HYDROGEN ATOM

J. Rydberg found experimentally that the spectral lines in hydrogen are given by

$$\frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right), \quad n, m \in \mathbb{Z}, n < m$$

The *Balmer series* is the series $n = 2$, $m = 3, 4, \ldots$ and the lines are named using the Greek alphabet, such that the first line, $\lambda = 656\text{nm}$ is the Balmer-α line (H_α). Subsequent lines have shorter and shorter wavelengths. Often one defines the wavenumber $\tilde{\nu}$:

$$\tilde{\nu} = \lambda^{-1}$$

as this is closely related to the energy of the transition:

$$E = hc\tilde{\nu}$$

Other series are more difficult for humans to observe (with their eyes): The *Lyman series*, which has $n = 1$ lies in the ultraviolet region, and the series with wave lengths longer than the Balmer series lie in and beyond the infra-red region.

Bohr's Model

Bohr assumed electrons were small masses that orbited the nucleus, setting the centripetal force equal and opposite to the Coulomb force you get:

$$\frac{m_e v^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

Now, using the classical Hamiltonian ($H = T + V$) Bohr showed that the total energy of the electron in orbit about the hydrogen nucleus would have negative energy:

$$E = -\frac{1}{2r}\frac{e^2}{4\pi\varepsilon_0}$$

In order to remove the dependence on the unknown quantity (r), Bohr assumed that the angular momentum was quantised in units of $\hbar$:

$$m_e v r = n\hbar, \quad n \in \mathbb{Z}$$

which implies

$$r = a_0 n^2, \quad a_0 = \frac{\hbar^2}{m_e}\frac{4\pi\varepsilon_0}{e^2}$$

where a_0 is the **Bohr radius**. This gives us the following expression for the hydrogen energy:

$$E = -\frac{1}{2a_0 n^2}\frac{e^2}{4\pi\varepsilon_0}$$

This fits very closely to what was observed experimentally, as we can define the Rydberg constant as

$$hcR_\infty = \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{2\hbar^2}$$

The subscript R_∞ denotes that the Bohr model has assumed that the nucleus (one proton) has infinite mass – i.e the proton is stationary. In reality though the electron-proton pair orbit about their centre of mass. The classical Hamiltonian for the two body problem is normally solved using the reduced mass:

$$\mu = \frac{m_e M}{m_e + M}$$

where M is the mass of the nucleus. Hence for hydrogen we get a correction that is of order $m_e/M \approx {}^1\!/\!{}_{1836}$:

$$R_H = R_\infty \frac{M}{m_e + M} \approx R_\infty\left(1 - \frac{m_e}{M}\right)$$

This leads to a small but observable shift in energy-levels between different isotopes, known as the **isotope shift**.

Einstein's A and B coefficients

Consider a two-level atomic system, with populations N_1 and N_2 of the lower and upper levels respectively. These atoms are placed into an environment with a continuous radiation density $\rho(\omega)$. The excitation $|1\rangle \rightsquigarrow |2\rangle$ occurs with a rate that is proportional to $\rho(\omega_{12})$ where $\omega_{12} \equiv (E_2 - E_1)/\hbar$. The proportionality constant is B_{12}. Similarly the radiation promotes decay $|2\rangle \rightsquigarrow |1\rangle$ at a rate proportional to $\rho(\omega_{12})$, however, with proportionality constant B_{21}. Additionally there is a non-zero probability to decay spontaneously; we treat this effect qualitatively, and merely say that this occurs with a lifetime $\tau = \frac{1}{A_{21}}$. Hence

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = N_1 B_{12}\rho(\omega_{12}) - N_2 B_{21}\rho(\omega_{12}) - N_2 A_{21}$$

additionally, because the total number of atoms is constant

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = -\frac{\mathrm{d}N_1}{\mathrm{d}t}$$

Let us look at an example: Assume that $\rho(\omega) = 0$ (the radiation is switched off), and that there are some excited atoms, say $N_2(0)$ of these. This means that

$$N_2(t) = N_2(0)e^{-A_{21}t}$$

Next let us look at the rate equations within a black body. That is, let us assume that the radiation density is given by Planck's distribution law:

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

This gives us an expression for $\rho(\omega_{12})$ at equilibrium. Additionally we must use that the population of each state (divided by its degeneracy) is given by the Boltzmann factor :

$$\frac{N_2}{g_2} = \frac{N_1}{g_1} \exp\left(-\frac{\hbar\omega}{k_B T}\right)$$

From this we find

$$A_{21} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{21}$$

and

$$B_{12} = \frac{g_2}{g_1} B_{21}$$

INTERACTION OF ATOMS WITH RADIATION

Suppose our time-dependent Hamiltonian can be split into a constant H_0 term, and a perturbative time-dependent part, $H_I(t)$. Using H_0 wave functions we can express the wave-function similarly to how we would have expressed it without $H_I(t)$'s effect, however, now our coefficients are time-dependent*:

$$\Psi(t) = c_1(t) \left|1\right\rangle e^{-i\omega_1 t} + c_2(t) \left|2\right\rangle e^{-i\omega_2 t}, \quad \omega_i = \frac{E_i}{\hbar}$$

We still have the normalisation condition:

$$|c_1(t)|^2 + |c_2(t)|^2 = 1$$

Hence it would be beneficial to describe any time-dependent perturbation by solving the differential equations for $c_i(t)$.

Oscillating electric field

An oscillatory electric field, $\boldsymbol{E}(t) = \boldsymbol{E}_0(t)\cos(\omega t)$, produces the following perturbation:

$$H_I(t) = e\boldsymbol{r} \cdot \boldsymbol{E}_0 \cos(\omega t)$$

which gives us the following Schrödinger equation

$$\dot{c}_1 = -i\Omega \cos(\omega t) e^{-i\omega_0 t} c_2$$
$$\dot{c}_2 = -i\Omega^* \cos(\omega t) e^{i\omega_0 t} c_1$$

where the **Rabi frequency** is defined as

$$\Omega = \frac{e}{\hbar} \left\langle 1\right| \boldsymbol{r} \cdot \boldsymbol{E}_0 \left|2\right\rangle$$

The **dipole approximation** simplifies these calculations significantly, by assuming that the amplitude of the electric field does not change on the scale of the problem (we assume $\|\boldsymbol{E}_0\|$ is approximately constant, which allows to take it outside the integral), hence

$$\Omega = \frac{eX_{12}\|\boldsymbol{E}_0\|}{\hbar}, \quad X_{12} \equiv \left\langle 1\right| \boldsymbol{r} \left|2\right\rangle$$

commonly we choose $\boldsymbol{E} \parallel \hat{\boldsymbol{x}}$, which turns X_{12} into $\left\langle 1\right| x \left|2\right\rangle$.

Rotating wave approximation

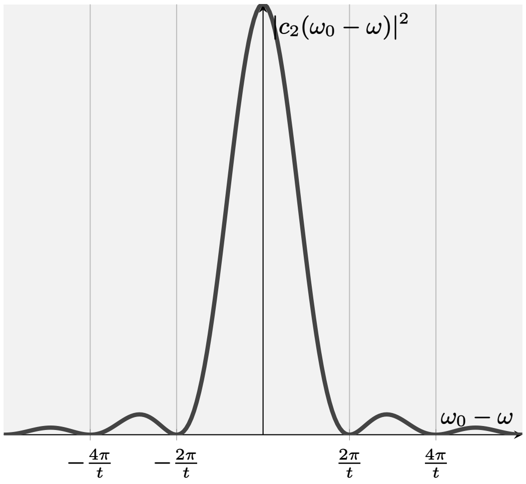
The solution to Equations and , with the initial conditions $c_1(0) = 1$ and $c_2(0) = 0$ is

$$c_1(t) = 1$$
$$c_2(t) = \frac{\Omega^*}{2}\left(\frac{1 - e^{i(\omega_0+\omega)t}}{\omega_0 + \omega} + \frac{1 - e^{i(\omega_0-\omega)t}}{\omega_0 - \omega}\right)$$

Assuming the detuning $\delta \equiv \omega_0 - \omega$ is small compared to the atomic resonance, ω_0, we can neglect the first term:

$$|c_2(t)|^2 = \left|\Omega \frac{\sin\left((\omega_0 - \omega)t/2\right)}{\omega_0 - \omega}\right|^2 = \frac{1}{4}|\Omega|^2 t^2 \frac{\sin^2 x}{x^2}$$

which is a sinc-squared in $\omega_0 - \omega$, with a width that decreases as $t \to \infty$. In the limit $t \to \infty$ it becomes a Dirac-delta.



Figur 1: $|c_2(\omega_0 - \omega)|^2$ *at a set value of* t.

Einstein's B coefficient

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* Is this a result due to the adiabatic theorem? Saying that we remain in the two eigenstates of the unperturbed Hamiltonian, even after we add our time-dependent perturbation, however, changing the coefficients at each instant of time?

By relating the radiation density $\rho(\omega)$ to the intensity, and hence the electric field, we can find an expression for $\Omega(\omega)$, which we would want to integrate over ω to get the total $c_2(t)$:

$$|c_2(t)|^2 = \frac{2e^2|X_{12}|^2}{\varepsilon_0\hbar}\int_{\omega_0-\Delta/2}^{\omega_0+\Delta/2}\rho(\omega)\frac{\sin^2\left((\omega_0-\omega)t/2\right)}{\omega_0-\omega}\mathrm{d}\omega$$

For large t, (in fact $t\to\infty$) the sinc function can be approximated as a Dirac delta, which spits out $\rho(\omega_0)$, giving us a transition rate of

$$R_{12} = \frac{|c_2(t)|^2}{t} = \frac{\pi e^2|X_{12}|^2}{\varepsilon_0\hbar^2}\rho(\omega_0)$$

and hence

$$B_{12} = \frac{\pi e^2\|\boldsymbol{D}_{12}\|^2}{3\varepsilon_0\hbar^2}$$

where we have used that $|X_{12}| \rightsquigarrow \|\boldsymbol{D}_{12}\|/3$ and

$$\boldsymbol{D}_{12} = \langle 1|\,\boldsymbol{r}\,|2\rangle$$

Our relation between A_{21} and B_{12} tells us that:

$$A_{21} = \frac{g_1}{g_2}\frac{4\alpha}{3c^2}\omega^3|D_{12}|^2$$

INTERACTION WITH MONOCHROMATIC RADIATION

Instead of treating the problem of the interaction between a two-level system and monochromatic radiation perturbatively, we can solve the full Schrödinger equation. This means we can allow the electric field to be strong. Initially we assumed that most of the population stayed in the ground state, i.e that $|c_1| \gg |c_2|$, however, now we will not make that approximation. Writing the Schrödinger equation:

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} = -ic_2\left(e^{i(\omega_0-\omega)t} + e^{-i(\omega_0+\omega)t}\right)\frac{\Omega}{2}$$

If ω is "close"to ω_0 the sum $\omega_0+\omega$ will oscillate far quicker than $\omega_0-\omega$, so the term with the sum will average out during one period of $\frac{1}{\omega_0-\omega}$. Therefore we can ignore its effect:

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} = -ic_2e^{i(\omega-\omega_0)t}\frac{\Omega}{2}$$
$$\frac{\mathrm{d}c_2}{\mathrm{d}t} = -ic_1e^{-i(\omega-\omega_0)t}\frac{\Omega^*}{2}$$

These coupled first-order differential equations can be decoupled to a second-order differential equation

$$\frac{\mathrm{d}^2c_2}{\mathrm{d}t^2} + i(\omega-\omega_0)\frac{\mathrm{d}c_2}{\mathrm{d}t} + \left|\frac{\omega}{2}\right|^2c_2 = 0$$

Whose solution, assuming that $c_1(0)=1$ and $c_2(0)=0$ can be written as

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

When the detuning is zero this simplifies to

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

for $\Omega t = \pi$ we get that $|c_2\left(\frac{\pi}{\Omega}\right)|^2 = 1$ and hence that $|c_1\left(\frac{\pi}{\Omega}\right)|^2 = 0$ – we have inverted the population. This population inversion is more general:

$$c_1\,|1\rangle + c_2\,|2\rangle \overset{\pi}{\rightsquigarrow} -i\left(c_2\,|1\rangle + c_1\,|2\rangle\right)$$

For $\Omega t = \frac{\pi}{2}$ this process hasn't finished completely, as $\sin^2\left(\frac{\pi}{2}\right) = \frac{1}{2}$, hence this takes us from $|1\rangle \rightsquigarrow \frac{1}{\sqrt{2}}\left(|1\rangle + e^{i\phi}\,|2\rangle\right)$.

Bloch Sphere and Bloch Vector

This simple example from before allows us to introduce the Bloch sphere and Bloch vector rather naturally. The density matrix is defined as

$$|\Psi\rangle\langle\Psi| = \begin{pmatrix} |c_1|^2 & c_1c_2^* \\ c_1^*c_2 & |c_2|^2 \end{pmatrix} \equiv \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix}$$

The diagonal entries are the populations of the two levels, and the off-diagonal elements are referred to as the *coherences*. By changing basis we can write hence rewrite the following expression for the dipole moment

$$D_x = c_1c_2^*X_{21}e^{i\omega_0t} + c_1^*c_2X_{12}e^{-i\omega_0t}$$

as follows:

$$D_x = X_{12}\left(u\cos(\omega t) - v\sin(\omega t)\right)$$

This is done by going into the *rotating frame*, which just means that we can think of our change of basis as a constant rotation with respect to the intrinsic phases of the two levels. We chose the rotating frame's frequency to be equal to the detuning $\delta = \omega - \omega_0{}^\dagger$, hence

$$\tilde{c}_1 = c_1e^{i\delta t/2}$$
$$\tilde{c}_2 = c_2e^{-i\delta t/2}$$

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† Is this the right way of thinking about it?

Using this transformation we define

$$\tilde{\rho}_{11} = \rho_{11}, \qquad \tilde{\rho}_{22} = \rho_{22}$$
$$\tilde{\rho}_{12} = \rho_{12}e^{-i\delta t}, \quad \tilde{\rho}_{21} = \rho_{21}e^{i\delta t}$$

Which allows us to rewrite the Schrödinger equation as

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} 0 & \delta & 0 \\ -\delta & 0 & \Omega \\ 0 & -\Omega & 0 \end{pmatrix}\begin{pmatrix} u \\ v \\ w \end{pmatrix}$$

where

$$\boldsymbol{R} = \begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} \tilde{\rho}_{12} + \tilde{\rho}_{21} \\ -i\left(\tilde{\rho}_{12} - \tilde{\rho}_{21}\right) \\ \tilde{\rho}_{11} - \tilde{\rho}_{22} \end{pmatrix}$$

The matrix, call it M, in equation screams "antisymmetric tensor", and can in fact be written as

$$M_{ij} = \varepsilon_{ijk}W_k, \quad \boldsymbol{W} = \begin{pmatrix} \Omega \\ 0 \\ \delta \end{pmatrix}$$

Thus

$$\dot{R}_i = \varepsilon_{ijk}R_jW_k \rightsquigarrow \dot{\boldsymbol{R}} = \boldsymbol{R} \times \boldsymbol{W}$$

$\boldsymbol{R}$ is the Bloch vector that describes our state (for example $\boldsymbol{R} = \hat{\boldsymbol{e}}_3$ is the state $|1\rangle$, whereas $\boldsymbol{R} = \hat{\boldsymbol{e}}_1$ is the state $\frac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right)$). $\boldsymbol{R}$ precesses about $\boldsymbol{W}$ at angular frequency W.

Optical Bloch Equations

By introducing the natural decay rate Γ, to the differential equations above, we modify the differential equation that describes ρ_{22}:

$$\dot{\rho}_{22} = -\Gamma\rho_{22} + \frac{\Omega}{2}v$$

which leads to the **Optical Bloch Equations**:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} -\frac{\Gamma}{2} & \delta & 0 \\ -\delta & -\frac{\Gamma}{2} & \Omega \\ 0 & -\Omega & -\Gamma \end{pmatrix}\begin{pmatrix} u \\ v \\ w \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \Gamma \end{pmatrix}$$

In steady state, i.e for $t \gg \Gamma^{-1}$ the solution reads

$$\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \frac{1}{\delta^2 + \frac{\Omega^2}{2} + \frac{\Gamma^2}{4}}\begin{pmatrix} \Omega\delta \\ \Omega\frac{\Gamma}{2} \\ \delta^2 + \frac{\Gamma^2}{4} \end{pmatrix}$$

This is not particularly intuitive, but for example, by putting this into the definitions given above you can see that $\rho_{22} = \frac{\Omega^2/4}{\delta^2+\Omega^2/2+\Gamma^2/4} \rightsquigarrow \frac{1}{2}$ for increasing intensities (and hence increasing Ω)

Optical absorption cross-section

The intensity of light propagating through a medium with N atoms per unit volume will decrease exponentially. The attenuation can be described by

$$\frac{\mathrm{d}I}{\mathrm{d}z} = -\kappa(\omega)I = -N\sigma(\omega)I$$

where $\sigma(\omega)$ is the **absorption cross-section**. Using the results from the previous sections we can express this as a function of Ω, δ and Γ:

$$\sigma(\omega) = \frac{\Omega^2/4}{\delta^2 + \Gamma^2/4}\frac{A_{21}\hbar\omega}{I}$$

Note that Ω^2 is a function of I, therefore the differential equation still has an exponential solution. Additionally note that omission of Ω^2 in the denominator, which must be because we assume that the field is sufficiently weak. We can rewrite this as

$$\sigma(\omega) = \frac{3\pi^2c^2}{\omega_0^2}A_{21}g_H(\omega), \quad g_H(\omega) = \frac{1}{2\pi}\frac{\Gamma}{\delta^2 + \Gamma^2/4}$$

where the subscript, H, in the distribution functions is to show that this line width is *homogeneous* – it affects all atoms in the sample in the same way. The pre-factor of 3 can range from 0 to 3, depending on how the incident light is polarised. For unpolarised light, propagating through a two-level system, with degeneracies on both levels, the cross-section becomes

$$\sigma(\omega) = \frac{g_2}{g_1}\frac{\pi^2c^2}{\omega_0^2}A_{21}g_H(\omega)$$

This broadening is often referred to as **natural linewidth.**

Peak radiative broadening

For $\delta = 0$ we reach the largest cross-section:

$$\sigma(\omega_0) = \frac{6\pi^2c^2}{\omega_0^2}\frac{A_{21}}{\Gamma}$$

In a two-level system $\Gamma = A_{21}$, because the only possible decay is from $|2\rangle \rightsquigarrow |1\rangle$. Hence

$$\sigma(\omega_0) \approx \frac{\lambda_0^2}{2}, \quad \lambda_0 \equiv \frac{2\pi c}{\omega_0}$$

This wavelength is often in the visible region, for example $\lambda_0 = 589\text{nm}$ for sodium, therefore the cross-section is often *huge* compared to the size of atoms, close to resonance. However, the cross-section decreases rapidly, off-resonance. For the example above, when we use light with wavelength $\lambda = 600\text{nm}$ the cross section is $\sigma(\omega) \sim 10^{-25}\text{m}^2$ – which is small, even compared to the Bohr radius squared.

Saturation Intensity

The population difference from before, can now be written as

$$w = \frac{1}{1 + {}^{I}/_{I_s(\omega)}}$$

where the saturation intensity is defined as

$$I_s(\omega) = \frac{\hbar\omega A_{21}}{2\sigma(\omega)}$$

which reaches its minimum at resonance – we define

$$I_{\text{sat}} \equiv \min\{I_s(\omega)\} = I_s(\omega_0) = \frac{\pi}{3}\frac{hc}{\lambda_0^3\tau}, \quad \tau = \Gamma^{-1}$$

where λ_0 is the aforementioned transition wavelength. From Equation we recognise that

$$\frac{I}{I_{\text{sat}}} = \frac{2\Omega^2}{\Gamma^2}$$

Power broadening

Using what we have found, we can rearrange the expression for the attenuation $\kappa(\omega)$:

$$\kappa(\omega) = N\sigma(\omega_0)\frac{{}^{\Gamma^2}/_4}{\delta^2 + {}^{\Gamma^2}/_4\left(1 + {}^{I}/_{I_{\text{sat}}}\right)}$$

which is a Lorentzian distribution, and tells us that the line shape due to the radiation has a full-width-half-maximum (FWHM) of

$$\Delta\omega_{\text{FWHM}} = \Gamma\left(1 + \frac{I}{I_{\text{sat}}}\right)^{1/2}$$

TRANSITIONS

When looking at dipole transitions, one will have to calculate the dipole moment, as in, for example Equation . In order to do this there are some selection rules that help get an overview of which dipole-transitions are legal. First let us split the dipole moment into an angular and a radial integral:

$$\langle 2|\,\boldsymbol{r}\cdot\hat{\boldsymbol{e}}_{\text{rad}}\,|1\rangle = D_{12}\mathcal{I}_{\text{ang}}$$

where

$$D_{12} = \int_0^\infty R_{n_2,\ell_2} r R_{n_1,\ell_1} r^2 \mathrm{d}r$$

$$\mathcal{I}_{\text{ang}} = \int_0^{2\pi}\int_0^\pi Y^*_{\ell_2,m_2}(\theta,\phi)\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{e}}_{\text{rad}} Y_{\ell_1,m_1}\sin\theta\mathrm{d}\theta\mathrm{d}\phi$$

The radial part measures the overlap in radial wave functions, hence for large differences in n_1 and n_2 this integral can be negligible. However, it is usually the radial integral that is zero, unless very strict selection rules hold true.

Generally the dot product $\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{e}}_{\text{rad}}$ can be written in terms of the $Y_{1,m}$ functions:

$$\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{e}}_{\text{rad}} \propto A_{\sigma^-}Y_{1,-1} + A_z Y_{1,0} + A_{\sigma^+}Y_{1,1}$$

Hence we have split up the radiation into π-radiation (linearly polarised light along the z-axis) and two σ-radiations (circular polarised light each rotating in the opposite direction)

π-transitions

π-polarised light does not have an angular momentum along the z-axis, thus we would expect that π-transitions leave m unchanged:

$$\mathcal{I}^\pi_{\text{ang}} = \int_0^{2\pi}\int_0^\pi Y_{\ell_2,m_2}\cos\theta Y_{\ell_1,m_1}\sin\theta\mathrm{d}\theta\mathrm{d}\phi$$

using the cylindrical symmetry, we can show that

$$\mathcal{I}^\pi_{\text{ang}} = e^{i(m_1-m_2)\phi_0}\mathcal{I}^\pi_{\text{ang}} \quad \rightsquigarrow \quad \Delta m = 0$$

as expected.

σ-transitions

σ^+-light rotates anticlockwise (seen from positive z, for light propagating in the z-direction), hence the angular momentum vector is pointing in the positive z-direction. This would lead us to believe that σ^+-transitions increase m by one, and this is in fact the case. Similarly σ^--transition decrease m by one:

$$\Delta m = \begin{cases} 1 & \sigma^+ - \text{transitions} \\ -1 & \sigma^- - \text{transitions} \end{cases}$$

Generally therefore the angular integral is zero unless

$$\Delta m = 0, \pm 1$$

Using the expression we got for $\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{e}}$ before we can see that

$$\mathcal{I}_{\text{ang}} \propto \int_0^{2\pi}\int_0^{\pi} Y^*_{\ell_2,m_2} Y_{1,m} Y_{\ell_1,m_1} \sin\theta \mathrm{d}\theta \mathrm{d}\phi, \quad m = 0, \pm 1$$

Using the orthogonality of the angular functions (and a rule for multiplication of angular functions) we get an additional selection rule, which constrains $\Delta\ell$. In summary the selection rules are

$$\Delta\ell = \pm 1$$
$$\Delta m = 0, \pm 1$$

FINE STRUCTURE

The fine structure has three contributing components: Spin-orbit coupling, the Darwin term and a relativistic correction to the kinetic energy.

Spin-orbit coupling

The calculation of the correction due to spin-orbit calculation is normally carried out in the electron's reference frame, which is not an inertial reference frame. Therefore our calculations will be off by approximately a factor of two, due to what is known as **Thomas precession.**

In the electron's reference frame, the proton is moving, and therefore creates a magnetic field:

$$\boldsymbol{B} = \frac{\hbar}{m_e c^2}\left(\frac{1}{er}\frac{\partial V}{\partial r}\right)\boldsymbol{\ell}$$

where $V(r)$ is the potential due to the proton and $\hbar\boldsymbol{\ell} = m_e\boldsymbol{r}\times\boldsymbol{v}$ is the quantised angular momentum of the electron. The intrinsic magnetic moment of the electron will couple to this magnetic field. This magnetic moment is related to its spin:

$$\boldsymbol{\mu} = -g_s\mu_B\boldsymbol{s}$$

where μ_B is the Bohr magneton and $g_s \approx 2$. The interaction energy is given by

$$H_{\text{SO}} = -\boldsymbol{\mu}\cdot\boldsymbol{B} = g_s\mu_B\frac{\hbar}{m_e c^2}\left(\frac{1}{er}\frac{\partial V}{\partial r}\right)\boldsymbol{s}\cdot\boldsymbol{\ell}$$

Evaluating the expectation value of this requires you to evaluate $\langle r^{-3}\rangle$ as well as $\langle\boldsymbol{s}\cdot\boldsymbol{\ell}\rangle$, the latter of which can be done by introducing $\boldsymbol{j} = \boldsymbol{s}+\boldsymbol{\ell}$, which is a conserved quantity. This gives us

$$E_{\text{SO}} = \frac{\beta}{2}\left(j(j+1) - s(s+1) - \ell(\ell+1)\right)$$

where the spin-orbit constant is

$$\beta = \frac{\hbar^2}{2m_e^2c^2}\frac{e^2}{4\pi\varepsilon_0}\frac{1}{(na_0^3)\ell\left(\ell+{}^1\!/\!{}_2\right)(\ell+1)}$$

The values of j can be

$$j = |\ell - s|, |\ell - s| + 1, \ldots, (\ell + s) - 1, (\ell + s)$$

Relativistic kinetic energy

The classical Hamiltonian $H = T + V$ is only accurate for small momenta, and using accurate measurement techniques there will always be a discrepancy between results obtained using $T + V$ and results using the relativistic Hamiltonian: $H = \sqrt{m^2c^4 + c^2\|\boldsymbol{p} - e\boldsymbol{A}(\boldsymbol{x},t)\|^2} + e\Psi(\boldsymbol{x},t)$. By Taylor approximating this Hamiltonian for low velocities we get

$$H \approx T + V + \mathcal{O}\left(\frac{v^2}{c^2}\right)$$

Hence the relativistic correction we make would be of order v^2c^{-2}. We find that the ratio vc^{-1} is

$$\frac{v}{c} = \frac{\alpha}{n}, \quad \alpha = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{\hbar c}$$

where α is the **fine structure constant**, and $\alpha \approx \frac{1}{137}$. Therefore, the relativistic correction is of order α^2, as are all other fine structure corrections.

Darwin Term

For electrons with $\ell = 0$ there is a non-zero probability to be at (and near) the site of the nucleus, where the energy density is so high that we must take into account the effects described by the Dirac equation. The Dirac equation predicts that there will be a *Zitterbewegung*, due to electron-positron pairs created from the vacuum (vacuum fluctuations). The interaction of the electron with this EP-pair causes the Zitterbewegung. This correction is proportional to $|\psi(r = 0)|^2$, and therefore only affects s-electrons

Lamb shift

HELIUM

The Hamiltonian that describes a Helium atom is

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)$$

where Ze is the nuclear charge and $r_{12} = \|\boldsymbol{r}_1 - \boldsymbol{r}_2\|$. We begin by neglecting the electron-electron interaction;

the Hamiltonian uncouples and the total wave function is the product of hydrogenic electron wave functions. This means the total energy would be

$$E^{(0)} = E_1 + E_2 \approx -109\text{eV}, \quad \text{ignoring repulsion}$$

where I have used that $Z = 2$ for Helium and hence $E = -4hcR_\infty$. Now we treat the electron-electron repulsion as a perturbation:

$$E^{(1)} = \langle V_{12} \rangle = \frac{e^2}{4\pi\varepsilon_0} \left\langle (1s)^2 \right| r_{12}^{-1} \left| (1s)^2 \right\rangle = 34\text{eV}$$

This implies that it is not appropriate to treat the electron-electron repulsion as a perturbation. However adding this value gives us an energy in the right region:

$$E^{(0)} + E^{(1)} = -75\text{eV}$$

whereas the experimentally measured value is -78.95eV.

Excited states

For excited states we follow the same procedure, however using different wave functions. We assume that only one electron is excited, hence we look at the configuration $(1s)(n\ell)$. However, electrons are indistinguishable[‡], therefore there is an **exchange degeneracy**, which implies we should use degenerate perturbation theory. Let us look at the wave function:

$$|\psi\rangle = a\,|(1s)(n\ell)\rangle + b\,|(n\ell)(1s)\rangle$$

Using which we can construct the perturbation matrix:

$$\begin{pmatrix} J & K \\ K & J \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \Delta E \begin{pmatrix} a \\ b \end{pmatrix}$$

where

$$J \equiv \frac{e^2}{4\pi\varepsilon_0} \langle (1s)(n\ell)| \frac{1}{r_{12}} |(1s)(n\ell)\rangle$$
$$K \equiv \frac{e^2}{4\pi\varepsilon_0} \langle (1s)(n\ell)| \frac{1}{r_{12}} |(n\ell)(1s)\rangle$$

This gives us a correction of

$$\Delta E = J \pm K$$

with the following eigenstates:

$$\left|\psi^{\mathrm{S}}_{\text{space}}\right\rangle = \frac{1}{\sqrt{2}} \left(|(1s)(n\ell)\rangle + |(n\ell)(1s)\rangle \right)$$
$$\left|\psi^{\mathrm{A}}_{\text{space}}\right\rangle = \frac{1}{\sqrt{2}} \left(|(1s)(n\ell)\rangle - |(n\ell)(1s)\rangle \right)$$

The symmetric wave function has energy $E^{(0)} + \Delta E$, whereas the antisymmetric wave function has $E^{(0)} - \Delta E$.

Spin states

Fermions have antisymmetric wave functions under particle-label interchange. This implies that the total wave function (space times spin) must be of the form

$$|\Psi\rangle = \begin{cases} \left|\psi^{\mathrm{S}}_{\text{space}} \psi^{\mathrm{A}}_{\text{spin}}\right\rangle \\ \left|\psi^{\mathrm{A}}_{\text{space}} \psi^{\mathrm{S}}_{\text{spin}}\right\rangle \end{cases}$$

Note that there is only one antisymmetric spin configuration, forming a singlet:

$$\left|\psi^{\mathrm{A}}_{\text{spin}}\right\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right)$$

which has $S = M_S = 0$. The symmetric spin configuration forms a triplet

$$\left|\psi^{\mathrm{S}}_{\text{spin}}\right\rangle = \begin{cases} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right) \\ |\downarrow\downarrow\rangle \end{cases}$$

all with $S = 1$ and $M_S = 1, 0, -1$ respectively. Using spectroscopic notation, the terms $({}^{2\mathrm{S}+1}L)$ of the ground state would be ${}^1S$ and ${}^3S$ for the singlet and triplet respectively.

ALKALIS

The alkalis are the first group of the periodic system, hence they have one electron in the outermost shell, and all inner shells are filled. For example

$$\begin{aligned} \text{Lithium}: &\quad (1s)^2\,2s \\ \text{Sodium}: &\quad (1s)^2(2s)^2(2p)^6 3s \\ \text{Potassium}: &\quad (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6 4s \\ &\quad \vdots \end{aligned}$$

The quantum defect

The $3s$, $3p$ and $3d$ configurations all have the same energy for hydrogen, however this is not the case for atoms with more than one electron – the electron-electron repulsion breaks this degeneracy. This is in part due to the fact that the inner electrons "screen"the nucleus – the outermost electrons see a nucleus with a charge $< Ze$. This shows why the $3s$ has a different energy than the $3p$ configuration: $3s$ has a higher probability to be closer to the nucleus, where it experiences a larger effective charge. Despite this complication,

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[‡] we can't tell the difference between $(1s)(n\ell)$ and $(n\ell)(1s)$.

Bohr's formula works well, as long as we introduce a new parameter:

$$E(n,\ell) = -hc\frac{R_\infty}{(n-\delta_\ell)^2}$$

where δ_ℓ is the *quantum defect*. For example sodium has the following quantum defects:

$$\delta_s = 1.35, \ \ \delta_p = 0.86, \ \ \delta_d = 0.01, \ \ \delta_\ell \approx 0 \ \text{ for } \ \ell > 2$$

The decrease of δ_ℓ with increasing ℓ is because the higher ℓ the smaller the probability is of the electron being inside the electron cloud of the closed shells.

Central-field approximation

The result from the previous example is purely empirical, and can't tell us anything more than what we have measured experimentally. In order to, for example, find the wave functions for the outermost electrons in alkalis, we must approximate the Schrödinger equation. Commonly one uses the central field approximation, which uses the spherical symmetry of closed subshells. This repulsion between subshell-electron and the outermost electron is shoved into a central potential, $S(r)$. Note that we assume that all electron-electron interactions are spherically symmetric, which is why this approximation is only realistic for the alkalis. We define the central-field potential

$$V_{\text{CF}}(r) = -\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r} + S(r)$$

and hence the central-field Hamiltonian is

$$H_{\text{CF}} = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2 + V_{\text{CF}}(r_i)\right)$$

this is a separable Hamiltonian, hence

$$\psi_{\text{atom}} = \prod_{i=1}^{N}\psi_i, \quad E = \sum_{i=1}^{N}E_i$$

where

$$\left(-\frac{\hbar^2}{2m}\nabla_i^2 + V_{\text{CF}}(r_i)\right)\psi_i = E_i\psi_i$$

The central potential can be thought of as a spherically symmetric potential, where the effective nuclear charge eZ_{eff} is a function of the radius, due to shielding. The radial dependence of this effective nuclear charge can be estimated by treating the subshell-electrons as hydrogenic electrons, and then evaluating the total electric field due to the closed subshell together with the nucleus.

Self-consistent solutions

Once we go through the calculations of the central field potential, we realise that the potential changing will cause our wave-functions to change, which in turn causes the potential to change etc. What one can do, numerically, is repeat this process over and over again, until the corrections one makes between each iteration are negligible. Once this is done one has made a self-consistent solution.

Slater determinant

The product wave function in the central-field approximation does not automatically respect the Pauli exclusion principle. For fermions the wave function must be antisymmetric under exchange of any two electrons, which we can enforce by writing the N-electron wave function as a **Slater determinant**. If $\chi_i(q_j)$ denotes the i-th spin-orbital evaluated at the coordinates and spin of electron j, then

$$\Psi(q_1,\ldots,q_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(q_1) & \chi_2(q_1) & \cdots & \chi_N(q_1) \\ \chi_1(q_2) & \chi_2(q_2) & \cdots & \chi_N(q_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(q_N) & \chi_2(q_N) & \cdots & \chi_N(q_N) \end{vmatrix}$$

Exchanging two electron labels exchanges two rows of the determinant, and therefore changes the sign of the wave function. If two electrons are put into the same spin-orbital, two columns are identical and the determinant vanishes. Thus the Slater determinant encodes Pauli's exclusion principle directly.

Fine structure in the alkalis

The fine structure of the alkalis can be approximated quite well using the Landé formula:

$$\Delta E_{\text{FS}} = \frac{Z_{\text{i}}^2 Z_{\text{o}}}{(n-\delta_\ell)^3\ell(\ell+1)}\alpha^2 hcR_\infty$$

Where Z_{i} and Z_{o} are the inner and outer atomic numbers respectively. For neutral alkali atoms $Z_{\text{o}} \approx 1$ and generally $Z_{\text{i}} \sim Z$, because no shielding occurs on the inside of the atom. This formula can be justified by looking at how we would evaluate the fine structure splitting using the central-field approximation. We would need to evaluate the value of

$$\langle\frac{Z_{\text{eff}}(r)}{r^3}\rangle = \langle\frac{1}{er}\frac{\partial V_{\text{CF}}(r)}{\partial r}\rangle$$

which indeed results in the Landé formula.

LS- AND jj-COUPLING SCHEMES

In reality the Hamiltonian is not spherically symmetric and in fact the complete Hamiltonian cannot be written with just the central-field term, therefore we should write the full Hamiltonian as

$$H = H_{\mathrm{CF}} + H_{\mathrm{RE}}$$

where H_{RE} is the residual electrostatic interaction between the electrons. This interaction would be of the form

$$H_{\mathrm{RE}} = \sum_i \sum_{j>i} \left(\frac{e^2}{4\pi\varepsilon_0 r_{ij}} - S(r_i) \right)$$

The residual electrostatic interaction causes the i and j-th electrons' angular momentum to precess (ℓ_i and ℓ_j interact with each other), therefore these are no longer good quantum numbers[§]. However, the residual interaction results in an internal force/torque, which cannot change the total angular momentum $\boldsymbol{L} = \boldsymbol{\ell}_1 + \boldsymbol{\ell}_2$. H_{RE} does not affect the spin, hence $\boldsymbol{S} = \boldsymbol{s}_1 + \boldsymbol{s}_2$ is still a good quantum number. Thus $|S\ M_S\ \ L\ M_L\rangle$ are the good quantum states.

If $E_{\mathrm{SO}} \ll E_{\mathrm{RE}}$ we can treat the spin-orbit interaction as a perturbation, and use the states $|S\ M_S\ \ L\ M_L\rangle$ as the unperturbed states, however, the perturbation affects the z-components of S and M_L, which no longer are constant, which is why it is beneficial to use the coupled basis $|S\ L\ \ J\ M_J\rangle$– this is what is referred to as the **LS-coupling scheme**. In this scheme we speak of **terms**, which is just what we call the states where we have specified L and S. For example $(3p)(4p)$ in silicon. Here

$$\ell_1 = \ell_2 = 1 \to L \in \{0, 1, 2\}$$
$$s_1 = s_2 = \frac{1}{2} \to S \in \{0, 1\}$$

We denote each of these states with the **term**, ${}^{2S+1}L$, where we replace $L = 1$ with S, $L = 2$ with P, $L = 3$ with D etc. Thus we get six terms that correspond to the configuration

$$(3p)(4p) \quad \rightsquigarrow \quad {}^1S,\ {}^1P,\ {}^1D,\ \ {}^3S,\ {}^3P,\ {}^3D$$

$2S + 1$ is the multiplicity of the term; for example ${}^1S$ is a singlet state, whereas ${}^3P$ is a triplet state.

An important point to make here, which is relevant only for *equivalent electrons*, is that the Pauli exclusion principle requires the total wave function of electrons to be anti-symmetric under label exchange. The spatial wave functions that give an odd numbered angular momentum L are antisymmetric under label exchange, and hence must be multiplied with a symmetric spin state (for example the triplets that have $S = 1$). This holds generally and it can be shown that

$$L + S \equiv 0 \mod 2, \quad \text{for equivalent electrons}$$

For example one would expect that the ground state configuration of helium $(1s)^2$ has the following terms:

$$(1s)^2 \quad \rightsquigarrow \quad {}^1S,\ {}^3S$$

because $\ell_1 = \ell_2 = 0$ and $s_1 = s_1 = 1/2$. However the greyed out state has an odd numbered $L+S$ and hence it can quickly be seen that this state is not allowed by Pauli's exclusion principle.

Spin-orbit interaction in the LS-coupling scheme

The spin-orbit interaction for each electron is summed up for the total interaction:

$$H_{\mathrm{SO}} = \beta_1 \boldsymbol{s}_1 \cdot \boldsymbol{\ell}_1 + \beta_2 \boldsymbol{s}_2 \cdot \boldsymbol{\ell}_2$$

however, $\boldsymbol{s}_i$ and $\boldsymbol{\ell}_i$ precess about $\boldsymbol{S}$ and $\boldsymbol{L}$ respectively. $\boldsymbol{S}$ and $\boldsymbol{L}$ in turn precess about $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$, however in the LS-coupling scheme this precession is slow, which is why we can use L and S. Using the projection theorem[¶] we can write the spin-orbit interaction in terms of the total spin and angular momenta:

$$H_{\mathrm{SO}} = \beta_{\mathrm{SO}} \boldsymbol{L} \cdot \boldsymbol{S}$$

From here we can express the spin-orbit energy as a function of J, L and S:

$$E_{\mathrm{SO}} = \frac{\beta_{\mathrm{SO}}}{2} \left(J(J+1) - L(L+1) - S(S+1) \right)$$

where $J \in \{|L-S|, |L-S|+1, \ldots, L+S-1, L+S\}$.

The difference between two adjacent J values' spin orbit energies is given by the **interval rule**:

$$\Delta E_{\mathrm{SO}} = E_J - E_{J-1} = \beta_{\mathrm{SO}} J$$

The spin-orbit interaction lifts the J degeneracy, which means we should now additionally specify the J value,

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[§] Good quantum numbers correspond to classical conserved quantities.

[¶] The projection theorem states that, because $\boldsymbol{\ell}_i$ precesses quickly about $\boldsymbol{L}$, we need only consider the (expectation value of the) projection of $\boldsymbol{\ell}_i$ onto $\boldsymbol{L}$: $\langle \boldsymbol{\ell}_1 \cdot \boldsymbol{L} \rangle$

this turns a term into a level, $^{2S+1}L_J$. For example the ^3P term of ground state silicon splits into three level:

$$^3P \quad \rightsquigarrow \quad ^3P_0, ^3P_1, ^3P_2$$

However, we know that, due to the residual electrostatic interaction and due to spin-orbit coupling, that the degeneracy in L and J is lifted. The question now is: how do these levels' energies order themselves, with H_{RE} and H_{SO} taken into account? The answer is given by Hund's rules. However, this rule is only accurate for *equivalent electrons* in the *ground state*, and hence cannot be used for excited states. These are **Hund's rules:**

1. The lowest energy state has largest S consistent with Pauli's exclusion principle
2. If there are several of these the lowest energy term has the largest value of L.
3. For a given term in an atom with outermost subshell half-filled or less, the level with the lowest value of J will have the lowest energy level. Otherwise it is the level with the greatest value of J that has the lowest energy.

On the other side of the scale would be where $E_{\text{SO}} \gg E_{\text{RE}}$, in which case we need to use the spin-orbit interactions eigenstates as the unperturbed eigenstates. This is generally the case for heavy atoms. Here $\boldsymbol{s}_i$ and $\boldsymbol{\ell}_i$ couple to $\boldsymbol{j}_i$. Here it is common to denote the levels as $(j_1, j_2)_J$, for example an *sp* configuration splits into four levels:

$$(sp) \quad \rightsquigarrow \quad (1/2, 1/2)_0\,,\ (1/2, 1/2)_1\,,\ \ (1/2, 3/2)_1\,,\ (1/2, 3/2)_2$$

In conclusion:

LS-coupling scheme: $\quad E_{\text{SO}} \ll E_{\text{RE}}$

jj-coupling scheme: $\quad E_{\text{SO}} \gg E_{\text{RE}}$

Selection rules in the LS-coupling scheme:

Selection Rule	Exception
$\Delta J = 0, \pm 1$	$J = 0 \nleftrightarrow J' = 0$
$\Delta M_J = 0, \pm 1$	$M_J = 0 \nleftrightarrow M'_J = 0$ if $\Delta J = 0$
Parity changes	
$\Delta \ell = \pm 1$	One electron jump
$\Delta L = 0, \pm 1$	$L = 0 \nleftrightarrow L' = 0$
$\Delta S = 0$	

Tabel I: *Selection rules for electric dipole transitions.*

Zeeman effect in the LS-coupling scheme

In this scheme we can treat the Zeeman effect for monovalent atoms. The magnetic moment of an atom** is

$$\boldsymbol{\mu} = -\mu_B \boldsymbol{L} - g_s \mu_B \boldsymbol{S}$$

where the spin g-factor $g_s = 2$ according to Dirac, however QED increases that value by about one per mille. The *anomalous* Zeeman effect the effect where the second term $g_s \mu_B \boldsymbol{S}$ contributes. If we can treat the Zeeman effect as a perturbation to the spin-orbit coupling, which in the LS-coupling scheme is a perturbation to the residual electrostatic scheme, then we can use $|L\ S\ J\ M_J\rangle$ as our unperturbed states. The energy relations are:

$$E_{\text{Ze}} \ll E_{\text{SO}} \ll E_{\text{RE}}$$

The interaction energy between a magnetic moment and a magnetic field is $H = -\boldsymbol{\mu} \cdot \boldsymbol{B}$. Once again using the projection theorem and assuming that $\boldsymbol{B} \parallel \hat{\boldsymbol{z}}$ we get

$$H_{\text{Ze}} = \frac{\langle \boldsymbol{L} \cdot \boldsymbol{J} \rangle + g_s \langle \boldsymbol{S} \cdot \boldsymbol{J} \rangle}{J(J+1)} \mu_B B J_z \rightsquigarrow E_{\text{Ze}} = g_J \mu_B B J_z$$

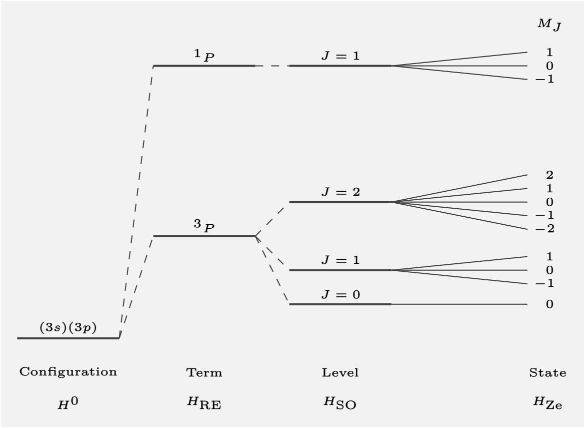
where††:

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

for singlets $g_J = 1$. Additionally singlets have $S = 0$, therefore these experience the normal Zeeman effect.

** neglecting the nuclear magnetic moment

†† assuming $g_s = 2$, exactly.



Figur 2: *The hierarchy of atomic structure for the* $(3s)(3p)$ *configuration of an alkaline earth metal atom.*

HYPERFINE STRUCTURE AND ISOTOPE SHIFT

The nucleus has a magnetic moment:

$$\boldsymbol{\mu}_I = g_I \mu_{\mathrm{N}} \boldsymbol{I}$$

where $\mu_N \approx \mu_B/1836$ is the nuclear magneton. The hyperfine structure is given by the interaction between the nuclear and electronic magnetic moments:

$$H_{\mathrm{HFS}} = -\boldsymbol{\mu}_I \cdot \boldsymbol{B} = A\boldsymbol{I} \cdot \boldsymbol{J}$$

where A is the hyperfine constant. Similar to what we did for the spin-orbit interaction we define the total angular momentum $\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{J}$. The hyperfine interaction causes $\boldsymbol{I}$ and $\boldsymbol{J}$ to precess about $\boldsymbol{F}$, which means that their magnitudes are constant, however, their z-components are not- just like how it was for the spin-orbit interaction. Thus we go from the uncoupled basis, $|I\ M_I\ \ J\ M_J\rangle$ to the coupled basis $|I\ J\ \ F\ M_F\rangle$, this is sometimes referred to as the IJ-coupling scheme. This means that

$$E_{\mathrm{HFS}} = \frac{A}{2}\left(F(F+1) - I(I+1) - J(J+1)\right)$$

Here we also have an interval rule, exactly like with the spin-orbit interaction:

$$\Delta E_{\mathrm{HFS}} = E_F - E_{F-1} = AF$$

Isotope shift

There are two contributions towards isotope splitting. The first we have already encountered in the Bohr model: the mass shift (because the nucleus does not have infinite mass). The second contribution is due to the nonzero volume of the nucleus.

Mass shift

As with the Bohr model we can perform the effective-mass substitution: $m_e \rightsquigarrow \frac{m_e M_N}{m_e + M_N}$, which gives us a true wavenumber

$$\tilde{\nu} = \tilde{\nu}_\infty \left(\frac{M_N}{m_e + M_N}\right)$$

where M_N is the nuclear mass. However $\tilde{\nu}_\infty$ is not measurable. But we *can* measure is the difference wavenumbers between two isotopes, say with nuclear masses $A'M_p$ and $A''M_p$ respectively. This gives us

$$\Delta\tilde{\nu}_{\mathrm{Mass}} = \tilde{\nu}_{\mathrm{A}'} - \tilde{\nu}_{\mathrm{A}''} \approx \frac{m_e}{M_p}\frac{A' - A''}{A'A''}\tilde{\nu}_\infty$$

For light atoms this correction is relevant. For example it is greater than the fine structure in Hydrogen.

We see from Equation that the heavier isotope always has larger wavenumbers.

Volume shift

The nucleus has a nonzero volume, which will cause a shift for s-electrons. The nuclear charge distribution, ρ_N, will interact with the electric potential due to the electron, ϕ_e:

$$E_{\mathrm{Vol}} = \int \mathrm{d}\boldsymbol{r} \rho_N \phi_e = \frac{Ze^2}{6\varepsilon_0}|\psi(0)|^2 \langle r_N^2 \rangle$$

The "liquid drop model"gives a formula for the radius of the nucleus:

$$r_N \approx 1.2 A^{1/3}\mathrm{fm}$$

where AM_p is the nuclear mass. This gives us an expression for the isotope shift:

$$\Delta\tilde{\nu}_{\mathrm{Vol}} = \frac{\Delta E_{\mathrm{Vol}}}{hc} \approx \frac{\langle r_N^2 \rangle}{a_0^2}\frac{\Delta A}{A}\frac{Z^2}{(n+\delta_\ell)^3}R_\infty$$

Using the mass shift and the volume shift, we can, using photonic excitations draw conclusions about the structure of nuclei.

Zeeman effect and hyperfine structure

We will treat the Zeeman effect for weak, intermediate and strong magnetic fields. The strength of the magnetic field is compared to the hyperfine structure constant, A/μ_B.

The magnetic moment of an atom is

$$\boldsymbol{\mu}_{\mathrm{atom}} = -g_J \mu_B \boldsymbol{J} + g_I \mu_N \boldsymbol{I} \approx -g_J \mu_B \boldsymbol{J}$$

We can neglect the nuclear magnetic moment and still be accurate within about one per mille, as $\mu_B \approx 1836\mu_N$. This gives us the interaction energy for the Zeeman effect:

$$H_{\mathrm{Ze}} = g_J \mu_B \boldsymbol{J} \cdot \boldsymbol{B}$$

Weak-field Zeeman effect, $\mu_B B < A$.

In this limit the hyperfine interaction is stronger than the Zeeman effect, therefore we should use the IJ-coupling scheme. This is because $\boldsymbol{I}$ and $\boldsymbol{J}$ precess rapidly about $\boldsymbol{F}$, whereas $\boldsymbol{F}$ precesses slowly about $\boldsymbol{B}$. Hence we should use the projection theorem once again:

$$H = g_J \mu_B \frac{\langle \boldsymbol{J} \cdot \boldsymbol{F} \rangle}{F(F+1)} \boldsymbol{F} \cdot \boldsymbol{B} = g_F \mu_B B F_z$$

where

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

This gives us

$$E = g_F \mu_B B M_F$$

Intermediate-field Zeeman effect, $\mu_B B \approx A$

In this case one treats $H_{\mathrm{Ze}} + H_{\mathrm{HFS}}$ as a perturbation. In this limit one can still use the IJ-coupling scheme, as the unperturbed basis. For example the ground state of hydrogen would have the following perturbation matrix:

$$H' = \begin{pmatrix} \frac{A}{4} & -\mu_B B \\ -\mu_B B & -\frac{3A}{4} \end{pmatrix}$$

which gives a splitting of

$$E' = -\frac{A}{4} \pm \sqrt{\frac{A^2}{4} + \mu_B^2 B^2}$$

which is a hyperbola in B. This is the splitting for the two $M_F = 0$ states. The $M_F = \pm 1$ states have a linear splitting.

Strong-field Zeeman effect, $\mu_B B > A$

In this regime the IJ-coupling scheme is no longer applicable, because F no longer is a good quantum number ($\boldsymbol{I}$ and $\boldsymbol{J}$ precess quickly and independently about $\boldsymbol{B}$). Instead it can be shown that

$$E = g_J \mu_B B M_J + A M_I M_J$$

The quick precession of $\boldsymbol{I}$ and $\boldsymbol{J}$ about $\boldsymbol{B}$ cause the x- and y-components to average out.

Measurement of the Zeeman effect

Optical techniques are, generally, not suitable for the measurement of the Zeeman effect, because the Zeeman effect is of the same order of magnitude as the Doppler broadening. Instead one can use the atomic-beam technique, which in principle is two Stern-Gerlach apparatus in succession. The first apparatus gathers the for example $M_J = \pm 1/2$ states. Then the a radio frequency apparatus is used to induce transitions. The second apparatus is the either

1. used to gather the states again (by having a magnetic field gradient that points in the same direction as the first apparatus' gradient). This would be a "flop-in"arrangement.
2. used to deflect the states (by having a magnetic field gradient that points in the opposite direction to the first apparatus' gradient). This would be a "flop-out"arrangement.

Generally it is true that the flop-in arrangement measures no flux, unless the radio-frequency waves have the correct frequency (corresponding to the hyperfine energy splitting), whereas the flop-out arrangement measures flux only when the radio-frequency waves have the correct frequency.

CAESIUM ATOMIC CLOCKS

The hyperfine splitting of Caesium splits the level into $F = 3$ and $F = 4$ states. Atomic clocks use the transition that has the smallest sensitivity to magnetic fields, which is the transition

$$|F = 4, M_F = 0\rangle \rightsquigarrow |F = 3, M_F = 0\rangle$$

For weak magnetic fields, usually in the μT region (atomic clocks usually use magnetic fields with about this strength) the $M_F = 0$ states feel no Zeeman splitting, however $M_F \neq 0$ states experience a linear Zeeman effect of the order $\Delta f_B = 6.998 M_F \cdot B \frac{\mathrm{MHz}}{\mu\mathrm{T}}$.

Atomic clocks have two regions (A and B) where the magnetic field is non-uniform (say it varies along the z-axis). This magnetic field gradient gives rise to a force on the atoms:

$$F_{\mathrm{atom}} = -\frac{\partial W}{\partial z} = -\frac{\partial W}{\partial B} \frac{\partial B}{\partial z} = -\mu_{\mathrm{eff}} \frac{\partial B}{\partial z}$$

note that μ_{eff} is as function of M_F. At non-zero magnetic fields the states $|F=4, M_F=0\rangle$ and $|F=3, M_F=0\rangle$ will experience an opposite force (the $|F=3, M_F=0\rangle$ state is a high-field seeker, as its energy is reduced for increasing magnetic fields). The polariser field (A-field) is used to pick out either $|F=4, M_F=0\rangle$ or $|F=3, M_F=0\rangle$.

The atoms are then sent through a C-region with a homogeneous magnetic field, where the atoms are allowed to evolve naturally. We will get to the C-region momentarily.

Then the atoms fly through the B-field, also known as the analyser, where we do the same thing as in the A-region, but with an opposite magnetic field. This means that if the evolution truly is free in the C-region, then we will not see any atoms hit the detector.

If we now use a Ramsey cavity within the C-region, which will drive the transition $|4,0\rangle \leftrightsquigarrow |3,0\rangle$, using two $\pi/2$-pulses. Beginning in the north pole of the Bloch Sphere the first $\pi/2$-pulse takes us to the equatorial-plane, where we evolve naturally for some time.

If we are in the rotating frame, then this free evolution has phase $e^{i\delta t}$. The second $\pi/2$-pulse will take us to the south pole if and only if $e^{i\delta T} = 1$ which is true if $T = \frac{2\pi}{\delta}$ or $\delta = 0$. The former is extremely unlikely, therefore we can use this method to determine whether the radio synthesiser has zero detuning– whether or not $\omega = \omega_0$.

Scanning through frequencies in the frequency synthesiser will give us a Ramsey resonance structure, which allows us to very precisely pin-point the value of ω_0.

It is very important that the two $\pi/2$-pulses are temporally coherent.

DIATOMIC MOLECULES

Energy contributions

Diatomic molecules have more degrees of freedom that atoms, however, the additional degrees of freedom do not affect the gross structure, but rather fine tune the energy scales. That is to say the gross structure is still due to electronic energies. The additional degrees of freedom are two rotational degrees of freedom and two vibrational degree of freedom $(T+V)$. Here are the energy scales:

1. Electronic energies: $E_e \sim \frac{\hbar^2}{ma^2} \sim$ eV
2. Vibrational energies: $E_v \sim \sqrt{\frac{m_e}{M}} E_e \sim$ 0.1eV
3. Rotational energies: $E_r \sim \frac{m_e}{M} E_e \sim$ meV

where M is the molecular mass.

The full problem that we need to solve is:

$$[T_N + T_e + V]\Psi = E\Psi$$

where we use reduced mass of the nuclei $\mu = \frac{M_A M_B}{M_A + M_B}$ and define $\boldsymbol{R} = \boldsymbol{R}_A - \boldsymbol{R}_B$ to be the distance between nuclei:

$$T_N = -\frac{\hbar^2}{2\mu}\nabla^2_{\boldsymbol{R}}$$

$$T_e = -\frac{\hbar^2}{2m_e}\sum_i \nabla^2_{r_i}$$

$$V = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z_A Z_B}{R} + \sum_i \left(-\frac{Z_A}{\|\boldsymbol{r}_i - \boldsymbol{R}_A\|} - \frac{Z_B}{\|\boldsymbol{r}_i - \boldsymbol{R}_B\|} + \sum_{j\neq i}\frac{1}{\|\boldsymbol{r}_i - \boldsymbol{r}_j\|}\right)\right)$$

because $\mu \gg m_e$ we can use the **Born-Oppenheimer approximation**:

1. "Freeze"the nuclei; solve the electronic wave-functions, ϕ_q:

   $$\left(T_e + V(\boldsymbol{R}, \boldsymbol{r}_i)\right)\phi_q(\boldsymbol{R}, \boldsymbol{r}_i) = E_q(\boldsymbol{R})\phi_q(\boldsymbol{R}, \boldsymbol{r}_i)$$

2. We treat $\boldsymbol{R}$ as a variation-parameter and minimize $E_q(\boldsymbol{R})$. $\phi_q(\boldsymbol{R}, \boldsymbol{r}_i)$ form a complete set for each internuclear distance. Solve the Schrödinger equation for the nuclear part of the wave function with $eE_q(\boldsymbol{R})$ as the potential.

The potential energy surfaces $E_q(R)$ have minima, which is the most convenient internuclear distance. We Taylor expand the potential energy surfaces, assuming $R \approx R_0$[‡‡]:

$$E_q(R) \approx E_q(R_0) + \frac{1}{2}k(R - R_0)^2$$

[‡‡] This should be an accurate approximation for normal temperatures.

Treating this quantum mechanically will give us harmonic oscillator energy solutions:

$$E_v = \hbar\omega_0\left(v+\frac{1}{2}\right), \quad \omega_0 = \sqrt{\frac{k}{\mu}}$$

The rotational part is of the form $\frac{\hbar^2}{2\mu}\frac{J(J+1)}{R_0}$ where we have assumed that $R \approx R_0$, thus the total energy is

$$E_{q,v,J} = E_q(R_0) + \hbar\omega_0\left(v+\frac{1}{2}\right) + \frac{\hbar^2}{2\mu R_0}J(J+1)$$

for low energies. That higher excitations the nuclear potential can no longer be treated as a harmonic oscillator.

This leads to the **Franck-Condon principle**, which is a weak "selection rule". The electronic transitions occur on very fast time scales compared to the nuclear motion, thus the nuclear coordinates barely change during the transition. Thus we *favour* transitions for which $\Delta R = 0$. Or rather we favour transitions whose radial overlap is largest:

$$f_{v,v'}^{q,q'} = \int \left(\psi_{v'}^{q'}\right)^* \psi_v^q \mathrm{d}R$$

is known as the Franck-Condon factor, and the transition strength is proportional to this factor.

Diatomic electric dipole transitions

The harmonic oscillator approximation gives us selection rules:

$$\Delta v = \pm 1$$

and the quantised angular momentum gives us an additional selection rule:

$$\Delta J = \pm 1$$

This defines two sets of transition, during *absorption*:

1. R transitions, for which $\Delta J = 1$.
2. P transitions, for which $\Delta J = -1$.

these sets make up the R-branch and P-branch respectively.

DOPPLER FREE LASER SPECTROSCOPY

Doppler broadening, which will be discussed shortly causes a line-width, which often is not negligible, for fine structure, but especially for hyperfine structure. Therefore numerous methods have been developed to avoid the effect of Doppler broadening.

Doppler broadening

The velocity distribution of atoms in an ideal gas is given by the Maxwell distribution. This gives us the fraction of atoms in the range from v to $v + \mathrm{d}v$:

$$f(v)\mathrm{d}v = \frac{1}{u\sqrt{\pi}}\exp\left(-\frac{v^2}{u^2}\right)\mathrm{d}v, \quad u \equiv \sqrt{\frac{2k_BT}{M}}$$

where u is the most probable speed for atoms at temperature T. The Doppler effect says that a reference frame moving with velocity v with respect to a stationary reference frame, which sends out light with frequency ω, will measure a shifted frequency, ω', equal to

$$\omega' = \omega - \boldsymbol{k}\cdot\boldsymbol{v}$$

where $\boldsymbol{k}$ is the wave vector of the transmitted light. This gives us a Gaussian line shape function:

$$g_{\mathrm{D}}(\omega) = \frac{c}{u\omega_0\sqrt{\pi}}\exp\left(-\frac{c^2}{u^2}\left(\frac{\omega-\omega_0}{\omega_0}\right)^2\right)$$

where ω_0 is the resonant frequency (atomic transition frequency). This Gaussian has a FWHM of

$$\Delta\omega_{\mathrm{D}} = \left(2\sqrt{\ln 2}\frac{u}{c}\right)\omega_0 = 2\sqrt{\ln 2}\frac{u}{\lambda}$$

The crossed-beam method

A simple way to reduce Doppler broadening, is by minimising the component of the velocity of the gas that is parallel to the laser beam used for measurements. This can be done by sending the laser beam at a right angle to an atomic beam. The atomic beam is not collinear, however, if we send the atomic beam through a small slit at a large distance from the oven we can reduce the collimation angle significantly. For small collimation angles $\sin\alpha \approx \alpha$, hence

$$\Delta f \sim \alpha\Delta f_{\mathrm{D}}$$

where Δf_{D} is the normal Doppler broadening of the gas at the same temperature. Suppose we would like the Doppler broadening of Sodium vapour at 1000K to be comparable to the natural line width, in that case

$$\alpha\Delta f_{\mathrm{D}} \approx \Delta f_N \to \alpha \approx 4\cdot 10^{-3}\mathrm{rad}$$

where we have used that $v_{\mathrm{beam}} \approx 1000\mathrm{m\ s}^{-1}$. This corresponds to a right angle where the ratio between opposite and adjacent is about $^1/_{250}$, which is doable in a laboratory environment.

Saturated Absorption Spectroscopy

Suppose we have a gas of atoms, with some Doppler-broadening ω_D and natural transition frequency ω_0. We now begin by sending an intense $I \approx I_{\text{sat}}$ laser beam with frequency ω, through the atoms (call this the *pump beam*). This will promote about half the population in the velocity class $v = (\omega - \omega_0)/k$ to the excited level. This promotion will have a homogeneous power-broadening line width.

Now we send another laser beam through the atoms with low intensity $I \ll I_{\text{sat}}$ in the opposite direction (call this the *probe beam*). This will promote a few atoms in the velocity class $v = -(\omega - \omega_0)/k$ assuming that $\omega \neq \omega_0$ – some of the laser beam will be absorbed. However, assuming now that $\omega \approx \omega_0$ there will be about as much excitation as there is de-excitation, due to the pump beam. Thus there will be general shape of increasing absorption as $\omega \to \omega_0$, however, when $\omega \approx \omega_0$ there will be a sudden drop in absorption.

Cross-over resonances in saturation spectroscopy

The discussion above is only accurate for two-level systems. In reality there are more than one transition that can occur. Naturally each of which will occur at different frequencies. Suppose we have a three-level system with transition frequencies ω_1 and ω_2. Our spectroscopy will naturally have absorption drops at these two frequencies, however, there will be an additional drop, namely where

$$\frac{\omega_1 + \omega_2}{2} = \omega$$

This is exactly the point when the ω_1 excitations from the pump beam affect the ω_2 excitations of the probe beam and vice versa. In general there will be additional drops at

$$\frac{\omega_i + \omega_j}{2} = \omega, \quad i \neq j$$

There are $\frac{N(N-1)}{2}$ additional drops, if there are N true transitions. However note that, depending on what the nature of the transition is, some of these additional drops can lie within each other. For hyperfine structure the interval rule holds, therefore for small enough N you will be able to see all drops, however some may be in the form of double-drops.

Two-photon spectroscopy

By sending two counter-propagating photons with $\omega = {}^{\omega_0}/_2$ through the atomic gas the Doppler broadening will be cancelled completely:

$$\omega\left(1 + \frac{v}{c}\right) + \omega\left(1 - \frac{v}{c}\right) = 2\omega = \omega_0$$

The benefit of this vs saturation spectroscopy is that all atoms can absorb the two photons, not just those at rest in the laboratory frame. Therefore we can expect stronger signal and hence better measurements.

LASER COOLING AND TRAPPING

Scattering Force

Photons bear momentum, which is transferred to atoms during interactions. The force is equal to how much momentum is transferred per unit time, which equals rate at which the light delivers energy divided by the speed of light:

$$F_{\text{rad}} = \frac{IA}{c} \sim 10^{-9}\text{N}, \quad \text{for} \quad IA \sim 1\text{W}$$

The area, A can be taken as $\sigma(\omega)$ per atom. At its peak ($\omega \approx \omega_0$) the radiative cross-section is much greater than the size of atoms, which implies that F_{rad} can also spike around resonance. We needn't think about the effect of the atom having to give spontaneously emitted photons a part of their momentum, because this effect will average out.

The magnitude of this *scattering* force equals the rate at which absorbed photons impart momentum to the atom:

$$F_{\text{scatt}} = \hbar k \frac{\Gamma}{2} \frac{I/I_{\text{sat}}}{1 + I/I_{\text{sat}} + 4\delta^2/\Gamma^2}$$

which gives a maximum acceleration of

$$a_{\max} = \frac{\hbar k \Gamma}{2M} = \frac{v_r \Gamma}{2}$$

where we have defined the recoil velocity $v_r = \frac{\hbar k}{M}$. $a_{\max} \sim 10^5 \text{m s}^{-2}$ for sodium, which is much greater than the gravitational acceleration. We can define the stopping distance (ignoring any Doppler effects):

$$L_0 = \frac{v_0^2}{a_{\max}}$$

for $v_0 = 1000\text{m s}^{-1}$ the stopping distance is $\sim$ 1m.

Slowing an atomic beam

In practice one cannot neglect the Doppler shift, which changes as a function of z (assuming that the atoms propagate in the z-direction). One method uses the Zeeman effect to vary the transition-frequency as a function of z, by using a varying magnetic field. Using the assumption that the deceleration is constant we get that

$$v(z) = v_0 \left(1 - \frac{z}{L_0}\right)^{1/2}$$

We would like for the Doppler-corrected frequency $\omega - kv(z)$ to match with the transition frequency ω_0, this we can do by using the Zeeman effect, which perturbs the transition frequency $\omega_0 + \frac{\mu_B B}{\hbar}$, hence our condition is

$$\omega_0 + \frac{\mu_B B(z)}{\hbar} = \omega + kv(z) \rightsquigarrow B(z) = B_0 \left(1 - \frac{z}{L_0}\right)^{1/2} + B_{\text{bias}}$$

where

$$B_0 = \frac{\hbar k v_0}{\mu_B}$$

Chirp Cooling

Instead of adjusting the transition frequency as a function of z one can adjust the laser frequency as a function of time – we change the laser frequency such that the laser signal is always Doppler-corrected.

Optical Molasses Technique

Suppose we have an atom moving at some velocity v. If we now send light with frequency ω from both the left and the right then the atom will experience a force

$$F_{\text{molasses}} = F_{\text{scatt}}(\omega - \omega_0 - kv) - F_{\text{scatt}}(\omega - \omega_0 + kv)$$

This is, by definition an odd function of v. A first order Taylor approximation gives us

$$F_{\text{molasses}} \approx -2kv \frac{\partial F_{\text{scatt}}}{\partial \omega} = -\alpha v$$

where[§§]

$$\alpha = 2kv \frac{\partial F_{\text{scatt}}}{\partial \omega} = 4\hbar k^2 \frac{I}{I_{\text{sat}}} \frac{-2\delta/\Gamma}{(1 + (2\delta/\Gamma)^2)^2}$$

which is positive only for $\delta < 0$ which is equivalent to the condition

$$\omega < \omega_0$$

thus this technique only works for light that is red-shifted with respect to the atomic transition frequency. We want $\alpha > 0$ so that the molasses force points in the opposite direction than v. Note that we have once again neglected I/I_{sat} in the denominator, because we assume that $I/I_{\text{sat}} \ll 1$.

This gives us an exponential decay of energy:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = -\frac{2\beta}{M} E = -\frac{E}{\tau_{\text{damp}}}$$

However this does not continue forever, the Doppler-cooling techniques do have limits, which will be discussed shortly.

Doppler cooling limit

The momentum kicks during spontaneous emission as well as the randomness of the absorption are source of uncertainty in both the position and the momentum of the atoms. We find that Doppler cooling has temperature limit, T_D:

$$T_D = \frac{\hbar \Gamma}{2 k_B}$$

the *Doppler cooling limit.* For sodium this temperature is $T_D = 240\mu\text{K}$. Though in reality these techniques work better than expected.

Magneto-optical trap

The optical molasses technique could hold atoms in place in outer space, however down on earth we need to overcome gravity. This is done using the magneto-optical trap, which combines the optical molasses technique (optical) with an anti-Helmholtz magnetic field. However, here the laser beams have circular polarisation, and it has a frequency that is slightly less than the atomic resonance frequency $J = 0 \rightsquigarrow J = 1$ in fact slightly less than the lowest of these transitions (there are three).

In the middle of the coils the magnetic fields cancel and there is $B = 0$. In the vicinity of this point however, there is a uniform field gradient, which perturbs the atomic energies, causing the three $J = 1$ states' energies to vary linearly with their displacement from the middle. The Zeeman effect causes an energy shift $\omega_0 \pm \beta z$. The Doppler broadening makes the atom see an effective frequency of $\omega \pm kv$.

This σ^+-light comes from the bottom and σ^- comes from the top. Thus for $z < 0$ the $|0\,0\rangle \rightsquigarrow |1\,1\rangle$ will occur, whereas for $z > 0$ the $|0\,0\rangle \rightsquigarrow |1\,-1\rangle$ transition will occur. Due to the uniform magnetic-field-gradient the Zeeman shift will vary with z, hence the MOT force

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[§§] Not the same α as used previously... sorry is:

$$F_{\mathrm{MOT}} = F_{\mathrm{scatt}}^{\sigma^+}(\underbrace{\omega - kv}_{\text{Doppler}} - \underbrace{(\omega + \beta z)}_{\text{Zeeman}}) - F_{\mathrm{scatt}}^{\sigma^+}(\underbrace{\omega + kv}_{\text{Doppler}} - \underbrace{(\omega - \beta z)}_{\text{Zeeman}})$$

$$\approx -2kv\frac{\partial F}{\partial \omega} + 2\beta z\frac{\partial F}{\partial \omega_0}$$

Hence we have a damped harmonic oscillator, which will hold atoms in place, also in the presence of gravity (gravity will add a constant to the differential equation, just shift the equilibrium position slightly)

APPENDIX

Summary of atomic units

Bohr radius:

$$a_0 = \frac{\hbar^2}{m_e}\frac{4\pi\varepsilon_0}{e^2} = 5.29 \cdot 10^{-11}\mathrm{m}$$

Hydrogen ground-state energy:

$$hcR_\infty = \frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = 13.6\mathrm{eV}$$

Electron-volt to Joule conversion

$$1\mathrm{eV} = 1.602 \cdot 10^{-19}\mathrm{J}$$

Zeeman frequency shift, due to magnetic field:

$$\frac{\Omega_L}{2\pi B} = \frac{e}{4\pi m_e} = 14\mathrm{GHz\ T}^{-1}$$

Bohr magneton:

$$\mu_B = \frac{e\hbar}{2m_e} = 9.27 \cdot 10^{-24}\mathrm{J\ T}^{-1}$$