Atomic Physics

Lecture 1 : Introduction to hydrogen

1.1 Internal state of the atom

Consider a proton (mass m_p, charge e, position $\underline{r}_p$) and an electron (mass m_e, charge $-e$, position $\underline{r}_e$). We'll ignore spin for now so the wavefunction is $\psi(\underline{r}_p, \underline{r}_e)$. Accounting for the electric interaction between the charged particles, the total Hamiltonian is

$$\hat{H}_{total} = \left(\frac{-\hbar^2}{2m_p}\nabla_p^2\right) + \left(\frac{-\hbar^2}{2m_e}\nabla_e^2\right) + \left(\frac{-e^2}{4\pi\epsilon_0}\frac{1}{|\underline{r}_e - \underline{r}_p|}\right) \qquad (1)$$

where the final term is the electric potential energy.

We define

$$M = m_e + m_p \qquad \text{"total mass"}$$

$$\underline{R} = \frac{m_e\underline{r}_e + m_p\underline{r}_p}{M} \qquad \text{"Center-of-mass position"}$$

$$m = \frac{m_e m_p}{m_e + m_p} \qquad \text{"reduced mass"}$$

$$\underline{r} = \underline{r}_e + \underline{r}_p \qquad \text{"relative electron position"}$$

Rewriting (1) interms of the new variables:

$$\hat{H}_{total} = \hat{H}_c + \hat{H}$$

$$\hat{H}_c = \frac{-\hbar^2}{2M}\nabla_R^2$$

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla_r^2 + \frac{-e^2}{4\pi\epsilon_0}\frac{1}{|\underline{r}|} \qquad (5)$$

$\hat{H}_c$ describes a free particle with mass M and position $\underline{R}$. This is the KE of the atom as a whole. The term $\hat{H}$ describes the internal workings of the atom, in terms of kinetic and potential energy due to $\underline{r}$.

We solve for eigenstates of

$$\hat{H}_c u_c(\underline{R}) = E_c u_c(\underline{R})$$

$$\hat{H} u(\underline{r}) = E u(\underline{r})$$

We can then construct the total eigenstate as

$$u_t(\underline{R}, \underline{r}) = u_c(\underline{R})\, u(\underline{r})$$

$$\hat{H}_{total} u_t(\underline{R}, \underline{r}) = E_t u_t(\underline{R}, \underline{r})$$

where $E_t = E_c + E$

The problem nicely separates, we can focus entirely on internal states $u(\underline{r})$

1.2 A natural scale for distance

To understand the atom, we need to solve for energy eigenstates and energy eigenvalues for $\hat{H}$ given in (5). We have a central potential so we write the eigenstates in spherical coordinates as

$$u(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi) = \frac{1}{r}\chi(r)Y_{lm}(\theta,\phi) \qquad (10)$$

Plugging (10) into (5) yields the eigenvalue equation

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right]\chi(r) = E\chi(r) \qquad (11)$$

We define a length to tidy things up. a_0

$$\frac{e^2}{4\pi\epsilon_0}\frac{1}{a_0} \quad \text{and} \quad \frac{\hbar^2}{ma_0^2}$$

are both energies, equating these we find

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2 m} \approx 5.3\times10^{-11}\,m \qquad \text{"effective Bohr radius"}$$

1.3 A natural scale for energy

We rewrite (11) in terms of the scaled distance $r_0 = \frac{r}{a_0}$:

$$\frac{1}{2}\alpha^2 mc^2\left[-\frac{d^2}{dr_0^2} + l(l+1)\frac{1}{r_0^2} + -\frac{2}{r_0}\right]\chi(r) = E\chi(r) \qquad (14)$$

where

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = 0.007297 \qquad \text{"fine-structure constant"}$$

α has no dimensions; its value doesn't depend on the choice of units.
By expressing distances in terms of a_0, (14) shows dimensionless kinetic and potential terms that are unified by the prefactor

$$\frac{1}{2}\alpha^2 mc^2 \approx 13.6\,eV$$

which sets the energy scale for the atom

For the reduced mass, since

$$m_e = 9.1\times10^{-31}\,kg = 0.51\,MeV/c^2$$
$$m_p = 1.7\times10^{-27}\,kg = 940\,MeV/c^2$$

the approximation $m \approx m_e$ is accurate to better than 0.1%.

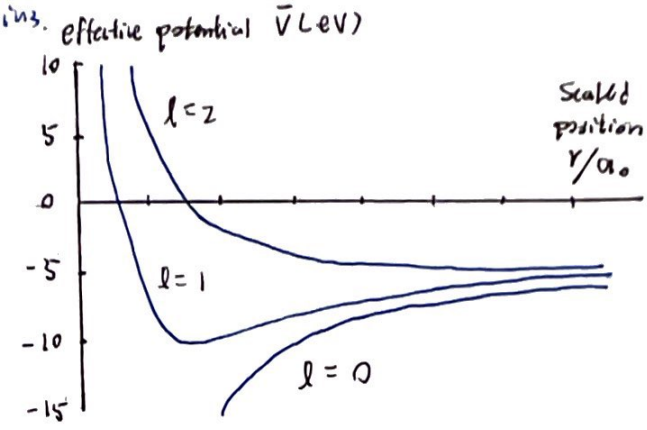
Lecture 2: The hydrogen gross structure

2.1 The effective radial potential

We found that the radial dependence of the energy eigenstates is captured by the function $\chi(r)$ that obeys (14). This is an eigenvalue equation that is analogous to the 1-D Schrödinger equation with an effective potential

$$\tilde{V}(r) = \frac{1}{2}\alpha^2 mc^2 \left[l(l+1)\frac{a_0^2}{r^2} - \frac{2a_0}{r} \right] \qquad (20)$$

where a_0 is the effective Bohr radius.



For large r, the electron is far from the proton. The $-\frac{1}{r}$ dominates as the potential approaches 0. For small, the electron is close to the proton. For $l=0$ the potential falls to $-\infty$ as expected. For $l>0$ however, the $\frac{1}{r^2}$ term dominates and the potential approaches ∞. Recall that the $\frac{1}{r^2}$ came from rotational kinetic energy. Here, it is effectively playing the role of a potential barrier (angular momentum barrier). The minimum of the potential occurs at larger r for larger l. For $l = 0, 1, 2$, the approximate mina $-\infty, -6.8\,eV, -2.3\,eV$ occur at $r = 0, 2a_0, 6a_0$.

2.2 1-D radial eigenfunctions: $\chi_{jl}(r)$

We seek eigenfunctions to

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dr^2} + \tilde{V}(r) \right] \chi(r) = E\chi(r) \qquad (21)$$

which has the appearance of a 1-D Schrödinger equation. We can write this second-order homogeneous ODE as

$$\frac{d^2y}{dx^2} - \left(\frac{a}{x^2} + \frac{1}{x} \right) y + cy = 0$$

which follows from (20) and (21)

Before we see the actual eigenfunctions, we can guess their shape using intuition from the 1-D square-well and harmonic potential problems that we previously solved. The eigenfunction must satisfy $\chi(0) = 0$ for the energy to be finite and $\chi(\infty) = 0$ to be normalisable. The curvature of $\chi(r)$ is proportional to $E - \tilde{V}$. Finally, the lowest-energy function has only the one node at $r=0$. The second-lowest has two nodes, the third lowest three...

2.3 Energy eigenvalues E_n

The energy eigenvalues are

$$E = -\frac{1}{2}\alpha^2 mc^2 \frac{1}{(j+l)^2}$$

The lowest-energy state has $l=0$ and $j=1$, and increasing either number corresponds to an increase in energy. This shouldn't be surprising: a state with larger orbital angular momentum or more radial nodes has a higher energy. However, increasing l or j by 1 results in the same increase in energy. It's an accidental degeneracy.

Fundamentally, we care more about the energy of an eigenstate than its number of nodes. Thus the convention is to define:

$n = j + l$ "principal quantum number"

so that

$$E_n = -\frac{1}{2}\alpha^2 mc^2 \frac{1}{n^2} \approx -13.6\,\text{eV}\frac{1}{n^2}$$

There are two consequences of this definition:

(1) For all eigenstates, n is an integer, $n>0$, and $l<n$.

(2) Two states with the same n have the same energy, regardless of their l values

Lastly, $E_n<0$ implies that magnitude of the mean potential energy is larger than that of the kinetic energy, which is for a state in which the electron and proton are bound together. In contrast, an energy $E \geq 0$ implies the atom is broken apart. For an atom in its ground state, 13.6eV must be added to irreversibly separate the particles, this is called the ionisation energy.

2.4 Radial eigenfunction : $R_{nl}(r)$

Once (21) is solved for the eigenfunctions $\chi(r)$, we write the radial eigenfunctions of the hydrogen atom as $R_{nl} = \frac{1}{r}\chi_{n-l,l}$. Let's skip to the solution

$$R_{n,l} = N_{nl}\left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left[\frac{2r}{na_0}\right]e^{-r/na_0}$$

The function $L_k^m(x)$ is polynomial of order k (up to x^k) known as an associated Laguerre polynomial. N_{nl} is a normalisation constant

Here we can use the $L_k^n(x)$ to calculate the first few radial wave functions

Here are two observations about these wavefunctions:

(1) All R_{nl} have the form of a polynomial in r, of order $n-1$, multiplied by an exponential with decay length na_0. Due to this exponent, wavefunctions with larger n extend to larger distances.

(2) Due to the angular momentum barrier, at the origin $R_{nl}(0)=0$ if $l>0$. For $l=0$, $R_{n,0}(0)>0$ for all n values. Note this is different than the χ functions, all of which have a node at $r=0$.

2.5 Angular eigenfunctions: $Y_{lm}(\theta,\phi)$

The spherical harmonic function Y_{lm}, which are the angular eigenfunctions for all systems with spherically symmetric potentials, including our atom. The general expression for $m \geq 0$ is

$$Y_{lm}(\theta,\phi) = \frac{(-1)^l}{2^l l!}\sqrt{\frac{(2l+1)(l+m)!}{4\pi(l-m)!}}\, e^{im\phi}\frac{1}{\sin^m\theta}\frac{d^{l-m}}{d(\cos\theta)^{l-m}}\sin^{2l}\theta$$

and for $m<0$

$$Y_{lm}(\theta,\phi) = (-1)^m[Y_{l,-m}(\theta,\phi)]^*$$

These are sometimes expressed in terms of another set of polynomials called the associated Legendre polynomials.

2.6 Total eigenfunctions: $u_{nlm}(r,\theta,\phi)$

The complete energy eigenfunction are given by $u_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$

These are the basis for understanding the physical structure of the atom.

2.7 Size of the atom

As an indication of the size of the ground state, we calculate

$$\langle r\rangle = \iiint r|u_{1,0,0}|^2 r^2\sin\theta\, dr\, d\theta\, d\phi = \int_0^\infty r^3|R_{1,0}(r)|^2 dr$$

$$= \frac{4}{a_0^3}\int_0^\infty r^3 e^{2r/a_0}dr = \frac{3}{2}a_0$$

For the last step the integral is solved by starting with the simpler integral $\int_0^\infty e^{-\alpha x}dx = \frac{1}{\alpha}$ and differentiating both sides by α a few times until the integral is in the desired form.

2.8 Dirac notation

The eigenstate for atoms can be specified by a list of quantum numbers. When we don't need the explicit wave function, we can use Dirac's notation

$$u_{n,l,m} \rightarrow |n,l,m\rangle$$

The ket symbol indicates a quantum state.

Lecture 3. Two-electron states

3.1 Notation for the position and spin of one electron

Recall that any kind of angular momentum can be described by a vector operator $\hat{\underline{J}} = (\hat{J}_x, \hat{J}_y, \hat{J}_z)$ with components that satisfy $[\hat{J}_i, \hat{J}_j] = i\hbar\varepsilon_{ijk}\hat{J}_k$.
In Dirac notation we can write quantum states as $|j,m\rangle$ and the eigenvalue relationship are thus

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

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

For spin angular momentum, we replace the letter J with S. The operator is $\hat{\underline{S}}$ and the quantum numbers are s and m_s. For a spin-$\frac{1}{2}$ particle, the two eigenstates $|s,m_s\rangle$ are

$$|\tfrac{1}{2},\tfrac{1}{2}\rangle = |\uparrow\rangle \quad \text{and} \quad |\tfrac{1}{2},-\tfrac{1}{2}\rangle = |\downarrow\rangle$$

Consider eigenstates of the electron in hydrogen, using the gross-structure model. Since the Hamiltonian does not depend on spin, an eigenstate can be written as a product state:

$$\psi(\underline{r},\underline{s}) = u_{n\ell m}(\underline{r})\,\xi(\underline{s})$$

In Dirac notation, we could simply express this total state as $|n,\ell,m,m_s\rangle$

3.2 Identical particles

To study this in a precise way, we introduce the exchange operator P:

$$\hat{P}\Psi(\underline{r}_1,\underline{r}_2) = \Psi(\underline{r}_2,\underline{r}_1)$$

This operation doesn't change the state in a meaningful way if the particles are identical. A valid two electron state must satisfy:

$$\Psi(\underline{r}_2,\underline{r}_1) = \lambda\Psi(\underline{r}_1,\underline{r}_2)$$

where $|\lambda| = 1$. We try applying $\hat{P}$ twice, we will get back to where we started:

$$\hat{P}^2\Psi(\underline{r}_1,\underline{r}_2) = \hat{P}\Psi(\underline{r}_2,\underline{r}_1) = \Psi(\underline{r}_1,\underline{r}_2) = \lambda^2\Psi(\underline{r}_1,\underline{r}_2)$$

Therefore $\lambda = 1$ or -1.

3.3 Symmetric and antisymmetric two-particle states

The eigenvalue λ relates to the symmetry of a two-particle wavefunction with respect to the exchange operation. $\lambda = -1$ is "antisymmetric".

$[\hat{H}, \hat{P}] = 0$, implying that the wavefunction symmetry remains constant. For example, if a two-particle wavefunction is symmetric, it remains so.

In nature, particles with integral spins $(s = 0, 1, 2, \cdots)$ which we call bosons, are in symmetric states. Particles with half-integral spin $(s = \frac{1}{2}, s = \frac{3}{2}, \ldots)$ which we call fermions, are in antisymmetric states.

3.4 Total spin of two spin-$\frac{1}{2}$ particles

Two particles states can be represented as a superposition of the four eigenstates of $(\hat{S}_1^2, \hat{S}_2^2, \hat{S}_{1z}, \hat{S}_{2z})$, which we can write as $|s_1, s_2, m_{s_1}, m_{s_2}\rangle$. Using the arrow notation, the four eigenstates are

$$|\uparrow,\uparrow\rangle, \ |\uparrow,\downarrow\rangle, \ |\downarrow,\uparrow\rangle, \text{ and } |\downarrow,\downarrow\rangle$$

The second state denotes $m_{s_1} = \frac{1}{2}$ and $m_{s_2} = -\frac{1}{2}$.

$\hat{S}_{1z}|\uparrow,\downarrow\rangle = \frac{\hbar}{2}|\uparrow,\downarrow\rangle$, $\hat{S}_{2z}|\uparrow,\downarrow\rangle = -\frac{\hbar}{2}|\uparrow,\downarrow\rangle$

If the two particles are identical, then $|\downarrow,\uparrow\rangle$ and $|\uparrow,\downarrow\rangle$ are invalid states.

$$\hat{P}|\uparrow,\downarrow\rangle = |\downarrow,\uparrow\rangle \neq \lambda|\uparrow,\downarrow\rangle$$

The problem is solved by using the symmetric and antisymmetric combinations $\frac{1}{\sqrt{2}}(|\uparrow,\downarrow\rangle \pm |\downarrow,\uparrow\rangle)$. If the particles are identical, it's impossible to measure $\hat{S}_{1z}$ or $\hat{S}_{2z}$ separately since it's meaningless to say which particle is which.

We can instead measure the total spin of the two-particle system defined as

$$\hat{\underline{S}} = \hat{\underline{s}}_1 + \hat{\underline{s}}_2$$

This implies a linear relationship between the components of the operators. $\hat{\underline{S}}$ commutes and the sum of two angular momentum operators is also an angular momentum operator.

To construct a new basis we use the complete set of compatible observables $(\hat{S}^2, \hat{S}_z, \hat{S}_1^2, \hat{S}_2^2)$. The basis states satisfy

$$\hat{S}^2|s, M_s\rangle = s(s+1)\hbar^2|s, M_s\rangle$$

$$\hat{S}_z|s, M_s\rangle = M_s\hbar|s, M_s\rangle$$

where s is the total spin quantum number and M_s the z component quantum

number of the total spin.

We can now interpret the symmetric and antisymmetric states in the single-spin basis in terms of their total spin. For example

$$\hat{S}^2\left[\frac{1}{\sqrt{2}}(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle)\right] = 2\hbar^2\left[\frac{1}{\sqrt{2}}(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle)\right]$$

$$\hat{S}_z\left[\frac{1}{\sqrt{2}}(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle)\right] = 0$$

which implies that the state $\frac{1}{\sqrt{2}}(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle)$ has quantum number $S=1$ and $M_S=0$. If we check all four states, we find:

Single-spin kets	total spin kets, $\lvert S, M_S\rangle$	exchange symmetry
$\lvert\uparrow,\uparrow\rangle$	$\lvert 1,1\rangle$	symmetric
$\frac{1}{\sqrt{2}}(\lvert\uparrow,\downarrow\rangle + \lvert\downarrow,\uparrow\rangle)$	$\lvert 1,0\rangle$	symmetric
$\lvert\downarrow,\downarrow\rangle$	$\lvert 1,-1\rangle$	symmetric
$\frac{1}{\sqrt{2}}(\lvert\uparrow,\downarrow\rangle - \lvert\downarrow,\uparrow\rangle)$	$\lvert 0,0\rangle$	antisymmetric

For two spin-$\frac{1}{2}$ particles, there are three $S=1$ states and they are symmetric. The state with $S=0$ is antisymmetric.

3.5 Position and spin of two electrons

In anticipation to the helium gross structure, we're interested in describing eigenstates of a Hamiltonian that does not depend on spin. These states are thus product states

$$\Psi(\underline{r}_1, \underline{s}_1, \underline{r}_2, \underline{s}_2) = \Phi(\underline{r}_1, \underline{r}_2)\,\chi(\underline{s}_1, \underline{s}_2)$$

where $\underline{r}$ and $\underline{s}$ label the position and spin degrees of freedom of each particle, Φ is a two particle waveform and χ is a two-particle spin state. Let's consider the action of $\hat{P}$ on the total state:

$$\hat{P}\Psi(\underline{r}_1, \underline{s}_1, \underline{r}_2, \underline{s}_2) = \Psi(\underline{r}_2, \underline{s}_2, \underline{r}_1, \underline{s}_1) = \Phi(\underline{r}_2, \underline{r}_1)\,\chi(\underline{s}_2, \underline{s}_1) = [\hat{P}\Phi(\underline{r}_1, \underline{r}_2)][\hat{P}\chi(\underline{s}_1, \underline{s}_2)]$$

Ψ is an eigenstate of $\hat{P}$ only if Φ and χ are also eigenstates of $\hat{P}$.

~~Since~~ Since electrons are fermions, $\hat{P}\Psi = -\Psi$. Thus $\lambda_\Phi \lambda_\chi = -1$

In other words if the spatial wavefunction is symmetric then the spin state is antisymmetric and vice versa.

- If one electron has wavefunction ψ and one electron has wavefunction ϕ, the possible wavefunctions are

$$\Phi_S(\underline{r}_1, \underline{r}_2) = N_S(\psi(\underline{r}_1)\phi(\underline{r}_2) + \phi(\underline{r}_1)\psi(\underline{r}_2))$$

$$\Phi_A(\underline{r}_1, \underline{r}_2) = N_A(\psi(\underline{r}_1)\phi(\underline{r}_2) - \phi(\underline{r}_1)\psi(\underline{r}_2))$$

where the symmetric state satisfies $\hat{P}\Phi_S = \Phi_S$ and the antisymmetric state satisfies $\hat{P}\Phi_A = -\Phi_A$.

Similarly, there are three possible symmetric spin states, which we could label as χ_{S,M_S}. So we have $\chi_{1,1}, \chi_{1,0}, \chi_{1,-1}$. The antisymmetric spin state is $\chi_{0,0}$. The possible two-electron ~~spin~~ states Ψ are therefore:

$$\Phi_S \chi_{0,0} \quad \text{and} \quad \Phi_A \chi_{1,i}$$

where $i = 1, 0,$ or -1. To specify the state, we only need the two wave functions and the quantum numbers S and M_S. In Dirac notation:

$$|\psi, \phi, S, M_S\rangle$$

If $S=1$ the spatial state must be antisymmetric and vice versa

3.6 Pauli's exclusion principle and Hund's rules

Pauli's principle state that two electrons can't have the same quantum state. The spin states $|\uparrow,\uparrow\rangle$ and $|\downarrow,\downarrow\rangle$ are both symmetric. The spatial wavefunction must therefore be antisymmetric. But if $\psi = \phi$ then there is no antisymmetric wavefunction.

$$\Phi_A(\underline{r}_1, \underline{r}_2) = N_A(\psi(\underline{r}_1)\psi(\underline{r}_2) - \psi(\underline{r}_1)\psi(\underline{r}_2)) = 0$$

We therefore conclude that if two electrons have the same spatial state, then their spatial wavefunction must be symmetric. In fact it is simply $\psi(\underline{r}_1)\psi(\underline{r}_2)$. Consequently, their spin state must be $S=0$.

This is related to Hund's rule used to explain electron configuration in atoms. The conventional idea is that there can be two electrons per orbital. It's not because the spins are opposite, the two spins are in the antisymmetric state with total spin 0.

Lecture 4: Helium gross structure

4.1 A three particle Hamiltonian

Helium atom: two e^-'s that are bound to a nucleus with two protons

Nucleus is treated as a particle with a charge, mass, and spin.

The total Hamiltonian for two e^-'s and a nucleus is:

$$\hat{H}_{total} = \left(\frac{-\hbar^2}{2m_n}\nabla_n^2\right) + \sum_{i=1}^{2}\left(\frac{-\hbar^2}{2m_e}\nabla_i^2 + \frac{-Ze^2}{4\pi\varepsilon_0}\frac{1}{|\underline{r}_i-\underline{r}_n|}\right) + \left(\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\underline{r}_1-\underline{r}_2|}\right)$$

$\underline{r}_n$ and m_n are the position and mass of the nucleus, $\underline{r}_i$ is the position of the ith electron. The first term is the KE of the nucleus. The second term is KE and electric PE for each electron w.r.t. the nucleus. Z is the number of protons in the nucleus ($Z=2$). The final term is the electric potential energy associated with the repulsion of the electrons.

We need approximation: We assume that from the perspective of the electrons, the nucleus is stationary.

4.2 Electron-electron repulsion as a perturbation

Assume nucleus fixed at $\underline{r}_n = 0$, the two-electron Hamiltonian can be written as

$$\hat{H}' = \hat{H}_0 + \hat{H}_1$$

where individual contributions from each electron are described by

$$\hat{H}_0 = \sum_{i=1}^{2}\left(\frac{-\hbar^2}{2m_e}\nabla_i^2 + \frac{-Ze^2}{4\pi\varepsilon_0}\frac{1}{|\underline{r}_i|}\right)$$

and the interaction of the two electrons is described by

$$\hat{H}_1 = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\underline{r}_1-\underline{r}_2|}$$

Since we know the solutions to $\hat{H}_0$, we can try using time-independent perturbation theory. This will only work if the influence of $\hat{H}_1$ is relatively small.

4.3 Ground State Energy

We start with zeroth-order perturbation theory i.e. solutions for $\hat{H}_0$

The ground state is:

$$U_g(\underline{r}_1, \underline{r}_2) = u_{1,0,0}(\underline{r}_1)\, u_{1,0,0}(\underline{r}_2)$$

where $u_{1,0,0}$ is a hydrogenic wavefunction. The total eigenenergy is $E_g = 2E_{(n=1)}$

There are $Z=2$ protons in the nucleus. The length and energy scales become

$$a_0 \to a_0/Z$$
$$\alpha \to Z\alpha$$

The length scale is thus reduced to $a_0/2$ due to stronger attraction.

$$E_g = 2 \times E_{(n=1)} = -2 \times \frac{1}{2} Z^2 \alpha^2 m_e c^2 = -8 \times (\tfrac{1}{2}\alpha^2 m_e c^2)$$
$$\approx -8 \times (13.6\,eV) = -108.8\,eV$$

First-order perturbation theory, we anticipate this will make electrons less strongly bound to the nucleus, which increases the ground state energy.

$$E_g' \approx E_g + \delta E_g^{(1)} \quad \text{where} \quad \delta E_g^{(1)} = \langle U_g, \hat{H}_1 U_g \rangle$$

$$\delta E_g^{(1)} = \frac{e^2}{4\pi\varepsilon_0} \iint \frac{1}{|\underline{r}_1 - \underline{r}_2|} |U_g(\underline{r}_1, \underline{r}_2)|^2 d\underline{r}_1 d\underline{r}_2 = \frac{5}{4}\frac{1}{a_0}$$

Using the definitions of a_0 and α:

$$\delta E_g^{(1)} = \frac{5}{4}\alpha^2 m_e c^2$$
$$= \frac{5}{16}(4\alpha^2 m_e c^2) = \frac{5}{16}|E_g|$$

To first order, we estimate the energy to be

$$E_g' \approx E_g + \delta E_g^{(1)} \approx -74.8\,eV$$

which is 34 eV higher than our zeroth-order estimate in ground state

If we extend to higher orders, answer converges to $-79.0\,eV$

We can now calculate the energy required to remove one electron from helium, to create He^+. This energy is $(E_{(n=1)} - E_g') = 24.5\,eV$

4.4 Excited state energies

We can use perturbation theory to estimate excited state energies. In 0th order approximation, an excited state consists of one e^- with $n=1$ while one electron is in a higher ~~state~~ (n,l) state.

... The two valid wavefunctions are

$$\Phi_+(\underline{r}_1,\underline{r}_2) = N_+[u_g(\underline{r}_1)u_e(\underline{r}_2) + u_e(\underline{r}_1)u_g(\underline{r}_2)] \quad (73)$$

$$\Phi_-(\underline{r}_1,\underline{r}_2) = N_-[u_g(\underline{r}_1)u_e(\underline{r}_2) - u_e(\underline{r}_1)u_g(\underline{r}_2)] \quad (74)$$

u_g, u_e : ground state & excited state wavefunctions

Φ_+, Φ_- : symmetric and antisymmetric wavefunctions

The first order energy shifts are :

$$\delta E_\pm^{(1)} = \langle \Phi_\pm, \hat{H}_1 \Phi_\pm \rangle$$

$$= N_\pm^2 \left(\langle u_g u_e, \hat{H}_1 u_g u_e \rangle \pm \langle u_e u_g, \hat{H}_1 u_g u_e \rangle \pm \langle u_g u_e, \hat{H}_1 u_e u_g \rangle + \langle u_e u_g, \hat{H}_1 u_e u_g \rangle \right)$$

The first inner product is evaluated with the integral

$$\langle u_g u_e, \hat{H}_1 u_g u_e \rangle = N_\pm^2 \frac{e^2}{4\pi\varepsilon_0} \iint \frac{1}{|\underline{r}_1 - \underline{r}_2|} |u_g(\underline{r}_1)|^2 |u_e(\underline{r}_2)|^2 \, d\underline{r}_1 \, d\underline{r}_2$$

Since this integral is unchanged by exchanging $\underline{r}_1$ and $\underline{r}_2$, the first and last term are equal.

$$\langle u_g u_e, \hat{H}_1 u_g u_e \rangle = \langle u_e u_g, \hat{H}_1 u_e u_g \rangle$$

We define

$$J = \langle u_g u_e, \hat{H}_1 u_g u_e \rangle + \langle u_e u_g, \hat{H} u_e u_g \rangle$$

which we call the direct integral. J can be interpreted as the mean electric potential energy of two charges with probability densities $|u_g|^2$ and $|u_e|^2$.

Similarly,

$$\langle u_e u_g, \hat{H}_1 u_g u_e \rangle = N_\pm^2 \frac{e^2}{4\pi\varepsilon_0} \iint \frac{1}{|\underline{r}_1 - \underline{r}_2|} u_e(\underline{r}_1)^* u_g(\underline{r}_2) u_g(\underline{r}_1)^* u_e(\underline{r}_2) \, d\underline{r}_1 \, d\underline{r}_2$$

$$= N_\pm^2 \frac{e^2}{4\pi\varepsilon_0} \iint \frac{1}{|\underline{r}_1 - \underline{r}_2|} f(\underline{r}_1)^* f(\underline{r}_2) \, d\underline{r}_1 \, d\underline{r}_2$$

where $f(\underline{r}) = u_g(\underline{r}) u_e(\underline{r})$, therefore

$$\langle u_e u_g, \hat{H}_1 u_g u_e \rangle = \langle u_g u_e, \hat{H}_1 u_e u_g \rangle^*$$

We define

$$K = \langle u_e u_g, \hat{H}_1 u_g u_e \rangle + \langle u_g u_e, \hat{H}_1 u_e u_g \rangle$$

which we call the exchange integral. We can see it as a neighbor overlap of the single-particle wavefunction. J and K are both positive and $J > K$

Putting together these integrals, we calculate the first order energy shift

$$\delta E_{\pm}^{(1)} = J \pm K$$

Recall (+) is for symmetric wavefunction (spin state $S=0$) and vice versa.

4.5 Excited state energies: results

We have estimated the energy of a helium state starting with one e^- in the $(1,0,0)$ wavefunction and one electron in a higher (n, l, m_l) wavefunction. Including spin, there are 4 such states, which we can write as $|u_1, u_2, S, M_S\rangle$

$$|(u_{1,0,0}), (u_{n,l,m_l}), 0, 0\rangle \text{ and } |(u_{1,0,0}), (u_{n,l,m_l}), 1, M_S\rangle$$

where the second states have values $M_S = -1, 0, 1$

To 0th order, we ignore electron-electron repulsion and the four states have the same energy. In first order perturbation, we estimated the influence of electron-electron repulsion by calculating two integrals. First, energy of all four states is increased by the ~~exchange~~ direct integral J. Second, the energy of the $S=0$ state is further increased by the exchange integral K, while decreased for the same amount for $S=1$. The energy shift is due to the required symmetry of the total two-electron state.

The integral values, thus the first order energies, depends on both n and l, which differs from the zeroth-order hydrogenic energies

We can look back at (73), (74). Electron-electron repulsion is proportional to $|\underline{r}_1 - \underline{r}_2|^{-1}$, so its importance is largest when the electrons are close together. More precisely, the repulsion is large for parts of the two-e^- wavefunction $\Phi_{\pm}(\underline{r}_1, \underline{r}_2)$ where $\underline{r}_1$ is close to $\underline{r}_2$. We see that $\Phi_-(\underline{r}_1, \underline{r}_2)$ is very small in this case.

If both e^-s are in excited states, the lowest energy of such a doubly-excited state would have both e^-s in a $n=2$ state. It turns out the energy in this case will be higher than that of a single electron in ground state.

4.6 Nomenclature

Standard nomenclature for atomic states comes from conventions in spectroscopy that predate quantum theory.

l quantum number	notation
0	s
1	p
2	d
3	f

$(n=1, l=0) \rightarrow 1s$

$(n=2, l=1) \rightarrow 2p$

$(n=3, l=2) \rightarrow 3d$

To partly specify a helium in the zeroth-order approximation, we simply give the designation for two states:

helium ground state $\rightarrow$ 1s 1s or $1s^2$

$(n,l) = (3,1)$ state $\rightarrow$ 1s 3p

S value also needs to be stated to specify an energy eigenvalue.

1s3p, $S=1$

This specifies an energy in the helium gross structure model, but m_l and M_s are needed to specify a quantum state. Each of them have possible values $(-1,0,1)$ so there are 9 orthogonal states with this energy.

4.7 Multielectron atoms and the electron configuration

The starting point is a model that describes the zeroth order ~~mult~~ multielectron states as a product of single-electron wavefunctions. When the $e^- - e^-$ repulsion is fully accounted for, the actual eigenstates differ from the zeroth-order state. But the latter still gives a practical way to describe the state.

lithium ($3e^-$s)	$1s^2 2s$
nitrogen ($7e^-$s)	$1s^2 2s^2 2p^3$
argon ($18e^-$s)	$1s^2 2s^2 2p^6 3s^2 3p^6$

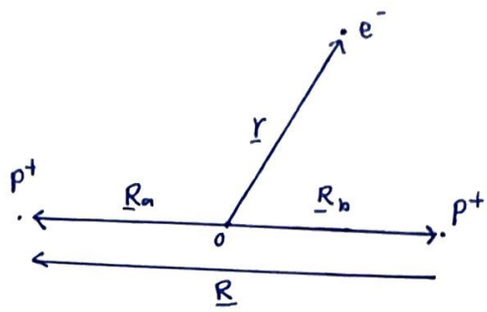
The n values are referred to as a "shell" of the atom. A particular (n,l) is referred to as a "subshell" of the atom. The maximum number of electrons in a subshell is the degeneracy of the

corresponding (n,l) value. Any full subshell has spherically symme total charge distribution since $\sum_m |Y_{lm}|^2$ is a constant.
Its total angular momentum and total spin are both 0, due to symmetry requirements.

Lecture 5 : The hydrogen molecular ion

5.1 Electronic ground state

We have a 3-particle problem.
Again assume that the nuclei are essentially stationary over time scales relevant to electronic motion.
$\underline{R} = \underline{R}_a - \underline{R}_b$



The Hamiltonian is then:

$$\hat{H} = \left(\frac{-\hbar^2}{2m_e}\nabla_r^2\right) + \left(\frac{-e^2}{4\pi\varepsilon_0}\frac{1}{|\underline{r}-\underline{R}/2|} + \frac{-e^2}{4\pi\varepsilon_0}\frac{1}{|\underline{r}+\underline{R}/2|}\right) + \left(\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\underline{R}|}\right)$$

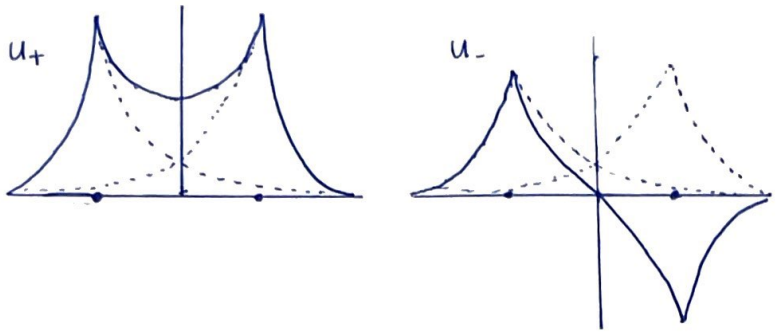
From left to right: KE of electron, the electric interaction of the electron and each proton, and the electric interaction of the two protons.
The last term is a constant for fixed $\underline{R}$.
Unlike the hydrogen atom, this is not symmetrical. But there is still a reflective symmetry. If we align the z-axis with $\underline{R}$, we see that $\hat{H}$ doesn't change if we reflect the electron's position across the x-y plane, corresponding to $z \to -z$
This type of symmetry like the square well and harmonic oscillator have symmetrical potentials $V(x)$ which leads to the eigenstates having definite parity. A similar result can be expected for H_2^+, so the ground state will be an even function of z, the first odd, etc.

when $|\underline{R}| \gg a_0$, the ground state is essentially a hydrogen atom in one location, and a proton in the other.
We expect $u_{1,0,0}(\underline{r}-\underline{R}/2)$ and $u_{1,0,0}(\underline{r}+\underline{R}/2)$ and any linear combination of these to be ground state wavefunctions
We can approximate the ground and first-excited state wavefunctions for large proton-proton separation to be then even and odd functions

$$u_+(\underline{r}) = N_+\left[u_{1,0,0}(\underline{r}-\underline{R}/2) + u_{1,0,0}(\underline{r}+\underline{R}/2)\right] \quad (87)$$

$$u_-(\underline{r}) = N_-\left[u_{1,0,0}(\underline{r}-\underline{R}/2) - u_{1,0,0}(\underline{r}+\underline{R}/2)\right] \quad (88)$$

where $N_\pm$ are normalization constants which depend on $\underline{R}$.
These functions are :

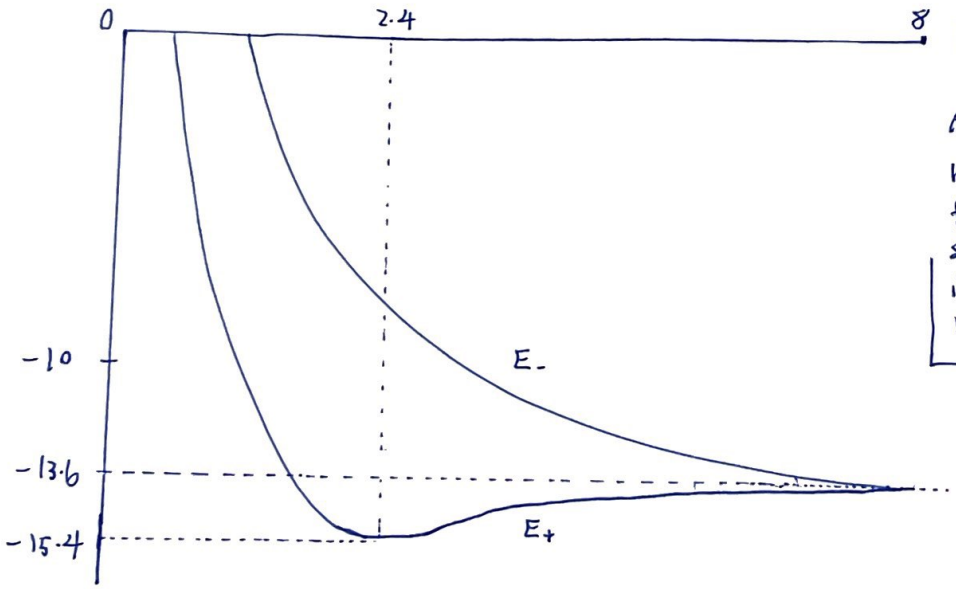


* The approximate H_2^+ eigenstates (solid line) made from hydrogen orbitals (dashed) plots are along the z-axis and nuclear positions are the dots.

- The eigenstates in (87) & (88) are truely correct only in the limit $|\underline{R}|/a_0 \to \infty$.

For some particular $R = |\underline{R}|$, called the internuclear distance, the energy eigenvalues can be estimated as an expectation value of $\hat{H}$

$$E_\pm(R) = \langle u_\pm, \hat{H} u_\pm \rangle$$



Approximate energy of the H_2^+ eigenstates as a function of proton-proton separation R. The minimum in the energy curve E_+ represents a molecular bond.

For large R, the two states are degenerate and the energies approach $-13.6\,eV$
For small R, nucleus-nucleus repulsion dominates and both energies rise toward ∞.

For u_+, addition of the hydrogenic wavefunctions causes an increase in amplitude in the region between the two protons. In this region, the electron is shared between the protons, and the electric energy from both electron-neutron interactions can outweigh the repulsion by the nuclei.
In contrast for u_- subtraction of the two hydrogenic wavefunctions cause a decreased electron amplitude in the central region, and repulsion of the ~~nucleiha~~ nuclei has the larger influence.

5.2 Molecular bonding

The minimum in $E_+(R)$ shows that it is energetically favourable for the nuclei to stay at a certain separation. This is a molecular bond. $R = 2.4a_0$ is called the bond length, and the difference by 1.8 eV the binding energy. u_+ is called a bonding molecular orbital, u_- is the antibonding molecular orbital.

H_2^+ also has higher energy electronics states, which are approximated as a linear combination of two hydrogenic wavefunctions. Each (n, l, m) yields a bonding and antibonding orbital, each has a unique $E(R)$

For H_2, In the ground state, both electrons occupy the 1s-1s orbital which is u_+. Since they have identical spatial wavefunction, they are symmetric under exchange and total spin $S=0$. With two electrons being shared, the binding energy increases to 4.7 eV. Therefore hydrogen exists as a diatomic molecule.

5.3 Molecular motion

Focusing on the relative motion of the nuclei leads to the 3D Hamiltonian:

$$\hat{H}_n = \frac{-\hbar^2}{2\mu} \nabla_{\underline{R}}^2 + E_+(R) \qquad (90)$$

where ∇_R^2 is the Laplacian w.r.t. the relative position of the two nuclei. $\mu = m_p/2$ is the ~~reduced~~ reduced mass of the system. $E_+(R)$ now plays the potential energy for nuclear motion.

(90) has a central potential, the eigenfunction $\psi(\underline{R})$ can be written as:

$$\psi(R, \theta, \phi) = f(R)\, Y_{l,m}(\theta, \phi)$$

$$\left(\frac{-\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{l(l+1)\hbar^2}{2\mu R^2} + E_+(R) \right) f(R) = E f(R)$$

where E is the total energy of the molecule.

Unless the molecule is in a highly excited state, ψ will be non-zero only for values of R close to the bond length R_0. We can make simplifying approximations: For rotational KE term, replace R with constant R_0. The E_{rot} will then only depend on the total angular momentum.

$$E_{rot} = \frac{l(l+1)\hbar^2}{2\mu R_0^2} = l(l+1)\hbar\omega_r$$

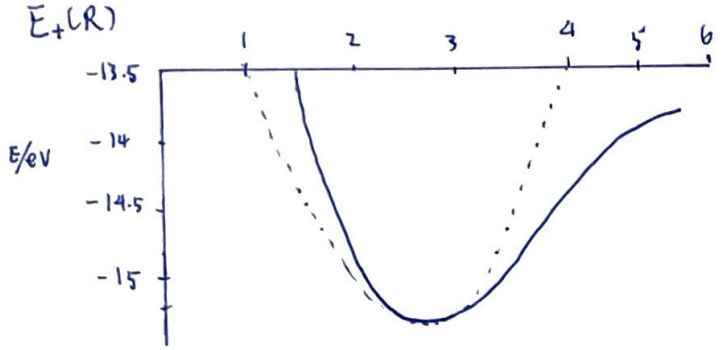
This is equivalent to saying the two nuclei are attached to the end of a rotating rigid rod.

Second, we approximate $E_+(R)$ with the second order Taylor series around $R = R_0$

$$E_+(R) = E_+(R_0) + \frac{dE_+}{dR}\Big|_{R_0}(R-R_0) + \frac{1}{2}\frac{d^2E_+}{dR^2}\Big|_{R_0}(R-R_0)^2 + \cdots$$

$$\approx E_+(R_0) + \frac{1}{2}\mu\omega_v^2(R-R_0)^2 \qquad (94)$$

where ω_v is the natural frequency, related to the second-order derivative of $E_+(R)$



Harmonic approximation (dashed) to the electronic energy $E_+(R)$ as described by Eq. (94)

The resulting radial equation centered at R_0 is

$$\left(\frac{-\hbar^2}{2\mu}\frac{d^2}{dR^2} + \frac{1}{2}\mu\omega_v^2\right)f(R-R_0) = (E - E_{rot} - E_+(R_0))\,f(R-R_0) \qquad (95)$$

which gives the usual solutions for the harmonic oscillator with eigenvalues

$$E_{vib} = \hbar\omega_v(n+\tfrac{1}{2})$$

where n denotes the eigenstate. From (95) the total energy is

$$E = E_{elec} + E_{vib} + E_{rot}$$

Takeaways

1: We can calculate all of these characteristics of the molecule from foundamental quantum theory.

2: There is a hierarchy of energy scales with a factor of roughly 40 x separating the excitation energy for rotations and vibrations, and also vibrations and electronic states. The energy scales for H_2^+ are typical of all molecules.

Lecture 6: Hydrogen fine structure

6.1 The spin-orbit interaction

electrons have a magnetic dipole moment proportional to their spin

$$\hat{\underline{\mu}} \approx -2\mu_B\hat{\underline{S}}/\hbar$$

where $\mu_B = e\hbar/2m_e$ is the Bohr magneton.

The energy due to the interaction of an electron with a magnetic field is $\hat{H} = -\hat{\underline{\mu}}\cdot\underline{B}$ The dot product means the energy depends on the alignment of the moment and field.

In the frame of the electron, the proton is moving, which creates a magnetic field. A particle moving at $\underline{v}$ through an electric field E experiences a magnetic field $\underline{B} = -\underline{v} \times \underline{E}/c^2$. This is a Lorentz transformation of the field due to special relativity.

Combining these ideas leads to a new interaction given by

$$\hat{H}_{s-o} = \left[2\mu_B \frac{\hat{\underline{s}}}{\hbar}\right] \cdot \left[\frac{\hat{\underline{l}}}{2m_e r} \frac{e}{4\pi\varepsilon_0 r^2} \frac{1}{c^2}\right]$$

$$= \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{m_e^2 c^2} \frac{1}{r^3} \hat{\underline{s}} \cdot \hat{\underline{l}}$$

The last line highlights that we have an effective interaction between the spin and orbital angular momentum of the electron. We thus call it the spin-orbit interaction

$$\hat{H}_{s-o} = \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{m_e^2 c^2} \frac{\hbar^2}{a_0^3} \frac{a_0^3}{r^3} \frac{\hat{\underline{s}}\hat{\underline{l}}}{\hbar^2}$$

$$= \alpha^2 \left(\frac{1}{2}\alpha^2 m_e c^2\right)\left(\frac{a_0^3}{r^3}\right) \frac{\hat{\underline{s}} \cdot \hat{\underline{l}}}{\hbar^2} \qquad (100)$$

Rearranging the terms, we see that the natural energy scale for the spin-orbit interaction is a factor of $\alpha^2 \approx (1/137)^2$ smaller than the gross energy scale of $\alpha^2 m_e c^2/2 = 13.6\,eV$.

6.2 Perturbation theory

The spin-orbit Hamiltonian needs to be added to the gross-structure Hamiltonian. Since the energy scale is comparatively small, we treat it as a perturbation.

The first order correction to each energy level can be calculated as

$$\delta E^{(1)}_{s-o} = \langle u_{nlm}, \hat{H}_{s-o} u_{nlm} \rangle \qquad (101)$$

where u_{nlm} is the gross is the gross-structure hydrogen wavefunction for quantum numbers (n, l, m_l)

The radial part of the spatial overlap integral is

$$\left\langle \frac{1}{r^3} \right\rangle_{nl} = \int \frac{1}{r^3} |R_{nl}(r)|^2 r^2 dr = \frac{1}{a_0^3} \frac{1}{l(l+1/2)(l+1)n^3} = \frac{1}{a_0^3} \beta_{n,l} \qquad (102)$$

where the constant $\beta_{n,l}$ is introduced to capture this dependence on n and l. $0 < \beta_{n,l} < 1$ and overall $\beta_{n,l}$ decreases with increasing l and n.

6.3 Total electron angular momentum, j

The term $\hat{\underline{s}} \cdot \hat{\underline{l}}$ is an interaction between two sources of angular momentum. A vector component of either angular momentum is not constant in time. $[\hat{s}_z, \hat{H}_{s-o}] \neq 0$ and similarly for $\hat{l}_z$. Consequently, the eigenstates of $\hat{H}_{s-o}$ are not simultaneous eigenstates of $\hat{s}_z$ and $\hat{l}_z$ and therefore the eigenstates are not specified by quantum numbers m_s and m_l. If we view the whole picture we recognize that there aren't external torques on the atom as a whole. Define

$$\hat{\underline{j}} = \hat{\underline{l}} + \hat{\underline{s}}$$

which is an operator corresponding to the total angular momentum, including both orbital and spin contributions.

$[\hat{\underline{j}}^2, \hat{H}_{s-o}] = [\hat{\underline{j}}_z, \hat{H}_{s-o}] = 0$, Our eigenstates can be specified by the quantum numbers j and m_j in the usual way.

$[\hat{\underline{s}}^2, \hat{H}_{s-o}] = [\hat{\underline{l}}^2, \hat{H}_{s-o}] = 0$, so the amount of orbital and spin angular momenta is still conserved, just the specific components that are not.

$$\hat{j}^2 = \hat{\underline{j}} \cdot \hat{\underline{j}} = (\hat{\underline{l}} + \hat{\underline{s}}) \cdot (\hat{\underline{l}} + \hat{\underline{s}}) = \hat{l}^2 + \hat{s}^2 + 2\hat{\underline{l}} \cdot \hat{\underline{s}}$$

$$\hat{\underline{s}} \cdot \hat{\underline{l}} = \frac{1}{2}(\hat{j}^2 - \hat{l}^2 - \hat{s}^2) \qquad (105)$$

6.4 Spin-orbit energy and eigenstates

To evaluate $\delta E^{(1)}_{s-o}$ using Eq. (101), we should express the eigenstates in terms of the quantum numbers (j, m_j) in addition to (n, l)

$$|n, l, j, m_j\rangle$$

In Dirac notation, the inner product $\langle \phi, \hat{A}\psi \rangle$ is written as $\langle \phi | \hat{A} | \psi \rangle$

We use (100), (102), (105):

$$\delta E^{(1)}_{s-o} = \langle n, l, j, m_j | \hat{H}_{s-o} | n, l, j, m_j \rangle$$

$$= \alpha^2 \times 13.6\,eV \times \beta_{n,l} \times \frac{j(j+1) - l(l+1) - s(s+1)}{2}$$

The total spin could be either $S = 1$ or $S = 0$. Similarly $\hat{L} = \hat{l}_1 + \hat{l}_2$. The possible values for L runs from $|l_1 - l_2|$ to $l_1 + l_2$ in integer steps. The possible values for j are thus

$$j = \frac{1}{2} \quad \text{if } l = 0$$

$$j = l \pm \frac{1}{2} \quad \text{if } l > 0$$

For $l > 0$, the two different values for j correspond to slightly different energies:

$$\text{for } j = l - \tfrac{1}{2}: \quad \delta E^{(1)}_{s\text{-}o} = \frac{-(l+1)}{2} \times (\alpha^2 \beta_{n,l})(13.6\,eV)$$

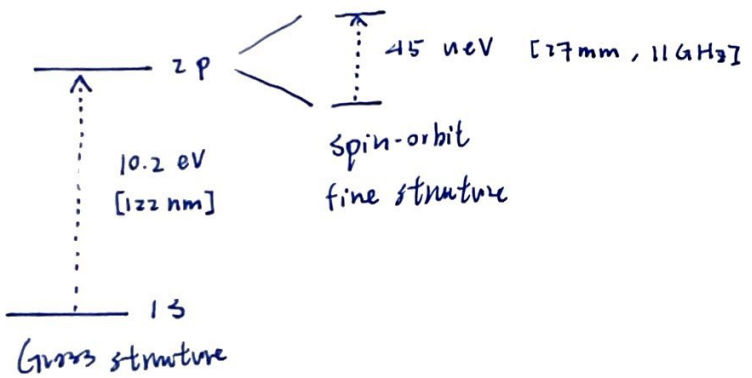
$$\text{for } j = l + \tfrac{1}{2}: \quad \delta E^{(1)}_{s\text{-}o} = \frac{l}{2} \times (\alpha^2 \beta_{n,l})(13.6\,eV)$$

The first case is a slight decrease in energy while the second a slight increase. These correspond to the cases when the magnetic moment and field are aligned and anti-aligned.

To first-order in the perturbation, the energy of a state is

$$E'(n,l,j) = E_n + \delta E^{(1)}_{s\text{-}o}$$
$$= 13.6\,eV \left[\frac{-1}{n^2} + \alpha^2 \beta_{n,l} \left(\frac{j(j+1) - l(l+1) - 3/4}{2} \right) \right]$$

where E_n is the gross structure energy. Two states of the same n and l have the same energy in the gross structure model.



For $l > 0$ the degeneracy is lifted by the spin-orbit interaction and states of different j have different energies

6.5 other relativistic effects

1: Adjustment to KE, for which the non-relativistic $\hat{p}^2/2m$ is only an approximation.

2: The Darwin term, it adjusts the $l = 0$ state energies.

6.6 Other atoms

The spin-orbit effect also occurs in helium and other multielectron atoms and molecules.

Lecture 7: Hyperfine structure and the Zeeman Effect

There is one more degree of freedom that we've yet to consider for our atoms the spin of the nucleus. In hydrogen, the relevant property is the magnetic dipole moment of the proton. The resulting hyperfine structures are very small compared to the previous levels of structure, but play an important role in physics.

The spin of a nucleus is described by the angular momentum operator $\hat{\underline{I}}$. The magnetic moment associated with this spin is

$$\hat{\underline{\mu}}_I = g_I \mu_N \hat{\underline{I}}/\hbar$$

where $\mu_N = e\hbar/2m_p$ is the nuclear magneton. $\mu_N/\mu_B \approx 1/2000$. The gyromagnetic factor g_I differs from the electron's value of approximately 2 due to the composite nature of the nuclei, which are made of protons and neutrons. The nuclear g factors are typically between 0.2 to 6. For a single proton, $g_I = 5.6$

The interaction of a nuclear magnetic moment with a magnetic field is described by $\hat{H} = -\hat{\underline{\mu}}_I \cdot \underline{B}$. In an atom this $\underline{B}$ is generated by the orbital and spin angular momentum of the electron. $\therefore$ $\underline{B} \propto$ total electron angular momentum. which we represented by $\hat{\underline{j}}$ for hydrogen.

For hydrogen, the resulting hyperfine structure Hamiltonian can be written as

$$\hat{H}_{hfs} = A_{hfs} \frac{1}{\hbar^2} \hat{\underline{I}} \cdot \hat{\underline{j}}$$

where A_{hfs} includes the energy state & geometric aspects of the interaction.

7.2 Hyperfine structure energy and eigenstates.

The interaction of $\hat{\underline{I}}$ and $\hat{\underline{j}}$ motivates the introduction of a total angular momentum

$$\hat{\underline{f}} = \hat{\underline{j}} + \hat{\underline{I}}$$

Use first order perturbation theory to calculate how $\hat{H}_{hfs}$ influences energy levels. The eigenstates of the spin-orbit Hamiltonian are specified by the quantum numbers (n, l, j, m_j, m_I). We don't need to specify the quantum numbers s or I, which are always $\frac{1}{2}$ for the electron and proton. We instead use a basis in total atom angular momentum so that states are specified by (n, l, j, f, m_f). This is analogous to our use of j to solve the spin-orbit problem. The first order correction to energy levels are

$$\delta E^{(1)}_{hfs} = \langle n, l, j, f, m_f | \hat{H}_{hfs} | n, l, j, f, m_f \rangle$$
$$= A_{nlj} \times \left(\frac{f(f+1) - j(j+1) - I(I+1)}{2} \right) \qquad (11b)$$

where $A_{nlj} = \langle A_{hfs} \rangle$ is called the hyperfine structure constant

For hydrogen, $I = \frac{1}{2}$ so the two possible values for f are $j+\frac{1}{2}$ and $j-\frac{1}{2}$

for $f = j - \frac{1}{2}$: $\delta E^{(1)}_{hfs} = -(\frac{j}{2} + \frac{3}{4}) A_{nlj}$

for $f = j + \frac{1}{2}$: $\delta E^{(1)}_{hfs} = (\frac{j}{2} - \frac{1}{4}) A_{nlj}$

Thus every energy level in the fine structure, denoted by j, is split into a pair of hyperfine ~~structures~~ levels.

7.3 The ground state of hydrogen

Since $l=0$ the magnetic field at the nucleus due to the electron is entirely due to its magnetic moment $\hat{\underline{\mu}} \approx -2\mu_B \hat{\underline{S}}/\hbar$

To estimate δE_{hfs}, inner product of Eq. 116 includes integral over electron position weighted by magnetic field. The electron's probability density gives an effective magnetization $\underline{M}(\underline{r})$.

The M-field inside a uniform sphere of magnetisation $\underline{M}_0$ is $\frac{2}{3}\mu_0 \underline{M}_0$ where μ_0 is magnetic constant.

We approximate the electron density as constant over the nucleus. We have $\underline{M} = \hat{\underline{\mu}} |u_{1,0,0}(0)|^2$ where $|u_{1,0,0}(0)|^2$ is the electron's ground state probability density at the origin.

Magnetic field at the nucleus due to the electron:

$$\hat{\underline{B}}_0 = \frac{2}{3}\mu_0 |u_{1,0,0}(0)|^2 \hat{\underline{\mu}}$$

$$= \frac{2}{3}\mu_0 |u_{1,0,0}(0)|^2 \left(\frac{-2\mu_B \hat{\underline{S}}}{\hbar}\right)$$

$$= -\frac{4}{3\pi a_0^3}\mu_0 \mu_B \frac{\hat{\underline{S}}}{\hbar}$$

We looked up $|u_{1,0,0}(0)|^2 = (\pi a_0^3)^{-1}$ from an earlier lecture. The effective Hamiltonian for the ground state is

$$\hat{H}^{(13)}_{hfs} = -\hat{\underline{\mu}}_I \cdot \underline{B}_0$$

$$= (g_I \mu_N \frac{\hat{\underline{I}}}{\hbar}) \cdot (\frac{4}{3\pi a_0^3}\mu_0 \mu_B \frac{\hat{\underline{S}}}{\hbar})$$

$$= \frac{4 g_I}{3\pi} \frac{\mu_0 \mu_B \mu_N}{a_0^3} \frac{\hat{\underline{I}} \cdot \hat{\underline{S}}}{\hbar^2}$$

$$= \frac{8 g_I}{3} \left(\frac{m_e}{m_p}\right) \alpha^2 (\frac{1}{2}\alpha^2 m_e c^2) \frac{\hat{\underline{I}} \cdot \hat{\underline{S}}}{\hbar^2} = A_{(13)} \frac{\hat{\underline{I}} \cdot \hat{\underline{S}}}{\hbar^2}$$

We see that the characteristic energy scale of hyperfine structure is reduced from fine structure by the ratio m_e/m_p.

$$\Delta E^{(13)} = \delta E^{(f=1)}_{hfs} - \delta E^{(f=0)}_{hfs} = A_{(13)}$$

7.4 The Zeeman effect

Our atomic models all contain degeneracy related to the orientation of the atom in space. In the hyperfine structure model, this occurs for $f > 0$. The energy does not depend on how much of the total atomic angular momentum points along the z-axis, which corresponds to the quantum number m_f. This final degeneracy is lifted if we consider an interaction of the atom with an external field.

To illustrate the concept, we return to the Zeeman effect, which was discussed briefly in previous lectures. In particular we consider a weak external magnetic field $\underline{B}$ that we approximate as uniform over the atom. The atom interacts with the field through its three magnetic dipole moments, resulting in $\hat{H}_Z = -(\hat{\underline{\mu}}_S + \hat{\underline{\mu}}_L + \hat{\underline{\mu}}_I) \cdot \underline{B}$

we neglect the nuclear contribution as it is smaller by a factor of $\mu_N / \mu_B = m_e / m_p$

Let's choose to align our coordinates so that the $\underline{B}$ field points along the z-axis. We then have

$$\hat{H}_Z = \mu_B B \left(\frac{2\hat{S}_z}{\hbar} + \frac{\hat{L}_z}{\hbar} \right)$$

where we have approximated the electron spin gyromagnetic factor as 2, and the orbital gyromagnetic factor as 1.

We calculate resulting energy shifts using first-order perturbation theory:

$$\delta E_Z^{(1)} = \langle n, l, j, f, m_f | \hat{H}_Z | n, l, j, f, m_f \rangle$$

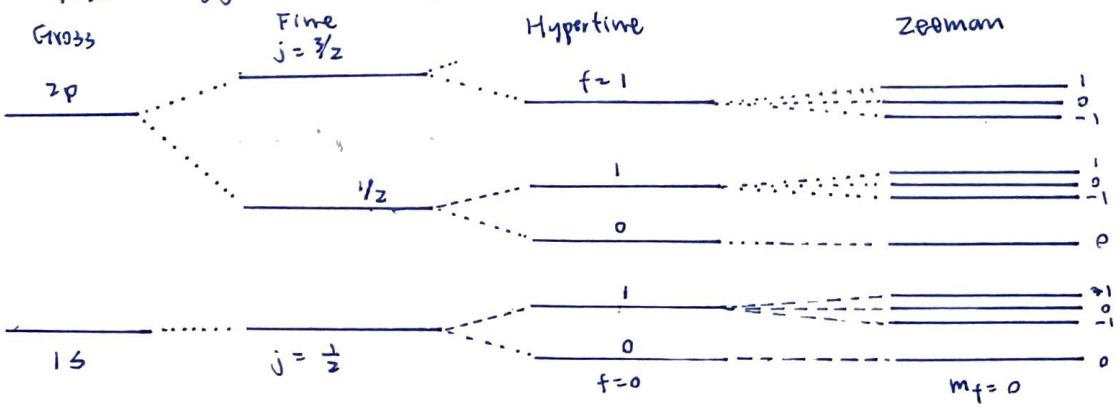
The EV of the z component of the atom's total magnetic moment must be proportional to EV of z component of the total angular momentum

$$\delta E_Z^{(1)} = g_f \mu_B B m_f$$

g_f is the state-dependent effective gyromagnetic factor

The hydrogen hyperfine ground state is 1s, $f = 0$. Therefore $m_f = 0$ and there is no first order shift. For the 1s, $f = 1$ level, we calculate $g_f = 1$

The energy of the $m_f = \pm 1$ levels therefore change by $\pm \mu_B \underline{B}$



Lecture 8: The electric dipole Hamiltonian

8.1 Interaction with an oscillating electric field

Consider a single atom sitting at rest, surrounded by a single-frequency electromagnetic field radiated from a distant source.

$$\hat{H} = \hat{H}_0 + \hat{H}_I$$

where $\hat{H}_0$ is the bare atom Hamiltonian and $\hat{H}_I$ the interaction Hamiltonian

What is $\hat{H}_I$? We describe the electric field in the vicinity of the atom as a travelling plane wave

$$\underline{E}(x,t) = \underline{e}_z \mathcal{E}_0 \cos(\omega t - kx)$$

where the electric field is characterized by its amplitude $\mathcal{E}_0$, wave number k, and angular frequency ω. The light propagates in the x-direction, the field points in $\hat{z}$.

We now determine the potential energy for the electron to be located at $\underline{r}$ by calculating the work required to displace it from the origin to $\underline{r}$.

$$U = -W = -\int_0^{\underline{r}} \underline{F} \cdot d\underline{s} \quad \text{where} \quad \underline{F} = q\underline{E}$$

Electrons are typically within 0.1nm of the nucleus but electric field varies gradually over a larger scale determined by $\lambda = 2\pi/k$. We approximate the electric field to be constant over the region of interest, so

$$\underline{E}(x,t) \approx \underline{E}(0,t) = \underline{e}_z \mathcal{E}_0 \cos(\omega t)$$

The classical potential energy is thus

$$U \approx -q\underline{E}(0,t) \cdot \underline{r} = -q\mathcal{E}_0 \cos(\omega t) z$$

Turning to quantum theory, we simply need to express the potential energy as an operator that acts on the atomic wave functions.

$$\hat{H}_I = e\mathcal{E}_0 \cos(\omega t)\hat{\underline{z}}$$

For atoms with multiple electrons the total interaction Hamiltonian is just the sum over terms for each electron i (position operator $\hat{z}_i$)

We define the electric dipole ~~moment~~ operator $\hat{\underline{d}} = \sum q_i \hat{\underline{r}}_i$, then:

$$\hat{H}_I = -\underline{E} \cdot \hat{\underline{d}}$$

$\underline{E}$ is the electric field at the origin. We refer to this approximation as the "electric dipole approximation" and $\hat{H}_I$ is the electric dipole Hamiltonian.

8.2 Transitions and selection rules

when we studied time-independent perturbation theory, we showed that an eigenstate for a total Hamiltonian is approximately

$$\psi_i' = \psi_i + \sum_{j \neq i} \frac{\langle \psi_j | \hat{H}_I | \psi_i \rangle}{E_i - E_j} \psi_j$$

This doesn't apply to the atom-light system, since the interaction Hamiltonian varies in time and its influence may not be small.

$\langle \psi_j | \hat{H}_I | \psi_i \rangle$ is a general expression that tells us how $\hat{H}_I$ connects the state ψ_i to the state ψ_j.

8.2.1 Example: 1s-2s and 1s-2p transitions in hydrogen

For our electric dipole Hamiltonian, the relevant inner product is proportional to $\langle \psi_j | \hat{\underline{d}} | \psi_i \rangle$. We'll call this the "electric dipole matrix element" and denote it $\underline{d}_{ij}$. As example, we calculate the z-component for a transition between the $i = (n, l, m_l, m_s)$ and $j = (n', l', m_l', m_s')$ states of hydrogen.

$$\langle \psi_j | \hat{d}_z | \psi_i \rangle = -e \iiint \phi^*_{n', l', m_l'} z \phi_{n, l, m_l} dV$$

$$= -e \left(\int_0^\infty R_{n', l'}(r) \, r \, R_{n, l}(r) \, r^2 dr \right) \left(\int_0^{2\pi} \int_0^\pi Y^*_{l', m_l'}(\theta, \phi) \cos(\theta) Y_{l, m_l}(\theta, \phi) \sin\theta \, d\theta \, d\phi \right)$$

where the spatial wavefunction of hydrogen is written as ϕ_{n, l, m_l}

For a 2p to 1s transition, for example, we could have $i = (2, 1, 0, 1/2)$ and $j = (1, 0, 0, 1/2)$. The relevant angular functions are $Y_{0,0} = \sqrt{1/4\pi}$ and $Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos\theta$

The angular integral gives

$$\langle \psi_j | \hat{d}_z | \psi_i \rangle \propto \int_0^{2\pi} \int_0^\pi \sqrt{\frac{3}{4\pi}} \cos(\theta) \cos(\theta) \sqrt{\frac{1}{4\pi}} \sin(\theta) \, d\theta \, d\phi$$

$$= \frac{\sqrt{3}}{2} \int_0^\pi \cos^2(\theta) \sin(\theta) \, d\theta = \frac{1}{\sqrt{3}}$$

If we consider a 2s to 1s transition, we find

$$\langle \psi_j | \hat{d}_z | \psi_i \rangle \propto \frac{1}{2} \int_0^\pi \cos(\theta) \sin(\theta) \, d\theta = 0$$

This is due to even/odd parity

8.2.2 Parity selection rule

Let's use a coordinate system that has been inverted through the origin, $\underline{r}' = -\underline{r}$

In Cartesian this implies $(x', y', z') = (-x, -y, -z)$

Similarly in spherical $(r', \theta', \phi') = (r, \pi - \theta, \phi - \pi)$

$$\langle \psi_j | \hat{\underline{d}} | \psi_i \rangle = -e \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \phi^*_{n', l', m_l'}(r, \theta, \phi)\, \underline{r}\, \phi_{n, l, m_l}(r, \theta, \phi)\, r^2 \sin(\theta)\, dr\, d\theta\, d\phi$$

$$= -e \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \phi_{n', l', m_l'}(r', \pi - \theta', \phi' + \pi)(-\underline{r}')\phi_{n, l, m_l}(r', \pi - \theta', \phi' + \pi)\, r^2 \sin(\theta')\, dr'\, d\theta'\, d\phi'$$

To proceed, we see that the radial function $R(r')$ is unchanged. The spherical harmonic functions transform according to $Y_{l, m_l}(\pi - \theta, \phi + \pi) = (-1)^l Y_{l, m_l}(\theta, \phi)$

If l is even, Y_{l, m_l} is unchanged by inversion and we say that it has even parity. If l is odd, the sign of Y_{l, m_l} flips and it is odd parity.

$$\iiint \underline{r}\, \phi^*_{n', l', m_l'}(r, \theta, \phi)\, \phi_{n, l, m_l}(r, \theta, \phi)\, dV = \iiint (-\underline{r}')(-1)^{l'} \phi^*_{n', l', m_l'}(r', \theta', \phi')(-1)^{l} \phi_{n, l, m_l}(r', \theta', \phi')\, dV'$$

For this equality to be true, either $(-1)^{(l'+1)} = -1$ or the integral is zero. Therefore the electric dipole matrix element is zero unless $\Delta l = l' - l$ is odd

8.2.3 Angular momentum selection rules

There are additional selection rules. Atom's angular momentum comes from motion of electrons and intrinsic spin

The electric dipole Hamiltonian interacts only with the spatial wave function, and therefore for d_{ij} to be nonzero, states i and j must have compatible spin states

In helium, a non-zero dipole element requires $\Delta S = S' - S = 0$

The total angular momentum of the atom and the radiation field must be conserved when the atom's state changes by absorbing or emitting a photon.

For a hydrogen, the orbital angular momentum can change by at most 1 when a photon is absorbed or emitted and only $\Delta l = \pm 1$ is permitted.

- For hydrogen: $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$, $\Delta m_j = 0, \pm 1$
- For helium and other multielectron atoms, $\Delta S = 0$
- When electron-dipole transition is forbidden due to selection rules, weaker, higher-order transitions become significant.

Lecture 9 : Rabi oscillations

9.1 Equations of motion

Consider atom with two possible energy eigenstates ψ_1 and ψ_2 with energy eigenvalues E_1 and E_2. These states both satisfy $\hat{H}_0\psi_i = E_i\psi_i$

Frequency of the electromagnetic field is ω, resonant frequency for two atomic states is $\omega_0 = (E_2 - E_1)\hbar$, which corresponds to energy difference.

We consider the case $\omega \approx \omega_0$ in our calculations.

Time-dependent calculations are used to solve the dynamics of the atom.

Start by describing the state of an atom as an arbitrary superposition of the two states.

$\psi(t) = \alpha(t)\psi_1 + \beta(t)\psi_2$

Solving for dynamics means finding the correct complex valued functions $\alpha(t)$ and $\beta(t)$

Time evolution of the state:

$$i\hbar \frac{d}{dt}\psi(t) = (\hat{H}_0 + \hat{H}_I)\psi(t) \qquad (9.1)$$

Rewriting $\psi(t)$ to simplify working:

$$\psi(t) = [c_1(t)e^{-iE_1t/\hbar}]\psi_1 + [c_2(t)e^{-iE_2t/\hbar}]\psi_2 \qquad (9.2)$$

where each amplitude is written as a product of $c_i(t)$ and the explicit time dependence $e^{-iE_it/\hbar}$.

Plug (9.2) into (9.1) to find

$$[(c_1(t)E_1 + i\hbar\frac{dc_1}{dt})e^{-iE_1t/\hbar}]\psi_1 + [(c_2(t)E_2 + i\hbar\frac{dc_2}{dt})e^{-iE_2t/\hbar}]\psi_2$$
$$= [(c_1(t)E_1 + c_1(t)\hat{H}_I)e^{-iE_1t/\hbar}]\psi_1 + [(c_2(t)E_2 + c_1(t)\hat{H}_I)e^{-iE_2t/\hbar}]\psi_2$$

Subtracting identical terms yields

$$[i\hbar\frac{dc_1}{dt}e^{-iE_1t/\hbar}]\psi_1 + [i\hbar\frac{dc_2}{dt}e^{-iE_2t/\hbar}]\psi_2 = [c_1(t)e^{-iE_1t/\hbar}]\hat{H}_I\psi_1 + [c_2(t)e^{-iE_2t/\hbar}]\hat{H}_I\psi_2$$

To turn this to an equation relating only the amplitudes, take inner product of both sides with ψ_1.

$$i\hbar\frac{dc_1}{dt}e^{-iE_1t/\hbar} = c_1(t)e^{-iE_1t/\hbar}\langle\psi_1|\hat{H}_I|\psi_1\rangle + c_2(t)e^{-iE_2t/\hbar}\langle\psi_1|\hat{H}_I|\psi_2\rangle$$

$\langle\psi_i|\hat{H}_I|\psi_i\rangle = 0$, multiply both sides by $e^{iE_1t/\hbar}$ and repeat for ψ_2:

$$i\hbar\frac{dc_1}{dt} = c_2(t)e^{-i\omega_0t}\langle\psi_1|\hat{H}_I|\psi_2\rangle$$

$$i\hbar\frac{dc_2}{dt} = c_1(t)e^{i\omega_0t}\langle\psi_2|\hat{H}_I|\psi_1\rangle$$

9.2 Resulting dynamics

Recall from last lecture $\hat{H}_I = -E_0 \cos(\omega t)\hat{d}_z$, $\hat{d}_z = -e\hat{z}$, we introduce Ω:

$$\Omega = -\frac{E_0}{\hbar}\langle \psi_1 | \hat{d}_z | \psi_2 \rangle$$

which we call the Rabi frequency

Expanding $\cos(\omega t) = (e^{i\omega t} + e^{-i\omega t})/2$ and rearranging, we find

$$\frac{dc_1}{dt} = -i\frac{\Omega}{2}\left(e^{i(\omega-\omega_0)t} + e^{-i(\omega+\omega_0)t}\right)c_2(t)$$

$$\frac{dc_2}{dt} = -i\frac{\Omega}{2}\left(e^{-i(\omega-\omega_0)t} + e^{i(\omega+\omega_0)t}\right)c_1(t)$$

where we used the fact that Ω is real-valued, so $\Omega = \Omega^*$

Note that $(\omega-\omega_0)$ and $(\omega+\omega_0)$ can be used to simplify things, as $\omega \approx \omega_0$ and typical optical transitions have $\omega_0 \approx 10^{15} - 10^{16}$ rads^{-1}. With this approximation:

$$\frac{dc_1}{dt} = -i\frac{\Omega}{2}e^{i\delta t}c_2(t)$$

$$\frac{dc_2}{dt} = -i\frac{\Omega}{2}e^{-i\delta t}c_1(t)$$

where $\delta = \omega - \omega_0$, is called detuning.

Taking time derivative of the second equation and substituting in for the resulting c_1 term yields

$$\frac{d^2c_2}{dt^2} + i\delta\frac{dc_2}{dt} + \frac{\Omega^2}{4}c_2(t) = 0$$

This is a second order homogeneous differential equation with constant coefficients. Let's say that initially the atom is in state 1, the I.C. are $c_1(0) = 1$ and $c_2(0) = 0$

$$c_2(t) = -ie^{-i3\delta t/2}\frac{\Omega \sin(t\sqrt{\Omega^2+\delta^2}/2)}{\sqrt{\Omega^2+\delta^2}}$$

If we measure the state of the atom at time t, the probability to find it in state 2 is therefore

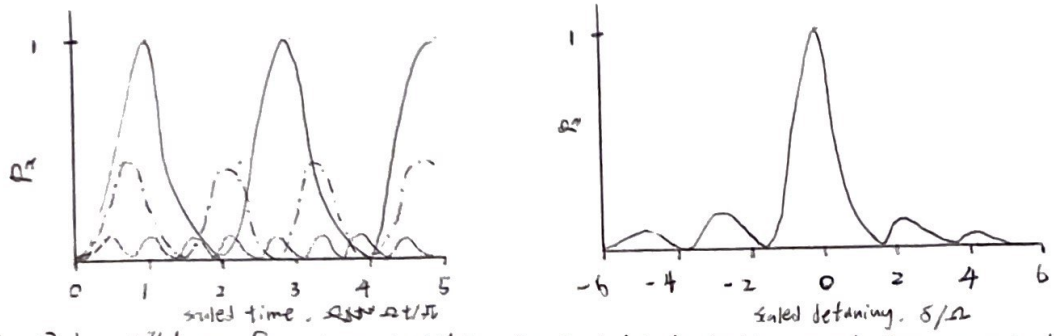
$$P_2(t) = |c_2(t)|^2 = \frac{\Omega^2}{\Omega^2+\delta^2}\sin^2\left(\frac{\sqrt{\Omega^2+\delta^2}}{2}t\right)$$

9.2.1 Oscillations

The incident light would excite the atom, causing transition from state 1 to 2. A main feature of our result is that the behavior is in fact periodic. The probability P_2 oscillates in time, with angular frequency $\sqrt{\Omega^2+\delta^2}$.

These Rabi oscillations describe an exchange of energy back and forth between the atom and field. If the atom starts in state 1 and then changes to state 2, an energy $\hbar\omega_0$ must have been absorbed from the field. The energy $\hbar\omega_0$ is returned to the field for the other way around. The processes are called absorption and stimulated emission.

If the light is resonant with the atom $\delta = 0$ and the oscillation has frequency Ω. After an interaction time $t = \pi/\Omega$ the state of the atom is ψ_2 and we have $P_2(\pi/\Omega) = 1$. For non-zero detuning, the frequency of the oscillation is increased. The amplitude of the oscillation, $\Omega^2/(\Omega^2+\delta^2)$, is maximal for resonant light.



Left: Rabi oscillations for $\delta = 0$ (solid), $\delta = \Omega$ (dot-dashed), and $\delta = 3\Omega$ (dashed)
Right: Resonance, the probability P_2 after a time $t = \pi/\Omega$ shown as a function of detuning

9.2.2 Resonance

From the figure on the right, the interaction is the strongest when ω is close to the resonant frequency ω_0. More precisely, we see that $|\delta|$ must be on the order of Ω or smaller. If the radiation is nearly resonant with the transition between ψ_1 and ψ_2, then any additional excited states would be of little consequence if the detunnings to these states were sufficiently large.

9.2.3 Example: 2s-3p transition in hydrogen

An realistic Rabi frequency Ω: Imagine laser with $r = 0.5$ mm, $P = 100$ mW that interacts with hydrogen atom in its metastable 2s state. The frequency of the light is resonant with the 2s-3p transition in hydrogen. We calculate $\langle 2s|\hat{z}|3p\rangle = (27\sqrt{2}/128)a_0$. Using the relationship between intensity and electric field, $I = P/\pi r^2 = \varepsilon_0 c E_0^2/2$, $E_0 = 10^4\ \mathrm{V\,m^{-1}}$. The Rabi frequency $\Omega = 2\times10^8\ \mathrm{rad\,s^{-1}}$

Ω is much smaller than the resonant frequency ($\omega_0 = 3\times10^{15}\ \mathrm{rad\,s^{-1}}$).

Even though $\Omega \ll \omega_0$, we should recognize that we've made an effort to achieve a large Ω. In more common settings the Rabi frequency would be too small to observe oscillations.

Lecture 10 Spontaneous emission

Real atoms naturally decay from excited states to lower-energy states by emitting a photon, even if there is no applied field, this is called spontaneous emission.

10.1 Modelling decay

A complete quantum description of spontaneous emission requires a modification to the Hamiltonian, so that the bare-atom eigenstates were no longer stationary states. If we have a quantum description of the radiation field, we find that the electric field is not strictly zero, even when radiation is in its ground state.

To make progress without a quantum treatment of the field, we model the effect by adding a decay term to the equation of motion. In particular a damping is added to the c_2 amplitude:

$$\frac{dc_1}{dt} = -i\frac{\Omega}{2} e^{i\delta t} c_2(t)$$

$$\frac{dc_2}{dt} = -i\frac{\Omega}{2} e^{-i\delta t} c_1(t) - \frac{\Gamma}{2} c_2(t) \qquad (10.1)$$

The $-\frac{\Gamma}{2}c_2$ causes the amplitude c_2 to decrease in time.

10.2 Damped oscillations of a free atom

- No applied field, $\Omega = 0$. We can immediately integrate (10.1)

$$c_2(t) = c_2(0) e^{-\Gamma t/2}$$

therefore the probability is

$$P_2(t) = |c_2(t)|^2 = c_2(0)^2 e^{-\Gamma t}$$

10.2.1 Visualizing the atom

Consider a hydrogen atom, the total spatial wave function is

$$\phi(\underline{r},t) = [c_1(t) e^{-iE_1 t/\hbar}]\phi_0(\underline{r}) + [c_2(t) e^{-iE_2 t/\hbar}]\phi_1(\underline{r})$$

where the spatial wave-function for ψ_i is $\phi_i(\underline{r})$. We assume ψ_1 and ψ_2 spin states are identical. To visualize the state, calculate the probability to find the electron at different positions. Take c_1, c_2, and wave functions to be real-valued.

$$P(\underline{r}) = |\phi(\underline{r},t)|^2$$

$$= [c_1(t)\phi_1(\underline{r})]^2 + [c_2(t)\phi_2(\underline{r})]^2 + [c_1(t)c_2(t)\phi_1(\underline{r})\phi_2(\underline{r})](e^{i(E_2-E_1)t/\hbar} + e^{-i(E_2-E_1)t/\hbar})$$

$$= [c_1(t)\phi_1(\underline{r})]^2 + [c_2(t)\phi_2(\underline{r})]^2 + 2[c_1(t)c_2(t)\phi_1(\underline{r})\phi_2(\underline{r})]\cos(\omega_0 t)$$

The probability has a third term that we can think of as the interference term between the two parts. At $t=0$, the sign of the interference term is positive at positions where the two functions have the same sign and negative otherwise. Interference terms oscillates at ω_0 as time advances.

10.2.2 Oscillating dipole moment

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:

$$\langle \hat{d}_z \rangle = \langle \psi(t) | \hat{d}_z | \psi(t) \rangle$$

$$= c_1^2 \langle \psi_1 | \hat{d}_z | \psi_1 \rangle + c_2^2 \langle \psi_2 | \hat{d}_z | \psi_2 \rangle + c_1 c_2 \langle \psi_1 | \hat{d}_z | \psi_2 \rangle e^{-i(E_2-E_1)t/\hbar} + c_1 c_2 \langle \psi_2 | \hat{d}_z | \psi_1 \rangle e^{-i(E_2-E_1)t/\hbar}$$

$$= 2 c_1 c_2 d_{12} \cos(\omega_0 t)$$

We see that $\langle \psi_1 | \hat{d}_z | \psi_1 \rangle = 0$ due to parity, similarly for state 2. The dipole matrix element $\langle \psi_2 | \hat{d}_z | \psi_1 \rangle = \langle \psi_1 | \hat{d}_z | \psi_2 \rangle$ is labeled d_{12} as before.

10.3 Weakly driven atom

We'll study the case where the atom starts in state 1 and the radiation is very weak. We write the c_2 equation of motion as

$$\frac{dc_2}{dt} = -i \frac{\Omega}{2} e^{-i\delta t} - \frac{\Gamma}{2} c_2(t)$$

We used the approximation that $c_1(t) = 1$. Take I.C. $c_2(0) = 0$, we find

$$c_2(t) = \frac{i\Omega}{\Gamma - 2i\delta} \left(e^{-\Gamma t/2} - e^{-i\delta t} \right) \qquad (10.9)$$

The upper state probability is thus

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

The time-dependent parts of $P_2(t)$ are transients due to the choice of I.C.s, which decay over a timescale of $1/\Gamma$. For longer times, the steady state expression is

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

The terms in the bracket is a Lorentzian function, and is 1 for the resonant condition $\omega = \omega_0$.

This tells us how likely a weakly driven atom will be found to be in excited state.

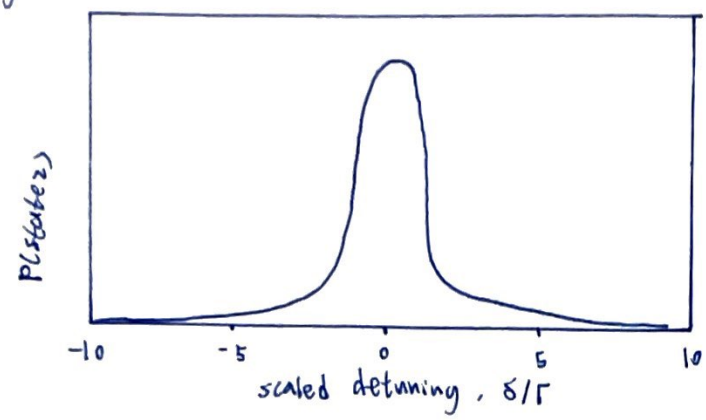
10.3.1 Lorentzian response.

The Lorentzian function characterizes the strength of atom-light interaction as a function of the detuning. In the figure below, the Lorentzian describes a peak with a full width at half maximum of Γ. For large detuning, the function dimishes with a scaling of $1/\delta^2$.

For typical electric-dipole transitions, $\Gamma/\omega_0 \approx 10^{-6}$ to 10^{-8} so the response is very sharply peaked, and is caused by the fraction of total radiation that has a frequency very close to a resonant frequency of the atom.

Imagine $\Omega = 10 \times \Gamma$. An atom will begin Rabi oscillations, but at some

point, the atom will spontaneously emit a photon and return to the ground state. Rabi oscillation will then restart and proceed until they are interrupted by another emission event.



Steady-state probability $P_2(t\to\infty)$ to find a weakly driven atom in its excited state, as a function of scaled detunning.

10.3.2 Damped driven oscillator

Let's consider the electric dipole moment for the weakly driven atom. Using the expression for $c_2(t)$ in (10.9) we calculate

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

where c.c. stands for the complex conjugate of the preceding term. Again we assumed $c_1(t)=1$ and consider the long time limit.

It is instructive to rewrite the expression

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

$$a = \frac{2\Omega d_{12}}{[\Gamma^2 + 4(\omega-\omega_0)^2]^{\frac{1}{2}}} \quad \text{and} \quad \theta = \tan^{-1}\left(\frac{\Gamma}{2(\omega-\omega_0)}\right)$$

The electric dipole now oscillates at the driving frequency ω, rather than its resonant frequency ω_0. The phase also depends on the detunning of the driving field from the resonance. In the limit of weak excitation, the atom behaves just like a harmonic oscillator.

Lecture 11: The Lorentz Model and Scattering

Despite its flawed microscopic depition of the atom, the model makes accurate predictions of the scattering of light in the case of a weak driving field.

11.1 The Lorentz model: a driven, damped harmonic oscillator

Consider the atom as a classical object. An electron of mass m and charge $-e$ is attached to a much more massive nucleus by a spring with spring constant k and damping coefficient b. A force on the electron comes from its interaction with an oscillating electric field.

The electric field is parallel to the z-axis with magnitude $\mathcal{E}_0 \cos(\omega t)$.
The classical equation of motion for the electron's displacement is

$$m\frac{d^2z}{dt^2} = -b\frac{dz}{dt} - kz - e\mathcal{E}_0\cos(\omega t)$$

It is convient to re-write this as

$$\frac{d^2z}{dt^2} + \Gamma\frac{dz}{dt} + \omega_0^2 z = -\frac{e\mathcal{E}_0}{m}\cos(\omega t)$$

The resonant frequency is defined as $\omega_0 = \sqrt{\frac{k}{m}}$ and the decay rate $\Gamma = \frac{b}{m}$
Using a trial solution $z(t) = \mathrm{Re}[z_0 e^{i\omega_0 t}]$ yields

$$-\omega^2 z_0 + i\omega\Gamma z_0 + \omega_0^2 z_0 = \frac{-e\mathcal{E}_0}{m}, \text{ thus } z_0 = \frac{-e\mathcal{E}_0}{m(\omega_0^2 - \omega^2 - i\Gamma\omega)}$$

Re-writing z_0 in $ae^{-i\theta}$ where a and θ are real, we find

$$z(t) = \mathrm{Re}(z_0 e^{i\omega_0 t}) = \cancel{a(\cos(\omega t - \theta)}\ a\cos(\omega t - \theta)$$

$$a = \frac{-e\mathcal{E}_0}{m[(\omega^2-\omega_0^2)^2 + \Gamma^2\omega^2]^{\frac{1}{2}}} \quad \text{and} \quad \theta = \tan^{-1}\left(\frac{-\Gamma\omega}{\omega^2-\omega_0^2}\right) \qquad (11.5)$$

The electron oscillates at the drive frequency ω with amplitude a and a phase lags behind the drive by θ.

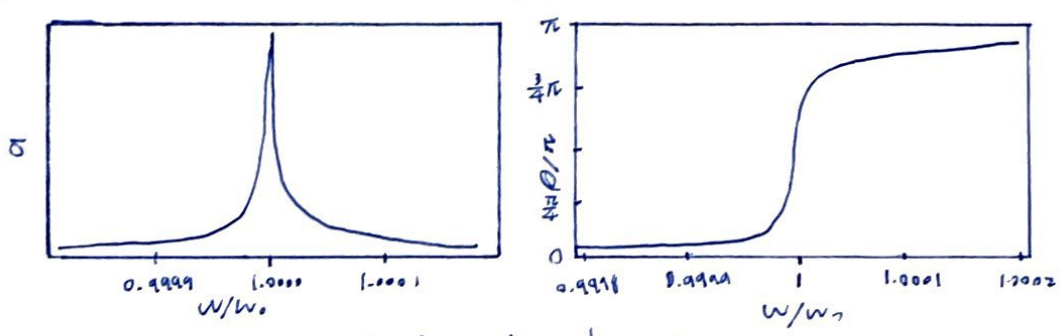


Fig 16. Amplitude and phase lag of a damped, driven harmonic oscillator as functions of ω/ω_0. The decay rate for the plots is $\Gamma = 10^{-5}\omega_0$

Drawing a parallel to our previous study, we consider a classical electric dipole moment, which is ~~the~~

$$d(t) = -ez(t)$$

So we have a dipole moment oscillating at the frequency of the applied field, much like what we found with our quantum model.

The Lorentz ~~mod~~ expression is more general as it describes the behavior of any detuning $\delta = \omega - \omega_0$

11.2 Scattering

We use the result from electromagnetism. The total power radiated by an oscillating electric dipole moment $d(t) = d_0 \cos(\omega t)$ is given by

$$P_{sc} = \frac{d_0^2 \omega^4}{12\pi\varepsilon_0 c^3}$$

Substituting in the amplitude from 11.5 we find

$$P_{sc} = \frac{e^4 E_0^2}{12\pi\varepsilon_0 m^2 c^3}\left[\frac{\omega^4}{(\omega^2-\omega_0^2)^2+\Gamma^2\omega^2}\right] = \frac{e^4 I_{in}}{6\pi\varepsilon_0^2 m^2 c^4}\left[\frac{\omega^4}{(\omega^2-\omega_0^2)^2+\Gamma^2\omega^2}\right]$$

where the intensity of the incoming radiation, $I_{in} = \frac{1}{2}\varepsilon_0 c E_0^2$.

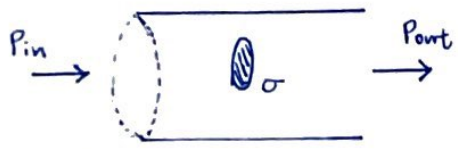
The total scatter power, P_{sc}, is proportional to the incident intensity I_{in}.

Introduce the proportionality factor σ_{sc} so that $P_{sc} = \sigma_{sc} I_{in}$ where

$$\sigma_{sc} = \frac{8\pi r_0^2}{3}\left[\frac{\omega^4}{(\omega^2-\omega_0^2)^2+\Gamma^2\omega^2}\right] \quad \text{with } r_0 = \frac{e^2}{4\pi\varepsilon_0 m c^2}$$

σ_{sc} has dimension of area, and is called the scattering cross-section

r_0 is the classical electron radius which has value $r_0 = 2.82 \times 10^{-15}$



Toy model of a scattering cross-section. An incident beam with uniform power P_{in} over an area A encounters a completely scattering object of area σ. The scattered power $P_{sc} = (P_{in} - P_{out})$ is seen to be $P_{sc} = \frac{\sigma}{A} P_{in} = \sigma I_{in}$

Warning: σ_{sc} doesn't actually correspond to physical dimensions of anything

11.2.1 Thomson scattering ($\omega \gg \omega_0$)

When $\omega \gg \omega_0$. A good example is a plasma, where $\omega_0 = 0$. In this limit $(\omega_0^2 - \omega^2)^2 \approx \omega^4$. Also for typical transitions in atoms $\Gamma \ll \omega_0$. These approximations yield a σ that has no dependency on the driving frequency:

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

11.2.2 Rayleigh scattering ($\omega \ll \omega_0$)

The opposite limit implies that $(\omega^2 - \omega_0^2)^2 \approx \omega_0^4$. Once again we ignore spontaneous decay as $\Gamma \ll \omega_0$. The resulting cross-section is

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

Nitrogen ~~atom~~ molecules in air scatter visible light through Rayleigh scattering. Scattering cross-section depends on the fourth power of radiation frequency. Blue light scatters more than red light due to the cross-section property. The sky appears blue during the day due to high-frequency components having a higher probability of scattering. When the sun is setting, light needs to pass through more atmosphere so blue light scatters away.

11.2.3 Resonant scattering ($\omega \approx \omega_0$)

This implies that $(\omega^2 - \omega_0^2) \approx 2\omega_0 \delta$. This approximation yields

$$\sigma_{sc} = \frac{8\pi r_0^2}{3} \frac{\omega_0^2}{\Gamma^2} \left[\frac{\Gamma^2}{\Gamma^2 + 4(\omega - \omega_0)^2} \right], \text{ with } r_0 = \frac{e^2}{4\pi\varepsilon_0 m c^2}$$

where the bracketed term is the Lorentzian function. On resonance, the bracketed term is 1. For a typical transition with $\Gamma = 10^{-8} \times \omega_0$, this resonant cross-section is 16 orders of magnitude larger than for Thomson scattering, which is itself higher than the cross-section for Rayleigh scattering.

Lecture 12 : Radiative Rate Equations

12.1 Radiative processes

Absorption : atom initially in its ground state goes to excited state after interacting with resonant radiation.

Stimulated emission : Atom is initially in excited state and goes to ground state after interacting with the radiation field, returning energy $\hbar\omega_0$

Spontaneous emission : an excited atom can transition to its ground state even if there is no incident radiation field. A photon will be emitted in a random direction, at a random time with a characteristic ~~rate~~ exponential decay.

12.2 Rate equations

Consider N atoms in a small volume interacting with a radiation field. To keep things simple, we only include two atomic states in the model. At any given time N_1 atoms are in state 1, $N_2 = N - N_1$ atoms are in state 2. The number of atoms in each state called the population of the state, changes in time according to the coupled rate equations.

$$\frac{dN_2}{dt} = \begin{pmatrix}\text{absorption}\\ \text{rate}\end{pmatrix} N_1 - \begin{pmatrix}\text{stimulated}\\ \text{emission rate}\end{pmatrix} N_2 - \begin{pmatrix}\text{spontaneous}\\ \text{emission rate}\end{pmatrix} N_2 \qquad (12.1)$$

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt} \qquad (12.2)$$

where each radiative process is associated with its own rate. The atoms behave independently. The second equation shows that the system is closed.

Assumptions about the rates : For monochromatic radiation, ~~you~~ the energy density ρ is given by

$$\rho = \frac{I}{c} = \frac{1}{2}\varepsilon_0 E_0^2 \qquad (12.3)$$

where I is the intensity and E_0 the electric field amplitude.
Let's assume that the rate is proportional to this energy density.
If the radiation is not monochromatic, we characterize it by a spectral energy density $\rho(\omega)$, where $\int \rho(\omega) d\omega$ gives the total energy.

Atoms only respond to a narrow range of frequency close to resonance, we therefore assume the absorption and stimulated emission rates $\propto \rho(\omega_0)$
We also assume that both rates are constant in time.
For the spontaneous emission rate we assume that it is independent of time and state of any incident radiation.
These result in :

$$\frac{dN_2}{dt} = B_{12}\rho(\omega_0)N_1 - B_{21}\rho(\omega_0)N_2 - A_{21}N_2 \qquad (12.4)$$

The remaining unknown proportionality constants are written as B_{12}, B_{21}, and A_{21}. They are called the Einstein A and B coefficients. If there is no radiation field the N_2 simply decays with the rate A_{21}, hence $A_{21} = \Gamma$.

12.3 Thermal equilibrium of a black body

A closed box will opaque walls and held at temperature T. The radiation field in the box comes to equilibrium with walls, resulting in a spatial energy density.

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\left(\frac{1}{e^{\hbar\omega/kT}-1}\right) \qquad (12.5)$$

Now put N two-state atoms within the box. At the steady state, we have $dN_2/dt = 0$. We therefore can rearrange (12.4) to find another expression for the spectral energy density.

$$\rho(\omega_0) = \frac{A_{21}/B_{21}}{\frac{N_1}{N_2}\frac{B_{12}}{B_{21}}-1} = \frac{A_{21}}{B_{21}}\left(\frac{1}{\left(\frac{B_{12}}{B_{21}}\right)e^{\hbar\omega_0/kT}-1}\right) \qquad (12.6)$$

In the second equlity we have utilized the Boltzmann distribution.
For the consistency of Planck's law, (12.5), and (12.6), for any possible temperature T the coefficients must satisfy

$$B_{12} = B_{21} \qquad \text{and} \qquad \frac{A_{21}}{B_{21}} = \frac{\hbar\omega_0^3}{\pi^2 c^3}$$

12.4 The spontaneous decay rate

For a monochromatic radiation field, neglating any spontaneous decay, we found that the probability of an atom to be in a state oscillates in time. In particular, for an atom initially in state 1, we calculated

$$P_2(t) = \frac{\Omega^2}{\Omega^2+\delta^2}\sin^2\left(\frac{\sqrt{\Omega^2+\delta^2}}{2}t\right) = \left(\frac{\Omega t}{2}\right)^2 \mathrm{sinc}^2\left(\frac{\Omega' t}{2}\right) \qquad (12.9)$$

for Rabi frequency Ω and detuning $\delta = \omega - \omega_0$, $\Omega' = \sqrt{\Omega^2+\delta^2}$
For black body radiation light is incoherent, we integrate the single-frequency probability in (12.9) over the entire frequency range:

$$P_2(t) = \int_0^\infty \frac{\rho(\omega) d_{12}^2 t^2}{\varepsilon_0 \hbar^2}\mathrm{sinc}^2\left(\frac{\Omega' t}{2}\right) d\omega$$

$$= \frac{d_{12}^2}{\varepsilon_0 \hbar^2}\rho(\omega_0) t^2 \int_0^\infty \left[\mathrm{sinc}^2\left(\frac{\Omega' t}{2}\right)\right] d\omega$$

We have re-written Ω^2 in terms of $\rho(\omega)$ using (12.3) and the definition of Ω. We then replaced $\rho(\omega)$ with $\rho(\omega_0)$ since it is approximately constant over the frequency range in which the sinc function is non-zero.
Using the approximation that $\Omega t \ll 1$ and the standard integral

$$\int_{-\infty}^{\infty} \mathrm{sinc}^2(x)\,dx = \pi$$

It can be shown that

$$P_2(t) = \frac{\pi d_{12}^2}{\varepsilon_0 \hbar^2} \rho(\omega_0) t = B\rho(\omega_0) t \qquad (12.11)$$

The excitation ~~pop~~ probability is proportional to time and the spatial energy density. Also we identify the remaining factor as the previously unknown B coefficient.

Recall that the radiation components have random polarization directions. For the square dipole matrix element d_{12}^2, we should use the average of the three Cartesian components $(d_x^2 + d_y^2 + d_z^2)/3$

Finally using the relationship between A and B coefficients defined above, along with the observation that $A = \Gamma$, we have

$$\Gamma = \frac{\omega_0^3}{3\varepsilon_0 \pi \hbar c^3} |\langle \psi_2 | \hat{\underline{d}} | \psi_1 \rangle|^2 .$$

We can calculate spontaneous decay in terms of the wave functions and energies of the states. The rate equations are valid in other examples, such as when collisions between atoms, which scrambles the phase of their superposition states, are frequent.

Lecture 13 : Laser Spectroscopy

13.1 Narrowband rate equations

We assume the bandwidth is so small that the response of the atoms is constant over this range. In this limit the total absorption and stimulated emission rates will depend on the total energy density $\rho = \int \rho(\omega) d\omega$ rather than the spatial energy at resonance $\rho(\omega_0)$.

The rates also depend on detuning, so frequency dependence of the atomic response needs to be accounted. We write the narrowband rate equation as:

$$\frac{dN_2}{dt} = g(\omega) B\rho N_1 - g(\omega) B\rho N_2 - \Gamma N_2$$

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt}$$

where $g(\omega)$ characterizes the response of the atoms to radiation. $B = \frac{\pi d_{12}^2}{\varepsilon_0 \hbar^2}$

Imagine the populations have reached steady state thus $dN_2/dt = 0$. The fraction of atoms that are in the excited state is

$$\frac{N_2}{N_2 + N_1} = \frac{g(\omega) B\rho}{2 g(\omega) B\rho + \Gamma} \qquad (13.3)$$

Consider the case of a weak radiation field, so that ρ is very small. The spontaneous decay rate is much larger than the stimulated emission rate. We therefore recognize that $2g(\omega)B\rho \ll \Gamma$ which simplifies the expression to:

$$\frac{N_2}{N_1+N_2} = B\rho \frac{g(\omega)}{\Gamma}$$

$$= \left(\frac{\pi d_{12}^2}{\varepsilon_0 \hbar^2}\right)\left(\frac{1}{2}\varepsilon_0 \mathcal{E}_0^2\right)\frac{g(\omega)}{\Gamma} = \frac{\pi}{2}\frac{\Omega^2}{\Gamma} g(\omega)$$

We ~~all~~ already found the ~~the~~ probability for one atom to be in the excited state and it is:

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

where $t\to\infty$ is used to denote steady-state value.

Equating the two expressions yields

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

which we recognize as the Lorentzian function with full width at half maximum of Γ. $g(\omega)$ is the normalized lineshape, $\int g(\omega)d\omega = 1$.

13.2 Absorption spectroscopy

We shine a beam of single-frequency light through a gas of atoms, and we aim to measure resonant frequencies of the atoms by observing how their response depends on radiation frequency.

One approach is to detect the amount of light scattered by the atoms by measuring how much light is emitted perpendicular to the incident beam. The total rate of scattering event is ΓN_2. We calculate the total scattered power to be

$$P_{sc} = \hbar\omega \times \Gamma N_2 = N\hbar\omega \frac{\pi\Omega^2}{2} g(\omega)$$

where $N = N_1+N_2$. It turns out that the classical calculation with radiation from an oscillating dipole is incorrect by a small factor.

13.2.1 Absorption

A superior approach to spectroscopy. We need to consider how the intensity of light beam changes as it propagates through the gas of atoms.

Consider a beam traveling the x direction, with an intensity $I(x)$ that is uniform over its cross section A. Each absorption event reduces the beam energy by $\hbar\omega$. Therefore absorption at rate R reduces the power of the beam by $R\hbar\omega$. Stimulated emission similarly increases the beam's power. Thus as the beam travels from x to $x+\Delta x$, the net loss in power is

$$P_{abs} = g(\omega)B\rho N_1\hbar\omega - g(\omega)B\rho N_2\hbar\omega$$

$$= (N_1-N_2)\frac{B\hbar\omega}{c} g(\omega) I(x) = (N_1-N_2)\sigma I(x)$$

due to the interaction with N atoms as the radiation travels over the volume $A\Delta x$. This equation shows a proportionality between the absorbed power and incident intensity. Drawing a parallel to the treatment of scattering, we've introduced the absorption cross section.

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

which has the dimension of area.

Rather than counting individual atoms, we describe the gas as a continuous density of n atoms per unit volume. As the beam travels from x to $x+\Delta x$ it interacts with $N = nA\Delta x$ atoms in total. The change in intensity is:

$$I(x+\Delta x) - I(x) = -\frac{P_{abs}}{A}$$

$$= -\frac{(n_1-n_2)A\Delta x}{A}\sigma I(x)$$

Dividing by Δx yields

$$\frac{dI}{dx} = -(n_1 - n_2)\sigma I(x)$$

The rate intensity decreases is proportional to population imbalance, the absorption cross-section, and the intensity.

Approximating that atomic populations are independent of I, which is valid for a weak drive, integrating our equation shows that

$$I(x) = I(0)e^{-\Delta n\sigma x}$$

where $\Delta n = n_1 - n_2$, note that $n_1 > n_2$.

The intensity decreases exponentially with a characteristic attenuation length of $\Delta n\sigma$.

Summary

- Rate equations can be formulated for narrowband radiation. The B-coefficients rates are modified by the normalized lineshape function $g(\omega)$
- The intensity of a beam of light decreases according to $I(x) = I(0)\exp(-\Delta n\sigma x)$
- The intrinsic lineshape function is a Lorenzian function. The FWHM, Γ, is called the natural linewidth.
- The motion of atoms in a gas causes an effective broadening of the line shape function. When this effect is large compared to the natural linewidth, the lineshape becomes a normal distribution with a FWHM proportional to $\sqrt{KT/M}$.