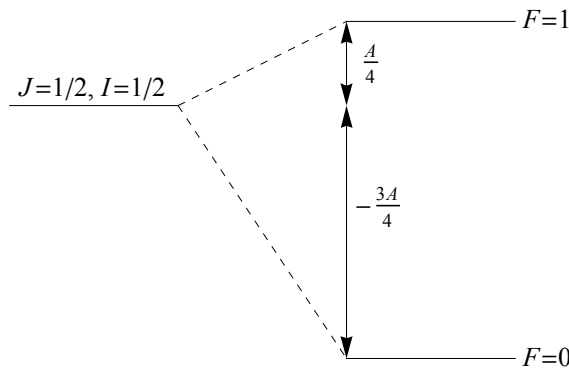
which has the same form as equation (7.3), with the quantity A now specified: $A = \frac{2}{3} g_s g_I \mu_0 \mu_B \mu_N \left| \psi_{1s}(0) \right|^2$. We found the hydrogenic wavefunctions in lecture 3. For the s state with principal quantum number n :

$$\left| \psi_{ns}(0) \right|^2 = \frac{1}{\pi a_0^3 n^3}.$$

So, for the specific case of the ground state of hydrogen, we get

$$A = \frac{2}{3} g_s g_I \mu_0 \mu_B \mu_N \frac{1}{\pi a_0^3}. \quad (7.10)$$

The proton spin is $I = 1/2$, and the electron spin is $J = 1/2$. So the ground state is split into two hyperfine components, $F = 1$ and $F = 0$, separated by the amount A (see equation (7.6)). The splitting is shown in the diagram below. All of the quantities in the above formula for A are known (for a proton, the g_I factor is 5.585694713). You can look up the values in a table and thus calculate the expected value of the hyperfine splitting in the ground state of hydrogen. Calculate it as a frequency - you should get 1.42 GHz, close to the (extremely precisely!) measured value - $\Delta E_{\text{hfs}}/h = 1\,420\,405\,751.7667 \pm 0.0009$ Hz.



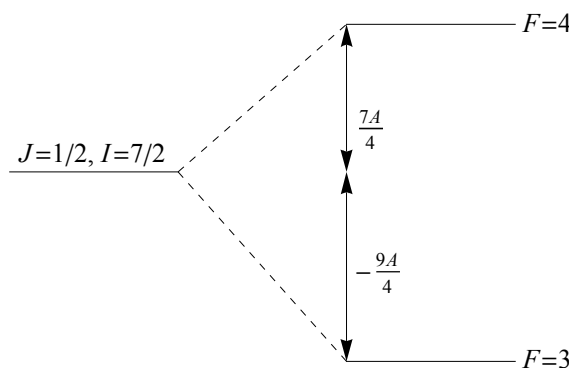
If a hydrogen atom is in the upper of the two hyperfine states ($F = 1$), it can decay to the ground state ($F = 0$) by emitting radiation at this frequency. The wavelength of this radiation is 21cm. This radiation is emitted by the vast quantities of hydrogen in our own galaxy and all the galaxies in the universe. It can be detected and mapped using radio telescopes and is extremely important in astronomy and cosmology

The hydrogen maser

In a hydrogen maser, the frequency of the ground-state hyperfine interval of hydrogen is used as an extremely precise and stable frequency reference. Look it up (e.g. on wikipedia).

7.3. Hyperfine structure in the ground state of caesium

The hyperfine structure in the ground state of Cs is enormously important because the frequency of this hyperfine interval defines the second. Cs has just one stable isotope, Cs-133, and its nuclear spin is $I = 7/2$. The ground electronic state of Cs is $6s^2 S_{1/2}$. The $J = 1/2$ couples to the $I = 7/2$ to give two hyperfine components with total angular momentum $F = 3, 4$, with $F = 3$ having the lower energy. The splitting is shown below.



The calculation of the size of the hyperfine splitting is similar to that for hydrogen given above. The only difference is in the wavefunction at the origin, which of course has a different value in Cs than it does in hydrogen. For the ground state of the alkalis, a good approximation

for the wavefunction at the origin is

$$|\psi(0)|^2 = \frac{Z}{\pi a_0^3 (n - \delta_0)^3}.$$

The only change relative to hydrogen is the appearance of the nuclear charge, Z , in the numerator, and the replacement of n by $n - \delta_0$ in the denominator, where δ_0 is the quantum defect for s-states that we met in lecture 4. For Cs, $Z = 55$, $n - \delta_0 = 1.87$, $g_I = 0.74$. So, scaling from the hydrogen result we would expect the hyperfine interval for Cs to be given approximately as

$$\frac{\Delta E_{\text{Cs}}}{\Delta E_H} \approx \frac{Z_{\text{Cs}}}{(n - \delta_0)_{\text{Cs}}^3} \frac{g_{I,\text{Cs}}}{g_{I,H}} \frac{F_{\text{max,Cs}}}{F_{\text{max,H}}} = \frac{55}{1.87^3} \frac{0.74}{5.59} \frac{4}{1} = 4.5.$$

This gives an estimate for the Cs hyperfine frequency of 6.4 GHz. In fact, the frequency is higher - 9.2GHz - but our estimate is not too bad given that it's non-relativistic. The important point to notice is that, unlike the fine-structure splitting which increases enormously as we go to heavier atoms, the size of the hyperfine splitting does not change very much between light and heavy atoms.

The caesium clock and the definition of the second

The hyperfine interval in the ground state of Cs defines the SI unit of time, the second. In a caesium atomic clock, the frequency of this interval is used as an extremely precise and stable frequency reference. Look this up (e.g. on wikipedia, or the website of the UK National Physical Laboratory (NPL)).

7.4. Summary of the main points

- Hyperfine structure is due to properties of the nucleus other than its charge, most importantly its magnetic dipole moment and its electric quadrupole moment.
- The hyperfine hamiltonian is of the form $A \hat{\mathbf{I}} \cdot \hat{\mathbf{J}}$.
- It leads to the splitting of energy levels into hyperfine components labelled by the total angular momentum F , which takes values from $|J - I|$ to $J + I$.
- Hyperfine structure is much smaller than fine structure.
- The ground state hyperfine splitting of hydrogen can be calculated quite accurately, and has also been measured to very high precision. It is the origin of the ubiquitous 21cm radiation and is the basis of the hydrogen maser.
- The hyperfine splitting of the ground states of all the alkalis lie in the 1-10 GHz range.
- The hyperfine frequency of the ground state of Cs defines the second.

7.5. To do

- Revise the material in this handout. Useful reading: chapter 9 of Woodgate and sections 6.1 & 6.4 of Foot.
- Read about the hydrogen maser and caesium atomic clock, e.g. on Wikipedia or the website of the National Physical Laboratory (NPL).
- Do questions 1 and 2 from problem set 3.

8. The Zeeman effect

The Zeeman effect describes the interaction of atoms with a static magnetic field. The total magnetic moment of the atom, $\hat{\mu}$, interacts with the applied field, \mathbf{B} , and the energy depends on the relative orientation of the magnetic moment and the magnetic field. The term that we have to add to the total Hamiltonian is

$$\hat{H}_Z = -\hat{\mu} \cdot \mathbf{B}, \quad (8.1)$$

which we treat as a small perturbation.

To find the total magnetic moment of the atom, we have to add up the contributions from all the electrons. For each electron there is a magnetic moment due the orbital motion,

$$\hat{\mu}_l = -g_l \mu_B \hat{\mathbf{l}},$$

and an intrinsic magnetic moment associated with the spin,

$$\hat{\mu}_s = -g_s \mu_B \hat{\mathbf{s}}.$$

Here, the g-factors (along with the constant μ_B) give the constant of proportionality between the magnetic moment and the associated angular momentum: $g_l = 1$ (exactly) and $g_s \approx 2$ (it's slightly greater than 2 because of small QED corrections). Note the sign as well - the magnetic moments point in the opposite direction to the angular momenta. The magnetic moments of the core electrons all cancel out, because their angular momenta add up to zero, so it's only the valence electrons that matter.

We will see that the energy shifts produced by the perturbation are small, even compared to the fine structure. So we suppose that we have already found the energy level structure of the atom down to the level of detail of the fine structure, and our job now is to calculate what happens to these levels when the magnetic field is applied. Remember that the fine structure levels are labelled by the quantum numbers L, S, J and M_J , so our job is to calculate the energy shift of the eigenstates $|L; S; J, M_J\rangle$ due to the perturbation - i.e. to calculate $\langle L; S; J, M_J | \hat{H}_Z | L; S; J, M_J \rangle$. We'll do a complete calculation in a moment, but first we'll make some simple arguments which will give us the correct energy shifts up to a factor of order 1.

8.1. Simple calculation

Since each valence electron has a magnetic moment of order μ_B , the total magnetic moment will also be of order μ_B . This total magnetic moment must be in the same direction as the total angular momentum of the atom, $\hat{\mathbf{J}}$. So, by analogy with the above, we can write

$$\hat{\mu} = -g_J \mu_B \hat{\mathbf{J}}, \quad (8.2)$$

where g_J is a proportionality constant which we expect to be of order 1 (we'll calculate it in a moment). It is customary to set up the coordinate system so that the z-axis is along the magnetic field direction, so that we have $\mathbf{B} = B \hat{\mathbf{z}}$, where $\hat{\mathbf{z}}$ is a unit vector along the z-axis. Using this, along with equations (8.1) and (8.2) we have

$$\hat{H}_Z = g_J \mu_B B \hat{J}_z. \quad (8.3)$$

The energy shift due to the perturbation is

$$\Delta E_Z = \langle L; S; J, M_J | \hat{H}_Z | L; S; J, M_J \rangle = g_J \mu_B B \langle L; S; J, M_J | \hat{J}_z | L; S; J, M_J \rangle = g_J \mu_B B M_J. \quad (8.4)$$

In the last step, we've used the fact that our states are eigenstates of J_z with eigenvalue M_J , i.e. $\hat{J}_z | L; S; J, M_J \rangle = M_J | L; S; J, M_J \rangle$. This result contains all the important information. First, we see that the energy levels of the atom split up into sub-levels with the energy being proportional to M_J (i.e. the projection of the total electronic angular momentum onto the z-axis). This is what we would expect - the energy depends on the relative orientation of μ and \mathbf{B} , and μ is parallel to \mathbf{J} while \mathbf{B} is parallel to the z-axis. We see that the energy splitting is proportional to the magnitude of the magnetic field, which again makes good sense. The approximate size of the energy shift is $\mu_B B$. The value of μ_B is $9.27 \times 10^{-24} \text{ J/T}$. Converting this to a frequency, we get $\mu_B/h \approx 14 \text{ GHz/T}$. Now, 1T is a very large magnetic field. The earth's field, for example, is about $5 \times 10^{-5} \text{ T}$. So in most situations, we expect the field to be less than 1T and the energy level shifts produced by the field to be less than about 10 GHz (this is $4 \times 10^{-5} \text{ eV}$). This is much smaller than the gross energy structure, the splitting of configurations into terms by the residual electrostatic interaction, and (for most atoms), the fine-structure splitting. This explains why we have applied this perturbation last - it's the smallest of all the effects.

8.2. Calculating g_J

Adding up all the contributions to $\hat{\mu}$, our perturbation is

$$\hat{H}_Z = \left(\sum_i g_l \mu_B \hat{\mathbf{l}}_i + g_s \mu_B \hat{\mathbf{s}}_i \right) \cdot \mathbf{B} = (g_l \mu_B \hat{\mathbf{L}} + g_s \mu_B \hat{\mathbf{S}}) \cdot \mathbf{B} = \mu_B B (g_L \hat{L}_z + g_s \hat{S}_z). \quad (8.5)$$

Here, we're using the total orbital and spin angular momenta once again ($\hat{\mathbf{L}} = \sum_i \hat{\mathbf{l}}_i$, $\hat{\mathbf{S}} = \sum_i \hat{\mathbf{s}}_i$, by definition). In the last step we've used the fact that the magnetic field is in the z-direction.

Note that if g_s were equal to g_l (i.e. 1), we would simply have $\hat{H}_Z = \mu_B B (\hat{L}_z + \hat{S}_z) = \mu_B B \hat{J}_z$, and thus $\Delta E_Z = \mu_B B M_J$ - i.e. our g_J factor would just be 1. But g_s is not equal to g_l , and that makes the calculation slightly more complicated.

We have to calculate the expectation values of \hat{L}_z and \hat{S}_z , but our states $|L; S; J, M_J\rangle$ are not eigenstates of \hat{L}_z and \hat{S}_z . Once again, we use the projection theorem, equation (2.18), which states that

$$\langle \hat{L}_z \rangle = \frac{\langle \hat{\mathbf{L}} \cdot \hat{\mathbf{J}} \rangle}{J(J+1)} \langle \hat{J}_z \rangle \quad (8.6)$$

Similarly

$$\langle \hat{S}_z \rangle = \frac{\langle \hat{\mathbf{S}} \cdot \hat{\mathbf{J}} \rangle}{J(J+1)} \langle \hat{J}_z \rangle \quad (8.7)$$

We can calculate these expectation values using methods we've used before. Since $\hat{\mathbf{S}} = \hat{\mathbf{J}} - \hat{\mathbf{L}}$, we have $\hat{\mathbf{L}} \cdot \hat{\mathbf{J}} = \frac{1}{2} (\hat{\mathbf{J}}^2 + \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2)$. So

$$\langle \hat{L}_z \rangle = \frac{\langle \hat{\mathbf{J}}^2 + \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2 \rangle}{2J(J+1)} \langle \hat{J}_z \rangle = \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} M_J \quad (8.8)$$

Similarly,

$$\langle \hat{S}_z \rangle = \frac{\langle \hat{\mathbf{J}}^2 + \hat{\mathbf{S}}^2 - \hat{\mathbf{L}}^2 \rangle}{2J(J+1)} \langle \hat{J}_z \rangle = \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} M_J \quad (8.9)$$

Using equations (8.5), (8.8) and (8.9), and using $g_l = 1$, $g_s = 2$, we find the energy shift to be

$$\Delta E_Z = \left(\frac{3J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \right) \mu_B B M_J \quad (8.10)$$

This has exactly the same form as equation (8.4) - $\Delta E_Z = g_J \mu_B M_J$ - but now we also find the value of g_J (which is known as the Landé g-factor):

$$g_J = \frac{3J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}. \quad (8.11)$$

8.3. An example - the Zeeman effect in helium

Let's apply these results to helium.

In the ground state $1s^2 \ ^1S_0$, there is no angular momentum at all, and so there is no Zeeman effect.

The level $1s2s \ ^1S_0$ also has no Zeeman effect, for the same reason.

For the level $1s2s \ ^3S_1$, we have $L = 0$, $J = S = 1$, and so $g_J = 2$. The level splits into three sub-levels, with $M_J = -1, 0, +1$, separated by $2 \mu_B B$.

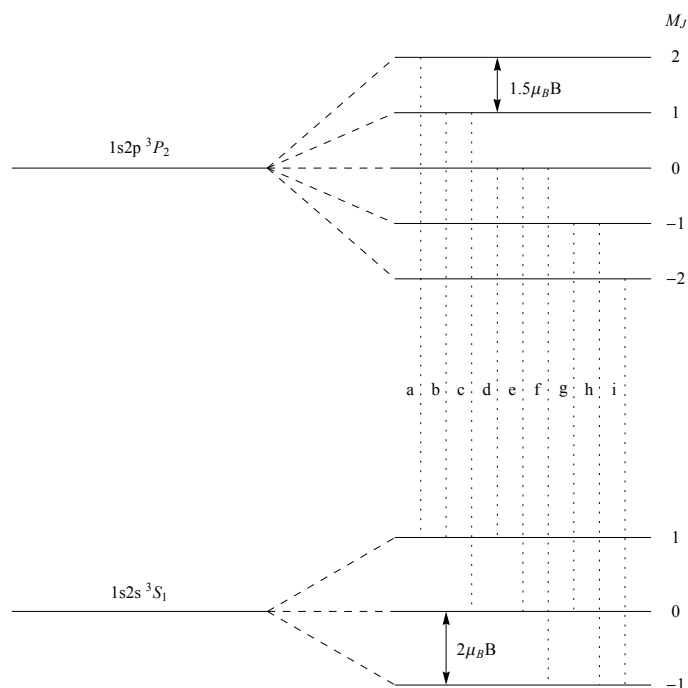
For the $1s2p \ ^1P_1$ level, we have $S = 0$, $J = L = 1$, and so $g_J = 1$. The level splits into three sub-levels, with $M_J = -1, 0, +1$, separated by $\mu_B B$.

For the $1s2p \ ^3P_0$ level, the total angular momentum is zero, so there is no Zeeman effect.

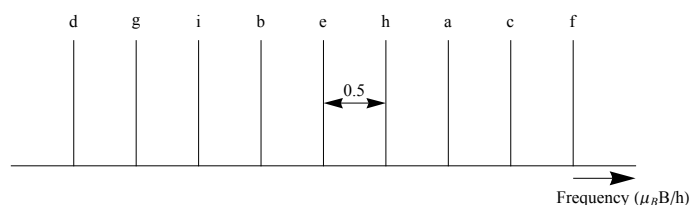
For the $1s2p \ ^3P_1$ level, we have $S = 1$, $L = 1$, $J = 1$, and so $g_J = 3/2$. The level splits into three sub-levels, with $M_J = -1, 0, +1$, separated by $3/2 \mu_B B$.

For the $1s2p \ ^3P_2$ level, we have $S = 1$, $L = 1$, $J = 2$, and so $g_J = 3/2$. The level splits into five sub-levels, with $M_J = -2, -1, 0, +1, +2$, separated by $3/2 \mu_B B$.

Now let's consider a specific transition in helium, say the transition $1s2s \ ^3S_1 - 1s2p \ ^3P_2$. The spectral line corresponding to this transition will be split into components in the presence of a magnetic field. Here's the energy level structure in the field B , with the levels labelled according to their values of M_J . To work out how many components there will be in the spectral line of this transition, we have to apply the selection rule $\Delta M_J = 0, \pm 1$. The allowed transitions are shown by the dotted lines labelled a-i in the figure.



The figure below shows how the spectral line is divided into its components. The labelling of the components is the same as in the figure above. We see that the magnetic field splits the spectral line into 9 components, with the frequency separation between each component being $0.5 \mu_B B/h$. For example, if the applied magnetic field is 1mT, the components will be separated by 7MHz. Satisfy yourself that all this is correct.



8.4. Summary of the main points

- The Zeeman effect splits fine-structure energy levels into sub-levels labelled by the M_J quantum number.
- For weak fields the energy shift is linear in B .
- The energy shift is $\Delta E_Z = g_J \mu_B B M_J$, where g_J is given by equation (8.11). There are $2J + 1$ sub-levels. The weak-field approximation means that the Zeeman splitting is small compared to the fine-structure splitting, which is almost always the case.
- The Zeeman splitting results in a spectral line being split into components whose spacing varies linearly with B (in the weak-field approximation). The spectrum can be worked out from the energy level diagram and the selection rule $\Delta M_J = 0, \pm 1$.

8.5. To do

- Revise the material in this handout. Useful reading: section 8.1 of Woodgate or section 5.5 of Foot.
- Do questions 3 and 4 from problem set 3.

Supplement to lecture 8

We have considered the Zeeman effect of fine-structure levels. It is almost always the case that Zeeman shifts are small compared to the fine-structure splitting, which is why we applied the perturbation due to the magnetic field last. You might also wonder how to calculate the Zeeman effect when there is hyperfine structure. This is an advanced topic which is beyond the syllabus for this course, but is given here in case you are interested.

8.7. Zeeman effect including hyperfine structure

So far we neglected the hyperfine structure in our discussion of the Zeeman effect. Now let's include it. Taking the Zeeman interaction and the hyperfine interaction together we have the perturbation

$$\hat{H}' = \hat{H}_{\text{hfs}} + \hat{H}_Z = A \hat{\mathbf{I}} \cdot \hat{\mathbf{J}} + \mu_B B (g_I \hat{L}_z + g_S \hat{S}_z), \quad (8.12)$$

where, as before, we have taken the magnetic field to be in the z direction, and we have $g_I = 1$, $g_S = 2$. The approach to finding the total energy shifts depends on whether the Zeeman shifts are small or large compared to the hyperfine structure.

Weak magnetic field

We'll first consider the case of small magnetic fields. Here, small means that the Zeeman splitting is much smaller than the hyperfine splitting (i.e. $\mu_B B \ll A$). In this case, we deal with the hyperfine structure first. For a first approximation, we neglect the Zeeman terms \hat{H}_Z in equation (8.12) and calculate the energy level shifts due to \hat{H}_{hfs} alone. This is the calculation we already did in lecture 7. Now we have energy levels split by the hyperfine interaction and labelled by the total angular momentum quantum number F (remember that $\hat{\mathbf{F}} = \hat{\mathbf{I}} + \hat{\mathbf{J}}$). We write the eigenstates using the labels $|I; J; F, M_F\rangle$ to remind us that they are eigenstates of $\hat{\mathbf{I}}^2$, $\hat{\mathbf{J}}^2$, $\hat{\mathbf{F}}^2$ and \hat{F}_z .

Next we calculate the energy shift due to the magnetic field using perturbation theory, with these states as our basis states. The perturbation is $\hat{H}_Z = \mu_B B (g_I \hat{L}_z + g_S \hat{S}_z)$. Following exactly the same arguments presented above, this can be re-written as $\hat{H}_Z = g_J \mu_B B \hat{J}_z$ where g_J is given by equation (8.11). The only remaining task is to calculate $\langle \hat{H}_Z \rangle$ using our $|I; J; F, M_F\rangle$ eigenstates:

$$\Delta E_Z = \langle \hat{H}_Z \rangle = g_J \mu_B B \langle I; J; F, M_F | \hat{J}_z | I; J; F, M_F \rangle. \quad (8.13)$$

Note that $|I; J; F, M_F\rangle$ is not an eigenstate of \hat{J}_z , but we can again use the vector model to sort this out. In fact, the calculation is almost exactly the same as in lecture 8. We project $\hat{\mathbf{J}}$ onto $\hat{\mathbf{F}}$, and then project $\hat{\mathbf{F}}$ onto the z-axis, obtaining

$$\langle \hat{J}_z \rangle = \left\langle \frac{(\hat{\mathbf{J}} \cdot \hat{\mathbf{F}}) \hat{F}_z}{\hat{\mathbf{F}}^2} \right\rangle = \frac{1}{2} \left\langle \frac{(\hat{\mathbf{F}}^2 + \hat{\mathbf{J}}^2 - \hat{\mathbf{I}}^2) F_z}{\hat{\mathbf{F}}^2} \right\rangle = \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} M_F \quad (8.14)$$

So the energy shift is now given by

$$\Delta E_Z = g_F \mu_B B M_F, \quad (8.15)$$

where the new g-factor that has appeared is

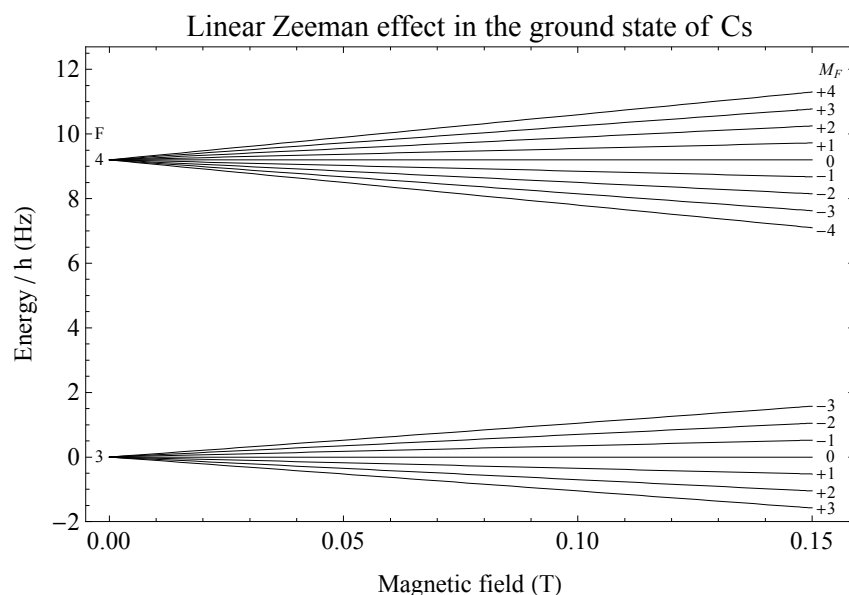
$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)}. \quad (8.16)$$

Notice that, just as before, the energy shift is linear in B and the levels are split according to the quantum number M_F - the projection of the total angular momentum onto the z-axis. The only thing that has changed is the g-factor - from g_J given by equation (8.11) to g_F given by equation (8.16).

Example: the Zeeman effect in the ground state of Cs

We looked at the ground state hyperfine structure of Cs in lecture 7. Now we can calculate the Zeeman effect of this hyperfine structure. In the ground state of Cs, we have $L = 0$, $S = J = 1/2$ and $I = 7/2$. So we get two hyperfine levels, $F = 3$ and $F = 4$, separated by the 9.2GHz hyperfine interval. The value of g_J for the ground state is $g_J = 2$. This should be obvious from the fact that the only contribution to the magnetic moment comes from the spin of the single valence electron, so we must have $g_J = g_S = 2$. Alternatively, you can see it from equation (8.11) with $L = 0$ and $J = S$. From equation (8.16) we get the values of g_F : $g_F = -1/4$ for $F = 3$, and $g_F = +1/4$ for $F = 4$.

The graph below shows the Zeeman splitting of the two hyperfine energy levels as a function of magnetic field. The zero of energy is placed (arbitrarily) at the $F = 3$ energy in zero field. Note that the Zeeman splitting is indeed small compared to the hyperfine splitting, at least for fields up to about 0.1T. In most applications of interest the magnetic fields tend to be quite a bit smaller than this and so our picture is good. If we go to higher fields the approximation that we've made starts to break down.



Strong magnetic field

Now let's consider the opposite extreme, where the Zeeman splitting is much larger than the hyperfine structure ($\mu_B B \gg A$). This is also easy to calculate. We simply reverse the order in which we apply the perturbations. First we neglect the hyperfine interaction, and calculate the Zeeman splitting of the fine structure levels. We already did the first step - calculating the Zeeman splitting with the hyperfine structure neglected. The Zeeman splitting is simply $\Delta E_Z = g_J \mu_B B M_J$. The eigenstates are eigenstates of \hat{J}^2 and \hat{J}_Z , and also of \hat{I}^2 and \hat{I}_Z (since the hyperfine interaction hasn't yet been introduced). So our basis states are $|I, M_I; J, M_J\rangle$.

Now we treat the hyperfine interaction as a perturbation using these basis states. The energy shift is given by

$$\Delta E_{\text{hfs}} = \langle A \hat{I} \cdot \hat{J} \rangle = \langle I, M_I; J, M_J | A \hat{I} \cdot \hat{J} | I, M_I; J, M_J \rangle. \quad (8.17)$$

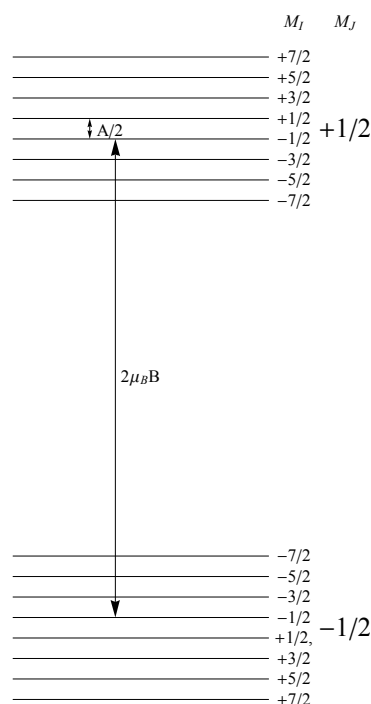
In the vector model, \hat{J} is precessing rapidly around the z-axis because of the strong Zeeman interaction and so the \hat{J}_x and \hat{J}_y components time-average to zero. So the only term in $\hat{I} \cdot \hat{J}$ that contributes to the expectation value is $\hat{I}_z \hat{J}_z$. So we obtain

$$\Delta E_{\text{hfs}} = \langle A \hat{I}_z \hat{J}_z \rangle = A M_I M_J. \quad (8.18)$$

The total energy shift in a strong field is thus given by

$$\Delta E = g_J \mu_B B M_J + A M_I M_J. \quad (8.19)$$

The picture below shows the energy levels for the ground state of Cs in a large magnetic field. Here the large interval is $2\mu_B B$ and the small interval is $A/2$.



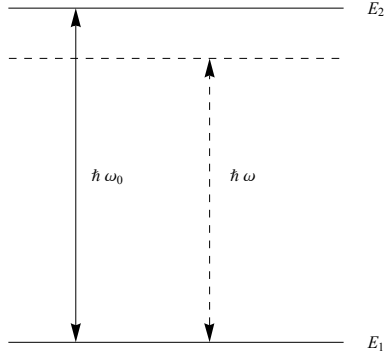
For intermediate strengths of magnetic field, we can't arrange the terms as a hierarchy of perturbations, and we have no choice but to set up the matrix representation of H' and diagonalize this to find the eigenvalues. However, without doing any calculations at all, we can easily link the energy levels obtained in the weak-field limit to those obtained in the strong field limit using the following two rules: (1) The total magnetic quantum number is $M_F = M_I + M_J$ and can be used to label the states at all values of the field, (2) States with the same values of M_F cannot cross one another. I'll leave it to you to make the diagram showing how the low-field levels connect to the high field ones.

Summary of this advanced topic

- The Zeeman effect splits a hyperfine level into sub-levels labelled by the M_F quantum number.
- For weak fields the energy shift is linear in B .
- For weak fields, the energy shift is $\Delta E_Z = g_F \mu_B B M_J$, where g_F is given by equation (8.16). There are $2F + 1$ sub-levels. The weak-field approximation means that the Zeeman splitting is small compared to the hyperfine-structure splitting, which is often the case, but not always.
- For strong fields, the perturbations are taken in the opposite order - first the Zeeman effect and then the hyperfine interaction. Energy levels are labelled by the quantum numbers M_J and M_I . There is a large splitting of $g_J \mu_B B M_J$ due to the magnetic field, and then a smaller splitting of $A M_I M_J$ due to the hyperfine interaction.
- There is no remaining degeneracy in a magnetic field.
- The spectrum can be worked out from the energy level diagram and the selection rule $\Delta M_F = 0, \pm 1$.

9. Interaction of atoms with an oscillating field

So far, we have studied in some detail the energy level structure of atoms. We have done this for free atoms, and for atoms in the presence of static fields. Next, we want to understand what happens when the atom is subjected to an oscillating field - i.e. to an electromagnetic wave. This is a complicated subject, but we will specialize to a particular case which is fairly simple and is of enormous practical importance. We consider an atom that has just two energy levels. We suppose that we have already solved the time-independent Schrödinger equation for the free atom - the eigenfunctions and eigenvalues are ϕ_1, ϕ_2 and E_1, E_2 , and the separation of the levels is $\hbar \omega_0 = E_2 - E_1$. Now we introduce an electric field that is oscillating at frequency ω , and we want to find out what happens. We are most interested in the case where the oscillating field is close to being in resonance with the atom, i.e. $\omega \approx \omega_0$, for it is at this frequency that we can expect something interesting to happen. A schematic representation of the situation we have is drawn below:



Because the electric field depends on time, we need to solve the time-dependent Schrödinger equation.

9.1. Solving the time-dependent Schrödinger equation for a two level atom interacting with an oscillating field

We write the electric field as $\mathcal{E} = \mathcal{E}_0 \cos(\omega t)$, where \mathcal{E}_0 contains all the spatial dependence of the wave. The time-dependent Schrödinger equation is

$$i \hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi, \quad (9.1)$$

where \hat{H} is the total Hamiltonian for the system. This we write as a sum of two parts, $\hat{H} = \hat{H}_0 + \hat{H}_I$. \hat{H}_0 is the Hamiltonian for the free atom, whose eigenfunctions and eigenvalues we've already found: $\hat{H}_0 \phi_1 = E_1 \phi_1$ and $\hat{H}_0 \phi_2 = E_2 \phi_2$. \hat{H}_I is the term that describes the interaction between the atom and the radiation, and the main part of this interaction is between the oscillating electric field and the charges of the electrons that make up the atom. The interaction Hamiltonian between the charges and the electric field of the light is

$$\hat{H}_I = -\hat{\mathbf{d}} \cdot \mathcal{E}_0 \cos(\omega t) \quad (9.2)$$

where $\hat{\mathbf{d}}$ is the atom's electric dipole moment operator. The derivation of this interaction Hamiltonian is covered in the Quantum Optics course, but you can easily see how it comes about by thinking about hydrogen in an applied electric field. If $\phi(\mathbf{r})$ is the electric potential of the applied field, then the interaction energy is $W = e \phi(0) - e \phi(r)$ where the first term is for the proton (at the origin) and the second for the electron (at r). For a field that doesn't change too rapidly over the size of the atom we can do a Taylor expansion of ϕ : $\phi(\mathbf{r}) \approx \phi(0) + \mathbf{r} \cdot \nabla \phi$. Using $\mathcal{E} = -\nabla \phi$, and the definition of a dipole moment $\mathbf{d} = -e \mathbf{r}$, we see that the interaction energy is $W \approx -\mathbf{d} \cdot \mathcal{E}$. This gives us the above interaction Hamiltonian. For definiteness, let's suppose that the electric field is pointing along the z-axis. Then

$$\hat{H}_I = -\hat{d}_z \mathcal{E}_0 \cos(\omega t). \quad (9.3)$$

In the absence of the radiation, ϕ_1 and ϕ_2 are stationary states, their only time-dependence being the usual $e^{-i E_1 t / \hbar}$ and $e^{-i E_2 t / \hbar}$. In the presence of the radiation, we can, quite generally, expand the full wavefunction in terms of these eigenstates:

$$\Psi(t) = c_1(t) \phi_1 e^{-i E_1 t / \hbar} + c_2(t) \phi_2 e^{-i E_2 t / \hbar}. \quad (9.4)$$

Here, c_1 and c_2 are coefficients that depend on time. Our whole task is to calculate these coefficients - once we know them we know the complete wavefunction at all times and so the problem is solved. We need to substitute this $\Psi(t)$ into the time-dependent Schrödinger equation. The left hand side is

$$i \hbar \frac{\partial \Psi}{\partial t} = c_1 \phi_1 E_1 e^{-i E_1 t / \hbar} + c_2 \phi_2 E_2 e^{-i E_2 t / \hbar} + i \hbar \frac{d c_1}{d t} \phi_1 e^{-i E_1 t / \hbar} + i \hbar \frac{d c_2}{d t} \phi_2 e^{-i E_2 t / \hbar}$$

and the right hand side is

$$\hat{H} \Psi = \hat{H}_0 \Psi + \hat{H}_I \Psi = c_1 \phi_1 E_1 e^{-i E_1 t / \hbar} + c_2 \phi_2 E_2 e^{-i E_2 t / \hbar} + c_1(t) \hat{H}_I \phi_1 e^{-i E_1 t / \hbar} + c_2(t) \hat{H}_I \phi_2 e^{-i E_2 t / \hbar}$$

So, the Schrödinger equation gives us

$$i \hbar \frac{d c_1}{d t} \phi_1 e^{-i E_1 t / \hbar} + i \hbar \frac{d c_2}{d t} \phi_2 e^{-i E_2 t / \hbar} = c_1(t) \hat{H}_I \phi_1 e^{-i E_1 t / \hbar} + c_2(t) \hat{H}_I \phi_2 e^{-i E_2 t / \hbar}. \quad (9.5)$$

Multiply by $\phi_1^* e^{i E_1 t / \hbar}$ and integrate over all space, using the orthonormality of the ϕ 's:

$$i \hbar \frac{dc_1}{dt} = c_1 \int \phi_1^* \hat{H}_I \phi_1 dV + c_2 e^{-i(E_2 - E_1)t/\hbar} \int \phi_1^* \hat{H}_I \phi_2 dV$$

Because the atom is so much smaller than the wavelength of light, the amplitude E_0 is very nearly a constant over the whole region where the eigenfunctions are non-zero and we can take it outside the integral. This is called the *dipole approximation*. Then, using $\omega_0 = (E_2 - E_1)/\hbar$ and $\cos(\omega t) = \frac{1}{2}(e^{i\omega t} + e^{-i\omega t})$, the above equation becomes

$$i \hbar \frac{dc_1}{dt} = -c_1 \frac{\mathcal{E}_0}{2} (e^{i\omega t} + e^{-i\omega t}) \int \phi_1^* \hat{d}_z \phi_1 dV - c_2 \frac{\mathcal{E}_0}{2} (e^{-i(\omega + \omega_0)t} + e^{i(\omega - \omega_0)t}) \int \phi_1^* \hat{d}_z \phi_2 dV$$

The eigenfunctions are states of definite parity, either odd or even. The electric dipole operator changes sign when we invert the coordinates ($r \rightarrow -r$), and so it is an odd operator. It follows that the first integral is an integral over all space of an odd function, and so it is zero. This leaves us with

$$i \hbar \frac{dc_1}{dt} = -c_2 \frac{\mathcal{E}_0}{2} (e^{-i(\omega + \omega_0)t} + e^{i(\omega - \omega_0)t}) \int \phi_1^* \hat{d}_z \phi_2 dV$$

The first term on the right hand side oscillates at frequency $\omega + \omega_0 \approx 2\omega_0$, whereas the second term oscillates at frequency $\omega - \omega_0$ which is very much slower. The effect of the rapidly oscillating term time-averages to zero on any timescale of interest to us, and so it is only the slowly-varying term that has any significant effect on the atom. Therefore, we keep only the slowly-varying term (this is known as the rotating-wave approximation) and end up with the following differential equation:

$$i \frac{dc_1}{dt} = \frac{\Omega}{2} e^{i(\omega - \omega_0)t} c_2, \quad (9.6)$$

where we have defined the quantity

$$\Omega = -\frac{\mathcal{E}_0}{\hbar} \int \phi_1^* \hat{d}_z \phi_2 dV = -\frac{\mathcal{E}_0}{\hbar} \langle 1 | \hat{d}_z | 2 \rangle. \quad (9.7)$$

Similarly, if we return to equation (9.5) and this time multiply by $\phi_2^* e^{i E_2 t / \hbar}$ and then integrate and apply the same rotating wave approximation we get

$$i \frac{dc_2}{dt} = \frac{\Omega}{2} e^{-i(\omega - \omega_0)t} c_1. \quad (9.8)$$

We can combine (9.6) and (9.8) to obtain an equation for just c_2 :

$$\frac{d^2 c_2}{dt^2} + i(\omega - \omega_0) \frac{dc_2}{dt} + \frac{\Omega^2}{4} c_2 = 0. \quad (9.9)$$

This differential equation tells us how the amplitude of state 2 changes with time. If at $t = 0$ the atom is in level 1 (i.e. $c_1(0) = 1$, $c_2(0) = 0$), the solution for the probability of being in level 2 (i.e. for $|c_2(t)|^2$) is

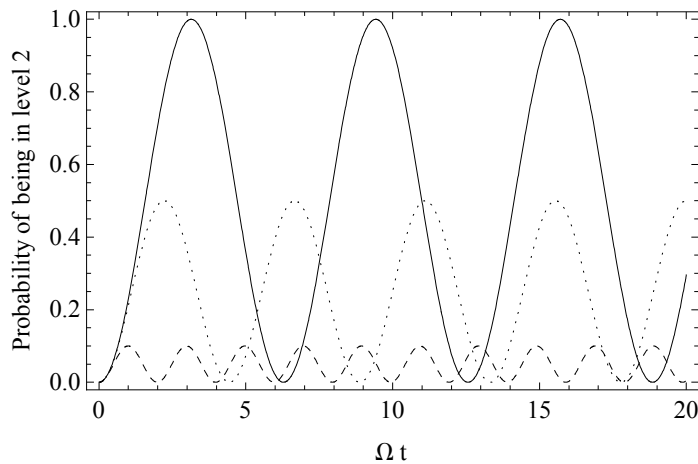
$$|c_2(t)|^2 = \frac{\Omega^2}{\Omega^2 + \delta^2} \sin^2\left(\frac{1}{2} \sqrt{\Omega^2 + \delta^2} t\right), \quad (9.10)$$

where we have defined $\delta = \omega - \omega_0$, which is the *detuning* of the light from the atom's resonance frequency.

9.2. Rabi oscillations and π -pulses

We see that *the probability oscillates sinusoidally between the two levels*. When the light is on resonance with the atom ($\delta = 0$), we have $|c_2(t)|^2 = \sin^2(\frac{1}{2} \Omega t)$ - the probability of being in the upper state oscillates between 0 and 1 with the characteristic angular frequency Ω - the oscillations are called *Rabi oscillations* and Ω is called the *Rabi frequency* (after I. I. Rabi, who first demonstrated the effect). As we increase the frequency detuning of the light from the atomic resonance frequency (increase $|\delta|$), the amplitude of the oscillations gets smaller, and the frequency gets larger.

The plot below shows the probability of finding the atom in level 2 as a function of time (expressed as the product Ωt), for three different values of the detuning - $|\delta| = 0$ (solid line), $|\delta| = \Omega$ (dotted line) and $|\delta| = 3\Omega$ (dashed line).



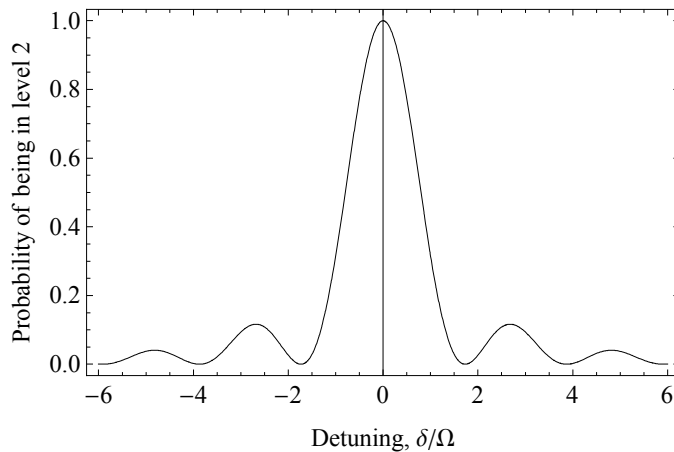
Suppose the atom is in level 1 and we apply a pulse of radiation which is on resonance. We can control the Rabi frequency Ω by controlling the intensity of the radiation, and we can choose the duration of the pulse, T . If we make $\Omega T = \pi$, the atom will be transferred from level 1 to level 2 with 100% probability. A pulse that satisfies this condition is called a π -pulse.

To get a feel for the numbers, let's calculate an approximate size for the Rabi frequency. It is given by equation (9.7) - $|\Omega| = \frac{\mathcal{E}_0}{\hbar} \langle 1 | \hat{d}_z | 2 \rangle$. Let's suppose we use a 100mW laser, focussed to a round spot of 1mm diameter, to drive the 2s-3p transition in hydrogen at 656nm. Using the hydrogenic eigenfunctions we find that $\langle 2s | e \hat{z} | 3p \rangle = \frac{27}{128} \sqrt{2} e a_0$. The intensity of the light is related to the electric field by $I = \frac{1}{2} \epsilon_0 c \mathcal{E}_0^2$. If we suppose that the intensity is uniform inside the round spot, we get an electric field $\mathcal{E}_0 \approx 10^4 \text{ V/m}$. In this case, the Rabi frequency is $2.4 \times 10^8 \text{ rad/s}$. This is very slow compared to the transition angular frequency (which is $2.9 \times 10^{15} \text{ rad/s}$ in this case).

Note that although we have treated the case of an atom with just two energy levels, the same theory works extremely well for multi-level atoms where the radiation is tuned close to resonance to one of the transition frequencies - the atom undergoes Rabi oscillations between these two particular levels, and nothing happens to any of the other levels.

9.3. Resonance lineshape

We might also wonder how the transition probability depends on the detuning from resonance. To see this, we set $\Omega T = \pi$, so that the transition probability is 1 on resonance, and then plot equation (9.10) as a function of the detuning δ . The result is plotted below - this is the characteristic resonance lineshape for an atom interacting with monochromatic radiation.



9.4. Types of transition

The atom interacts most strongly with the electric part of the electromagnetic field. However, there are many transitions where $\langle 1 | \hat{d}_z | 2 \rangle = 0$, meaning that the Rabi frequency is zero and so the transition cannot be driven by the oscillating electric field. In this case, we say that this *electric dipole transition* is forbidden. Then, the weaker interaction with the oscillating magnetic field becomes important. To give an example, the transition between the two hyperfine levels of ground state hydrogen cannot be driven by an oscillating electric field, but can be driven by an oscillating magnetic field - the electric dipole transition is forbidden, but the magnetic dipole transition is allowed. Recall that the hyperfine interaction is an interaction between the magnetic moments of the electron and nucleus. The difference in energy between hyperfine levels arises due to the relative orientations of the magnetic moments - the energy depends on whether these magnetic moments are parallel, antiparallel, or somewhere in-between. A transition between hyperfine levels requires the re-orientation of the magnetic moments, and so it is no surprise that it's the oscillating magnetic field that drives this transition. In this case, the interaction Hamiltonian changes from equation (9.2) to

$$\hat{H}_I = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B}_0 \cos(\omega t) \quad (9.11)$$

where $\hat{\boldsymbol{\mu}}$ is the atom's magnetic dipole moment operator, and \mathbf{B}_0 is the magnetic field of the electromagnetic radiation. With this, we can follow exactly the same theory as before, and all our results will be exactly the same, except that now we have an alternative Rabi frequency given by

$$\Omega' = -\frac{B_0}{\hbar} \langle 1 | \hat{\mu}_z | 2 \rangle. \quad (9.12)$$

The hyperfine transition in ground-state hydrogen is the 1.42GHz (21cm wavelength) transition that we calculated in lecture 7. So using microwave radiation tuned exactly to this transition frequency, it is possible to drive Rabi oscillations between the two hyperfine components of the ground state.

There are other higher-order transitions too, for example electric quadrupole transitions. All of these have much slower rates than electric dipole transitions and are only important when the electric dipole transition is forbidden. You do not need to know about these higher-order transitions for this course.

9.5. Summary of the main points

- When a two-level atom interacts with radiation near resonance the probability oscillates between the two states.
- The behaviour is the same for a multi-level atom - only the two levels that are close to resonance with the radiation matter.
- On resonance, the probability oscillates fully (i.e. between 0 and 1). The angular frequency of this oscillation is the Rabi frequency.
- The Rabi frequency is proportional to the amplitude of the oscillating electric field, and to the matrix element of the electric dipole moment operator between the two states.
- As the radiation is detuned from the resonance frequency, the oscillation goes faster and the amplitude gets smaller.

9.6. To do

- Revise the material in this handout. Useful reading: sections 7.1 & 7.3 of Foot.
- Do questions 6 and 7 from problem set 3.

10. The atom as an oscillating dipole

In the last lecture, we found that when an atom interacts with a near-resonant oscillating field, the probability of being in the excited state oscillates back and forth. When the resonance condition is met, the amplitude of these oscillations is maximal (from 0 to 1), and the angular frequency of the oscillations occurs at the Rabi frequency. According to our theory, these oscillations continue for as long as the oscillating field is turned on. The atom starts out in state 1, absorbs energy from the oscillating field as it gradually transitions to state 2, and then returns the energy to the field as it returns to state 1. It's like a continual process of absorption from the field followed by stimulated emission back into the field. Spontaneous emission seems to play no role in our theory.

If we include spontaneous emission in our theory, we find that the Rabi oscillations are damped out and the populations in the two levels eventually reach a steady state. The characteristic damping time is simply the excited state lifetime. We will find that for an electric dipole transition between two different electronic states, which typically lies in the visible or ultra-violet part of the spectrum, the lifetime is typically just a few nanoseconds, and the Rabi oscillations are damped out on this timescale. In fact, it is very difficult indeed to observe Rabi oscillations in this case, because the damping time is so fast. At the opposite extreme is the hyperfine transition in the ground state of hydrogen. The natural lifetime of the upper level turns out to be about 10 million years, so then you only see the Rabi oscillations, with no damping, exactly as described by the above theory.

But why does spontaneous emission not just appear naturally in our theory. What is it that we left out? The answer is that we've used a quantized atom interacting with a classical electromagnetic field. For a complete and proper description, we should quantize the electromagnetic field as well. When you quantize the electromagnetic field, you find that there are zero-point fluctuations (just like in a harmonic oscillator where the ground state energy is not zero but $1/2 \hbar \omega$) - they are the fluctuations of the vacuum. These vacuum fluctuations drive the electron, in much the same way as real radiation drives it. For an atom in an excited state, resonant radiation causes stimulated emission, whereas the vacuum fluctuations cause spontaneous emission. It is only when you quantize the electromagnetic field that an excited atom is able to decay. *Vacuum really does have these zero-point fluctuations - if it did not there would be no light!*

10.1. Introducing damping

A proper treatment of the spontaneous decay comes from quantum electrodynamics, but this is outside the scope of this course. Instead, we introduce the decay by adding a decay term to the equation for the excited state amplitude. Recall from lecture 9 that we wrote the time-dependent amplitudes of the two states of an atom as c_1 and c_2 , and we found the equations for these amplitudes by solving the time-dependent Schrodinger equation - these are equations (9.6) and (9.8) which we repeat here:

$$\frac{dc_1}{dt} = -i \frac{\Omega}{2} e^{i(\omega - \omega_0)t} c_2, \quad (10.1)$$

$$\frac{dc_2}{dt} = -i \frac{\Omega}{2} e^{-i(\omega - \omega_0)t} c_1. \quad (10.2)$$

We add a damping term to equation (10.2) so that it reads

$$\frac{dc_2}{dt} = -i \frac{\Omega}{2} e^{-i(\omega - \omega_0)t} c_1 - \frac{\Gamma}{2} c_2. \quad (10.3)$$

The extra term just says that the decay rate of the amplitude is proportional to the amplitude and to a decay constant $\Gamma/2$. We might wonder whether we should also modify the equation for c_1 , equation (10.1), but we won't actually need this equation in what follows.

10.2. Free atom

First suppose that there is no driving field, $\Omega = 0$. Then the solution of equation (10.3) is

$$c_2(t) = c_2(0) \exp(-\Gamma t/2), \quad (10.4)$$

and the corresponding probability of being in the upper state is

$$|c_2(t)|^2 = |c_2(0)|^2 \exp(-\Gamma t). \quad (10.5)$$

So we get the required exponential decay of the upper state population, which justifies the form of the damping term we added. The decay rate Γ is the inverse of the upper state lifetime.

Let's now return to the complete wavefunction of the atom:

$$\Psi = c_1 \phi_1 e^{-i E_1 t/\hbar} + c_2 \phi_2 e^{-i E_2 t/\hbar}.$$

We'll take c_1 and c_2 to be real to keep things simple. The probability distribution is

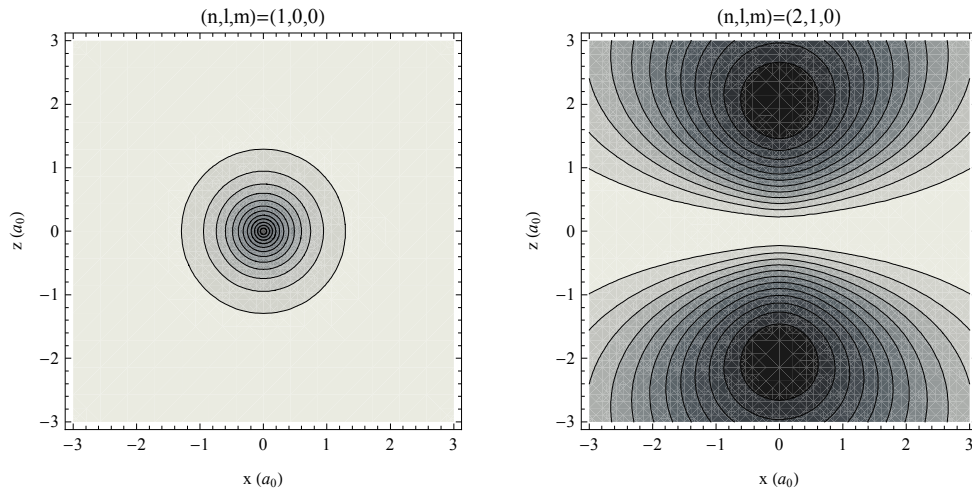
$$P = |\Psi|^2 = c_1^2 \phi_1^2 + c_2^2 \phi_2^2 + c_1 c_2 \phi_1 \phi_2 (e^{i(E_2 - E_1)t/\hbar} + e^{-i(E_2 - E_1)t/\hbar}).$$

Writing $\hbar \omega_0 = E_2 - E_1$, this is

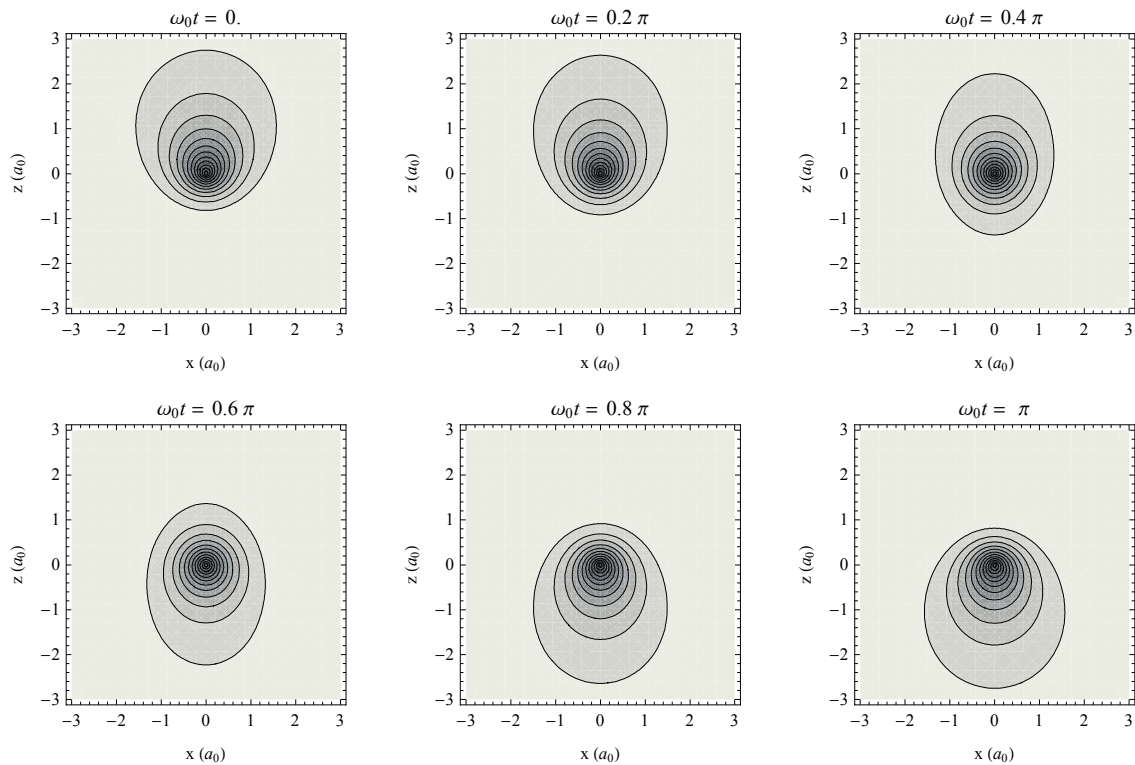
$$P = c_1^2 \phi_1^2 + c_2^2 \phi_2^2 + 2 c_1 c_2 \phi_1 \phi_2 \cos(\omega_0 t). \quad (10.6)$$

The probability distribution is not just the sum of the two individual probability distributions for ϕ_1 and ϕ_2 (weighted by the square of their amplitudes in the superposition). There is an extra term, which we can think of as an interference term between the two parts of the superposition. This term oscillates at the transition angular frequency ω_0 .

Let's look at the example of the hydrogen atom prepared in the superposition of states $\phi_1 = \phi_{1,0,0}$ and $\phi_2 = \phi_{2,1,0}$, where $\phi_{n,l,m}$ is the hydrogen wavefunction with quantum numbers (n, l, m) . First, it's helpful to remind ourselves of what the individual eigenstates look like. Here are their probability distributions in the xz -plane. The axes are in units of the Bohr radius a_0 . The shading indicates the probability density (black for high probability, white for low), and the lines are contours of constant probability density. These distributions don't depend on the ϕ coordinate so you get the full 3D picture by rotating these 2D pictures around the z -axis.



Now look at the probability distribution for the superposition state. The time-dependence comes both from the $\cos(\omega_0 t)$ factor, and the $e^{-\Gamma t/2}$ dependence of c_2 (and correspondingly, c_1). However, for an atom, ω_0 is vastly larger than Γ . For a typical visible transition for example, $\omega_0 \sim 4 \times 10^{15}$ rad/s, while $\Gamma \sim 4 \times 10^7$ rad/s. So, for looking at the rapid oscillation at ω_0 we can just take c_1, c_2 to be constant. We'll choose $c_1^2 = 1/4$, $c_2^2 = 3/4$ and plot the probability distribution at various moments in time, using the same representation as above. Here they are, for times spanning one half-cycle of the oscillation.



We see the electron probability distribution changing in time, oscillating back and forth with an angular frequency of ω_0 corresponding to the energy difference between the two states. This probability distribution is just the electron's charge distribution (after multiplying by $-e$), and so we see that the electron charge distribution is oscillating back and forth around a (very nearly) stationary nucleus. This looks very similar indeed to a classical oscillating electric dipole (just that the electron charge is smeared out a bit).

An electric dipole moment is the charge times the displacement, and so for the one-electron atom the electric dipole moment operator is $\hat{d} = -e\hat{r}$, where r is the distance of the electron from the origin. For a many-electron atom, we have to sum over all electrons. We can get a step closer to the classical picture of an oscillating electric dipole by calculating the expectation value of the electric dipole moment operator, i.e. $\langle \hat{d} \rangle = \langle \Psi | \hat{d} | \Psi \rangle$:

$$\langle \hat{d} \rangle = \langle \Psi | \hat{d} | \Psi \rangle = \int \Psi^* \hat{d} \Psi dV = |c_1|^2 \int \phi_1^* \hat{d} \phi_1 dV + |c_2|^2 \int \phi_2^* \hat{d} \phi_2 dV + c_1^* c_2 e^{-i(E_2-E_1)t/\hbar} \int \phi_1^* \hat{d} \phi_2 dV + c_1 c_2^* e^{i(E_2-E_1)t/\hbar} \int \phi_2^* \hat{d} \phi_1 dV$$

The first two integrals on the right hand side are both zero because their integrands are odd functions of the coordinates. This is because $\hat{d} = -e\hat{r}$ is odd (changes sign when $\mathbf{r} \rightarrow -\mathbf{r}$), and ϕ_1 and ϕ_2 are both states of definite parity (i.e. they are either even or odd functions). The last two integrals are equal to one another and can be non-zero, provided ϕ_1 and ϕ_2 are of opposite parity. So, using the notation $d_{12} = \langle 1 | \hat{d} | 2 \rangle = \int \phi_1^* \hat{d} \phi_2 dV$, we get

$$\langle \hat{d} \rangle = d_{12} (c_1^* c_2 e^{-i\omega_0 t} + c_1 c_2^* e^{i\omega_0 t}). \quad (10.7)$$

In the case where c_1, c_2 are real, this becomes

$$\langle \hat{d} \rangle = 2 c_1 c_2 d_{12} \cos(\omega_0 t). \quad (10.8)$$

So we see that the expectation value of the dipole moment oscillates at angular frequency ω_0 . The amplitude of the oscillation is proportional to the product $c_1 c_2$ (whose maximum possible value is 1/2), and to d_{12} which is the *matrix element of the dipole operator between states 1 and 2*. Its value depends on the chosen states, but is typically about $-ea_0$. The oscillation decays away with a characteristic rate Γ , but we would have to watch a vast number of cycles to notice that (about 100 million cycles for a transition in the visible, and vastly more than that for lower frequencies).

Recall from year 2 electromagnetism that radiation is produced by an accelerating charge. In fact, you studied exactly this problem of an oscillating electric dipole moment and the radiation that it emits. Since our atom looks very much like this oscillating dipole, it should emit radiation at angular frequency ω_0 . Once again, the oscillation is damped, and so the emitted radiation will be a damped wave, lasting a time of approximately $1/\Gamma$ (i.e. the upper state lifetime). The radiation carries away energy, which is why the atom's oscillation must be damped. This is a semi-classical picture of how atoms emit light ("semi-classical" because the atom is quantized but the light is not).

10.3. An atom being driven by an electromagnetic field

Now let's return to the more general case of an atom interacting with an electromagnetic field, equations (10.1) and (10.3). To make the equations easier to solve, we make the approximation that the atom is being driven only weakly by the field, so that the upper state population is always very small. This is a very good approximation for most situations - for example, a typical atom with a transition in the visible, exposed to direct sunlight on Earth, will have $c_2 \sim 10^{-14}$. So we solve equation (10.3) with $c_1 = 1$:

$$\frac{dc_2}{dt} = -i \frac{\Omega}{2} e^{-i(\omega-\omega_0)t} - \frac{\Gamma}{2} c_2. \quad (10.9)$$

The solution to this equation, with initial condition $c_2(0) = 0$ is

$$c_2(t) = \frac{i\Omega}{\Gamma - 2i\delta} (e^{-\Gamma t/2} - e^{-i\delta t}), \quad (10.10)$$

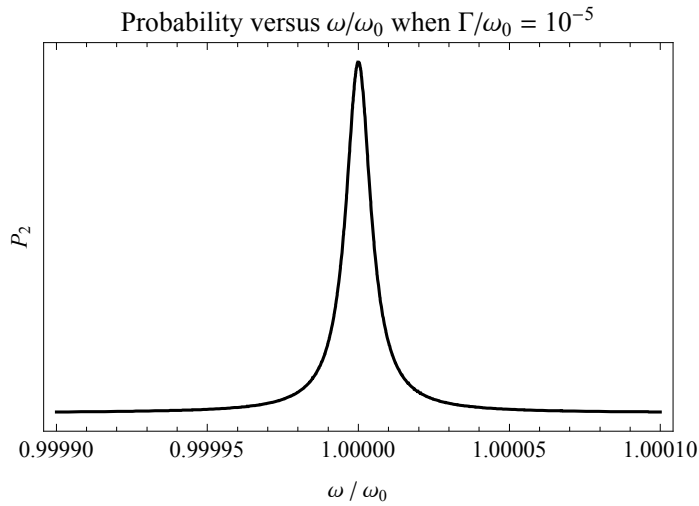
where, as before, we've used the shorthand $\delta = \omega - \omega_0$. The upper state probability is

$$P_2(t) = |c_2(t)|^2 = \frac{\Omega^2}{\Gamma^2 + 4\delta^2} (1 + e^{-\Gamma t} - 2e^{-\Gamma t/2} \cos(\delta t)). \quad (10.11)$$

We see that there is an initial transient which decays away on a timescale of order $1/\Gamma$ (i.e. the upper state lifetime) towards a steady state. For transitions in the visible, the transient typically only lasts about 10ns, so we usually are interested only in the steady-state probability which is

$$P_2(t \rightarrow \infty) = \frac{\Omega^2}{\Gamma^2} \left(\frac{\Gamma^2}{\Gamma^2 + 4(\omega - \omega_0)^2} \right). \quad (10.12)$$

This is an important result because it tells us how (in the weakly-driven limit) the transition probability of an atom depends on the frequency of the light. The term in brackets will keep appearing over the next few lectures. The function is a Lorentzian, and it is plotted below versus ω/ω_0 for the case where $\Gamma/\omega_0 = 10^{-5}$. We see that the result is very strongly peaked around the atom's resonant frequency ω_0 . It is easy to show that the full width at half maximum of this function is Γ . So the atom only responds strongly when the angular frequency of the light is in the range $\omega_0 \pm \Gamma$.



Now let's look at the behaviour of $\langle \hat{d} \rangle$, just as we did for the free atom case. The expression for $\langle \hat{d} \rangle$ is still equation (10.7), and since we are in the weak-excitation limit we take $c_1 = 1$ and c_2 to be the steady-state limit of equation (10.10). This gives us

$$\langle \hat{d} \rangle = -i \frac{\Omega}{\Gamma - 2i\delta} d_{12} e^{-i\omega_0 t} e^{-i\delta t} + c.c. = -i \frac{\Omega}{\Gamma - 2i\delta} d_{12} e^{-i\omega t} + c.c.$$

where *c.c.* stands for complex conjugate. Writing the complex number as an amplitude times a phase factor, we get

$$\langle \hat{d} \rangle = a \cos(\omega t + \theta), \quad (10.13)$$

where

$$a = \frac{2\Omega d_{12}}{[\Gamma^2 + 4(\omega - \omega_0)^2]^{1/2}}, \quad (10.14)$$

$$\theta = \tan^{-1} \left(\frac{\Gamma}{2(\omega - \omega_0)} \right). \quad (10.15)$$

So we see that the dipole is now oscillating at the driving frequency ω , rather than at its natural frequency ω_0 . This makes sense - harmonically driven systems oscillate at the driving frequency. The expressions for the amplitude and phase of the oscillating dipole should look familiar to you - they are exactly the results you get for a driven, damped harmonic oscillator. In the limit of weak excitation, the *atom behaves exactly like a harmonic oscillator*.

10.4. The damping rate

We can find an expression for the damping rate, Γ , as follows. For a classical oscillating dipole $d_0 \cos(\omega t)$, the total radiated power (see electromagnetism course) is

$$P_r = \frac{d_0^2 \omega^4}{12\pi\epsilon_0 c^3}.$$

We have a quantum mechanical oscillating dipole, so we use the expectation value of the dipole moment in place of d_0 . Using (10.8), this gives us

$$P_r = \frac{\omega_0^4}{12\pi\epsilon_0 c^3} 4c_1^2 c_2^2 d_{12}^2.$$

If the atom is in the excited state at time $t = 0$, then it decays according to $c_2^2 = \exp(-\Gamma t)$, $c_1^2 = 1 - c_2^2$. Furthermore, if we integrate the radiated power over all time, we get the total emitted energy, which is $\hbar\omega_0$:

$$\int_0^\infty P_r dt = \frac{\omega_0^4 d_{12}^2}{3\pi\epsilon_0 c^3} \int_0^\infty (1 - e^{-\Gamma t}) e^{-\Gamma t} dt = \frac{\omega_0^4 d_{12}^2}{3\pi\epsilon_0 c^3} \frac{1}{2\Gamma} = \hbar\omega_0$$

This gives us the following expression for Γ :

$$\Gamma = \frac{\omega_0^3 d_{12}^2}{6\pi\epsilon_0 \hbar c^3}. \quad (10.16)$$

In lecture 12, we will find an expression for Γ in a different way, and then we will see that the correct expression is twice the value found here, but otherwise identical.

10.5. Summary of the main points

- When an atom is in a superposition of two states, the probability distribution oscillates at the angular frequency $\omega_0 = (E_2 - E_1)/\hbar$.
- The expectation value of the dipole moment of a free atom also oscillates at ω_0 .
- This oscillating dipole produces electromagnetic radiation.
- The oscillation is damped as the excited state probability decays away. The decay constant, Γ , is the inverse of the excited state lifetime.
- The excited state lifetime is extremely long for microwave transitions between hyperfine levels and the damping can then be neglected. It is extremely short (~ 10 ns) for the higher frequency transitions between different electronic states of an atom.
- For an atom driven by an electromagnetic field at frequency ω , the transition probability follows a Lorentzian curve with a full width at half maximum of Γ .
- For a driven atom, the expectation value of the dipole moment behaves exactly like a driven, damped harmonic oscillator.

10.6. To do

- Revise the material in this handout.
- Do problem 1 from problem set 4.

11. Electron oscillator model, scattering and refractive index

In the last lecture we discovered that, for a weak driving field, an atom interacting with light is just like a driven, damped harmonic oscillator. We found this amazing result by solving the time-dependent Schrodinger equation, adding in the decay of the excited state “by hand”, and making a few approximations that are good ones in most situations. So this picture is firmly based in quantum mechanics. As it happens, Lorentz already put forward this model of the atom-light interaction in the late 19th century, before quantum mechanics. He described the atom as an electron attached to the nucleus by a spring, having a natural frequency ω_0 , and being driven by the oscillating electric field of light.

11.1. The driven, damped, harmonic oscillator

The equation of motion for the displacement of the electron (mass m , charge $-e$) is

$$m \frac{d^2 x}{dt^2} + b \frac{dx}{dt} + kx = -e \mathcal{E}_0 \cos(\omega t), \quad (11.1)$$

where \mathcal{E}_0 and ω are the amplitude and angular frequency of the driving electric field, k is the spring constant, and b the damping coefficient. We like to write this in the form

$$\frac{d^2 x}{dt^2} + \gamma \frac{dx}{dt} + \omega_0^2 x = \frac{-e \mathcal{E}_0}{m} \cos(\omega t), \quad (11.2)$$

where we have made the substitutions $\omega_0^2 = k/m$ and $\gamma = b/m$. This is the equation of a damped harmonic oscillator with a sinusoidal driving force, which is a system you have studied in detail previously. To find the solution, it's helpful to write the right hand side as the real part of $e \mathcal{E}_0/m e^{i\omega t}$, and take the trial solution to be $x = x_0 e^{i\omega t}$, where x_0 is not a function of t . We have to remember that we should take the real part of this solution at the end. With this trial solution, the above equation becomes

$$-\omega^2 x_0 + i \omega \gamma x_0 + \omega_0^2 x_0 = \frac{-e \mathcal{E}_0}{m}, \quad (11.3)$$

giving us

$$x_0 = \frac{-e \mathcal{E}_0}{m(\omega_0^2 - \omega^2 + i \gamma \omega)}. \quad (11.4)$$

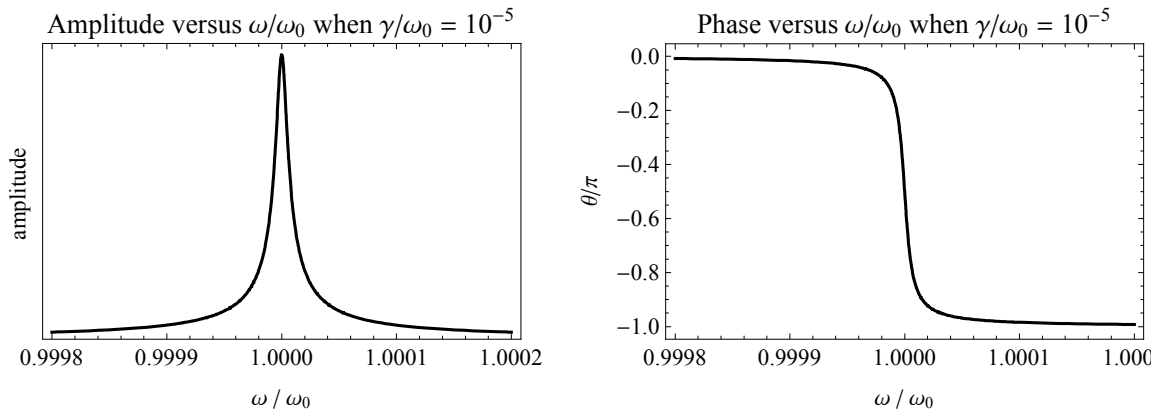
Let us write this x_0 as an amplitude factor times a phase factor, $x_0 = a e^{i\theta}$, where both a and θ are real. The amplitude factor is

$$a = \frac{-e \mathcal{E}_0}{m[(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]^{1/2}}, \quad (11.5)$$

and the phase factor is

$$\theta = \tan^{-1} \left(-\frac{\gamma \omega}{\omega_0^2 - \omega^2} \right). \quad (11.6)$$

Putting everything together, and taking the real part as we should, we get the displacement to be $x = a \cos(\omega t + \theta)$, with a given by (11.5) and θ given by (11.6). The electric dipole moment, let's call it d , is simply $d = -ex$. So we have an oscillating electric dipole, one that oscillates at the same frequency as the driving field, but with a phase difference, and with an amplitude that has the typical resonant response to the driving frequency. This is all exactly the same as we found (from quantum mechanics) in the last lecture.



Notice that the response is very strongly peaked around ω_0 (in fact, even more so than in the plots, because $\gamma/\omega_0 \sim 10^{-8}$ is more typical). So we are usually interested in the region where $\omega - \omega_0$ is very small compared to ω_0 . This means we can write $\omega_0^2 - \omega^2 = (\omega_0 + \omega)(\omega_0 - \omega) \approx 2\omega_0(\omega_0 - \omega)$. With this approximation, equations (11.5) and (11.6) become

$$a = \left(\frac{e \mathcal{E}_0}{m \omega_0} \right) \frac{1}{[4(\omega - \omega_0)^2 + \gamma^2]^{1/2}}, \quad (11.7)$$

$$\theta = \tan^{-1} \left(\frac{\gamma}{2(\omega - \omega_0)} \right). \quad (11.8)$$

These are identical in form to the equations we found in the last lecture for the expectation value of the dipole moment operator (see problem 1 in problem set 4 for the complete analogy between the two).

11.2. Scattering

In the year 2 electromagnetism course, you learned that an accelerating charge produces electromagnetic radiation, and you studied the particular case of an oscillating electric dipole, $d = d_0 e^{i\omega t}$. An important result is the total power radiated by this oscillating dipole, which is

$$P_r = \frac{d_0^2 \omega^4}{12 \pi \epsilon_0 c^3}. \quad (11.9)$$

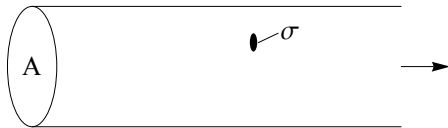
Using this result, and our d_0 worked out above, the power radiated by our driven electric dipole is

$$P_r = \frac{e^4 \mathcal{E}_0^2}{12 \pi \epsilon_0 m^2 c^3} \frac{\omega^4}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}. \quad (11.10)$$

Remember that the electron is oscillating because it is being driven by an incident electromagnetic wave, whose electric field amplitude is \mathcal{E}_0 . The intensity of this incident wave is $I_{\text{in}} = \frac{1}{2} \epsilon_0 c \mathcal{E}_0^2$. Using this to replace \mathcal{E}_0^2 in the above equation we get

$$P_r = \frac{e^4 I_{\text{in}}}{6 \pi \epsilon_0^2 m^2 c^4} \frac{\omega^4}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}.$$

What we have found is the amount of the incident power that is scattered by the atom. We often think about scattering problems in terms of the cross-sectional area of the target. The situation is shown below, where a beam of particles or light with cross-sectional area A is being scattered by a target whose cross-sectional area is σ .



Every particle, or photon, that hits the target is scattered, and all the rest are not. So the scattered flux is simply the input flux times the ratio σ/A . In the case of light we can say that the scattered power is $P_r = P_{\text{in}} \sigma/A$, and since the incident intensity is P_{in}/A , we get $P_r = I_{\text{in}} \sigma$. This is the same relation that we have above, the scattered power being the product of the incident intensity and a quantity that has the units of an area. This area we call the scattering cross-section,

$$\sigma = \frac{8 \pi r_0^2}{3} \frac{\omega^4}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}, \quad (11.11)$$

where we have introduced the constant $r_0 = e^2/(4 \pi \epsilon_0 m c^2)$ which is called the *classical electron radius* and has the value $r_0 = 2.81794 \times 10^{-15} \text{ m}$. Now let's examine some limiting cases.

Thomson scattering

First, consider the case where the driving frequency is high compared to the resonant frequency, $\omega \gg \omega_0$. A good example is when the electrons are actually not bound at all, in a plasma for example, meaning that $\omega_0 = 0$. Another example is high frequency radiation such as x-rays interacting with atoms that have their resonant frequencies in the visible. In this limit, $(\omega_0^2 - \omega^2)^2 \approx \omega^4$. Also, for typical transitions in atoms $\gamma \sim 10^{-8} \omega_0$ or even smaller, and so we can neglect $\gamma^2 \omega^2$ in the denominator in comparison to ω^4 . So the whole denominator is simply ω^4 , which cancels the ω^4 in the numerator. The cross-section has no frequency dependence, and is simply a constant known as the *Thomson scattering cross-section*,

$$\sigma_T = \frac{8 \pi r_0^2}{3} = 6.65 \times 10^{-29} \text{ m}^2 \quad (\omega \gg \omega_0). \quad (11.12)$$

Rayleigh scattering

The opposite limit, where the driving frequency is low compared to the resonant frequency, is known as *Rayleigh scattering*. In this case $\omega \ll \omega_0$ and so $(\omega_0^2 - \omega^2)^2 \approx \omega_0^4$. Once again, we can neglect $\gamma^2 \omega^2$ in the denominator by comparison to ω_0^4 and so we find the cross-section for Rayleigh scattering to be

$$\sigma_R = \frac{8 \pi r_0^2}{3} \left(\frac{\omega}{\omega_0} \right)^4 \quad (\omega \ll \omega_0). \quad (11.13)$$

The electronic transitions in many atoms and molecules are in the ultra-violet part of the spectrum, and this low frequency limit then applies to all frequencies lower than uv frequencies, including the visible part of the spectrum. This is true of the constituents of air for example, and so scattering of visible light by air is Rayleigh scattering. The scattering cross-section depends on the fourth power of the frequency, or

inversely as the fourth power of the wavelength, and so blue light is scattered much more strongly than red light. When we look at the sky we are seeing sunlight that has been scattered by the atmosphere into our eyes, and this scattering is far stronger for the blue light which is why the sky appears blue. Similarly, when we look at the setting sun, the red light reaches us through the atmosphere, but the blue light is scattered away, and so the sun appears red. It is only red when it's close to the horizon, because then the light has to pass through so much more atmosphere.

After light has travelled a distance L through the atmosphere, the fraction of the incident power scattered away is $n \sigma_R L$, where n is the density. Air is mostly molecular nitrogen, whose main electronic transition frequencies are at about 150nm. So taking light from the middle of the visible spectrum (e.g. 550nm), and using the formula above, we get a Rayleigh scattering cross-section of $4 \times 10^{-31} \text{ m}^2$. At atmospheric pressure (10^5 Pa), and at 273K, the density of air is $n = 2.65 \times 10^{25} \text{ m}^{-3}$ (use the ideal gas law). So we find that each kilometre of the atmosphere scatters about 1% of the light, which explains why you can see a long way, on a clear day. We are actually neglecting something important here: at such high density, the distance between atoms is smaller than the wavelength of light, and we have to think about interference between the light scattered by many different atoms. The interference tends to be constructive in the direction of propagation of the light, and destructive in all other directions, so that there's less scattering than you would otherwise expect. This is even more important when it comes to scattering in solids.

It's interesting to wonder why the visibility is so much worse on a foggy day. To understand this, we have to think about what happens to the scattering when atoms clump together, as they do in a tiny water droplet. You might think that each atom scatters with the above cross-section and so N atoms together have N times the above cross-section, but that is not right. As long as the little clump is much smaller than the wavelength of the light, then all the electrons in the clump are being driven together by the incident field, all in phase. This means they all scatter in phase, and so the light scattered by one interferes constructively with the light scattered by all of the others. The total electric field of the scattered light is N times that of a single scatterer, and so the intensity of the scattered light scales as N^2 . Now, the number of atoms in the droplet is proportional to its volume, which is proportional to d^3 , where d is the droplet diameter, and so the Rayleigh scattering cross-section for a sub-wavelength droplet scales as d^6 - the sixth power of the droplet diameter. This explains why on a foggy day you may only be able to see a few metres, even though you can see for many kilometres on a clear day. Note that this d^6 scaling does not continue indefinitely. Once the size of the droplet approaches the wavelength of the light, the electrons on one side of the droplet are driven with a different phase to those on the other side, and so the scattered light will not interfere constructively any more. This is a different scattering regime to Rayleigh scattering.

Resonant scattering

Finally, look at the case where the light is nearly resonant with the atom $\omega \approx \omega_0$. In this case, we can write $\omega_0^2 - \omega^2 = (\omega_0 + \omega)(\omega_0 - \omega) \approx 2\omega(\omega_0 - \omega)$, and equation (11.11) becomes

$$\sigma = \frac{8\pi r_0^2}{3} \frac{\omega_0^2}{\gamma^2} \left(\frac{\gamma^2}{4(\omega - \omega_0)^2 + \gamma^2} \right). \quad (11.14)$$

The bracketed factor contains the frequency dependence of the scattering, and this is the same Lorentzian dependence that we have seen several times before (e.g. equation (10.12)). On resonance, the bracketed factor is 1. As already noted, visible transitions typically have $\gamma \sim 10^{-8} \omega_0$, meaning that the cross-section for resonant scattering is about 16 orders of magnitude larger than for Thomson scattering (and even larger than for Rayleigh scattering). In the next lecture, we will find the expression for γ and show that the resonant scattering cross-section is of order λ^2 - i.e. it is set by the wavelength of the light, not by the size of the atom.

11.3. Refractive index

In electromagnetism and optics, we frequently use the idea of a refractive index to describe how light propagates through materials. Using this, we can understand the refraction, dispersion and absorption of light. We can now use our electron oscillator model to understand the microscopic origin of the refractive index. Recall that the refractive index (n) is related to the relative electric permittivity (ϵ_r) and the relative magnetic permeability (μ_r) via $n = \sqrt{\epsilon_r \mu_r}$. Most materials have μ_r very close to 1, especially at optical frequencies, so we'll concentrate on this case and take $n = \sqrt{\epsilon_r}$. Recall that when a material is placed in an electric field it is polarized by the field and we define the polarization density \mathbf{P} related to the applied field \mathbf{E} by

$$\mathbf{P} = (\epsilon_r - 1) \epsilon_0 \mathbf{E}. \quad (11.15)$$

We can use our electron oscillator model to find a relation between \mathbf{P} and \mathbf{E} . The polarization density \mathbf{P} is the electric dipole moment per unit volume. We have an expression for the dipole moment of one atom, $d = -e x_0 e^{i\omega t}$, where x_0 is given by equation (11.4). So, for the polarization density we have

$$\mathbf{P} = \frac{N e^2}{m(\omega_0^2 - \omega^2 + i\gamma\omega)} \mathbf{E} \quad (11.16)$$

where N is the number of atoms per unit volume, i.e. their number density. Combining these last two equations we get

$$\epsilon_r = 1 + \frac{N e^2}{m \epsilon_0(\omega_0^2 - \omega^2 + i\gamma\omega)}. \quad (11.17)$$

The refractive index is just the square root of this. We are often interested in cases where the refractive index is only a little different from 1, and then we can use the expansion $\sqrt{1+x} \approx 1 + x/2$, giving us

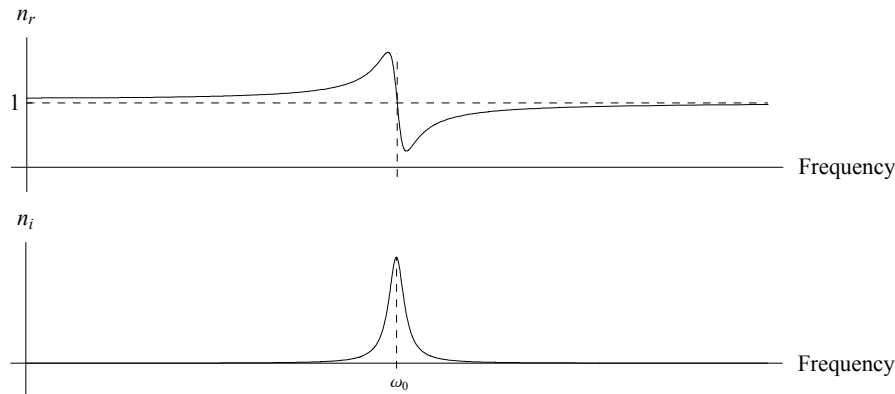
$$n = 1 + \frac{N e^2}{2 m \epsilon_0 (\omega_0^2 - \omega^2 + i \gamma \omega)}. \quad (11.18)$$

There are several interesting things about this result. We see that the refractive index deviates from 1 by an amount that is proportional to the number density of the medium. So, for example, the refractive index of a gas will depend on its pressure. We also see that the refractive index depends on the frequency of the light, and it is this that leads to the dispersion of light, blue light being refracted differently to red light for example. Also, we see that the refractive index has both a real and an imaginary part. Let us separate these out:

$$n = n_r - i n_i = \left(1 + \frac{N e^2 (\omega_0^2 - \omega^2)}{2 m \epsilon_0 [(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]} \right) - i \left(\frac{N e^2 \gamma \omega}{2 m \epsilon_0 [(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]} \right). \quad (11.19)$$

Recall that a wave propagating in the z direction can be written $\exp[i \omega (t - n z / c)] = \exp(i \omega t) \exp(-i \omega n_r z / c) \exp(-\omega n_i z / c)$. We see that the real part of the refractive index gives us the phase velocity of the wave and so is responsible for dispersion, while the imaginary part attenuates the wave and so is responsible for absorption in the medium.

Plotted below are the real and imaginary parts of the refractive index as a function of frequency in a region around the resonance frequency, ω_0 . Let's look first at the real part. At almost all frequencies the refractive index increases as frequency increases (graph has a positive slope). This means, for example, that n_r is higher for blue light than for red light, explaining how light is dispersed in a medium and the "blue bends best" rule. There is, however, a small region close to the resonance where n_r decreases with frequency. Here, the dispersion goes the opposite way to normal and so is called "anomalous dispersion". There is a typically a huge change in the refractive index close to the resonance, though the resonances can be very narrow and so the frequency of the light has to be carefully tuned to observe the resonant region. Note also that, above the resonance frequency, the refractive index can be less than 1. This means that the phase velocity is higher than c .



For most regular gases, and many other materials, the lowest resonance frequency is in the ultra-violet. For all frequencies that are smaller than this, e.g. frequencies in the visible, we are in the regime where $\omega \ll \omega_0$ and so we can neglect ω relative to ω_0 . Also, atomic and molecular resonances are usually very narrow, meaning that $\gamma \ll \omega_0$, and so we can also neglect the $\gamma^2 \omega^2$ term in the denominator. That leaves us with

$$n \approx \left(1 + \frac{N e^2}{2 m \epsilon_0 \omega_0^2} \right) - i \left(\frac{N e^2 \gamma \omega}{2 m \epsilon_0 \omega_0^4} \right) \quad (\omega \ll \omega_0). \quad (11.20)$$

In this approximation, the real part of the refractive index is the same for all frequencies, and its value depends only on the resonance frequency ω_0 , and on the density.

11.4. Summary of the main points

- The interaction of atoms with light can be understood using a classical harmonic oscillator picture.
- This leads to an equation for the cross-section of an atom scattering light.
- When $\omega \gg \omega_0$, we have Thomson scattering, and the cross-section is a constant.
- When $\omega \ll \omega_0$, we have Rayleigh scattering, and the cross-section scales as ω^4 .
- When $\omega = \omega_0$, we have resonant scattering and the cross-section is vastly larger than either of the other limits.
- The classical electron oscillator model leads to a microscopic understanding of the refractive index of materials.
- The refractive index is complex. The real part is responsible for dispersion, while the imaginary part is responsible for absorption.
- Close to the resonance frequency the absorption is large and the real part of the refractive index changes rapidly.

11.5. To do

- Revise the material in this handout. Useful reading is Feynman Lectures Volume I, chapters 31 and 32.
- Do problems 2 and 3 from problem set 4.

12. Transitions and atomic spectra

When an atom is excited in some way, it emits light at a set of definite frequencies corresponding to the frequencies of the allowed transitions between the energy levels of the atom. This is the emission spectrum of the atom. Similarly, when light passes through a sample of atoms, they absorb light at the particular frequencies that correspond to allowed transitions. This is the absorption spectrum. In both cases, the spectrum is determined by the energy level structure and by the selection rules which dictate which transitions are allowed. It is through the careful study of these spectra that the energy level structure of atoms has been determined. The spectral lines are typically narrow, but they do have some width and they have a particular intensity profile. This lecture is about these spectra.

12.1. The Einstein A and B coefficients

The Einstein A and B coefficients describe the fundamental processes of absorption, stimulated emission and spontaneous emission. You already studied this in the 2nd year Atomic, Nuclear and Particle physics course. Here is a review of the ideas and the relations between the coefficients.

Consider a population of atoms with two non-degenerate energy levels, a ground state of energy E_1 and an excited state of energy E_2 . The population in levels 1 and 2 are N_1 and N_2 respectively. If we put an atom in the excited state we know that it will not remain there forever - it decays back to the ground state, emitting a photon in the process. This is spontaneous emission. The excited state decays with a certain rate, let's call it A_{21} . *This rate is a property of the atom.* The decay of level 2 is described by the rate equation

$$\frac{dN_2}{dt} = -A_{21} N_2. \quad (12.1)$$

This equation states that the rate of change of the population in level 2 is proportional to the decay rate and to the level 2 population itself. The solution to this equation is

$$N_2(t) = N_2(0) \exp(-t/\tau), \quad (12.2)$$

where

$$\tau = \frac{1}{A_{21}} \quad (12.3)$$

is the lifetime of the excited state. The excited state decays with a characteristic time τ , which is the inverse of the rate A_{21} . Note that this A_{21} is exactly the same as the decay rate Γ that we introduced in lecture 10.

Now let's shine some light on the atoms. This introduces two new processes - absorption and stimulated emission.

Atoms in level 1 absorb light and are excited to level 2, so the absorption rate must be proportional to the population in level 1. What else does the absorption rate depend on? It should depend on some property of the atomic transition - how strongly this particular transition in this particular atom absorbs light - we call this property the absorption coefficient B_{12} . We expect the absorption rate to depend very strongly on the frequency of the light. Let's introduce a lineshape function, $g(\omega)$, normalized so that

$$\int_0^\infty g(\omega) d\omega = 1, \quad (12.4)$$

which tells us how the absorption probability depends on the frequency. We expect this function to be strongly peaked around the resonance frequency ω_0 . An example is the Lorentzian lineshape function that we've seen in previous lectures, e.g. in equation (11.11), though other lineshape functions are also possible (see later). Finally, the absorption rate depends on how much light there is. The quantity that matters is the energy density per unit angular frequency interval $\rho(\omega)$ (sometimes called the spectral energy density). So, the contribution to the absorption rate due to the light whose angular frequency is in the range $\omega \rightarrow \omega + d\omega$ is $B_{12} N_1 \rho(\omega) g(\omega) d\omega$. To get the total absorption rate, we integrate over all frequencies:

$$\frac{dN_1}{dt} = -B_{12} N_1 \int \rho(\omega') g(\omega') d\omega' \quad (\text{absorption only}). \quad (12.5)$$

Atomic resonances are narrow, and so it's very common for the light to be extremely broadband compared to the width of the resonance. In this case, $\rho(\omega)$ has a constant value of $\rho(\omega_0)$ over the whole region where $g(\omega)$ is significant, and we can take this constant outside the integral. Then, we are simply left with

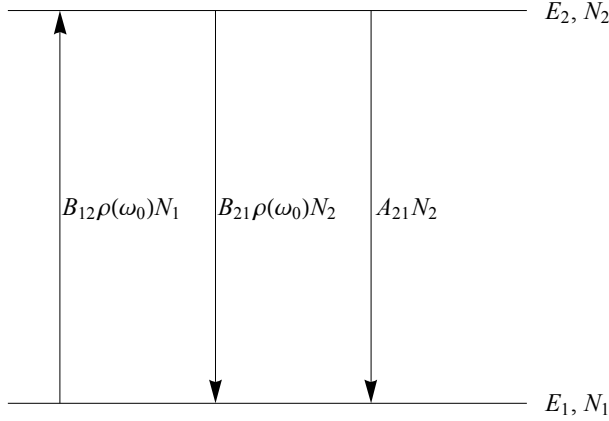
$$\frac{dN_1}{dt} = -B_{12} N_1 \rho(\omega_0) \quad (\text{absorption only, broadband light}). \quad (12.6)$$

This is the way the absorption rate appears in most textbooks (also in your 2nd year course). The opposite limit of monochromatic light is also important (e.g. for laser light). In this limit, we write $\rho(\omega') = \rho \delta(\omega' - \omega)$, where ρ is the total energy density, ω is the angular frequency of the light, and δ is a delta function. In this case, the integral is $\rho \int g(\omega') \delta(\omega' - \omega) d\omega' = \rho g(\omega)$, which tells us that we should multiply the energy density by the value of the lineshape function at the angular frequency of the light. We get

$$\frac{dN_1}{dt} = -B_{12} N_1 \rho g(\omega) \quad (\text{absorption only, monochromatic light at } \omega). \quad (12.7)$$

Stimulated emission is the inverse process to absorption, so its rate is given in a similar way. The coefficient for stimulated emission is B_{21} . In stimulated emission, one photon comes in and two come out. Importantly, the two that come out are identical in every way - they have exactly the same frequency, propagation direction and polarization.

Below is the diagram that shows the fundamental processes that can happen, and their rates (in the case of broadband excitation).



The complete rate equation that describes the population of level 2, in the case of broadband excitation, is

$$\frac{dN_2}{dt} = B_{12} \rho(\omega_0) N_1 - B_{21} \rho(\omega_0) N_2 - A_{21} N_2, \quad (12.8)$$

We can also write the equivalent equation for dN_1/dt (simply change all the signs!).

12.2. Relation between the A and B coefficients (revision)

Einstein found the relationships between the coefficients A_{21} , B_{21} , B_{12} using the following clever argument. Suppose we put the atoms in a box whose walls are at temperature T , and allow the atoms to come into thermal equilibrium with the blackbody radiation in the box. The energy density per unit angular frequency of blackbody radiation inside the box is given by the Planck distribution law:

$$\rho(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{\exp(\hbar \omega / k_B T) - 1}. \quad (12.9)$$

In thermal equilibrium the populations are not changing, so we have $dN_2/dt = 0$. From equation (12.8) we then have

$$B_{12} \rho(\omega_0) N_1 - B_{21} \rho(\omega_0) N_2 - A_{21} N_2 = 0, \quad (12.10)$$

which we can rearrange to give

$$\rho(\omega_0) = \frac{A_{21}}{B_{21}} \frac{1}{(B_{12}/B_{21})(N_1/N_2) - 1}. \quad (12.11)$$

But in thermal equilibrium, the way population is distributed between two energy levels is given by the Boltzmann distribution:

$$\frac{N_2}{N_1} = \frac{\exp(-E_2/k_B T)}{\exp(-E_1/k_B T)} = \exp\left(-\frac{\hbar \omega_0}{k_B T}\right). \quad (12.12)$$

Substituting equation (12.12) into equation (12.11) we get

$$\rho(\omega_0) = \frac{A_{21}}{B_{21}} \frac{1}{(B_{12}/B_{21}) \exp(\hbar \omega_0 / k_B T) - 1}. \quad (12.13)$$

In order to make this equation consistent with equation (12.9), we must have

$$A_{21} = \frac{\hbar \omega_0^3}{\pi^2 c^3} B_{21}, \quad (12.14)$$

and

$$B_{12} = B_{21}. \quad (12.15)$$

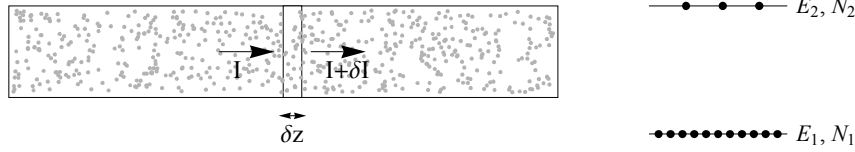
Now remember - *the A and B coefficients are properties of the atom*. They do not depend on the light, or on the atom's environment. So, although we have derived the relationships between the A and B coefficients by considering the special case of thermal equilibrium with blackbody radiation, *they must always be true*.

Equation (12.15) tells us that the coefficients for absorption and stimulated emission are equal. This makes good sense, since one process is the inverse of the other. Equation (12.14) tells us that the A and B coefficients are proportional to one another. So if an atom absorbs strongly (large B_{12}), its decay rate will be high (large A_{21}), meaning that the upper state lifetime is short.

12.3. Absorption

Suppose we have a beam of monochromatic light of energy density ρ that passes through a gas of atoms, and the frequency of the light, ω , is close to the atomic transition frequency ω_0 . Atoms in level 1 undergo absorption which removes photons from the light beam, while those in level 2 undergo stimulated emission which adds photons to the light beam. The level 2 atoms can also undergo spontaneous emission, but

these photons are emitted in a random direction, not back into the beam. When the gas is in thermal equilibrium, there are always more atoms in the lower level than in the upper level, and so there is more absorption than stimulated emission and the light is absorbed as it passes through the medium.



We can work out what happens to the light intensity by considering how it changes as it passes through a thin slice of thickness Δz and cross-sectional area A . Suppose that inside this slice there are N_1 atoms in the lower level and N_2 atoms in the upper levels. Then, the rate of absorption is $B \rho g(\omega) N_1$, and the rate of stimulated emission is $B \rho g(\omega) N_2$, where B is the Einstein B-coefficient. The first is also the rate at which photons are removed from the beam, and the latter the rate at which photons are added. Each photon carries an energy $\hbar\omega_0$, and so the change in intensity (energy per unit time per unit area) of the light is

$$\delta I = (-B \rho g(\omega) N_1 + B \rho g(\omega) N_2) \frac{\hbar \omega}{A}.$$

The relation between ρ and I is simply $\rho = I/c$, so our equation becomes

$$\delta I = -(N_1 - N_2) B \frac{I}{c} g(\omega) \frac{\hbar \omega}{A \delta z} \delta z.$$

Now $A \delta z$ is just the volume of the slice, and we can write $N_i/(A \delta z) = n_i$, where n_i is the density of atoms in level i . Then, taking the limit of very small δz , we get a differential equation for the intensity:

$$\frac{dI}{dz} = -(n_1 - n_2) \frac{B \hbar \omega}{c} g(\omega) I.$$

The quantity $B \hbar \omega g(\omega)/c$ has the dimensions of an area, and we identify it as the absorption cross-section and give it the symbol σ . Then,

$$\frac{dI}{dz} = -(n_1 - n_2) \sigma I, \quad (12.16)$$

$$\sigma = \frac{B \hbar \omega g(\omega)}{c}, \quad (12.17)$$

with solution

$$I = I_0 \exp(-(n_1 - n_2) \sigma z). \quad (12.18)$$

For a gas in thermal equilibrium, $n_1 > n_2$ (see next lecture) and so the intensity falls exponentially as it propagates through the gas.

12.4. The natural width

If there are no other line-broadening mechanisms, the lineshape function $g(\omega)$ is the natural linewidth of the transition, given by a Lorentzian function of FWHM $\Gamma (= A_{21})$. For this case

$$g(\omega) = \frac{2}{\pi \Gamma} \frac{\Gamma^2}{\Gamma^2 + 4(\omega - \omega_0)^2}. \quad (12.19)$$

This is the lineshape we first found in lecture 10. It is the Fourier transform of the wave emitted by the atom, which has angular frequency ω_0 and an amplitude which decays exponentially with the time constant of the upper state lifetime, $\tau = 1/\Gamma$. The pre-factor ensures that the lineshape function is normalized so that $\int g(\omega) d\omega = 1$ [see equation (12.4)]. For this lineshape, equation (12.17) becomes

$$\sigma(\omega) = \frac{B \hbar \omega}{c} \frac{2}{\pi \Gamma} \frac{\Gamma^2}{\Gamma^2 + 4(\omega - \omega_0)^2}.$$

Using the fact that $\Gamma = A_{21}$, $\omega \approx \omega_0$, and the relation between the A and B coefficients given by equation (12.14), we get

$$\sigma(\omega) = \frac{2 \pi c^2}{\omega_0^2} \frac{\Gamma^2}{\Gamma^2 + 4(\omega - \omega_0)^2} = \frac{\lambda^2}{2 \pi} \frac{\Gamma^2}{\Gamma^2 + 4(\omega - \omega_0)^2}. \quad (12.20)$$

On resonance, $\omega = \omega_0$, and the absorption cross-section is

$$\sigma(\omega_0) = \frac{\lambda^2}{2 \pi}. \quad (12.21)$$

This remarkable result tells us that the cross-section for resonant absorption is given by the wavelength of the light, rather than by any property of the atom. The cross-section is enormous, e.g. $4 \times 10^{-14} \text{ m}^2$ for 500nm light - about 15 orders of magnitude larger than the cross-section for Thomson scattering!

12.5. Doppler broadening

It is usual to measure the spectra of atoms and molecules when they are in the gas phase (so that the levels are not shifted and broadened by interatomic interactions). The atoms in the source are excited and the light they emit is measured with a spectrometer. If an atom is moving towards the spectrometer with speed v the light it emits is Doppler shifted. The angular frequency of the light measured by the spectrometer will be $\omega = \omega_0(1 + v/c)$, where ω_0 is the angular frequency in the rest frame of the atom. The atoms in the source have a spread of velocities given by the Maxwell-Boltzmann distribution,

$$n(v) \propto \exp\left(-\frac{M v^2}{2 k_B T}\right),$$

where M is the atom's mass and T the temperature of the source. This distribution translates into a distribution of frequencies:

$$f(\omega) \propto \exp\left(-\frac{M \lambda^2}{8 \pi^2 k_B T} (\omega - \omega_0)^2\right),$$

where $\lambda = 2 \pi c / \omega_0$ is the wavelength of the light (in the atom's rest frame). This lineshape is a Gaussian distribution. It's easy to show that its full width at half its maximum height (normally called the Doppler width) is:

$$\delta\omega_{\text{Dopp}} = 2 \pi \sqrt{\frac{8 \ln 2 k_B T}{M \lambda^2}}.$$

In many practical situations, the Doppler width is considerably larger than the natural linewidth of the transition and is the limiting factor in the ability to resolve one spectral line from another.

12.6. Expression for the A coefficient

In lecture 9, we considered the interaction of a two-level atom with monochromatic radiation, and we used the time-dependent Schrödinger equation to find the probability of being in the excited state. Then in lecture 10, we introduced the decay of the excited state and made the approximation of weak excitation. In this limit, and in the steady-state, the probability of being in the excited state is given by equation (10.12), which we re-write here:

$$P_2 = \frac{\pi}{2} \frac{\Omega^2}{\Gamma} \left(\frac{2}{\pi \Gamma} \frac{\Gamma^2}{\Gamma^2 + 4(\omega - \omega_0)^2} \right),$$

where Ω is the Rabi frequency given by equation (9.7):

$$\Omega = -\frac{\mathcal{E}_0}{\hbar} \langle 1 | \hat{d}_z | 2 \rangle.$$

In the expression for P_2 above, the factor in brackets is the natural lineshape function $g(\omega)$, so we can write

$$P_2 = \frac{\pi}{2} \frac{\Omega^2}{\Gamma} g(\omega). \quad (12.22)$$

Now let's link this to the A and B coefficients. We already have an expression for the steady-state population in the upper-state - equation (12.8) with $dN_2/dt = 0$. This was written down for broadband light. In the case of monochromatic light, we replace $\rho(\omega_0)$ with $\rho g(\omega)$ as discussed above. Then, writing the total population as $N = N_1 + N_2$, we get

$$P_2 = \frac{N_2}{N} = \frac{B \rho g(\omega)}{A + 2 B \rho g(\omega)}.$$

Now we need to go to the weak excitation limit, since that's the limit where (12.22) holds. The weak excitation limit means that spontaneous emission dominates over stimulated emission, i.e. $A \gg B \rho g(\omega)$. So in this limit, we get

$$P_2 = \frac{N_2}{N} = \frac{B \rho g(\omega)}{A}. \quad (12.23)$$

Now we just have to compare (12.22) and (12.23), and use the expression for the energy density in terms of the electric field, $\rho = 1/2 \epsilon_0 \mathcal{E}_0^2$, and the relation between the A and B coefficients, equation (12.14):

$$\frac{\pi}{2} \frac{\mathcal{E}_0^2}{\hbar^2 \Gamma} |\langle 1 | \hat{d}_z | 2 \rangle|^2 g(\omega) = \frac{\pi^2 c^3}{\hbar \omega_0^3} \frac{1}{2} \epsilon_0 \mathcal{E}_0^2 g(\omega).$$

Re-arranging this, we get an expression for the decay rate Γ :

$$\Gamma = A_{21} = \frac{\omega_0^3}{\pi \epsilon_0 \hbar c^3} |\langle 1 | \hat{d}_z | 2 \rangle|^2.$$

Note that \hat{d}_z is the z-component of the dipole-moment operator. For spontaneous emission, there's nothing special about the z-axis, so it

makes more sense to express the answer in terms of $\left| \langle 1 | \hat{\mathbf{d}} | 2 \rangle \right|^2 = 3 \left| \langle 1 | \hat{d}_z | 2 \rangle \right|^2$. Here $\hat{\mathbf{d}}^2 = \hat{d}_x^2 + \hat{d}_y^2 + \hat{d}_z^2 = 3 \hat{d}_z^2$, where the last step comes from the fact that all three directions are equivalent. Then we get the result

$$\Gamma = A_{21} = \frac{\omega_0^3}{3 \epsilon_0 \pi \hbar c^3} \left| \langle 2 | \hat{\mathbf{d}} | 1 \rangle \right|^2 \quad (12.24)$$

This is an important result - it gives the rate of spontaneous emission, and hence the excited state lifetime ($\tau = 1/A_{21}$) in terms of atomic properties. The spontaneous emission rate is proportional to the square of the matrix element of the electric dipole operator and to ω_0^3 . The lifetime of an atomic state scales inversely as the transition frequency cubed. Consider hydrogen for example. The 2p state decays to the ground state, emitting ultra-violet light (around 2.5×10^{15} Hz), and the lifetime is just a few nanoseconds. By contrast, the lifetime of the upper hyperfine component of the 1s state, which is only separated from the lower hyperfine component by 1.4×10^9 Hz, is about 10 million years.

12.7. Selection rules (revision)

The main interaction between an electromagnetic field and an atom is the electric dipole interaction - the electric field of the light drives the electron in the atom. The electron's displacement from the nucleus is \mathbf{r} , and it has a charge $-e$, so it produces an electric dipole moment $\hat{\mathbf{d}} = -e \hat{\mathbf{r}}$. If there are many electrons, we just sum over them: $\hat{\mathbf{d}} = -e \sum_i \hat{\mathbf{r}}_i$. The electric field of the light, \mathbf{E} , interacts with this electric dipole moment, and the interaction Hamiltonian is $-\hat{\mathbf{d}} \cdot \mathbf{E}$. Let's write the electric field of the light as $\mathbf{E} = \epsilon E_0 \cos(\omega t)$. As we see above, the transition rate, R_{21} , between two states $|1\rangle$ and $|2\rangle$ is proportional to the squared matrix element of the electric dipole moment operator:

$$R_{21} \propto \left| \langle 2 | -e \hat{\mathbf{r}} | 1 \rangle \cdot \epsilon \right|^2 \quad (12.25)$$

If we want to calculate the transition rate, we have to calculate the above matrix element, which for a one-electron atom we can do using the hydrogenic eigenfunctions and evaluating the integrals. Very often the transition rate is zero, meaning that the transition is forbidden. This is important in understanding the spectra of atoms - only certain transitions are allowed. Whether a transition is allowed or forbidden depends on the quantum numbers of the two states involved in the transition - so we get selection rules that govern how these quantum numbers are allowed to change in a transition.

Similarly, the rate for a magnetic dipole transition is proportional to the square of $\langle 2 | \hat{\boldsymbol{\mu}} | 1 \rangle$ where $\hat{\boldsymbol{\mu}}$ is the atom's magnetic dipole moment. Again, a consideration of when this matrix element is zero gives us the selection rules for magnetic dipole transitions.

Parity and the parity selection rule

We often refer to the *parity* of the eigenstates. The parity operation P is the inversion of the coordinates through the origin, $\mathbf{r} \rightarrow -\mathbf{r}$. All the eigenstates of an atom are states of definite parity, either +1 or -1: $\hat{P}\psi = \pm\psi$. This is a consequence of the fact that electromagnetic interactions conserve parity. The parity of a state is usually referred to as even or odd depending on whether the sign is plus or minus. All the radial functions are even, and so the parity is specified entirely by the spherical harmonics. Their parity depends on l and is simply $(-1)^l$. So, states with even l have even parity, and states with odd l have odd parity.

The transition rate is proportional to the square of

$$\langle 2 | \hat{\mathbf{r}} | 1 \rangle = \int \psi_2^* \mathbf{r} \psi_1 dV,$$

where the integral is over all space. Clearly $\hat{\mathbf{r}}$ is an odd operator (it changes sign through the origin). So if the two states have the same parity (either both odd or both even), the integrand is odd and the integral evaluates to zero. So we have an important selection rule for an electric dipole transition: *the parity must change in the transition*. This is a strict selection rule that applies to many-electron atoms just as it does to a one-electron atom.

The magnetic dipole moment operator is an even operator. This is because the magnetic moment is proportional to the angular momentum, and the angular momentum does not change sign on reflection through the origin (think of orbital angular momentum, $\hat{\mathbf{r}} \times \hat{\mathbf{p}}$ - both $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ change sign and so their product does not). So - *the parity must not change in a magnetic dipole transition*.

We see that, in this sense, the two types of transition are complementary. If one type is forbidden by the parity selection rule, the other type will be allowed. Note that all the fine-structure levels of a particular term (levels labelled by J) have the same parity and so transitions between them are magnetic dipole transitions. The same is true for hyperfine levels.

Selection rules for the quantum numbers n , l , and m

Now let's find the electric dipole selection rules for the quantum numbers n , l and m . We'll do it for a one-electron atom, and then generalize. Suppose that the light is linearly polarized along the z -axis (which could be defined by an applied magnetic field for example). This means that ϵ is a unit vector in the z direction and so $\mathbf{r} \cdot \epsilon = z = r \cos \theta$. So the transition rate is proportional to the square of the following matrix element:

$$\langle n', l', m' | r \cos \theta | n, l, m \rangle = \text{normalization} \times \int_0^\infty R_{n',l'}^* r R_{n,l} r^2 dr \int_0^\pi P_{l',m'}^* \cos \theta P_{l,m} \sin \theta d\theta \int_0^{2\pi} e^{im'\phi} e^{-im\phi} d\phi.$$

Here, $R_{n,l}$ is the radial part of the hydrogenic wavefunction and depends only on the radial coordinate, and $P_{l,m} e^{im\phi}$ is the angular part of the wavefunction - the spherical harmonics. The $P_{l,m}$ are the associated Legendre polynomials and depend only on θ . The dependence on ϕ is contained entirely in the $e^{im\phi}$ factor. The integral over ϕ is zero unless $m' = m$.

Next suppose that the light is linearly polarized along x . Then we have $\mathbf{r} \cdot \epsilon = x = r \sin \theta \cos \phi$. Writing out just the ϕ integral this time:

$$\langle n', l', m' | r \cos \theta | n, l, m \rangle \propto \int_0^{2\pi} e^{i m' \phi} \cos \phi e^{-i m \phi} d\phi = \frac{1}{2} \int_0^{2\pi} e^{i(m'-m+1)\phi} d\phi + \frac{1}{2} \int_0^{2\pi} e^{i(m'-m-1)\phi} d\phi.$$

The integral is zero unless $m' = m \pm 1$. A moment's consideration shows that the same result applies for light linearly polarized along y . So we reach the following selection rules for m :

$$\Delta m = 0 \quad (\text{light linearly polarized parallel to } z), \quad (12.26)$$

$$\Delta m = \pm 1 \quad (\text{light linearly polarized perpendicular to } z). \quad (12.27)$$

Turning now to the l quantum number, we see that its change is governed by the integral over θ . To evaluate this integral, we need to know something about the associated Legendre polynomials, in particular the following recursion relations (don't try to remember these!):

$$\sin \theta P_{l,m} = \frac{P_{l+1,m} - P_{l-1,m}}{2l+1},$$

$$\cos \theta P_{l,m} = \frac{(l-m+1)P_{l+1,m} + (l+m)P_{l-1,m}}{(2l+1)}.$$

Using these, and the fact that the $P_{l,m}$ are orthogonal to one another, we see that (irrespective of the polarization) we must have $l' = l \pm 1$. So the selection rule is:

$$\Delta l = \pm 1 \quad (\text{electric dipole}). \quad (12.28)$$

Finally, consider the change in the n quantum number, which is governed by the radial integral. The integral is an overlap integral between the radial wavefunctions weighted by r (i.e. overlap in the outer regions contributes more to the integral than in the inner regions of the atom). The integral is always non-zero so there is no selection rule on the change in n .

$$\Delta n = \text{anything} \quad (\text{electric dipole}).$$

For a many-electron atom in the central field approximation, the many electron wavefunction is just a product of one-electron wavefunctions with angular parts given by the spherical harmonics just as in hydrogen. So the selection rules are the same (applied now to the particular electron that's making the transition). Note though that, for a many electron atom, these selection rules hold *within the central field approximation*. They hold to the extent that the central field approximation is a good approximation.

Selection rules for the quantum numbers L , S , J and M_J

The selection rule on J follows from the conservation of angular momentum, the fact that a photon has a spin of 1, and the addition of angular momentum in quantum mechanics (recall: adding J_1 and J_2 the allowed values go, in integer steps, from $|J_1 - J_2|$ to $J_1 + J_2$). So we have the selection rule $\Delta J = 0, \pm 1$, plus the additional rule that a transition between $J' = 0$ and $J = 0$ is forbidden (because you can't add 0 and 1 and get 0, not even in quantum mechanics!). Applying the same reasoning to the component of angular momentum in the z -direction, we get the selection rule $\Delta M_J = 0, \pm 1$. These selection rules are strict ones, as they are based on a conservation law. The selection rule for S is simple: $\Delta S = 0$. This follows from the fact that the electric dipole operator acts in the coordinate space of the electrons, and has nothing to do with the spin - so the spin can't change in the transition. The selection rule for L now follows directly from the other two and the fact that $\hat{J} = \hat{L} + \hat{S}$. Since S doesn't change in the transition, the change in L has to be the same as the change in J . So the selection rule for L is $\Delta L = 0, \pm 1$, with $L' = 0$ going to $L = 0$ forbidden.

12.8. Summary of the main points

- There are three fundamental interactions between light and atoms - absorption, stimulated emission, and spontaneous emission.
- The Einstein A and B coefficients relate the rate coefficients for these processes - equations (12.14) and (12.15).
- The intensity profile of a spectral line depends on the broadening mechanism. If there is no other broadening, the lineshape is a Lorentzian with FWHM given by the Einstein A coefficient, which is the inverse of the excited state lifetime. In this case, the resonant absorption cross-section is proportional to the square of the wavelength.
- The spread of atomic velocities in a gas leads to a spread of Doppler shifts which broadens a spectral line. The lineshape is a Gaussian, and the FWHM is proportional to the square root of the temperature.
- The A coefficient is proportional to the cube of the frequency, and is proportional to the square of the matrix element of the electric dipole operator between the two states of interest.
- When this matrix element is zero, the electric dipole transition is forbidden. This gives us the selection rules.
- There can be higher-order transitions - most notably magnetic dipole transitions and electric quadrupole transitions - but their rates are strongly suppressed relative to an allowed electric dipole transition. They have different selection rules and become important when an electric dipole transition is forbidden.

12.9. To do

- Revise the material in this handout. Useful reading: chapter 3 of Woodgate, sections 1.7, 2.2, 5.5 and 8.1 of Foot.
- Do questions 4-6 from problem set 4.

13. Lasers

13.1. Steady-state population for two-level atoms

Let's return to our picture of the basic processes that occur for a two level atom, and the rate equation that describes the population in the upper level, equation (12.8). In the steady-state, we have $dN_2/dt = 0$, giving

$$B_{12} \rho(\omega_0) N_1 - B_{21} \rho(\omega_0) N_2 - A_{21} N_2 = 0.$$

Using $B_{12} = B_{21}$, the ratio of the populations in the steady state is

$$\frac{N_2}{N_1} = \frac{B \rho(\omega_0)}{A + B \rho(\omega_0)}. \quad (13.1)$$

Here, we've used the shorter notation $B = B_{21}$, $A = A_{21}$.

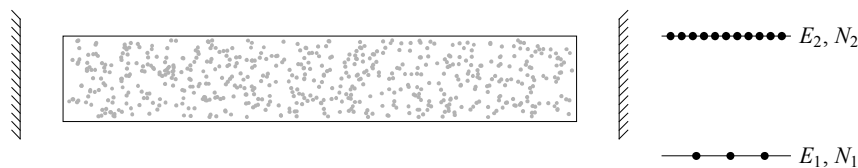
Remember that $\rho(\omega_0)$ is proportional to the intensity of the light at the resonance frequency. When the intensity is low, the rate of absorption (and stimulated emission) is small compared to the spontaneous emission rate (i.e. $B \rho(\omega_0) \ll A$). In this case, equation (13.1) tells us that $N_2 \ll N_1$ - most of the population stays in the ground state when the radiation is weak, as we would expect. To get a significant fraction of the population into the upper state, we have to make the absorption rate comparable to the spontaneous emission rate. When these two rates are equal ($B \rho(\omega_0) = A$), we have $N_2/N_1 = 1/2$ (meaning that 1/3 of the total population is in the upper state). The maximum possible upper state population occurs when the absorption (and stimulated emission) rate is much larger than the spontaneous emission rate, $B \rho(\omega_0) \gg A$. Then equation (13.1) tells us that $N_2 = N_1$ - i.e. half of all the population is in the upper state. *In the steady state, you cannot get more than half into the upper state, no matter how intense the radiation is.* This makes sense - in the limit where the radiation is very intense, the absorption and stimulated emission rates dominate (spontaneous emission is not important), and since their rates are equal we must end up with half the population in each state. It follows that if we send a beam of resonant light through a sample of two-level atoms, there must always be more absorption than stimulated emission, so the intensity of the light beam decreases as it propagates.

13.2. Amplification

In lecture 12 we found an expression for the way the intensity of a light beam changes as it propagates through a medium; this is equation (12.18):

$$I = I_0 \exp(-(n_1 - n_2) \sigma z).$$

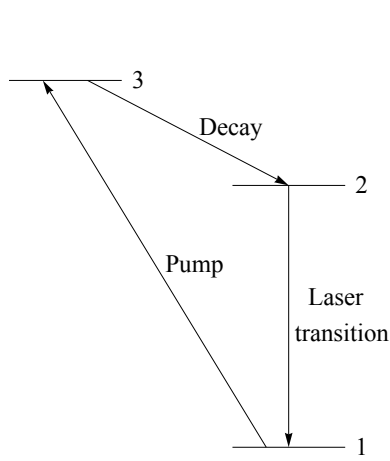
Here, σ is the absorption cross-section, n_1 and n_2 are the densities of atoms in levels 1 and 2, and z is the propagation distance. Let's imagine that we have found some way to make $n_2 > n_1$. This is called a *population inversion*. In this case, there is more stimulated emission into the beam than absorption from the beam - the exponent in equation (12.18) is positive and so the intensity of the light beam grows exponentially as it propagates. The stimulated emission amplifies the light intensity. Now suppose we put the cell of gas, where we have arranged this population inversion, between a pair of mirrors, as shown below. The mirrors make an *optical cavity*. The light bounces back and forth between the mirrors, being amplified each time it passes through the gas cell. If we make the right hand mirror partly reflective and partly transmissive, some fraction of the light will pass out towards the right, and the rest will go back for another round trip, being amplified once again. So a beam of light will come out of the cavity, and the intensity inside the cavity that is lost to that beam will be constantly replenished by the amplification process, as long as we maintain the population inversion. This is a laser. Note that a single spontaneously emitted photon that happens to be emitted straight towards one of the mirrors is enough to get the process started, and so the laser will start itself as soon as we make the population inversion.



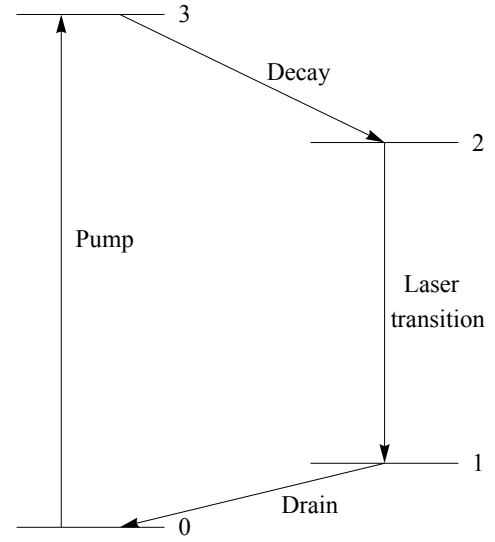
A population inversion placed between mirrors makes a laser

13.3. Population inversion, gain and loss

As shown above, when there are just two levels it's impossible to make a steady-state population inversion. This remains true when there are other processes that transfer population between the two levels, e.g. electron collisions. However, all real systems have more than just two levels, and then it becomes possible to create a population inversion. Consider, for example, the 3-level system shown in the picture below (part (a)). Population is pumped out of level 1 to level 3, which then rapidly decays to level 2. If this decay rate is much faster than the decay rate of level 2, then population will build up in level 2 and be depleted from level 1. This sets up the required population inversion. This scheme is not ideal because the stimulated emission in the laser builds up population in level 1 again. A better way, and more common in real lasers, is to have a 4th level, the one labelled 0 in part (b) of the figure. Now, level 1 can empty itself by draining to level 0, and that helps to set up a bigger population inversion.

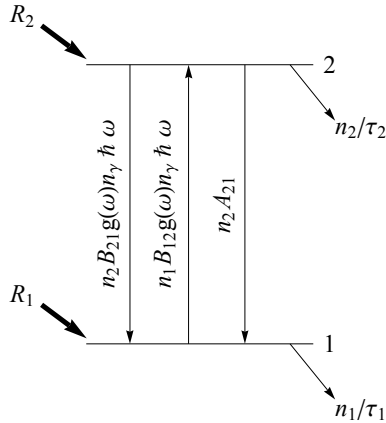


(a) Population inversion in a 3-level system



(b) Population inversion in a 4-level system

It can get quite complicated to analyze these schemes in detail, and we don't need to because we only really care about the populations in levels 1 and 2. We can analyze what happens using the general system shown below. Population is pumped into level 2 at the rate per unit volume R_2 . Note that this rate includes all processes that populate level 2 (e.g. decay from higher levels, collisional excitation, optical pumping). The lifetime of level 2 is τ_2 , and this is its total lifetime taking into account all processes that deplete the population of the level. Similarly, the pumping rate per unit volume into level 1 is R_1 , and the lifetime of level 1 is τ_1 . The Einstein-A coefficient for the spontaneous decay from 1 to 2 is A_{21} . Note that R_1 does not include the spontaneous decay from level 2. We assume monochromatic radiation at frequency ω , so that the absorption rate per unit volume out of level 1 is $n_1 B_{12} g(\omega) \rho$, where $g(\omega)$ is the lineshape function and ρ is the energy density of the light. Since each photon has energy $\hbar\omega$, we can write $\rho = n_\gamma \hbar \omega$, where n_γ is the photon density.



Let's first work out the steady-state population inversion that is reached when there is no laser action, meaning that the photon density, n_γ , is zero. In the steady state, we have

$$\frac{dn_1}{dt} = R_1 + A_{21} n_2 - \frac{n_1}{\tau_1} = 0, \quad (13.2)$$

$$\frac{dn_2}{dt} = R_2 - \frac{n_2}{\tau_2} = 0. \quad (13.3)$$

From these, we find the steady-state densities to be

$$n_2 = R_2 \tau_2, \quad n_1 = R_1 \tau_1 + A_{21} \tau_1 R_2 \tau_2. \quad (13.4)$$

For population inversion, we need $n_2/n_1 > 1$, which translates to the following *condition for population inversion*:

$$\frac{R_2 \tau_2}{R_1 \tau_1} (1 - A_{21} \tau_1) > 1. \quad (13.5)$$

This tells us several important things. First, the condition can clearly only be satisfied if the term in brackets is positive, and so a necessary (but not sufficient) condition is $\tau_1 < 1/A_{21}$. This simply means that the population must be removed from level 1 faster than the spontaneous decay rate from level 2 to level 1. Provided this is satisfied, it becomes possible to make a population inversion either by *selective pumping* of the upper level (i.e. large value of R_2/R_1) or by having a favourable lifetime ratio between the two levels (i.e. large value of

τ_2/τ_1).

Now let's see what happens to the photon density:

$$\frac{dn_\gamma}{dt} = (n_2 - n_1) B g(\omega) n_\gamma \hbar \omega - \beta n_\gamma.$$

The first terms are the rate of change of photon density due to stimulated emission and absorption, while the last term accounts for photon loss from the laser cavity at the rate β . Part of this loss will be the photons that are transmitted out of the cavity to make the laser beam, and part will be due to absorption losses in the mirrors or elsewhere. Using equation (12.17) [$\sigma(\omega) c = B \hbar \omega g(\omega)$], we can re-write the above equation as

$$\frac{dn_\gamma}{dt} = \Delta n \sigma(\omega) c n_\gamma - \beta n_\gamma, \quad (13.6)$$

where $\Delta n = n_2 - n_1$ is the population inversion. The solution is

$$n_\gamma(t) = n_\gamma(0) \exp[(\Delta n \sigma(\omega) c - \beta) t]. \quad (13.7)$$

We could just as well write this in terms of propagation distance z : $n_\gamma(z) = n_\gamma(0) \exp[(\Delta n \sigma(\omega) - \beta/c) z]$. If the gain medium completely fills the cavity of length L , the change after one complete round trip is

$$n_\gamma(2L) = n_\gamma(0) \exp[(2 \Delta n \sigma(\omega) L - 2L \beta/c)].$$

Let us define γ_{loss} to be the round-trip loss. It must be the loss rate (β) multiplied by the time taken to make one trip around the cavity ($2L/c$), i.e. $\gamma_{\text{loss}} = 2L \beta/c$. This is just the last factor in the exponent above, and so we get

$$n_\gamma(2L) = n_\gamma(0) \exp[(2 \Delta n \sigma(\omega) L - \gamma_{\text{loss}})]. \quad (13.8)$$

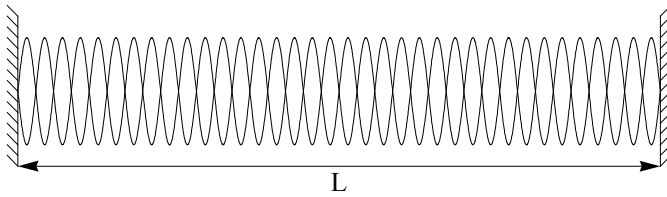
We can think of the first term in the exponent as the round-trip gain, and the second as the round-trip loss. Note that the round-trip gain is proportional to $\sigma(\omega)$ which in turn is proportional to the lineshape function, and so it is a strong function of the frequency. The equation above tells us that, from an initial small number, the photon density will increase exponentially provided $2 \Delta n \sigma(\omega) L > \gamma_{\text{loss}}$. This gives us a *threshold population inversion*:

$$\Delta n_{\text{th}} = \frac{\gamma_{\text{loss}}}{2 \sigma(\omega) L}. \quad (13.9)$$

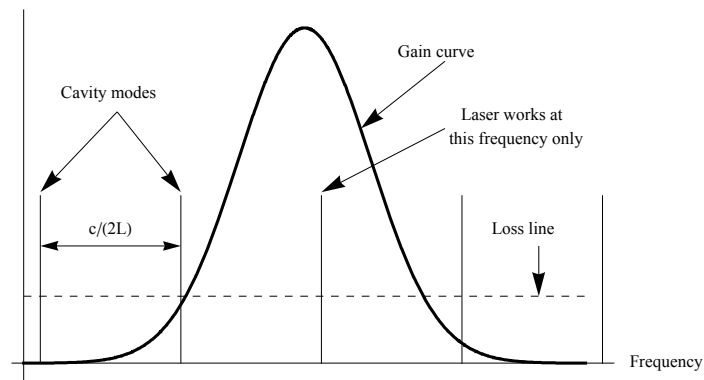
For the laser to work, we must get the population inversion above this threshold so that more photons are put into the cavity than are lost on each round trip. The photon density does not increase indefinitely, because as it increases the rate of stimulated emission increases, and this reduces the population inversion. A steady-state is quickly reached, where $dn/dt = 0$. We see that in the steady state, $\Delta n = \Delta n_{\text{th}}$ - so the photon density increases until the population inversion is pulled down to its threshold value.

13.4. The optical cavity

The laser mirrors make an optical cavity, and the light bounces back and forth between the mirrors of the cavity. There will be constructive interference between one round-trip of the cavity and the next only if the wavelength satisfies $n \lambda_n = 2L$, where n is an integer and L is the cavity length. This just says that a standing wave has to fit inside the cavity. The corresponding frequencies of these “cavity modes” are $f_n = n c / (2L)$. The frequency spacing between cavity modes is known as the *free spectral range* of the cavity and is simply $c / (2L)$.



Since only these discrete frequencies of light can circulate in the cavity, there is only optical feedback to the gain medium at these frequencies, and so the laser can only lase at one of these frequencies. For an example, consider a gas laser in a 10cm long cavity. The mode spacing (free spectral range) of the cavity is 1.5GHz, which is much larger than the natural linewidth of most atomic transitions, and may also be larger than the Doppler width. The situation is illustrated in the figure below. The bold line shows how the round-trip gain $2 \Delta n \sigma(\omega) L$ varies with frequency ω , following the lineshape function which is here chosen to be a Gaussian (e.g. Doppler broadening). The dashed horizontal line is the round-trip loss, and so the laser can only lase at frequencies where the bold line is above the dashed line. The vertical bars indicate the modes of the optical cavity formed by the two mirrors, separated in frequency by $c/2L$. We see in this illustration that there is only one mode of the cavity where the gain exceeds the loss, and so the laser will work exclusively on this mode.



13.5. Summary of the main points

- By producing a population inversion, stimulated emission exceeds absorption and light is amplified.
- A pair of mirrors makes a cavity for light.
- When the population inversion is placed in the cavity the light circulates around and is continuously amplified (the amplifier has feedback). This is a laser.
- It's impossible to produce a population inversion in a two-level system, but can be done when there are more than two levels.
- A necessary condition for a population inversion is for the population to be removed from the lower level faster than the spontaneous decay rate into that level.
- There is a threshold population inversion which is reached when the round-trip gain balances the round-trip loss.
- When the laser operates, the population inversion is pulled down by stimulated emission to the threshold value.
- The cavity supports a discrete set of modes and the laser can only operate on one (or possibly several) of these modes.

13.6. To do

- Suggested reading: Wikipedia for background on various types of laser, e.g. He-Ne laser, Nd:YAG laser, dye laser, diode laser.
- Do question 1 from problem set 5.

14. Electronic structure of diatomic molecules; bonding

When two atoms approach each other there is a re-distribution of the electron charge distribution which can result in a net attractive force between the atoms - then they can bind to form a molecule. We will only consider diatomic molecules - molecules made out of just two atoms.

14.1. The Born-Oppenheimer approximation

Molecules have electronic energy levels just like atoms. They have an electronic ground state and a set of electronically excited states, and the spacing between these is similar to the energy-level spacing in atoms, i.e. of order 10eV. But molecules can do more than atoms - they can also vibrate and rotate. The vibrational and rotational motion are, of course, quantized. So we have a discrete set of vibrational and rotational energies. The nuclei are much heavier than the electrons and so they move much more slowly. As a result, it's possible to separate the electronic motion from the nuclear motion, effectively treating them as two separate systems. This separation is called the Born-Oppenheimer approximation. In this approximation, the total wavefunction of the molecule is a product of an electronic function and a nuclear function:

$$\Psi = \psi_e \chi_N \quad (14.1)$$

Here, ψ_e is the “electronic wavefunction” and is a function of the coordinates of the electrons, while χ_N is the “nuclear wavefunction” and is a function of the coordinates of the nuclei. The nuclear motion can be further separated into an angular part and a radial part (much like in atoms). The angular part represents the rotation of the molecule and the radial part represents the vibration of the molecule. So we have

$$\Psi = \psi_e \psi_v \psi_r \quad (14.2)$$

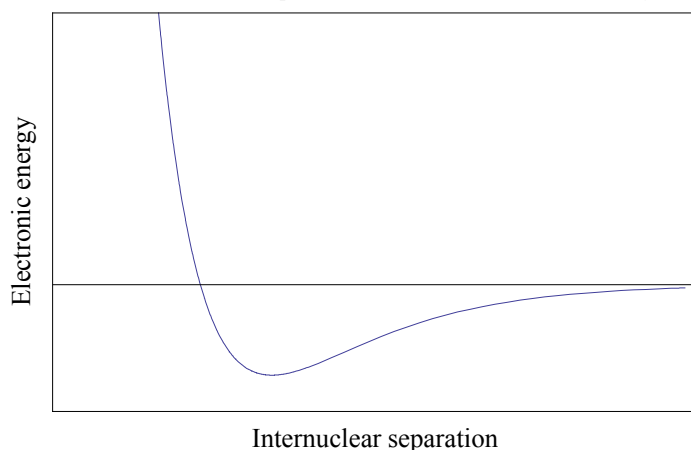
where ψ_v and ψ_r are vibrational and rotational functions respectively. The total energy is just the sum of the individual energies:

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}} \quad (14.3)$$

Since the nuclei move much more slowly than the electrons, the energy associated with nuclear motion (rotation and vibration) is much smaller than the electronic energy. It also turns out that the vibrational energy level spacing is much smaller than the rotational energy spacing. So:

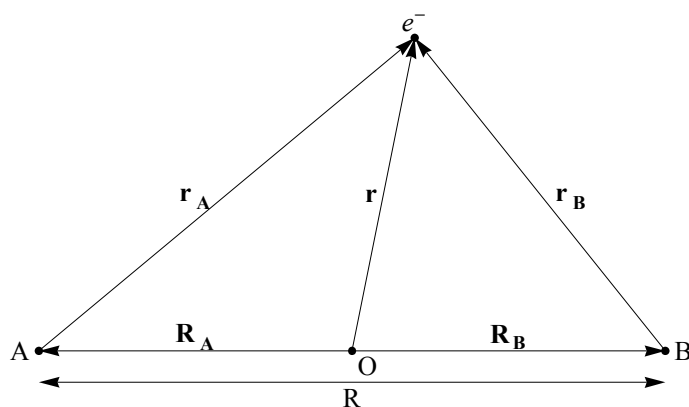
$$E_{\text{rotation}} \ll E_{\text{vibration}} \ll E_{\text{electronic}} \quad (14.4)$$

In the Born-Oppenheimer approximation, we find the electronic eigenfunctions and energies by solving the Schrödinger equation for the electrons with the nuclei at fixed positions. Of course, the answer we get will depend on how far apart the (fixed) nuclei are. So, we solve the electronic problem for a whole set of different distances R . This procedure gives us the electronic energies as a function of the internuclear separation R - these are called the potential curves of the molecule. The figure below is a sketch of one such molecular potential.



14.2. The H_2^+ molecule

We'll consider the simplest of all possible molecules - H_2^+ (singly ionized molecular hydrogen). It is a three-particle system consisting of two identical nuclei (protons) and a single electron. It nicely illustrates the ideas used to describe the electronic states of a molecule. The coordinates of the particles are shown below. The origin, O, of the coordinate system lies half way along the internuclear axis that joins the two nuclei A and B, which are separated by a distance R . The coordinates of the two nuclei relative to O are \mathbf{R}_A and \mathbf{R}_B respectively. The coordinate of the electron relative to O is \mathbf{r} , and relative to A and B is \mathbf{r}_A and \mathbf{r}_B . We have the following relations between these coordinates: $\mathbf{r}_A = \mathbf{r} - \mathbf{R}_A$ and $\mathbf{r}_B = \mathbf{r} - \mathbf{R}_B$.



Now let's write down the *electronic Hamiltonian* for this system - by electronic Hamiltonian we mean the one we get in the Born-Oppenheimer approximation where the nuclei are held a fixed distance R apart. The nuclei are not moving, so there is no nuclear kinetic energy term. We have

$$\hat{H}_{\text{el}} = \frac{-\hbar^2}{2m_e} \nabla_r^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R}. \quad (14.5)$$

The first term is the electron kinetic energy, the second and third the attraction of the electron to nuclei A and B, and the fourth the repulsion between the two nuclei.

Suppose the two nuclei are far apart. Then we would expect the electron to be bound to one of the protons - the asymptotic ground-state solution at large R is simply a ground-state hydrogen atom and a bare proton. In this case, the wavefunction is simply $\phi_{1s}(r_A)$ if the electron is bound to proton A, or $\phi_{1s}(r_B)$ if the electron is bound to proton B. Here, $\phi_{1s}(r)$ is the normalized wavefunction of ground state hydrogen:

$$\phi_{1s}(r) = \left(\frac{1}{\pi a_0^3} \right)^{1/2} \exp\left(-\frac{r}{a_0}\right). \quad (14.6)$$

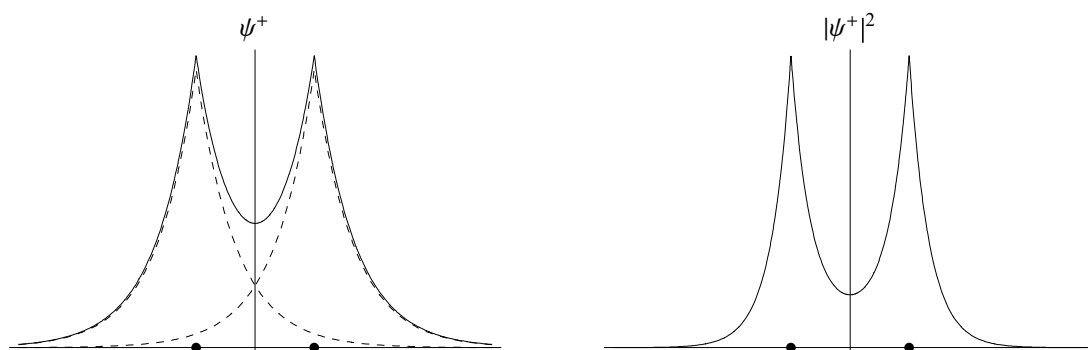
There is obviously no difference between the energies of the functions $\phi_{1s}(r_A)$ and $\phi_{1s}(r_B)$ - they are degenerate. We can form linear combinations of them, and in particular the symmetric and antisymmetric wavefunctions:

$$\psi^+(\mathbf{r}, R) = \frac{1}{\sqrt{2}} [\phi_{1s}(\mathbf{r}_A) + \phi_{1s}(\mathbf{r}_B)], \quad (14.7)$$

$$\psi^-(\mathbf{r}, R) = \frac{1}{\sqrt{2}} [\phi_{1s}(\mathbf{r}_A) - \phi_{1s}(\mathbf{r}_B)]. \quad (14.8)$$

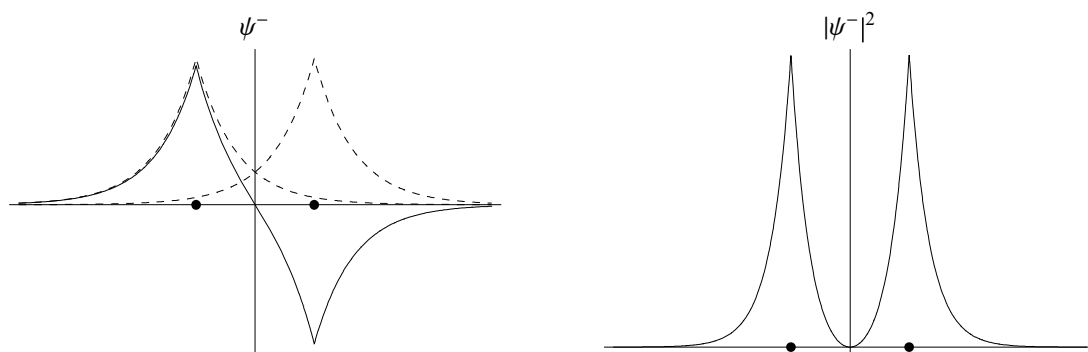
We have selected these particular linear combinations because they satisfy the symmetry requirement that the wavefunction be unchanged (up to a sign) on exchanging the two identical protons (i.e. swapping \mathbf{r}_A and \mathbf{r}_B). This is similar to the way we constructed wavefunctions that were symmetric or antisymmetric under exchange of electrons.

Below, on the left, is a plot of the symmetric wavefunction ψ^+ along the molecular axis, with the position of the two nuclei shown by the dots. It's easy to make this plot - it's simply $\frac{1}{\sqrt{2}} [\phi_{1s}(|r - R/2|) + \phi_{1s}(|r + R/2|)]$ - i.e. a sum of two exponential decay functions centred at $\pm R/2$, the positions of the two nuclei (each exponential decay is shown by the dashed lines in the plot). On the right is plotted the square of this same function, $|\psi^+|^2$. This is simply the electron density along the internuclear axis for an electron in the symmetric state ψ^+ . What we find is that, for ψ^+ , the electron density at the centre (half way between the two protons) is larger than if the electron is simply bound to one proton or the other. The two nuclei are attracted toward this enhanced electron density, and this allows them to bind together. So, ψ^+ is known as a *bonding orbital*. We see that the electron density is 'shared' between the two nuclei, with an excess of electron density near the mid-point - this is a covalent bond.



Similar plots for the antisymmetric wavefunction ψ^- are shown below. Here, we see that the electron density at the mid-point is reduced to

zero as a result of the antisymmetry. There is an absence of negative charge between the two nuclei which therefore repel each other more strongly. So ψ^- is known as an *antibonding orbital*.



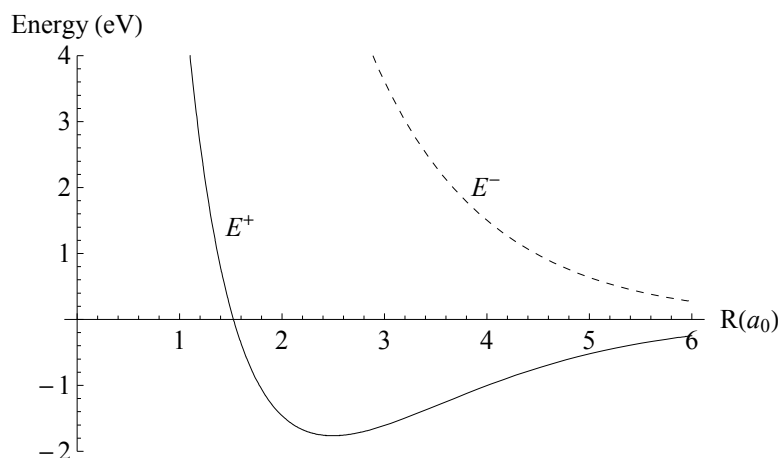
Look at the mathematical expression for the electron density. Using the fact that ϕ_{1s} is real, we get

$$|\psi^\pm|^2 = \frac{1}{2} |\phi_{1s}(r_A)|^2 + \frac{1}{2} |\phi_{1s}(r_B)|^2 \pm \phi_{1s}(r_A) \phi_{1s}(r_B). \quad (14.9)$$

It's the last term - the *interference term* - that makes the electron density different between the symmetric and antisymmetric functions. We can think of this as constructive or destructive interference of the atomic orbitals in the overlap region between the two nuclei. Constructive interference in the overlap region leads to enhanced electron density here and thus to bonding. Destructive interference in the overlap region leads to a reduction in electron density and to anti-bonding.

Now, we haven't actually found the energy eigenvalues yet! All we really know is that the wavefunctions ψ^\pm must be the correct eigenfunctions at large R . To find the energies for any value of internuclear distance R , we can use a method called the variational method. The variational principle tells us that the expectation value of \hat{H} evaluated using any arbitrary wavefunction (let's call it ψ) is always larger than or equal to the true ground-state energy, E_0 [$\int \psi^* \hat{H} \psi dV \geq E_0$. The proof is easy. You can look it up if you're interested]. So all we have to do is guess a wavefunction, then evaluate the expectation value of the Hamiltonian and we know for sure that the ground-state energy is less than this value. Usually, we leave some free parameters in the guess wavefunction and then vary them to find the parameters that gives us the minimum expectation value. This is a good way of getting close to the true energy. For our case of the H_2^+ molecule, we use the symmetric and antisymmetric wavefunctions ψ^\pm as our guess wavefunctions. This is a good idea, because these wavefunctions already have the symmetry that the problem demands. We calculate $\int (\psi^\pm)^* \hat{H}_{el} \psi^\pm dV$ with \hat{H}_{el} given by equation (14.5) and ψ^\pm given by equation (14.7) - the answer will be a function of the internuclear distance R - this gives us an approximation to the true ground state energy as a function of R . Then we repeat the procedure for ψ^- given by equation (14.8). The whole procedure is straightforward, though it involves the evaluation of some awkward integrals.

The result of the procedure is plotted below. It shows the approximate electronic energy obtained using this variational method. The solid curve (labelled E^+) is the one obtained using the symmetric wavefunction ψ^+ - we see that as the nuclei approach the energy decreases, meaning that a bond is formed. At a certain value of R , the energy has a minimum - this is the equilibrium internuclear separation, or *bond length*, R_0 . At values of $R < R_0$ the energy increases again because the two nuclei get too close together and their Coulomb repulsion dominates. The dashed curve (labelled E^-) is the one obtained using the antisymmetric wavefunction ψ^- - in this case, as the nuclei approach the energy keeps increasing - this is the antibonding orbital.



Notation

We have written the symmetric and antisymmetric functions as ψ^+ and ψ^- , so that it's easy to remember which is which. However, the conventional notation is to use the subscripts g and u which stand for "gerade" and "ungerade" ("even" and "odd" in German). So: ψ^+ becomes ψ_g while ψ^- becomes ψ_u .

14.3. Symmetry in diatomic molecules

A diatomic molecule has cylindrical symmetry about the internuclear axis. The internuclear axis defines a special axis in a molecule, and we make this our z-axis. The projection of the angular momentum onto the internuclear axis - characterized by the quantum number m_l - is a constant of the motion in a diatomic molecule. So the m_l quantum number has a special status. It cannot make any difference to the energy whether the electrons are going around the internuclear axis in the clockwise or anticlockwise direction, so there's a degeneracy with respect to $\pm m_l$. We introduce a new quantum number $\lambda = |m_l|$, and states are labelled according to their value of λ . The notation is the same as that used for atoms, except greek letters are used instead - so for $\lambda = 0, 1, 2, 3 \dots$ we use the letters $\sigma, \pi, \delta, \phi \dots$

Molecular orbitals are now labelled according to the value of λ , the atomic orbital used to construct the molecular one, and the letter g or u to denote the symmetry. Thus, the ground-state bonding orbital for H_2^+ is labelled $\sigma_g 1s$ - σ means that $\lambda = 0$, the subscript g tells us it's the "gerade" symmetry, and the $1s$ tells us that it's the $1s$ atomic orbital we've used to construct the molecular orbital. The antibonding orbital is labelled $\sigma_u^* 1s$. Here, we add the asterisk to denote the fact that this is an antibonding orbital.

14.4. Building up other diatomic molecules

Molecular orbitals are filled up according to the Pauli exclusion principle, with each orbital accommodating two electrons with opposite spin directions. So, now we can build some molecules.

- $H + H$. When two hydrogen atoms come together both electrons go into the $\sigma_g 1s$ orbital with opposite spins. The H_2 molecule is stable because both electrons are in bonding orbitals - this is why hydrogen gas is a diatomic gas.
- $He + He$. When two ground-state He atoms come together we have 4 electrons altogether, all of them in $1s$ states. Two of the electrons go into the $\sigma_g 1s$ orbital, but the other two have to go into the $\sigma_u^* 1s$ antibonding orbital. The net effect is to give a total binding energy very close to zero. This is why helium gas is a monatomic gas.
- $O + O$. The ground-state configuration of oxygen is $1s^2 2s^2 2p^4$. Now a $2p$ atomic orbital can give six molecular orbitals: they are $\sigma_g 2p$, $\sigma_u^* 2p$, $\pi_g 2p$ and $\pi_u^* 2p$ with the π orbitals being doubly degenerate because we can have $m_l = \pm 1$. Three of the six are bonding orbitals, and the other three antibonding. We have to accommodate 8 electrons from atomic p orbitals in total. The first 6 can go into the 3 bonding orbitals. The other two go into one of the antibonding orbitals. So - 3 filled bonding orbitals, 1 filled antibonding orbital, giving a net of two bonds. So the O_2 molecule is stable, having a "double bond". This is why oxygen gas is a diatomic gas.

14.5. Summary of the main points

- The Born-Oppenheimer approximation is based on the fact that the nuclei, being much heavier than the electrons, move much more slowly than the electrons.
- In the Born-Oppenheimer approximation, the total wavefunction of the molecule is written as a product of electronic, vibrational and rotational wavefunctions: $\Psi = \psi_e \psi_v \psi_r$. The total energy is the sum of the individual energies: $E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}}$.
- To find the electronic wavefunction and energy, the nuclei are fixed at a separation R . Then the nuclear kinetic energy term is absent in the electronic Hamiltonian. The electronic energy is a function of R - these are the potential energy curves of the molecule.
- Molecular orbitals are built up from linear combinations of atomic orbitals.
- For a homonuclear molecule, there has to be a symmetry through the origin, so we have symmetric ("gerade") and antisymmetric ("ungerade") states.
- In the H_2^+ molecule, the symmetric orbital is a bonding orbital. The bond is formed because of the excess electron density in the region between the nuclei. The antisymmetric orbital is an antibonding orbital because there is an absence of electron density in the region between the nuclei.

14.6. To do

- Revise the material in this handout. Useful reading is sections 5.1 and 5.2 of Thorne.
- Do questions 2 and 3 from problem set 5.

15. Vibrational and rotational structure of diatomic molecules

In the last lecture, we considered the Born-Oppenheimer approximation which tells us that the nuclear motion and the electronic motion can be treated separately. Then we looked at the electronic part of the problem. In this lecture, we look at the nuclear motion. As we will see, this gives us vibrational and rotational energy levels.

Let's begin with a sketch of the procedure involved in the Born-Oppenheimer separation of the electronic and nuclear motion. We begin with the Schrödinger equation for the diatomic molecule,

$$\hat{H} \Psi = E \Psi. \quad (15.1)$$

The full Hamiltonian \hat{H} contains the the nucletar kinetic energy \hat{T}_N , the electronic kinetic energy, \hat{T}_e , and the Coulomb potential for every charge interacting with every other charge, V :

$$\hat{H} = \hat{T}_N + \hat{T}_e + V. \quad (15.2)$$

For a diatomic molecule, with nuclei of charge $Z_A e$ and $Z_B e$, mass M_A and M_B , and having N electrons each labelled by the index i , these terms in the Hamiltonian are

$$\hat{T}_N = -\frac{\hbar^2}{2\mu} \nabla_R^2, \quad \hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2, \quad V = \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R} - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \left(\frac{Z_A}{r_{iA}} + \frac{Z_B}{r_{iB}} \right) + \frac{e^2}{4\pi\epsilon_0} \sum_{\text{all pairs}} \frac{1}{r_{ij}}. \quad (15.3)$$

Here, μ is the reduced mass of the two nuclei, given by

$$\mu = \frac{M_A M_B}{M_A + M_B}. \quad (15.4)$$

Now we write the wavefunction as a product of an electronic part and a nuclear part:

$$\Psi(\mathbf{r}_i, \mathbf{R}) = \psi_e(\mathbf{r}_i, R) \chi_N(R). \quad (15.5)$$

To find the electronic wavefunction, the electrons are fixed in place with a separation R . The nuclear kinetic energy then disappears from the Hamiltonian, and the equation we have to solve is

$$(\hat{T}_e + V) \psi_e(\mathbf{r}_i, R) = E_e(R) \psi_e(\mathbf{r}_i, R). \quad (15.6)$$

This equation is considerably easier to solve than the one where the nuclei are also allowed to move. The methods that are used are similar to the ones used to find the energy levels of an atom, e.g. the self-consistent field method. Solving this equation we get $E_e(R)$ - the electronic energy as a function of internuclear distance. This is called the potential energy curve.

It can then be shown that the nuclear wavefunctions satisfy the following equation:

$$\left(-\frac{\hbar^2}{2\mu} \nabla_R^2 + E_e(R) \right) \chi_N(R) = E \chi_N(R). \quad (15.7)$$

This is just a Schrödinger equation for the nuclear motion, where the potential that appears is the electronic energy as a function of R , $E_e(R)$. So the solution to the electronic part of the problem appears as the potential for the nuclear motion. This makes good sense. In order for the nuclei to move away from the equilibrium separation R_0 to some other R , they have to provide the energy necessary to change the electronic energy from $E_e(R_0)$ to $E_e(R)$ - which is just a way of saying that the nuclei are moving in the potential $E_e(R)$.

15.1. Rotational structure

The potential $E_e(R)$ depends only on the internuclear distance R . It does not depend on the angular coordinates of the nuclei. So, once again, we have a central potential. We know that whenever we have a potential that is not a function of the angular coordinates, we can separate the wavefunction into an angular part and a radial part. So, in the usual way, we write equation (15.7) in spherical coordinates (R, Θ, Φ) , and write the wavefunction as a product of a radial function $f(R)$ and an angular part $g(\Theta, \Phi)$:

$$\chi_N(R, \Theta, \Phi) = \frac{1}{R} f(R) g(\Theta, \Phi). \quad (15.8)$$

As always for a central potential, the angular solutions are the spherical harmonics, $g(\Theta, \Phi) = Y_{J,M}(\Theta, \Phi)$. They are angular momentum eigenfunctions satisfying

$$\hat{J}^2 Y_{J,M} = J(J+1) Y_{J,M}, \quad \hat{J}_z Y_{J,M} = M Y_{J,M}. \quad (15.9)$$

Then, we end up with the following radial equation:

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{J(J+1)\hbar^2}{2\mu R^2} + E_e(R) - E \right) f(R) = 0 \quad (15.10)$$

Next, we make the approximation that the molecular bond is quite rigid, and so the nuclear separation stays close to its equilibrium value R_0 . This is called the rigid rotor approximation. It allows us to replace R by R_0 in the second term of the above equation, so that this term is now just a constant. So the equation becomes

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + E_r + E_e(R) - E \right) f(R) = 0 \quad (15.11)$$

where

$$E_r = \frac{\hbar^2}{2\mu R_0^2} J(J+1). \quad (15.12)$$

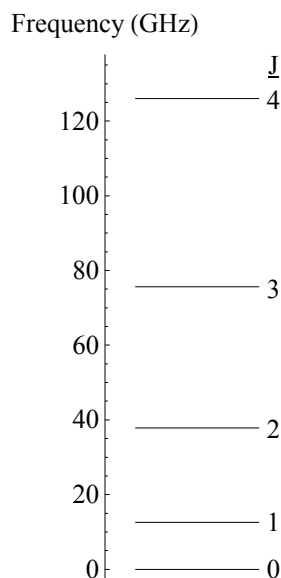
This is an expression for the rotational energy of the molecule, in this rigid rotor approximation. Note that (apart from the quantum number J and the constant \hbar), the rotational energy depends only on the reduced mass of the nuclei and on the bond length.

We can see why this is the rotational energy from a very simple model - a stick and ball model. We model the molecule as two balls (mass M_A and M_B) on the ends of a rod of length R_0 . Recall from classical mechanics that the energy of a rigidly rotating body is

$$E_r = \frac{L^2}{2I}, \quad (15.13)$$

where L is the angular momentum, and I is the moment of inertia. It's easy to show that the moment of inertia for our two balls on a stick is $I = \mu R_0^2$, where μ is the reduced mass. Using this, and the quantization of angular momentum which replaces L^2 by $J(J+1)\hbar^2$ (integer J), and we immediately have the rotational energy given by equation (15.12).

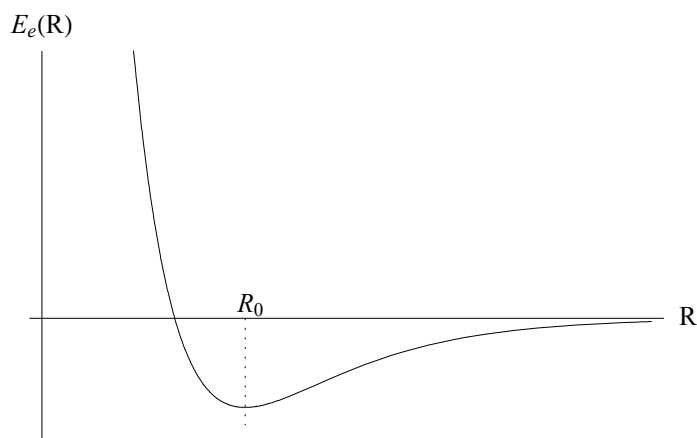
Let's look at an example - the NaCl molecule. It has a reduced mass of $\mu = 13.9$ atomic mass units, and a bond length of $R_0 = 0.24$ nm. This gives us, $E_r/h = 6.3 J(J+1)$ GHz, where we've expressed the result as a frequency. The plot below shows the ladder of rotational levels in the molecule, expressed in frequency units, with each level labelled by its value of J . The spacing of the two lowest levels is 12.6 GHz. This is in the microwave region of the electromagnetic spectrum. This is typical for the rotational states of all molecules. So transitions between rotational states of a diatomic molecule are in the microwave part of the spectrum.



15.2. Vibrational structure

We are left needing to solve the radial equation - equation (15.11). The equation contains the potential curve $E_e(R)$, and so the solutions will of course depend on the form of this potential. Whatever its form, the equation can always be solved numerically (i.e. on a computer) and the energy levels in the potential found - these are the vibrational energy levels of the molecule.

Let's look at a typical potential energy curve once again:



Whatever the exact form of the potential energy curve, we know that it has a turning point at R_0 . Let's make a Taylor expansion of $E_e(R)$ around R_0 :

$$E_e(R) \approx E_e(R_0) + \left(\frac{dE_e}{dR} \right)_{R_0} (R - R_0) + \frac{1}{2} \left(\frac{d^2 E_e}{dR^2} \right)_{R_0} (R - R_0)^2 + \dots \quad (15.14)$$

The first derivative is zero at the turning point, and so the second term in the above expression is zero. So, around the turning point we have

$$E_e(R) \approx E_e(R_0) + \frac{1}{2} k (R - R_0)^2. \quad (15.15)$$

where

$$k = \left(\frac{d^2 E_e}{dR^2} \right)_{R_0}. \quad (15.16)$$

This is simply telling us that, close enough to the turning point, the potential depends quadratically on the distance from the equilibrium point. This is the potential of a harmonic oscillator, where k is the "spring constant". In other words, provided the molecule doesn't stretch too much, it behaves like two masses connected by a spring (quantized, of course).

Substituting equation (15.15) into equation (15.11), and defining the vibrational energy, E_v by $E = E_e(R_0) + E_v + E_r$ we have

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2} k (R - R_0)^2 - E_v \right) f(R) = 0, \quad (15.17)$$

which is the equation for a quantum harmonic oscillator. You've studied the solutions to this equation before, so we can skip directly to the solution. In particular, the energy eigenvalues are

$$E_v = (v + 1/2) \hbar f_0, \quad (15.18)$$

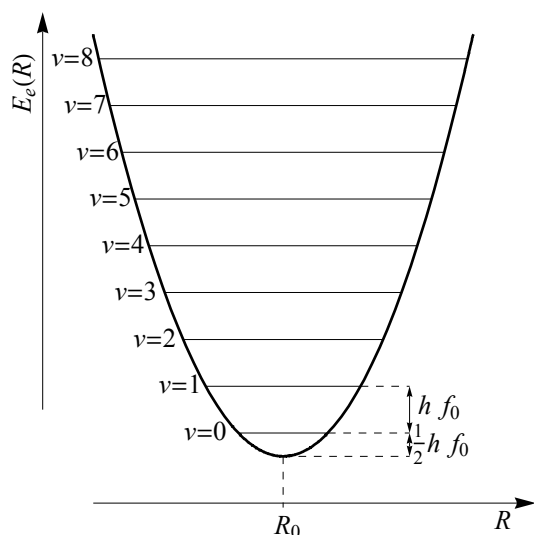
where $v = 0, 1, 2 \dots$ is the vibrational quantum number, and

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}. \quad (15.19)$$

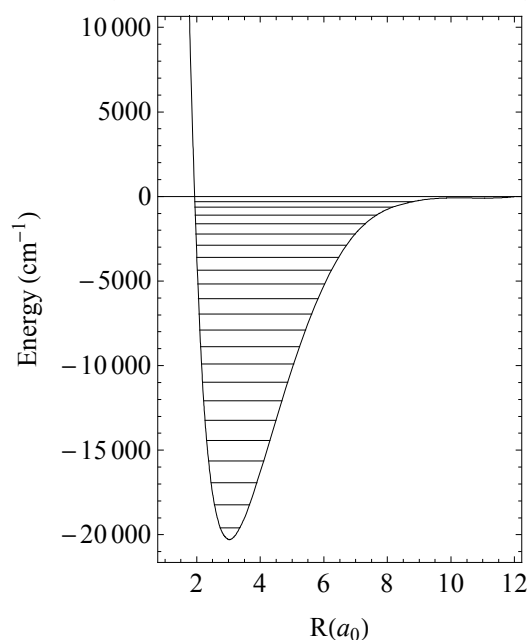
is the frequency of the oscillations. So we get a ladder of equally spaced vibrational energies, separated by the energy $\hbar f_0$, and with the lowest level being $1/2 \hbar f_0$ above the zero-point of the potential.

Let's look again at the example of the NaCl molecule. For this molecule, $f_0 = 1.1 \times 10^{13}$ Hz. This is the fundamental vibrational frequency of the molecule. The vibrational frequencies of other molecules are similar. Notice how the vibrational frequency is much larger than the rotational frequency (which for most molecules is in the $10^{10} - 10^{11}$ Hz range), but much smaller than a typical electronic energy spacing (which is usually in the $10^{14} - 10^{15}$ Hz range). Also, the vibrational frequency is small compared to the typical depth of the electronic potential - for NaCl, $\hbar f_0 = 0.045$ eV whereas the potential depth is 4.3 eV. This means that there are a very large number of vibrational energy levels inside the potential, and our harmonic-oscillator approximation is a very good approximation for all the low-lying levels.

The figure below shows schematically the bottom of the potential energy curve, and the low-lying vibrational energy levels within it.



If we go far enough up the vibrational ladder, we notice that the potential is not harmonic any longer. For this reason, the high-lying vibrational levels are no longer equally spaced. The spacing between the levels decreases as the vibrational quantum number increases. This is illustrated in the figure below which shows the vibrational energy levels for the ground-state molecular potential of the LiH molecule.



15.3. Summary of the main points

- The rotational energies of a diatomic molecule are given by $E_r = \frac{\hbar^2}{2\mu R_0^2} J(J+1)$, where μ is the reduced mass, R_0 is the bond length, and J is the rotational quantum number ($J = 0, 1, 2, \dots$). The rotational spacing increases as J increases.
- Rotational eigenfunctions are spherical harmonics. Rotational energy spacings are in the microwave region, typically 10-100 GHz.
- The low-lying vibrational energies of a diatomic molecule are given by $E_v = (v + 1/2) h f_0$ where f_0 is the vibrational frequency and v is the vibrational quantum number ($v = 0, 1, 2, \dots$). The vibrational frequency is related to the reduced mass and the spring constant via

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}. \text{ The vibrational spacing is a constant for the low-lying levels.}$$

- Vibrational eigenfunctions are those of a harmonic oscillator. Vibrational energy spacings are in the infra-red, typically 10 THz.
- Electronic energy spacings are in the visible and ultra-violet region, typically 100-1000 THz.

15.4. To do

- Revise the material in this handout. Useful reading is sections 5.3 & 5.4 of Thorne.
- Do question 4 from problem set 5.