285A Atomic, Molecular, Optical Physics A

Taylor Patti
Susanne Yelin

Sabina Dragoi
Haoyang Gao
Wenjie Gong
Derick Gonzalez-Acevedo
Timothy Guo
Caleb Heuvel-Horwitz
Abigail McClain Gomez
Abdullah Nasir
Avery Parr
Jonah Peter
Perrin Segura

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Introduction

This is an interactive course script - no guarantees!

In addition to the traditional topics of an AMO course — basic atomic model, interaction with light, all kinds of corrections — this course is trying to lay the foundation to read cutting edge papers (and take really advanced courses). There has been a lot of developments in the general area of AMO in the last few decades, including (but never limited to)

- lasers, e.g.
    - Ti:sapphire (high power, excellent coherence
    - diode + extended cavity (cheap, good)
    - fiber lasers (all of the above)
- cavity QEC
- ultracold temperatures,
  including techniques for cooling, trapping, manipulation of atoms, and including short pulse/ultrafast/high harmonics physics
- fundamental physics (e.g., EDM) and constants (e.g., new SI)
- metrology (clocks, GPS, ...)
- material engineering
- quantum information science

(What has not been found is new atoms. Why? They follow a very clear pattern that has been recognized and figured out long time ago.)

Chapter 1

Units and Fundamental Constants

Depending on the assumptions that we make, we will use two basic sets of quantities in this chapter:

- Assumption 1 - Non-Relativistic Atom: The atomic model of an electron orbiting an infinitely heavy nucleus. The interaction of the two in quantum mechanical and governed by the Coulomb force. The basic quantities that go into this model are the electron mass m_e, the electron charge e, and the Planck constant $\hbar$.
- Assumption 2 - Relativistic Atom: In addition to the quantities above, the fundamental constant of the speed of light, c, must be considered as well.

Please note that these assumptions can go either way: If we assume that these constants exist, then the basic properties of hydrogen must be derivable from these constants. Conversely, if we see the atom as the basic truth — the particular constants have to follow. Either way, the two are intricately related. In this chapter, we argue along the first line of reasoning using *dimensional analysis*.

1.1 Non-Relativistic Atomic Model

Atomic units should only depend on the three basic quantities that arise in Coulomb's law and quantum mechanics:

- m_e: the electron mass (if we assume $m_e \ll m_p$)
- e: the elementary charge (in SI units this has to be $k = \frac{e}{4\pi\epsilon_0}$ instead)
- $\hbar$: Planck's constant

An aside: In SI units, Coulomb's law has an extra multiplying factor that connects the dimensions. This can be scaled out:

$$F = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r^2} = \frac{q_2}{\sqrt{4\pi\epsilon_0}}\frac{q_1}{\sqrt{4\pi\epsilon_0}}\frac{1}{r^2} \equiv \frac{\tilde{q}_1\tilde{q}_2}{r^2}$$

(Here, F is the (Coulomb) force, ϵ_0 the vacuum permittivity, q_i the charge of particle i, and r their distance. We denote the dimensions as

$[M]$ – dimension of mass
$[L]$ – dimension of length
$[T]$ – dimension of time
$[Q]$ – dimension of charge or
$[\tilde{Q}]$ – dimension of charge scaled for SI units.

In order for the dimensions to be the same on both sides of the equation above, one needs

$$\frac{[M][L]}{[T]^2} = \frac{[\tilde{Q}]^2}{[L]^2}$$

and thus

$$[\tilde{Q}] = \frac{\sqrt{[M][L]^3}}{[T]}, \tag{1.1}$$

with

For the rest of this section, we will assume that the quantities we are dealing with are m_e, $\tilde{e}$, and $\hbar$.

Which quantities can one find on the basis of only these constants?

For this, we divide our search by dimensions:

1. Is there a dimensionless quantity/scale?

If this is the case, we have to find a quantity where some combination of these constants is dimensionless, i.e.,

$$m_e^k\,\tilde{e}^\ell\,\hbar^m \;\to\; [M]^k \left(\frac{[M]^{\frac{1}{2}}[L]^{\frac{3}{2}}}{[T]}\right)^\ell \left(\frac{[M][L]^2}{[T]}\right)^m \;=\; [M]^{k+\frac{\ell}{2}+m]}\,[L]^{\frac{3\ell}{2}+2m}\,[T]^{-\ell-m}.$$

In order for this expression to be dimensionless, we need all exponents to be 0, i.e.,

$$\left.\begin{array}{l} k+\frac{\ell}{2}+m \;=\; 0 \\ \frac{3\ell}{2}+2m \;=\; 0 \\ \ell+m \;=\; 0 \end{array}\right\} \quad \ell \;=\; 0, \quad m \;=\; 0, \quad k \;=\; 0.$$

Thus, there is no non-zero expression that would give us a dimensionless expression (which would amount to a scaling factor).

2. Is there a basic length scale? Repeating the calculation for

$$[M]^{k+\frac{\ell}{2}+m]}\,[L]^{\frac{3\ell}{2}+2m}\,[T]^{-\ell-m} \;=\; [L]^p$$

With this, we have

$$\left.\begin{array}{l} k+\frac{\ell}{2}+m \;=\; 0 \\ \ell+m \;=\; 0 \end{array}\right\} \quad \ell \;=\; 2k \;=\; -m$$

and

$$p \;=\; \frac{3\ell}{2}+2m.$$

Thus a basic length scale (let's call it a for now) would have to scale according to

$$a^{\frac{3\ell}{2}+2m} \;=\; a^{-k} \;=\; m_e^k\,\tilde{e}^{2k}\,\hbar^{-2k}.$$

With that we define the "Bohr radius" a_B as

$$a_B \;=\; \frac{\hbar^2}{m_e\,\tilde{e}^2} \;=\; \frac{4\pi\epsilon_0\hbar^2}{m_e\,e^2}. \tag{1.2}$$

3. Is there a basic time scale (τ)? Same procedure:

$$\left.\begin{array}{l} k+\frac{\ell}{2}+m \;=\; 0 \\ \frac{3\ell}{2}+2m \;=\; 0 \end{array}\right\} \quad \ell \;=\; 4k, \quad m \;==-3k.$$

Thus,

$$\tau^{-\ell-m} = \tau^{-k} = m^k\, \tilde{e}^{4k}\, \hbar^{-3k}$$

and so

$$\tau_B = \frac{\hbar^3}{m\, \tilde{e}^4} = \frac{(4\pi\epsilon_0)^2\hbar^3}{m\, e^4}$$

4. The basic mass scale is obviously the electron mass m.

5. The basic velocity scale can now be put together from the other quantities:

$$\frac{a_B}{\tau_B} = \frac{e^2}{4\pi\epsilon_0\hbar}$$

6. The same idea goes for energy:

$$\frac{[M][L]^2}{[T]^2} \rightarrow \frac{m\, a_B^2}{\tau_B^2} = \frac{m\, e^4}{(4\pi\epsilon_0)^2\hbar^2} \equiv E_0$$

This gives basically the "Rydberg unit of energy." $(Ry = E_0/2)$

These are all the (reasonable) quantities that one can get in this case. Recalling the basic hydrogen model, these are indeed the quantities that are needed!

1.2 Relativistic Atom

There is an fundamental constant describing a velocity: the vacuum speed of light, c. Since, in the previous section, a velocity has already been found, the obvious way to introduce c is to just compare these two quantities and with that define a *dimensionless* quantity α. (Please note that this is indeed the only dimensionless quantity that there is in atomic physics!)

$$\alpha \equiv \frac{a_B/\tau_b}{c} = \frac{e^2}{4\pi\epsilon_0\hbar c}$$

This quantity is known as the "fine structure constant." All quantities that depend on α are thus "relativistic effects."

Just as a side remark: The basic energy E_0, even though it is not relativistic, can be written in a simpler way as

$$E_0 = \alpha^2\, m\, c^2$$

1.3 Summary of important scales

- length:

$\alpha^0 a_B$	$= a_B$	Bohr radius
$\alpha^1 a_B$	$= \lambda_c$	reduced Compton wavelength
$\alpha^2 a_B$	$\approx r_e$	classical electron radius

- energy:

$\alpha^2 m\, c^2$	$\to E_0$	binding energy
$\alpha^4 m\, c^2$		fine structure splitting
$\frac{m_{\text{electron}}}{m_{\text{nucleus}}}\, \alpha^4 m\, c^2$		hyperfine splitting

With the use of these basic units one can then define the so-called **atomic units,** where one just gauges to

$$\hbar \;=\; e \;=\; m \;=\; 4\pi\epsilon_0 \;=\; 1. \tag{1.3}$$

An example of this simplification can be seen in the Schrödinger Equation for hydrogen:

$$\frac{\hbar^2}{2m}\nabla^2\psi - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}\,\psi \;=\; E\,\psi;$$

all the constants, $\hbar, m, 4\pi\epsilon_0, a_B$ and E_0 are all unity; thus one can define $x \equiv \frac{r}{a_B}$ and $\varepsilon \equiv \frac{E}{E_0}$ and get

$$\frac{1}{2}\nabla^2\psi - \frac{1}{x}\,\psi \;=\; \varepsilon\,\psi.$$

1.4 New SI units

Since 2019, the SI units are, in fact, entirely based on fundamental constants. Thus, the fundamental constants are set (to a very similar value to which they were before measured, such as not to change our daily life too much), but all as rational numbers that are now **exact**. The seven constant are

for Kilogram	$h = 6.62607015 \cdot 10^{-34}$ J·s	Planck's constant
for Ampere:	$e = 1.602176634 \cdot 10^{-19}$ C	electron charge
for Meter:	$c = 299792458$ m/s	speed of light in vacuum

for Second:	Frequency (^{133}Cs ground state hyperfine transition): $\nu_{\mathrm{Cs}} = 9162631770$ Hz	
for Kelvin:	$k_B = 1.380649 \cdot 10^{-23}$ J/K	Boltzmann's constant
for Mole:	$N_A = 6.02214076 \cdot 10^{23}$ mol^{-1}	Avogadro's number
for Candela	Luminous flux (luminar efficacy of 540 THz light): $K_{\mathrm{cd}} = 683$ lm/W	

Thus, the values of the quantities introduced above are (careful, these are **approximate**):

vacuum permittivity	$\epsilon_0 = 8.854187817 \cdot 10^{-12}$ F/m
Bohr radius	$a_B = 0.529177$ Å
Rydberg unit of energy	$E_0 = 2.17987236110 \cdot 10^{-18}$ J
Fine structure constant	$\alpha = 1/137.06$
basic time scale	$\tau_B = 2.4 \cdot 10^{-17}$ s

Chapter 2

Resonance: Physics of two-state systems

2.1 Introduction: A little history of resonances:

1. Measure lines with continuous spectra (example: Balmer series) :

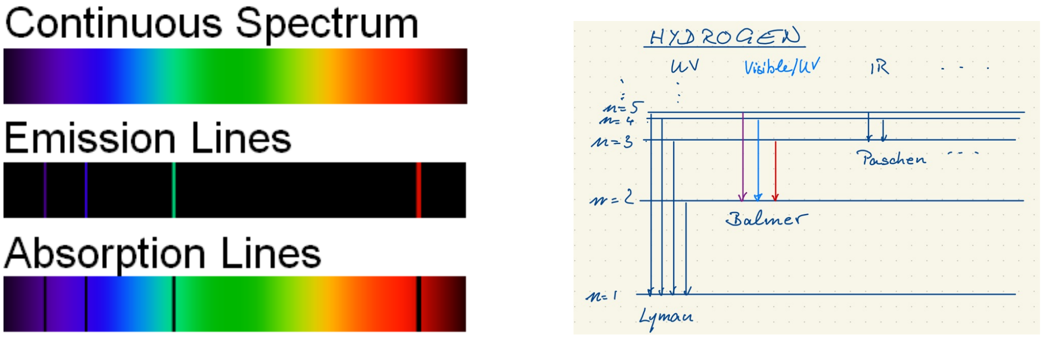


Figure 2.1: Balmer series

2. Magnetic (NMR) and electric (ESR) resonance: much narrower line widths

3. Advent of laser

The Nobel Prizes in AMO/resonances in the last three decades:

1981 Bloembergen, Shawlow: laser spectroscopy

1989 Ramsey, Dehmelt, Paul: hydrogen maser, ion traps

1997 Chu, Cohen-Tannoudji, Phillips: cooling and trapping atoms

2001 Cornell, Wieman, Ketterle: Bose-Einstein condensation

2005 Glauber, Hall, Hänsch: quantum theory of light, (frequency comb) spectroscopy

2009 Kao (et al): optical communication in fibers

2012 Haroche, Wineland: measureing and manipulation of quantum systems

2018 Ashkin, Mourou, Strickland: optical tweezers, high intensity fields

Some examples of accuracy of spectroscopy

1. Lamb shift (predicted by Pasternack 1937): $E(^2S_{1/2} > E(^2P_{1/2})$

   Measured by W. Lamb (1947): ESR with $\sim 1\%$ accuracy

2. Magnetic moment of electron: $\mu_e \overset{?}{=} \mu_B = \frac{e\hbar}{2m}$

   measured by P. Kusch 1948: $\frac{\mu_e}{\mu_B} - 1 \approx 1.6 \cdot 10^{-3}$ – the difference is due to multiplicity of lines etc. (Please note that this is basically the same as the famous"$g-2$"-measurements.)

3. Now EDM of electron in molecules (ACME): is measured to an accuracy of $\sim 10^{-29}$ e·cm.

2.2 Classical resonance: Language

The most common example of oscillator is an LRC circuit (+voltage change), in which the total voltage over the circuit components is:

$$\Delta V_{total} = -L\frac{dI}{dt} - IR - \frac{q}{C}$$

Using Kirchhoff's loop law, this leads to the following equation:

$$\ddot{q} + \gamma\dot{q} + \omega_0^2 q = f(t),$$

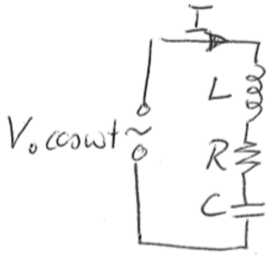


Figure 2.2: Typical LRC circuit

where we substituted $\gamma = \frac{R}{L}$, $\omega_0^2 = \frac{1}{LC}$, and the applied voltage oscillation, $f(t) = \frac{V_0}{L}\cos(\omega t)$.

Solving for complex solutions, we find two main components, one resulting from the homogeneous relation right from below, and one resulting from the non-homogeneous relation. We first deal with the homogeneous part, which we know contributes to the dampening of the amplitude with time:

$$\ddot{z} + \gamma\dot{z} + \omega_0^2 z = 0$$

We arrive at $z = z_0\, e^{\lambda t}$, leading to solutions $\lambda_\pm = \frac{1}{2}\Big(-\gamma \pm \sqrt{\gamma^2 - 4\omega_0^2}\Big)$. This breaks into 3 cases;

- If the quantity under the square root is negative, i.e. $\gamma/2 < \omega_0$, the movement is called weakly damped. In this case, there are oscillations.
- If the quantity under the square root is exactly 0, i.e. $\gamma/2 = \omega_0$, the movement is called critically damped.
- If the quantity under the square root is positive, i.e. $\gamma/2 > \omega_0$, the movement is called strongly damped. The strongly damped case does not display oscillations.

For the **atomic case**, i.e. $\gamma \ll \omega_0 \approx \frac{E_0}{\hbar}, \frac{1}{\tau_B}$, (see Fig. 2.3), we will have $\lambda_\pm = -\gamma/2 \pm i\tilde{\omega}_0$, where $\tilde{\omega}_0 = \omega_0\sqrt{1 - \frac{\gamma^2}{4\omega_0^2}}$. The frequencies ω_0 and $\tilde{\omega}_0$ are close, but keep in mind that they are still different. Finally, we get:

$$z(t) = e^{-\gamma t/2}\Big(z_+ e^{i\tilde{\omega}_0 t} + z_- e^{-i\tilde{\omega}_0 t}\Big)$$

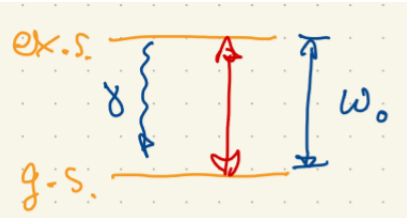


Figure 2.3: Atomic case: Ground and excited states – the excited state is the analog to a swinging classical oscillator. The decay rate γ is the inverse lifetime of the excited state, and ω_0 the energy difference to the ground state. A driving laser of frequency ω (red arrow) is the driving force.

The first term comes from the damping and the second term comes from the oscillating motion. The real solution is $q = Re(z)$, i.e.

$$q(t) = q_0 \, e^{-\gamma t/2} \cos(\tilde{\omega}_0 t + \phi)$$

The graph has the shape shown in Fig. 2.4.

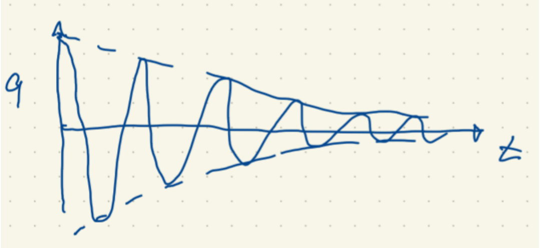


Figure 2.4: Weakly damped oscillator: charge of Fig. 2.2 as a function of time.

For the **driven system** , we have the particular solution:

$$z_{\text{part}} \;=\; A \, e^{i\phi} \, e^{i\omega t}$$

Plugging this into the original equation and solving it we get:

$$Ae^{i\phi} \;=\; \frac{f_0}{-\omega^2 + i\gamma\omega + \omega_0^2}$$

Thus, the (square of the) amplitude will read:

$$A^2 \;=\; \frac{f_0^2}{(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2}, \tag{2.1}$$

while the phase will be:

$$\tan\phi = \frac{\omega\gamma}{\omega^2 - \omega_0^2}. \tag{2.2}$$

We notice that the maximum of the amplitude is reached for $\omega^2 = \tilde{\omega}_0^2 - \gamma^2/2$ and has the value:

$$A^2_{max} = \frac{f_0^2}{\omega_0^2\gamma^2 - \gamma^4/4}.$$

Note that expressions like intensity or energy are proportional to A^2 – thus this form of the amplitude is the most physical one.

Other than expected in general, this is actually not a Lorentzian line shape, and is, in fact, a bit awkward, given that it is a fourth order expression. It turns out that a **Lorentzian** line shape is an excellent approximation that yields:

$$A^2 = \frac{f_0^2}{(\omega_0-\omega)^2(\omega_0+\omega)^2 + \omega^2\gamma^2} \approx \frac{f_0^2}{4\omega_0^2}\frac{1}{(\omega_0-\omega)^2 + \gamma^2/4}, \tag{2.3}$$

where we recognize that $\gamma/\omega_0 \approx 10^{-14} \ll 1$ in typical cases. Thus, the expression for A^2 is extremely small except where $\omega \approx \omega_0$ and we can replace ω by ω_0 except for the difference expression and get the resulting Lorentzian line shape, depicted (approximately) in Fig. 2.5.

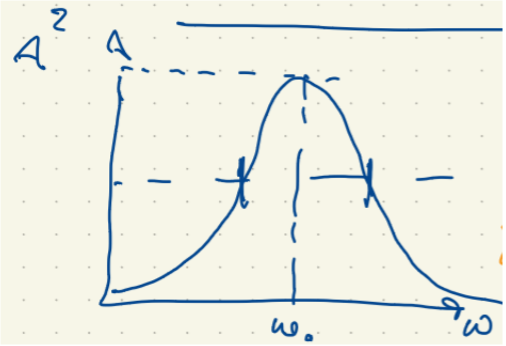


Figure 2.5: Amplitude as a function of frequency. The width depicts the FWHM

The line width $\Delta\omega$ is defined as the width of the curve at half of the maximum amplitude ("full width at half maximum" or FWHM), and for the case of a Lorentzian lineshape, this is equal to $\Delta\omega = \gamma$.

Question: How well can we measure this line width?
Answer: In theory, arbitrarily well! (We could just zoom into the perfect curve and find exactly where the maximum is. This procedure is called "splitting the line.") Experimentally, however, this is not what we typically see. The curve is noisy, like in Fig. 2.6.

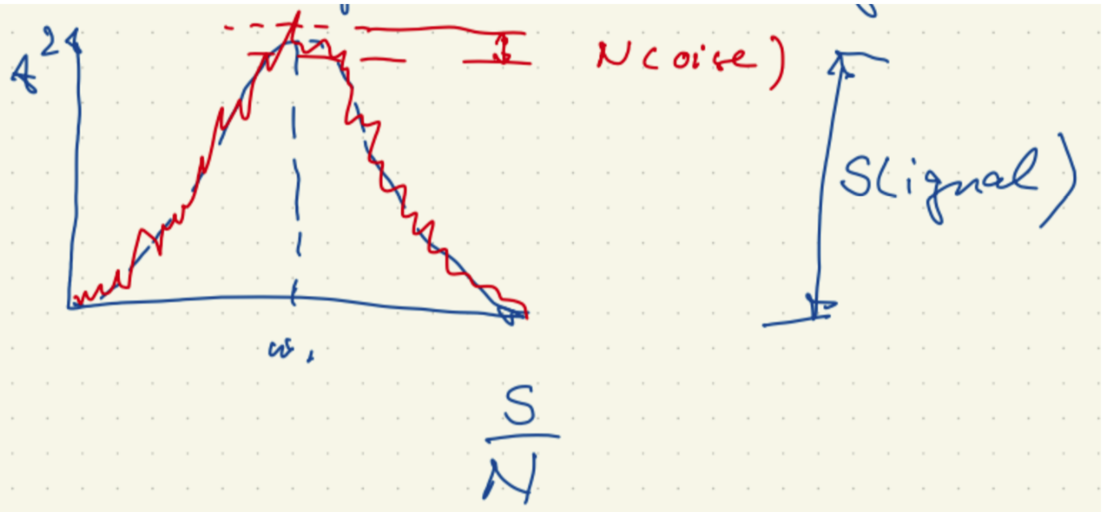


Figure 2.6: Noisy amplitude. S (the "signal") depicts the maximum amplitude and N the (amplitude of the) "noise."

In experiments, one typically defines the quality factor as the line width compared to the absolute frequency:

$$Q \equiv \frac{\omega_0}{\Delta\omega}.$$

That is, the line form is the narrower the higher Q is.

From Fig. 2.4, we see that the fall-off time (i.e., "life time") of the excitation is

$$\tau = \frac{1}{\gamma},$$

i.e., the time where the excitation amplitude goes down by a factor of $1/e$. Thus, γ is also called "decay rate."

2.2.1 Splitting the Line

First, we introduce the concept of ”splitting the line”. Previously, we had defined the Q factor, $\frac{\omega_0}{\Delta\omega}$ and the signal-to-noise ratio (SNR), $\frac{S}{N}$. In theory, it is possible to extract the resonant frequency with infinite precision, since theory curves are perfectly smooth. In practice, however, experiments are limited by sources of noise, which means we cannot arbitrarily zoom in to the absolute maximum of our peak. The SNR and Q factor thus independently contribute to how well we can make such measurements. We can introduce a new factor,

$$\delta\omega = \frac{\Delta\omega}{S/N},$$

which depends on the linewidth and the signal-to-noise. In practice, we cannot determine the accuracy of our measurement better than this factor, which is said to *split* the linewidth by a factor of the SNR, which is why this process as known as *splitting the line*.

In the below figures, we see some examples of lines that can be split very well. The Cesium fountain clock experiment, schematically shown in Fig. 2.7, results in a more traditional overall Lorentzian-like shape in Fig. 2.8, but with many closely spaced teeth. These oscillations result in a lower value for $\Delta\omega$, which in turn, splits the line even better. In Fig. 2.9, we see an incredibly smooth plot from the ACME EDM experiment, resulting in a very high SNR, and again, a very well split line.

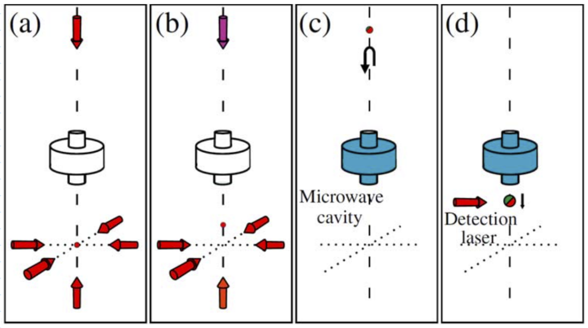


Figure 2.7: A diagram of the Cesium fountain clock experiment.

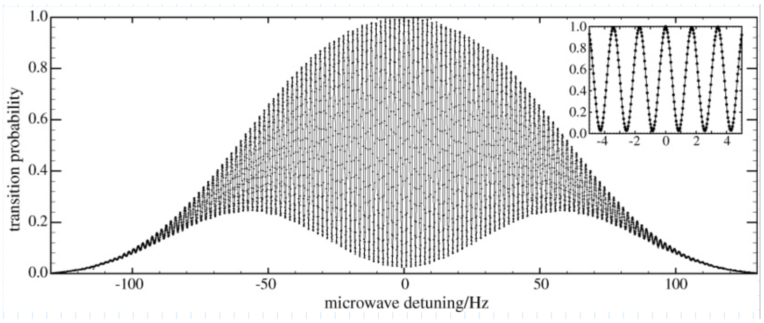


Figure 2.8: Spectrum of the Cesium fountain clock experiment, showing a fine fine tooth pattern resulting in a very well split line.

2.2.2 Phase

Previously, when we analyzed classical resonance, we defined the phase (Eq. (2.2)). With the same approximation that we did for the amplitude, we get.

$$\tan\varphi = \frac{-\gamma/2}{\omega_0 - \omega}, \tag{2.4}$$

which is plotted below in Fig. 2.10. In fact, we often intuitively think about phase. For example, when pushing someone on a swing, we know to always push at the point where they would get the largest boost, or when $\varphi = \frac{\pi}{2}$.

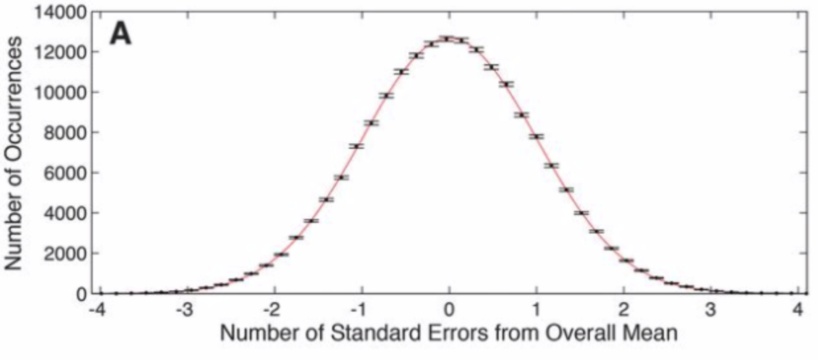


Figure 2.9: Spectrum from the ACME EDM experiment, with a very high SNR.

Figure 2.10: Phase Plot

2.2.3 Examples of typical Q values

One example of a Q value is that of the Earth's rotation, for which $Q = 10^7$. This is, of course, not perfect, due to the fact that the rotation of the Earth is measured taking the only Sun into account, despite the fact that many other celestial bodies affect it. Taking forward the astrophysical theme, pulsars, also known as astronomical clocks, have $Q = 10^{10}$.

This discussion leads to the question, what exactly are "useful resonances" in the context of AMO, and why do we care about them? One thinks of the hyperfine transition in a Cesium atom, which is used to define a second. Such a measurement has a high Q, is reproducible, and is certainly useful. Another such example is the study of the change in fundamental constants over time. Below are even more examples of useful resonances/quality factors:

- The anomalous Zeeman effect found by Thomas Preston which showed unexpected additional splittings due to what was then, the undiscovered spin.
- The Lamb Shift
- The typical quality factor for a visible line due to the Doppler effect at room temperature is 10^6
- An electron in a penning trap has $Q = 10^6 - 10^7$.
- The Hydrogen 1s - 2p line has $Q = 2 \times 10^7$.

- The Helium fine structure: $Q = 10^8 - 10^9$.

2.2.4 Definitions/Remarks

When it comes to measuring lines, the two most common quantities that show up are ω, the angular frequency, and f, the frequency, where $\omega = 2\pi f$. Theorists tend to favor the former, while experimentalists prefer the latter, where ω is measured in $1/s$ and f is measured in, well, $1/s$. This leads to some ambiguity, so it is common to see measurements with f written as some amount of Hz, while measurements made in ω are measured in $1/s$. Sometimes, if the scientist is feeling extra kind, a measurement can be written as $\omega = 2\pi \times 10$ MHz, which is completely unambiguous.

Typically, γ which has units of $1/s$ is given in units of s defined as $\tau = 1/\gamma$, or the lifetime of a particular state. If we were to to make a measurement for an infinitely long period of time, we would expect $\Delta\omega\tau = 1$, but in practice since we don't have forever, we can use the uncertainty principle (or Fourier transform) to obtain a bound whereby $\Delta\omega\Delta t \geq \frac{1}{2}$.

2.3 Coupling & Level Crossing

Suppose we have a two level system, with an excited state $|e\rangle$ and a ground state $|g\rangle$. We can take them as uncoupled, such that

$$H|e\rangle = \frac{1}{2}\hbar\omega_0|e\rangle, H|g\rangle = -\frac{1}{2}\hbar\omega_0|g\rangle.$$

We can define our states and the resulting Hamiltonian as

$$|e\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \ |g\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \ H = \begin{pmatrix} \frac{1}{2}\hbar\omega_0 & 0 \\ 0 & -\frac{1}{2}\hbar\omega_0 \end{pmatrix}$$

No off diagonal terms are present in this Hamiltonian, which means there is no coupling between the states. If we plot the eigenvalues, as done in Fig. 2.11, we see level crossing at exactly $\omega_0 = 0$. Pretty boring...

We can spice things up a little by adding coupling between the two states via a factor, which we will call α (not the fine structure constant). Our Hamiltonian is now

$$H = \frac{1}{2}\hbar \begin{pmatrix} \omega_0 & \alpha \\ \alpha & -\omega_0 \end{pmatrix},$$

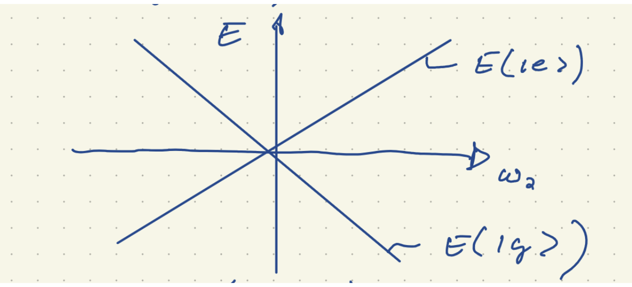


Figure 2.11: Plotted energy eigenvalues of an uncoupled two-level system as a function of ω_0.

with eigenvalues and eigenstates

$$\lambda_\pm = \pm\frac{\hbar}{2}\sqrt{\omega_0^2+\alpha^2}, \qquad |\lambda_\pm(\omega_0=0)\rangle = \frac{1}{\sqrt{2}}(|e\rangle \pm |g\rangle).$$

Now, if we plot these eigenvalues in Fig. 2.12, we see that there is no longer a zero-crossing. In fact, we see the curves crossing the y-axis at $\pm\frac{\hbar}{2}\alpha$, and asymptotically approach the plot for the uncoupled system in Fig. 2.11. This lack of crossing is known as an "avoided crossing" or "anti-crossing," and in tandem with the asymptotic behaviour is an indication that some sort of coupling is occurring.

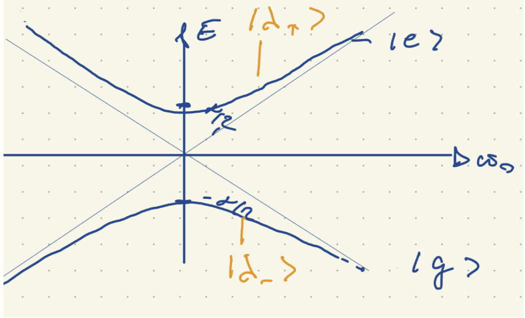


Figure 2.12: Plotted energy eigenvalues of a coupled two-level system as a function of ω_0.

2.3.1 Examples Involving Avoided Crossings

We first look at the ammonia molecule, NH_3, shown below in Fig. 2.13.

Figure 2.13: Two different orientations for the NH_3 molecule with degenerate energy.

Given that the two states are degenerate, we can write the Hamiltonian as

$$H = \frac{1}{2}\hbar \begin{pmatrix} 0 & \alpha \\ \alpha & 0 \end{pmatrix},$$

where the off diagonal term, α, is the tunneling rate between the two configurations. We can study the dynamics of the system by taking the up state $|u\rangle$ (the first state in Fig. 2.13, the second being the down state $|d\rangle$) as the initial state such that $|\psi(0)\rangle = |u\rangle$. Thus, we have

$$\begin{aligned} |\psi(t)\rangle &= e^{-\frac{i}{\hbar}Ht}|\psi(0)\rangle \\ &= \cos\frac{\alpha}{2}|u\rangle - i\sin\frac{\alpha}{2}|d\rangle. \end{aligned}$$

We can then plot the probability of being in, for example, the up state

$$P(t) = |\langle u|\psi(t)\rangle|^2,$$

where we have plotted the result in Fig. 2.14.

We can add a static electric field F (with energy $E = -\vec{F}\cdot\vec{p}$ for dipole moment $\vec{p}$) to break the degeneracy:

$$H = \frac{1}{2}\hbar \begin{pmatrix} -2\frac{p\cdot F}{\hbar} & \alpha \\ \alpha & 2\frac{p\cdot F}{\hbar} \end{pmatrix}.$$

Another example is that of H_2^+, shown below.

The Hamiltonian is similar to the ammonia example, except now α depends exponentially on the separation between the two protons, as shown below.

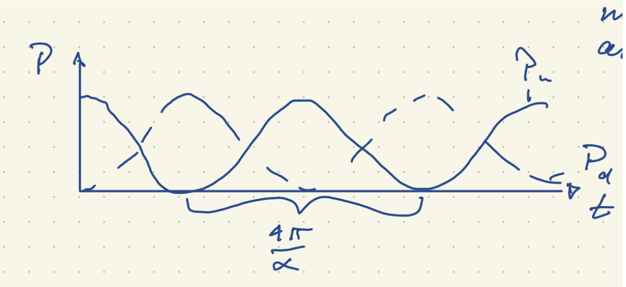


Figure 2.14: Probability of being in an up or down state for the ammonia molecule.

Figure 2.15: Two different ways of "orienting" H_2^+.

2.4 Spin-1/2 models

The spin 1/2 system is the most generic system. We can define its eigenstates, which we call spin operators, such that

$$S_z|e/g\rangle = \pm\frac{\hbar}{2}|e/g\rangle,\ S_z = \frac{\hbar}{2}(|e\rangle\langle e| - |g\rangle\langle g|).$$

We can then define

$$|e\rangle = \begin{pmatrix}1\\0\end{pmatrix},\ |g\rangle = \begin{pmatrix}0\\1\end{pmatrix},\ S_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix},$$

where the matrix divorced from the $\frac{\hbar}{2}$ in S_z is the Pauli matrix, σ_z. From this, it follows that

$$S^2 = S_z^2 + S_y^2 + S_x^2 \to S^2|e/g\rangle = \frac{3}{4}\hbar^2|e/g\rangle.$$

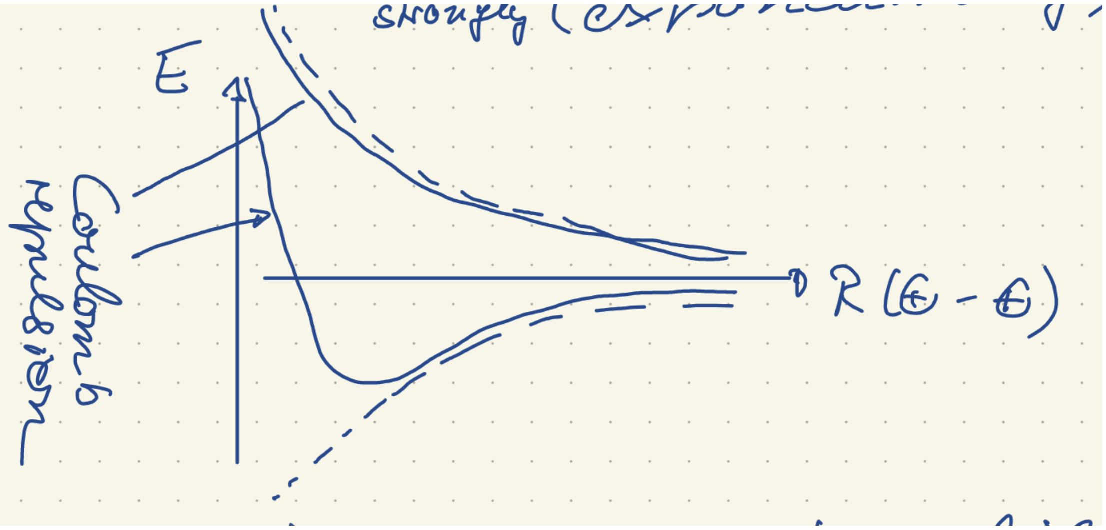


Figure 2.16: Energy diagram as a function of separation for H_2^+

We can define other spin projectors,

$$\begin{aligned}
S_x &= \frac{\hbar}{2}(|e\rangle\langle g| + |g\rangle\langle e|) &\rightarrow& \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} &=& \frac{\hbar}{2}\sigma_x, \\
S_y &= = i\frac{\hbar}{2}(-|e\rangle\langle g| + |g\rangle\langle e|) &\rightarrow& \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} &=& \frac{\hbar}{2}\sigma_y, \\
S_+ &= S_x + iS_y = \hbar|e\rangle|g\rangle &\rightarrow& \frac{\hbar}{2}\begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix}, \\
S_- &= S_x - iS_y = \hbar|g\rangle|e\rangle &\rightarrow& \frac{\hbar}{2}\begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix},
\end{aligned}$$

and thus the eigenstates of the x, y-components can be written as

$$\begin{aligned}
S_x|s_{x\pm}\rangle &= \pm\frac{\hbar}{2}\frac{1}{\sqrt{2}}\left(|e\rangle \pm |g\rangle\right) \\
S_y|s_{y\pm}\rangle &= \pm\frac{\hbar}{2}\frac{1}{\sqrt{2}}\left(|e\rangle \pm i|g\rangle\right).
\end{aligned}$$

Note the effect of the raising and lowering operators:

$$S_+|g\rangle = \frac{\hbar}{2}|e\rangle, \qquad S_-|e\rangle = \frac{\hbar}{2}|g\rangle, \qquad S_+|e\rangle = 0, \qquad S_-|g\rangle = 0.$$

The commutation and anti-commutation relations follow the typical angular momentum operations:

$$[S_i, S_j] = i\hbar\epsilon_{ijk}S_k, \qquad [\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k,$$
$$\{S_i, S_j\} = \frac{\hbar^2}{2}\delta_{ij}, \qquad \{\sigma_i, \sigma_j\} = 2\delta_{ij}.$$

Question: From these operations, are TLSs bosonic or fermionic?

Answer: They are always fermions - no TLS can be excited twice! (The comparison with "traditional" fermions can be understood by this analogy: TLS → one particular state, excitation of TLS → electron/spin.)

2.5 Transitions

Why study TLS? Aren't they very simplified cases of systems in nature only? In fact, they are much more general than that! For that it is good to take into account (details later):

- Typically, only one transition/two states are addressed by any given field/laser and can thus, to a point, be treated independently.
- Many-level systems/more complex setups nearly always use, at least approximately, TLSs as basic building blocks.

2.5.1 The Interaction Picture

First consider an uncoupled TLS described by the Hamiltonian H_0 as shown in the figure below.

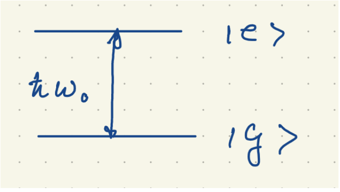


Figure 2.17: A generic TLS with ground state $|g\rangle$ and excited state $|e\rangle$ separated by an energy difference of $\hbar\omega_0$.

By convention we write the eigenvalues as:

$$H_0|e\rangle = \frac{\hbar}{2}\omega_0|e\rangle$$
$$H_0|g\rangle = -\frac{\hbar}{2}\omega_0|g\rangle$$

such that the uncoupled Hamiltonian is:

$$H_0 = \frac{\hbar}{2}\omega_0\sigma_z.$$

We now introduce a time-dependent interaction term $V(t)$ such that the full Hamiltonian reads:

$$H = H_0 + V(t).$$

Note that V is typically off-diagonal, that is: $V_{gg} = V_{ee} = 0$. More generally, if we have a known set of complete orthonormal eigenstates of H_0 given by

$$H_0|n\rangle = \hbar\omega_n|n\rangle$$

we can expand an arbitrary Schrodinger picture state $|\psi\rangle$ as a linear combination of eigenstates of H_0 as:

$$|\psi\rangle = \sum_n c_n(t)e^{-i\omega_n t}|n\rangle \tag{2.5}$$

where the exponential time dependence due to evolution with H_0 has been factored for convenience. This state obviously satisfies the Schrodinger equation:

$$i\hbar\partial_t|\psi\rangle = (H_0 + V)|\psi\rangle. \tag{2.6}$$

Plugging Eq. (2.5) into Eq. (2.6) yields:

$$i\hbar\sum_m(\dot{c}_m - i\omega_m c_m)e^{-i\omega_m t}|m\rangle = \sum_m c_m\hbar\omega_m e^{-i\omega_m t}|m\rangle + \sum_m Vc_m e^{-i\omega_m t}|m\rangle.$$

Acting on the left of both sides of this equation with the orthogonal state $\langle n|$ produces:

$$i\hbar\dot{c}_n = \sum_m c_m e^{-i(\omega_m-\omega_n)t}V_{nm}$$

where $V_{nm} = \langle n|V|m\rangle$. For a TLS this reduces to a system of two coupled differential equations:

$$\begin{aligned} i\hbar\dot{c}_e &= c_g e^{i\omega_0 t} V_{eg} \\ i\hbar\dot{c}_g &= c_e e^{-i\omega_0 t} V_{ge}. \end{aligned} \tag{2.7}$$

We now assume that the matrix elements of V are "rotating" such that

$$\begin{aligned} V_{eg}(t) &= -\frac{\hbar}{2}\Omega_R e^{-i\omega t} \\ V_{ge}(t) &= -\frac{\hbar}{2}\Omega_R^* e^{i\omega t} \end{aligned} \tag{2.8}$$

where ω is the driving frequency. Plugging Eq. (2.8) into Eq. (2.7) yields:

$$\begin{aligned} i\dot{c}_e &= -\frac{1}{2}\Omega_R e^{-i(\omega-\omega_0)t} c_g \\ i\dot{c}_g &= -\frac{1}{2}\Omega_R^* e^{i(\omega-\omega_0)t} c_e \end{aligned} \tag{2.9}$$

which motivates the definition of the "detuning": $\delta = \omega - \omega_0$. Typically one has $\delta \ll \omega, \omega_0$.

We are now ready to move to the **interaction picture**. We define the interaction picture coefficients as:

$$\begin{aligned} \tilde{c}_e &= e^{-i\omega_e t} c_e \\ \tilde{c}_g &= e^{-i\omega_g t} c_g \end{aligned} \tag{2.10}$$

with arbitrary ω_e and ω_g. Plugging these definitions into Eq. (2.9) and using the product rule, we have:

$$\begin{aligned} i(\dot{\tilde{c}}_e + i\omega_e\tilde{c}_e) &= -\frac{\Omega_R}{2}\,\tilde{c}_g\, e^{-i(\delta-\omega_g+\omega_e)t} \\ i(\dot{\tilde{c}}_g + i\omega_g\tilde{c}_g) &= -\frac{\Omega_R^*}{2}\,\tilde{c}_e\, e^{i(\delta-\omega_g+\omega_e)t}. \end{aligned}$$

If we choose $\delta = \omega_g - \omega_e$ we arrive at our final answer for time evolution in the **rotating frame**:

$$\begin{aligned} \dot{\tilde{c}}_e &= -i\,\omega_e\tilde{c}_e + i\frac{\Omega_R}{2}\,\tilde{c}_g \\ \dot{\tilde{c}}_g &= -i\,\omega_g\tilde{c}_g + i\frac{\Omega_R}{2}\,\tilde{c}_e. \end{aligned} \tag{2.11}$$

This system can be written succinctly as a Schrodinger-like equation with Hamiltonian

$$\tilde{H} = \hbar \begin{pmatrix} \omega_e & -\frac{\Omega_R}{2} \\ -\frac{\Omega_R^*}{2} & \omega_g \end{pmatrix}. \tag{2.12}$$

Some convenient choices for ω_e and ω_g are illustrated in the figure below.

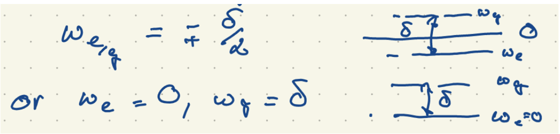


Figure 2.18: Two level diagrams showing possible choices of ω_e and ω_g. Note that their relative magnitude is always equal to δ.

2.5.2 Interaction picture for laser coupling

Frequently, the states will be coupled through a dipole interaction

$$V = -\mathbf{p} \cdot \mathbf{E} \tag{2.13}$$

where $\mathbf{p}$ is the electric dipole moment and $\mathbf{E}$ is the applied electric field (e.g. from a laser) with the form

$$\mathbf{E} = \mathbf{E}^{+} e^{-i\nu t} + \mathbf{E}^{-} e^{i\nu t}$$

where ν is the particular driving frequency. Note that the condition that $\mathbf{E}$ must be real implies $\mathbf{E}^{+*} = \mathbf{E}^{-}$. Another important point is that the dipole operator

$$\mathbf{p} = e\mathbf{r}$$

only couples states with opposite parity. That is:

$$\langle e|\mathbf{r}|e\rangle = \langle g|\mathbf{r}|g\rangle = 0$$

for symmetry reasons. Thus, the initial assumption that V be off-diagonal is well justified. It is instructive to expand the dipole operator by inserting two copies of the complete set of states. (From here on, the vector character of field and dipole is dropped, since for a TLS obviously only one spatial component of the polarization is needed.)

$$p \;=\; e\,r \;=\; e\mathbf{1}r\mathbf{1} \;=\; e\sum_i |i\rangle\langle i|\,r\sum_j |j\rangle\langle j| \;=\; e\sum_{i,j} r_{ij}|i\rangle\langle j|.$$

For a TLS this reduces to:

$$p \;=\; \wp\,|e\rangle\langle g| + h.c. \tag{2.14}$$

where $\wp \;=\; e\,r_{eg}$ is the "dipole matrix element" coupling constant. With the choice of interaction given by Eq. (2.13), the interaction matrix elements become:

$$V_{eg} \;=\; -\wp(E^+e^{-i\nu t} + E^-e^{i\nu t})$$

and similar for the Hermitian conjugate element. Plugging this into the first line of Eq. (2.7) yields:

$$i\,\hbar\,\dot{c}_e \;=\; -c_g\,\wp\,(E^+\,e^{-i(\nu-\omega_0)t} + E^-\,e^{i(\nu+\omega_0)t}).$$

We call the rapidly oscillating term with E^- the "counter-rotating" term. For $|\nu-\omega_0| << |\nu+\omega_0|$ the counter-rotating term averages to zero and we can drop it. Thus, in the so-called **rotating wave approximation** (RWA), the interaction matrix elements reduce to:

$$V_{eg} \approx -\wp\,E^+\,e^{-i\nu t}.$$

This is precisely the form we had previously for the purely rotating interaction. We therefore see that the purely rotating interaction is the limit of the dipole interaction within the RWA. Comparing the above expression to our previous form, we define the **Rabi frequency** as:

$$\frac{\Omega_R}{2} = \frac{\wp\,E^+}{\hbar}. \tag{2.15}$$

The Rabi frequency depends on both the material properties of the TLS (through $\wp$) and on the properties of the driving laser (through $\mathbf{E}^+$).

Briefly, we note that for magnetic interactions we have the interaction

$$V = -\mu\cdot\mathbf{B}$$

which describes, for example, a spin in a magnetic field.

2.6 Weak and strong driving fields: adiabatic passage and Rabi oscillations

2.6.1 Weak Near-Resonant Excitation

Consider a TLS where the excited state is allowed to decay into the ground state.

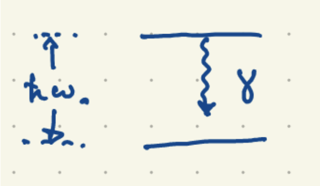


Figure 2.19: A TLS that is allowed to decay from the excited state to the ground state through the emission of a photon.

This is a non-unitary process, but can be treated with the Schrodinger equation in an ad-hoc way using perturbation theory. Phenomenologically speaking, we expect the decay to follow an exponential timescale. We can therefore "patch" this process into the Schrodinger equation by making the replacement:

$$|e\rangle \rightarrow e^{-\frac{\gamma}{2}t}|e\rangle$$

or equivalently,

$$e^{\pm i\omega_0 t} \rightarrow e^{\pm i\omega_0 t-\frac{\gamma}{2}t}.$$

For weak driving, we have $c_g(t) \approx c_g(0) \approx 1$ and $c_e(t) \ll 1$. Plugging this substitution into the equations of motion (2.7) with the rotating interaction we have:

$$c_e(t) = i\int_0^t dt' \frac{\Omega_R}{2} e^{-\delta t' -\frac{\gamma}{2}t'} \; = \; i\frac{\Omega_R}{2}\frac{1}{-i\delta-\gamma/2}(e^{-i\delta t-\frac{\gamma}{2}t}-1).$$

In the limit $t \rightarrow \infty$ this becomes:

$$c_e(t) = \frac{\Omega_R}{2}\frac{1}{\delta - i\gamma/2}$$

and therefore the transition probability from the ground to the excited state is:

$$P_e = |c_e(t \to \infty)|^2 = \frac{|\Omega_R|^2}{4} \frac{1}{\delta^2 + (\gamma/2)^2}. \tag{2.16}$$

As shown in the figure below, this probability distribution has a Lorentzian shape, and thus reproduces the classical solution for $t \to \infty$.

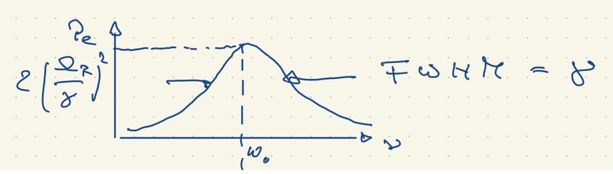


Figure 2.20: Lorentzian probability distribution for the ground to excited state transition in the weak driving regime.

This solution can be obtained exactly through the use of a non-Hermitian Hamiltonian. In the rotating frame:

$$\tilde{H} = \hbar \begin{pmatrix} -\delta - i\gamma/2 & -\frac{\Omega_R}{2} \\ -\frac{\Omega_R^*}{2} & 0 \end{pmatrix}. \tag{2.17}$$

Then,

$$\tilde{c}_e = \frac{i\Omega_R}{2\sqrt{(\gamma/2 + i\delta)^2 - |\Omega_R|^2}} e^{\frac{1}{2}(-\frac{\gamma}{2} + \sqrt{(\gamma/2+i\delta)^2 - |\Omega_R|^2})t} (1 - e^{-\sqrt{(\gamma/2+i\delta)^2 - |\Omega_R|^2}}) \tag{2.18}$$

which reproduces the previous result for $|\Omega_R| \ll \gamma$.

2.6.2 Strong Excitation

In the limit of strong excitation we have $\gamma \ll |\Omega_R|$ and we an neglect the decay process since the normal unitary evolution occurs on a much faster timescale than the decay. Working in the rotating frame (while dropping the tilde notation) the Hamiltonian is:

$$\frac{H}{\hbar} = \begin{pmatrix} -\delta & -\frac{\Omega_R}{2} \\ -\frac{\Omega_R^*}{2} & 0 \end{pmatrix}. \tag{2.19}$$

Near resonance, $\delta = 0$, the equations of motion in the rotating frame become:

$$\dot{c}_e = \frac{i\Omega_R}{2} c_g \tag{2.20}$$

$$\dot{c}_g = \frac{i\Omega_R^*}{2} c_e \tag{2.21}$$

Taking the time derivative of the equation for $\dot{c}_e$ and plugging in the expression for $\dot{c}_g$ yields:

$$\ddot{c}_e = -\frac{|\Omega_R|^2}{4} c_e$$

which is exactly the equation of motion for a harmonic oscillator. Plugging in the initial condition $c_g(0) = 1$ gives an expression for the transition probability:

$$P_e(t) = |c_e(t)|^2 = \sin^2 \frac{|\Omega_R|}{2} t = \frac{1}{2}(1 - \cos|\Omega_R|t) \tag{2.22}$$

which is plotted in the figure below. After a pulse of duration $t = \pi/|\Omega_R|$

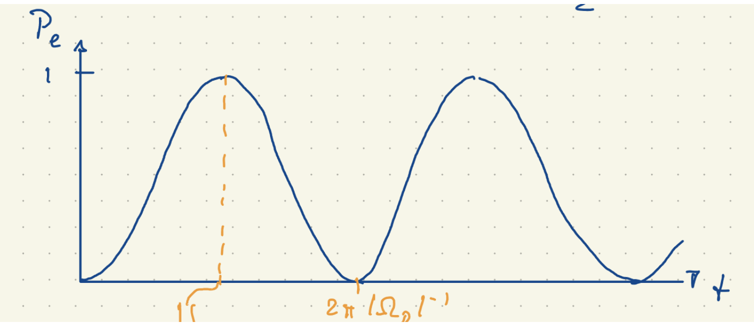


Figure 2.21: Oscillatory probability distribution for the ground to excited state transition in the strong driving regime.

the system is deterministically driven to the excited state $|g\rangle \to |e\rangle$ with probability 1. This pulse, known as a **π-pulse** is depicted schematically below.

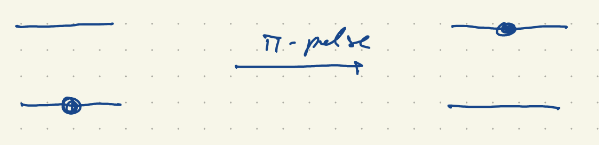


Figure 2.22: Schematic TLS diagram depicting a π-pulse.

Similarly, a pulse of duration $t = \pi/2|\Omega_R|$ is known as a **$\pi/2$-pulse** and drives the system into a superposition state $|g\rangle \rightarrow 1/\sqrt{2}(i|e\rangle + |g\rangle)$.

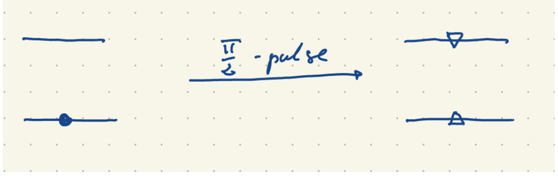


Figure 2.23: Schematic TLS diagram depicting a $\pi/2$-pulse.

2.6.3 Off Resonance ($\delta \neq 0$)

The π- and $\pi/2$-pulse are executed on resonance. What happens off resonance? Another term will appear in the equation for the excited state population amplitude, $\tilde{c}_e$, proportional to the detuning of the driving field.

$$\ddot{\tilde{c}}_e + i\delta\dot{\tilde{c}}_e + \frac{|\Omega_R|^2}{4}\,\tilde{c}_e \;=\; 0 \tag{2.23}$$

To solve this equation, the ansatz $\tilde{c}_e \propto e^{i\alpha t}$ is used. When this ansatz is plugged into the second order equation, the frequency α is found to be:

$$\alpha \;=\; -\frac{\delta}{2} \pm \frac{1}{2}\sqrt{\delta^2 + |\Omega_R|^2} \tag{2.24}$$

Defining the **generalized Rabi frequency** $\tilde{\Omega}$ as the factor $\sqrt{\delta^2 + |\Omega_R|^2}$:

$$\alpha \;=\; -\frac{\delta}{2} \pm \frac{1}{2}\tilde{\Omega} \tag{2.25}$$

If the excited state population amplitude is zero initially ($\tilde{c}_e(0) = 0$), the solution is simply:

$$\tilde{c}_e(t) \;=\; A\,e^{-i\frac{\delta}{2}t}\,\sin\left(\frac{\tilde{\Omega}}{2}t\right) \tag{2.26}$$

The amplitude A has yet to be determined, but it can be calculated from initial conditions as follows:

$$\begin{aligned}\dot{\tilde{c}}_e(0) &= i\frac{A}{2}\big[-i(\delta - \tilde{\Omega}) + i(\delta + \tilde{\Omega}\big]\\ &= -\frac{A}{2}\tilde{\Omega}\\ &= -i\delta\tilde{c}_e(0) - i\frac{\Omega_R}{2}\tilde{c}_g(0)\end{aligned} \tag{2.27}$$

The final step in the above calculation follows from the first order equation for the excited population amplitude. Using the same initial conditions (that is, $\tilde{c}_e(0) = 0$ and $\tilde{c}_g(0) = 1$), A is found to be:

$$A = i\frac{\Omega_R}{\tilde{\Omega}} \tag{2.28}$$

The definition of $\tilde{\Omega}$ requires that it be greater than or equal to the magnitude of the Rabi frequency, Ω_R. Thus, the amplitude $|A|$ must be less than or equal to 1, being equal only in the limiting case of perfect resonance ($\delta = 0$).

Now that all components of the excited state population amplitude have been found, the probability of occupying the excited state can be calculated:

$$\begin{aligned} P_e(t) &= \left|\frac{\Omega_R}{\tilde{\Omega}}\right|^2 \sin^2\left(\frac{\tilde{\Omega}}{2}t\right) \\ &= \left|\frac{\Omega_R}{\tilde{\Omega}}\right|^2 \frac{1-\cos\tilde{\Omega}t}{2} \end{aligned} \tag{2.29}$$

In the off-resonant case, the Rabi oscillations have an amplitude smaller than one (Fig. 2.24). Thus, full population transfer cannot be achieved while driving off resonance. The oscillations also occur at a higher frequency when compared to the on-resonant case.

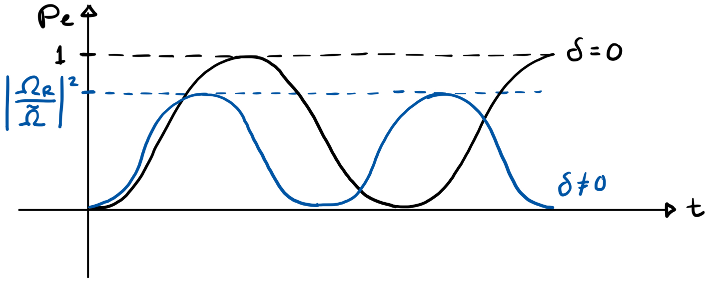


Figure 2.24: Comparison of resonant and off-resonant Rabi oscillations.

2.7 The Bloch Sphere

Because a relative phase can always exist between the ground and excited states, solving the equations of motion of a TLS is a two-dimensional problem that can best be represented on the surface of a sphere. This way of visualizing the state of a two-level system is known as the **Bloch sphere**.

The most general description for any spin-1/2 (and, thus, any two-level) system can be summarized by the x, y, and z components of spin. It is convenient to group these quantities in a vector:

$$\langle \vec{\sigma} \rangle = \langle \sigma_x \rangle \hat{x} + \langle \sigma_y \rangle \hat{y} + \langle \sigma_z \rangle \hat{z} \tag{2.30}$$

The vector $\langle \vec{\sigma} \rangle$ has its tip on the surface of the Bloch sphere, with the origin at its center and the z-axis defined vertically (Fig. 2.25). A vector that points along the positive z-axis is in the excited state; likewise, a vector that points along the negative z-axis is in the ground state. Any vector that lies along the equator of the sphere (in the xy-plane) is in an equal superposition of the excited and ground states, with some relative phase between them. This phase is specified by the angle ϕ between the vector and the positive x-axis.

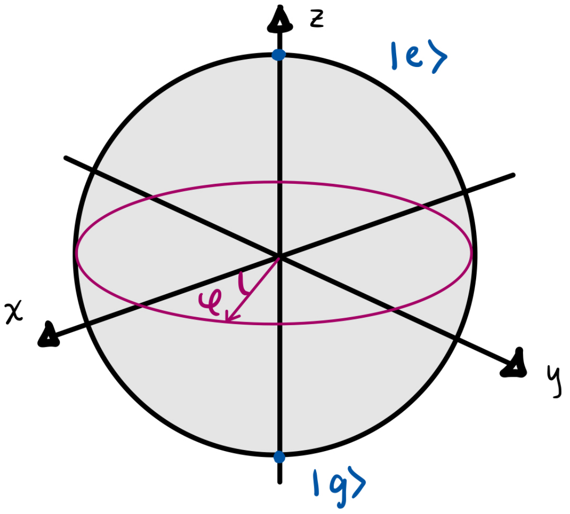


Figure 2.25: Visualization of the Bloch sphere.

The equations of motion of the two-level system can be rewritten in terms of this vector $\langle \vec{\sigma} \rangle$.

[This calculation is done as a homework. I'll add the details later. – SY]

2.8 Dressed States and Light Shifts

Dressed states are simply the eigenstates of the two-level system when diagonalized with respect to the driving field(s).

Start by solving the time-independent Schrödinger equation with Hamiltonian

$$\frac{H}{\hbar} = \begin{pmatrix} -\delta & -\Omega_R/2 \\ -\Omega_R^*/2 & 0 \end{pmatrix}. \tag{2.31}$$

Here, the Hamiltonian is represented in the basis $|e\rangle = [1,0]^T$, $|g\rangle = [0,1]^T$. Diagonalizing the Hamiltonian results in two eigenvalues and eigenvectors:

$$\begin{aligned} \lambda_\pm &= -\frac{1}{2}\big(\delta \pm \sqrt{\delta^2 + |\Omega_R|^2}\big) \\ |\lambda_-\rangle &= \mathcal{N}\begin{pmatrix} \sqrt{\delta^2 + |\Omega_R|^2} - \delta \\ -\Omega_R^* \end{pmatrix} \\ |\lambda_+\rangle &= \mathcal{N}\begin{pmatrix} \Omega_R \\ \sqrt{\delta^2 + |\Omega_R|^2} - \delta \end{pmatrix} \\ \mathcal{N}^{-2} &= |\Omega_R|^2 + \big(\sqrt{\delta^2 + |\Omega_R|^2} - \delta\big)^2 \end{aligned} \tag{2.32}$$

By definition, these eigenstates of the system with a driving field ($|\lambda_\pm\rangle$) are **dressed states**. Notice that the square root factor that repeatedly shows up in these expressions is the generalized Rabi frequency that was discussed in the previous section.

In the limiting case of resonance ($\delta = 0$), the eigenvalues and eigenstates of the driven system approach:

$$\begin{aligned} \lambda_\pm &= \mp\frac{|\Omega_R|}{2} \\ |\lambda_-\rangle &= \frac{1}{\sqrt{2}}\left(|e\rangle - e^{-i\phi}|g\rangle\right) \\ |\lambda_+\rangle &= \frac{1}{\sqrt{2}}\left(e^{i\phi}|e\rangle + |g\rangle\right) \end{aligned} \tag{2.33}$$

where the phase ϕ is defined by $\Omega_R = |\Omega_R|e^{i\phi}$. Notice that the dressed states of the resonantly driven system are equal superpositions of the excited and ground states.

In the limiting case of large detuning ($|\delta| \gg |\Omega_R|$), the generalized Rabi frequency can be Taylor expanded ($\sqrt{\delta^2 + |\Omega_R|^2} \approx |\delta| + |\Omega_R|^2/2|\delta|$). Recall that the detuning is defined as the driving frequency minus the transition frequency – $\delta = \omega - \omega_0$. In the case of an infinite positive (blue) detuning, the dressed states approach the ground and excited states:

$$\begin{aligned}
\lambda_- &\approx \frac{|\Omega_R|^2}{4\delta} \\
\lambda_+ &\approx -\delta - \frac{|\Omega_R|^2}{4\delta} \\
&\approx -\delta \\
|\lambda_-\rangle &\rightarrow |g\rangle \\
|\lambda_+\rangle &\rightarrow |e\rangle.
\end{aligned} \tag{2.34}$$

In the far red detuned limit (that is, $\delta \rightarrow -\infty$), the dressed states approach the opposite atomic states:

$$\begin{aligned}
\lambda_- &\approx -\delta \\
\lambda_+ &\approx \frac{|\Omega_R|^2}{4\delta} \\
|\lambda_-\rangle &\rightarrow |e\rangle \\
|\lambda_+\rangle &\rightarrow |g\rangle.
\end{aligned} \tag{2.35}$$

Knowing the two limiting behaviors of the dressed states as a function of detuning, as well as the on-resonant behavior, the full dependence can be inferred (Fig. 2.26). The dressed state $|\lambda_-\rangle$ ($|\lambda_+\rangle$) is asymptotically aligned with the excited (ground) state at large, negative detuning. As the detuning increases to zero, $|\lambda_-\rangle$ ($|\lambda_+\rangle$) approaches $|\Omega_R|/2$ ($-|\Omega_R|/2$). This is the point of closes approach of the two dressed states. As the detuning increases further to large positive values, the $|\lambda_-\rangle$ ($|\lambda_+\rangle$) approaches the ground (excited) state. The distinct manner in which the dressed states bend away from each other without intersecting is known as "anti-crossing".

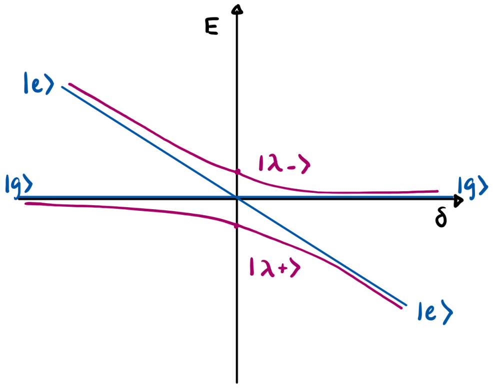


Figure 2.26: Dressed states as a function of detuning.

Note that if we shift the zero-energy point of our Hamiltonian such that $E(|e\rangle) = -\delta/2$ and $E(|g\rangle) = \delta/2$, the whole graph will be tilted (Fig. 2.27).

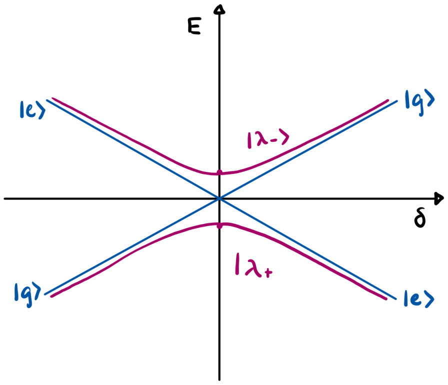


Figure 2.27: Dressed states as a function of detuning, with the zero-energy point shifted to between the excited and ground states.

Spectroscopy on the ground or excited state will reveal the energy shifts induced by the driving field. In the on-resonant case, the dressed states are equal superpositions of the ground and excited states. Thus. two equally strong lines will appear, shifted by $\pm|\Omega_R|/2$ from resonance. This is known as the **Autler-Townes effect** (Fig. 2.28).

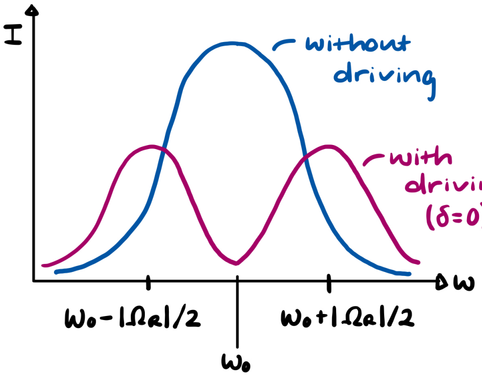


Figure 2.28: Spectroscopy on the two-level system with driving on resonance.

In the limit of large detuning, the principle peak will appear shifted by $|\Omega_R|^2/4\delta$. This is known as the **AC Stark shift**, or **light shift**. While the $-\delta$ shift is also visible in principle, it belongs to a state with a much smaller contribution (Fig. 2.29).

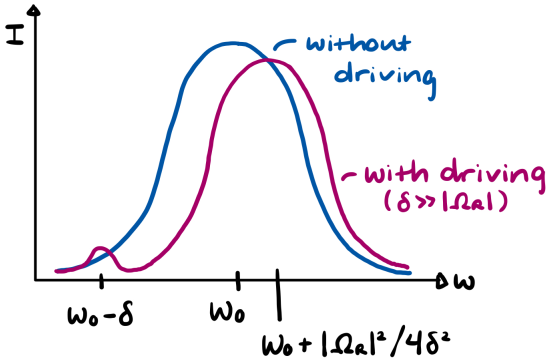


Figure 2.29: Spectroscopy on the two-level system with driving, with a large positive detuning.

Although the counter-rotating terms were neglected early on in this treatment of the two-level system, they also produce a small shift. The counter-rotating terms involve a frequency very far from resonance; thus, they can be treated as an independent field:

$$\frac{H}{\hbar} = \frac{1}{2}\begin{pmatrix} \omega + \omega_0 & -\Omega_R \\ -\Omega_R^* & -(\omega + \omega_0) \end{pmatrix} \tag{2.36}$$

This Hamiltonian is identical to the one treated previously with δ replaced by $\omega + \omega_0 \approx 2\omega_0$. The energy shift can be read off by comparison:

$$\Delta E_{BS\pm} = \pm \frac{\hbar}{2} \frac{|\Omega_R|^2}{4\omega_0} \tag{2.37}$$

This is known as the **Bloch-Siegert shift**. Because of the large enumerator – the transition frequency – it is only important for very strong driving fields.

NB: The two types of light shifts (from the co- and counter-rotating terms, respectively) are both typically very small compared to the transition frequency. Thus, they are treated to the lowest order in the intensity. Thus, assuming them independent of each other is justified.

2.9 Adiabatic Theorem and Passage

Adiabatic means that the system remains in its instantaneous eigenstate if any given perturbation is acting slowly enough. Thus, in principle, one can change the system into a non-trivial state by starting in the ground state of a Hamiltonian which often is easy to reach.

Note: In thermodynamics, "adiabatic" refers to a process that does not include heat transfer. Heat transfer, translated into quantum mechanics language, means a type of non-coherent/non-unitary transition between eigenstates; thus, the two definitions of adiabaticity fit!

It is good to keep in mind that all the physics that were discussed up to this point happen effectively in zero temperature. Why is this a good approximation? The energy of temperature is $k_B T$, and the energy scale of the TLS is the energy difference of the two levels. Since these values are typically orders of magnitude different, according to the Boltzmann distribution the probability of ground state occupation is ≈ 1. Thus, the thermodynamic expectation of adiabaticity is automatically satisfied.

Obviously, adiabaticity also depends on the gaps between the eigenstates. For a two-level system, this latter part does not really matter as the two levels are far apart.

In the rotating frame, the EOM we get for the Bloch vector is (see section/HW on Bloch vector):

$$\frac{\partial}{\partial t}\langle\vec{\sigma}\rangle = \vec{\tilde{\Omega}} \times \langle\vec{\sigma}\rangle, \tag{2.38}$$

where

$$\vec{\tilde{\Omega}} = -\delta\hat{z} + |\Omega_R|\hat{x} \tag{2.39}$$

The length of this vector is the generalized Rabi frequency, and $\vec{\tilde{\Omega}}$ obviously is the axis around which the vector rotates.

This can now be written in polar coordinates:

$$\langle\vec{\sigma}\rangle = \langle\sigma_r\rangle\hat{r} + \langle\sigma_\theta\rangle\hat{\theta} + \langle\sigma_\phi\rangle\hat{\phi}. \tag{2.40}$$

Note that σ_r, σ_ϕ, etc. are superpositions of the usual Pauli matrices (according to the transformation between coordinate systems). For now, it is easiest to just treat their expectation values as complex variables.

Now one can choose $\hat{r}$ to be the axis of rotation, i.e., $\hat{r} = \hat{\tilde{\Omega}}$. Thus,

$$\begin{aligned} \hat{r} &= \cos\theta\,\hat{z} + \sin\theta\,\hat{x} \\ \hat{\theta} &= -\sin\theta\,\hat{z} + \cos\theta\,\hat{x} \\ \hat{\phi} &= \hat{y} \end{aligned}$$

Note that due to Eq. (2.39), one gets $\cos\theta \propto -\delta$ and $\sin\theta \propto |\Omega_R|$. The unit vectors now on the Rabi frequency and the detuning which can be time dependent. Thus, $\dot{\hat{r}} = \dot{\theta}\,\hat{\theta}$, $\dot{\hat{\theta}} = -\dot{\theta}\,\hat{r}$, and $\dot{\hat{\phi}} = 0$. With that, Eq. (2.38) becomes

$$\begin{aligned} \frac{\partial}{\partial t}\langle\vec{\sigma}\rangle &= \langle\dot{\sigma_r}\rangle\hat{r} + \langle\dot{\sigma_\theta}\rangle\hat{\theta} + \langle\dot{\sigma_\phi}\rangle\hat{\phi} + \langle\sigma_r\rangle\underbrace{\dot{\hat{r}}}_{\propto\hat{\theta}} + \langle\sigma_\theta\rangle\underbrace{\dot{\hat{\theta}}}_{\propto\hat{r}} + \underbrace{\langle\sigma_\phi\rangle\dot{\hat{\phi}}}_{\text{goes to 0}} \\ &= \tilde{\Omega}\,\hat{r} \times \left(\langle\sigma_r\rangle\hat{r} + \langle\sigma_\theta\rangle\hat{\theta} + \langle\sigma_\phi\rangle\hat{\phi}\right) \end{aligned} \tag{2.41}$$

If one writes this out component by component, it yields

$$\begin{aligned} \langle\dot{\sigma_r}\rangle - \langle\sigma_\theta\rangle\,\dot{\theta} &= 0 \\ \langle\dot{\sigma_\theta}\rangle + \langle\sigma_r\rangle\,\dot{\theta} &= -\tilde{\Omega}\langle\sigma_\phi\rangle \\ \langle\dot{\sigma_\phi}\rangle &= \tilde{\Omega}\langle\sigma_\theta\rangle \end{aligned} \tag{2.42}$$

Note that θ depends on δ and $|\Omega_R|$. Thus, $\dot{\theta}$ gives us the change in input parameters. Thus, the assumption of adiabaticity should mean

$$|\dot{\theta}| \ll \tilde{\Omega} \tag{2.43}$$

To lowest order, the adiabatic EOM would thus read

$$\begin{aligned} \langle\dot{\sigma_r}\rangle &= \ 0 \\ \langle\dot{\sigma_\theta}\rangle &= -\tilde{\Omega}\langle\sigma_\phi\rangle \\ \langle\dot{\sigma_\phi}\rangle &= \tilde{\Omega}\langle\sigma_\theta\rangle \end{aligned}$$

From this, one sees that the θ and ϕ components (perpendicular to $\hat{\tilde{\Omega}}$) oscillate around $\hat{r}||\hat{\tilde{\Omega}}$ with frequency $\tilde{\Omega}$ while the r component does not change. This means that:

$$\langle\vec{\sigma}\rangle \text{ follows } \vec{\tilde{\Omega}} \tag{2.44}$$

This is a formulation of the "adiabatic theorem." A closer look at the math reveals

$$\begin{aligned} \frac{d}{dt}\tan(\theta) = \ \frac{\dot{\theta}}{\cos^2(\theta)} \ &= \ \frac{\dot{\theta}}{\delta^2}\tilde{\Omega}^2 \ = \ \frac{d}{dt}(-\frac{|\Omega_R|}{\delta}) \ = \ -\frac{|\dot{\Omega}_R|\delta - |\Omega_R|\dot{\delta}}{\delta^2} \\ \Longrightarrow \ \dot{\theta} = \ -\frac{|\dot{\Omega}_R|\delta - |\Omega_R|\dot{\delta}}{\tilde{\Omega}^2} \end{aligned} \tag{2.45}$$

Now, recall from before that $|\dot{\theta}| \ll \tilde{\Omega}$ is the assumption of adiabaticity. Using Eq. (2.45), this relation can be applied to the following scenarios:

1. If $\dot{\delta} \neq 0$, $|\dot{\Omega}_R| = 0$, then plugging into Eq. (2.45) yields:

$$\begin{aligned} |\dot{\delta}| &\ll \frac{\tilde{\Omega}^3}{|\Omega_R|} \\ \xRightarrow{\text{min. value of } \tilde{\Omega}=|\Omega_R|} \ |\dot{\delta}| &\ll \ |\Omega_R|^2 \end{aligned} \tag{2.46}$$

   This is usually seen as *the* adiabaticity condition.

2. If $\dot{|}\Omega_R| \neq 0$ but $\dot{\delta} = 0$, then the expression for $|\dot{\theta}|$ becomes:

$$\begin{aligned} \dot{\theta} = \ -|\dot{\Omega}_R|\,\frac{\delta}{\tilde{\Omega}^2} \\ \Longrightarrow \ |\dot{\Omega}_R|\frac{|\delta|}{\tilde{\Omega}^2} \ll \tilde{\Omega}^2 \end{aligned}$$

This is a relatively trivial condition since it is satisfied automatically for either very large or very small detunings. As a consequence, this is not usually shown as adiabaticity condition in most texts.

As an example, adiabatic passage for two-level systems can be examined. This is also known as rapid adiabatic passage, or RAP. Despite the fact that it is adiabatic, note that it can still potentially be a very fast process. Since the system is adiabatic, the relation of $\langle\vec{\sigma}\rangle$ follows $\vec{\tilde{\Omega}}$ is satisfied. Then, a change of $\vec{\tilde{\Omega}}||\hat{z}$ to $\vec{\tilde{\Omega}}||-\hat{z}$ yields a change of population between excited $|e\rangle$ and ground $|g\rangle$ states. There are four cases:

1. $t \to -\infty$: $\delta = -\infty$ and $\langle\vec{\sigma}(-\infty)\rangle\,||-\hat{z}$ (i.e. $|g\rangle$). Then:

   $$\vec{\tilde{\Omega}}(-\infty) = -\,\delta\hat{z} + |\Omega_R|\hat{x}$$
   $$\implies \vec{\tilde{\Omega}}||\hat{z}$$

   This implies $\langle\vec{\sigma}\rangle\,||-\vec{\tilde{\Omega}}$. Then, δ can be turned from $-\infty$ to $+\infty$ in time, causing $\vec{\tilde{\Omega}}$ to go from $||\hat{z}$ to $||-\hat{z}$. As a consequence, $\langle\vec{\sigma}\rangle$ will go from anti-parallel to $\hat{z}$ to parallel to $\hat{z}$, or from the ground state to the excited state, as shown in Fig. 2.30.

2. $t \to -\infty$: $\delta = +\infty$ and $\langle\vec{\sigma}(-\infty)\rangle\,||-\hat{z}$ (i.e. $|g\rangle$). Then:

   $$\langle\vec{\sigma}\rangle\,||\vec{\tilde{\Omega}}$$

   The behavior of $\vec{\tilde{\Omega}}$ and $\langle\vec{\sigma}\rangle$ are then shown in Fig. 2.31. Note that in both of these cases, $\langle\vec{\sigma}\rangle$ goes from the ground state to the excited state. Thus, no matter if the system changes from red detuned to blue detuned (1) or blue detuned to red detuned (2), if $\langle\vec{\sigma}\rangle$ starts in the ground state, it will go to the excited state.

3. (and 4.) $\langle\vec{\sigma}(-\infty)\rangle\,||\hat{z} \implies$ evolution from excited state to ground state ($|e\rangle \to |g\rangle$).

There is more decoherence when changing the system from one state to another using adiabatic passage than with the π pulse, since the $\dot{\theta}$ terms are approximated away. However, this method is advantageous because it is not as sensitive.

Figure 2.30: Movement of $\vec{\tilde{\Omega}}$ and $\langle\vec{\sigma}\rangle$ for case 1 of adiabatic passage.

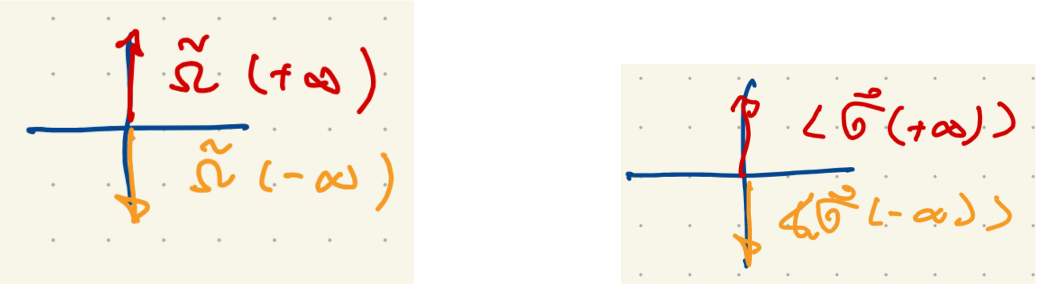


Figure 2.31: Movement of $\vec{\tilde{\Omega}}$ and $\langle\vec{\sigma}\rangle$ for case 2 of adiabatic passage.

2.10 Landau-Zener crossing

How does a system evolve between eigenstates depending on adiabaticity? In order to understand this it makes most sense to study a level crossing. (Note that this discussion happens fully in the rotating frame.)

$$\begin{aligned} i\dot{c}_e &= -\frac{\Omega_R}{2}\, e^{-i\delta(t)t} \\ i\dot{c}_g &= -\frac{\Omega_R^*}{2}\, e^{i\delta(t)t} \end{aligned} \tag{2.47}$$

Assume that $\delta(t) = \alpha t$, i.e., a linear sweep. Thus we have to solve Eq. (2.47) as follows:

$$0 \;=\; \ddot{c}_{e/g} \pm 2i\alpha\, t\, \dot{c}_{e/g} + \frac{|\Omega_R|^2}{4}\, c_{e/g} \tag{2.48}$$

A new time τ can be defined:

$$\tau \equiv \frac{|\Omega_R|}{2} t \tag{2.49}$$

Then, the equation becomes:

$$0 \;=\; c''_{e/g} \pm 2i\,\frac{\tau}{\Gamma}\,c'_{e/g} + c_{e/g} \tag{2.50}$$

The only scale in this equation is Γ,

$$\Gamma \;\equiv\; \frac{|\Omega_R|^2}{4\alpha}. \tag{2.51}$$

Γ is known as the Landau-Zener parameter. This was solved exactly in Ref. [6] and, for example, solved approximately in Ref. [5].

As an approximate solution, this can be treated as a perturbation with $c_g(-\infty) = 1$. Note that $\frac{\Omega_R}{|\Omega_R|} = e^{i\phi}$. Then,

$$\begin{aligned} c'_{e/g} \;=&\; i\,c_{g/e}\,e^{\mp i(\phi - \frac{4\alpha}{|\Omega_R|^2}\tau^2)} \;=\; i\,c_{g/e}\,e^{\mp i(\phi - \frac{\tau^2}{\Gamma})} \\ \Longrightarrow\; c_e(\infty) =&\; c_e(-\infty) + \int_{-\infty}^{\infty} d\tau\, \left(-i\,c_g(\tau)\,e^{-i(\phi - \frac{\tau^2}{\Gamma})}\right). \end{aligned}$$

As the approximation, one can now set $c_g(\tau) \approx c_g(-\infty) = 1$, and then gets

$$\begin{aligned} c_e(\infty) \;&\approx\; -ie^{-i\phi}\sqrt{i\pi\Gamma} \\ P_e(\infty) \;&=\; |c_e(\infty)|^2 \approx \pi\Gamma \\ \Longrightarrow\; P_g(\infty) \;&\approx\; 1 - \pi\Gamma \end{aligned}$$

An educated guess for larger Γ is then

$$\begin{aligned} &P_g \approx e^{-\pi\Gamma} \\ &P_e \approx 1 - e^{-\pi\Gamma}. \end{aligned} \tag{2.52}$$

Note that in this case, Γ is no longer small. The numerical plot of P_e is seen in Fig. 2.32. If the sweep is fast, meaning small Γ, then there is no transition. On the other hand, if the sweep is slow, meaning large Γ, then there is a transition. Recall the adiabaticity condition:

$$|\dot{\delta}| = |\alpha| \ll |\Omega_R|^2,$$

where

$$\alpha = \frac{|\Omega_R|^2}{4\Gamma}. \tag{2.53}$$

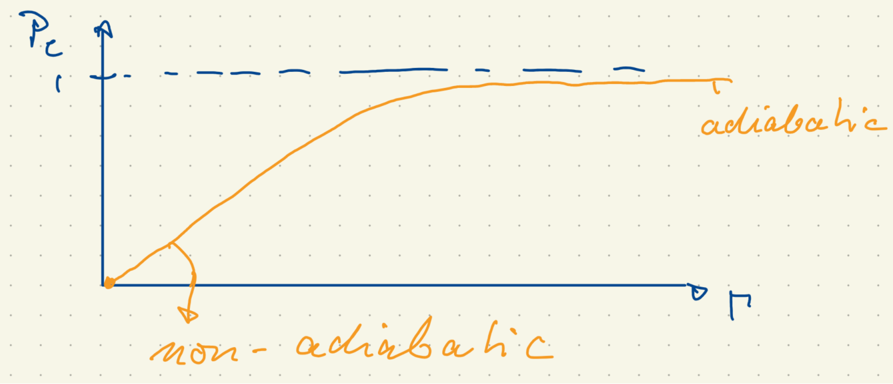


Figure 2.32: Plot of Eq. (2.52). The probability of excited state occupation increases with Γ.

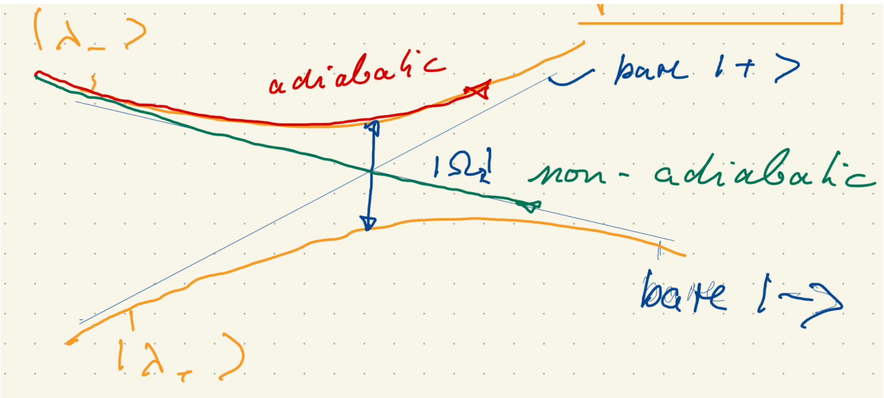


Figure 2.33: Schematic plot of Landau-Zener crossing.

This means that $\Gamma \gg 1$ is equivalent to the stated adiabaticity condition from before. If the system is changed adiabatically, the current state moves along the dressed state. But if the system is changed non-adiabatically, the state moves along the bare state. This is seen in Fig. 2.33. This is known as the Landau-Zener crossing, in which the state stays along the eigenstate for an adiabatic change, but crosses to another state with a non-adiabatic change.

NB: "Bare states" are eigenstates of H_0, whereas "dressed states" are eigenstates of $H = H_0 + V$.

Chapter 3

Open Systems & Density Matrix Formalism

All problems can, in principle, be solved using wave functions and the Schrödinger Equation (as long as we are non-relativistic). But taking into account *all* degrees of freedom that might at some point or other interact with the system of interest, this can become cumbersome. As an example, imagine a two-level system that interacts (mostly very weakly) with all light modes in order to capture spontaneous emission correctly. This would mean that the wave function does not only contain the atom degrees of freedom (two, for a two-level system) but also the infinite light degrees of freedom. (Note: We will derive how to get the exact formula for spontaneous emission from coupling to infinite light modes a little later in class.) Therefore, it is useful to find a treatment that is limited to the system only, and treats the environment only as far as its effect on the system is concerned. This is what is called an "open system." Obviously, one does not want to lose accuracy. This open system calculations are done with the density matrix.

This chapter starts by introducing the density matrix in the same picture as the already well-known wave function. The next section will then divide the universe into "system" and "environment" (often also called "reservoir") and trace out the degrees of freedom that one is not really interested in. This leads to the "master equation" or "Lindblad equation."

3.1 Properties of the density matrix

What is the density matrix for a system in state $|\psi\rangle$? This gives a density operator $\rho = |\psi\rangle\langle\psi|$. Note that where $|\psi\rangle$ is a "state" in the Hilbert space (of the universt) ρ is an operator in the same space. In the same wat one can represent $|\psi\rangle$ as a vector one can represent ρ as a matrix.

In order to find the equation of motion for ρ, the Schrödinger Equation is used:

$$\begin{aligned} i\hbar|\dot{\psi}\rangle &= H|\psi\rangle \implies \\ \dot{\rho} &= |\dot{\psi}\rangle\langle\psi| + |\psi\rangle\langle\dot{\psi}| = \frac{1}{i\hbar}\left[H|\psi\rangle\langle\psi| - |\psi\rangle\langle\psi|H\right] = \frac{1}{i\hbar}[H,\rho] \end{aligned} \tag{3.1}$$

This is called the *von Neumann* equation – in the case of $\rho = |\psi\rangle\langle\psi|$ it is equivalent to the Schrödinger equation. Thus, ρ must satisfy:

1. $\rho = \rho^\dagger$
2. $\mathrm{Tr}\ \rho = 1$
3. $\rho^2 = \rho \qquad \implies \qquad \mathrm{Tr}\ \rho^2 = \mathrm{Tr}\ \rho = 1$

In the example of a two-level system, one finds that

$$|\psi\rangle = \alpha|e\rangle + \beta|g\rangle \implies \rho = \begin{pmatrix} |\alpha|^2 & \alpha^*\beta \\ \alpha\beta^* & |\beta|^2 \end{pmatrix}$$

Note that this means that the system with two parameters (α and β) now in principle has four ($\rho_{ee}, \rho_{eg}, \rho_{ge}$, and ρ_{gg}) - obviously, there is more that one can describe with ρ than with $|\psi\rangle$. Also, the non-diagonal elements (e.g., ρ_{eg}) connect the states $|e\rangle$ and $|g\rangle$ with a (complex) phase, i.e., "coherently." (Note that the basic meaning of "coherent" in physics is "able to interfere", "with a definite phase relationship.") Obviously, there are cases where this coherence gets lost (especially over time). The most obvious example for this is the density matrix for thermally distributed states: Since the population in this case is distributed via the Boltzmann distribution and because, in the thermodynamic limit there are no coherences, one would expect a density matrix of the form

$$\rho \propto \begin{pmatrix} e^{-\frac{\Delta E}{k_B T}} & 0 \\ 0 & e^{\frac{\Delta E}{k_B T}}, \end{pmatrix}$$

where ΔE denotes the energy difference between the two levels and k_B is the Boltzmann constant.

More generally, one thus may write

$$\rho = \sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| \tag{3.2}$$

for p_α the probability of being in state $|\psi_\alpha\rangle$. If there is more than one nonzero p_α, it means that the system is not in a "pure" state; thus, these types of states are called "mixed states." Note that the von-Neumann equation Eq. (3.1) is still valid in this case (as can be checked easily). In this case, the properties above generalize to

1. $\rho = \rho^\dagger$
2. $\mathrm{Tr}\ \rho \ = \ 1$
3. $\mathrm{Tr}\ \rho^2 \ \leq \ 1$, where the "$=$"-sign always denotes a pure state and the "$<$"-sign a mixed state.

This is a useful check for whether the system is in a mixed state or not. In general, the density matrix is written in terms of its coefficients:

$$\rho = \sum_{n,m} |n\rangle\langle n|\rho|m\rangle\langle m| = \sum_{n,m} \rho_{nm}|n\rangle\langle m|, \tag{3.3}$$

where $\{|n\rangle\}/\{|m\rangle\}$ denote a basis of the Hilbert space. There is a simple interpretation for the diagonal elements ρ_{nn} as the probability of being in state $|n\rangle$. As explained above, the off-diagonal terms ρ_{nm} are called "coherences."

Expectation values of operators can now be derived from their form in pure states:

$$\begin{aligned}
\left\langle \hat{O} \right\rangle \ &= \ \sum_\alpha p_\alpha \langle\psi_\alpha|\hat{O}|\psi_\alpha\rangle \ = \ \sum_\alpha p_\alpha \langle\psi_\alpha|\hat{O}\,\mathbf{1}\,|p_\alpha\rangle \ = \\
&= \ \sum_{\alpha,n} p_\alpha \langle\psi_\alpha|\hat{O}|n\rangle\langle n||\psi_\alpha\rangle \ = \ \sum_n \langle n| \underbrace{\sum_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| p_\alpha}_{\rho} \hat{O}|n\rangle \ = \\
&= \ \mathrm{Tr}\,\rho\,\hat{O}
\end{aligned}$$

3.2 Open Systems & Master Equation

The most useful part of the density matrix formalism is for open systems: Divide the universe into the parts whose properties one cares about (the "system") and those whose properties one doesn't (the "environment"). One has to be able to track the time-evolution of the system, but due to the effects of the environment on the system, one cannot ignore it in calculations.

3.2.1 System and Environment

Assume that the universe's state is $|\psi\rangle$, a pure state. The system, however, will in general be a mixed state. How can one find a way of representing just the state of the system as simply as possible? The full basis of the universe Hilbert space can be written as $\{|n, e_k\rangle\}$, where $\{|n\rangle\}$ is a basis for the system only and $\{|e_k\rangle\}$ for the environment only, i.e.,

$$|\psi\rangle \;=\; \sum_{n,k} |n, e_k\rangle\langle n, e_k|\psi\rangle.$$

For a system operator $\hat{S}$ (i.e., an operator that acts only on the system degrees of freedom) one finds

$$\begin{aligned}\left\langle \hat{S} \right\rangle &= \langle\psi|\hat{S}|\psi\rangle \;=\; \sum_{n,k}\sum_{n',k'}\langle\psi|n, e_k\rangle \underbrace{\langle n, e_k|\hat{S}|n', e'_k\rangle}_{\langle n|\hat{S}|n'\rangle\delta_{kk'}}\langle n', e'_k|\psi\rangle \;= \\ &= \sum_{n,n'}\langle n|\hat{S}|n'\rangle\langle n'| \underbrace{\sum_k \langle e_k|\psi\rangle\langle\psi|e_k\rangle}_{\mathrm{Tr}_{\mathrm{env}}\,\rho_{\mathrm{total}} \,\equiv\, \rho_{\mathrm{sys}}} |n\rangle \;=\; \mathrm{Tr}_{\mathrm{sys}}\,\rho_{\mathrm{sys}}\,\hat{S}.\end{aligned}$$

Thus, the system operator expectation value needs only knowledge of the system, or, in other words, the formula for expectation values of operators is the same for the whole universe or any subsystem. It is useful to remember the definition of the system-only density matrix:

$$\rho_{\mathrm{sys}} \;=\; \mathrm{Tr}_{\mathrm{env}}\,|\psi\rangle\langle\psi|,$$

where the trace goes over all the environmental degrees of freedom.

The equation of motion for the system can now be found by taking the von-Neumann equation Eq. (3.1) for the universe and trace it over the environment degrees of freedom:

$$\dot{\rho}_{\text{sys}} = \frac{1}{i\hbar}\left[H_{\text{sys}} + H_{\text{env}} + H_{\text{sys}-\text{env}}, \rho_{\text{sys}}\right] = \frac{1}{i\hbar}\left[H_{sys} + H_{\text{sys}-\text{env}}, \rho_{\text{sys}}\right]$$

Both density matrix and Hamiltonians are here already traced over and where $[H_{\text{env}}, \rho_{\text{sys}}] = 0$. In order to work with this further, it is useful to move into the interaction picture where

$$\begin{aligned} U_{\text{sys}} \;&=\; e^{-\frac{i}{\hbar}H_{\text{sys}}t} \\ \tilde{\rho} \equiv\; &U_{\text{sys}}\,\rho\,U^{\dagger}_{\text{sys}}, \qquad \tilde{H}_{\text{sys}-\text{env}} \;\equiv\; U_{\text{sys}}\,H_{\text{sys}-\text{int}}\,U^{\dagger}_{\text{sys}}. \end{aligned}$$

The von-Neumann equation in the interaction picture reads then

$$\dot{\tilde{\rho}}_{\text{sys}} \;=\; \frac{1}{i\hbar}\left[\tilde{H}_{\text{sys}-\text{env}}, \tilde{\rho}_{\text{sys}}\right]$$

3.2.2 Kraus operators and Lindblad form

Any system evolution (of the density operator) can be described as a linear map, i.e., a unitary transformation. Recall $\rho_{\text{sys}} = \text{Tr}_{\text{env}}\,\rho_{total}$. To simplify the following derivation, assume that at some time in the past $\rho_{\text{total}} = \rho_{\text{sys}} \otimes |e\rangle\langle e|$ (typically $t_0 = -\infty$), i.e., at some point that one can completely unentangle the system and the environment and, for simplicity, that the environment at that point is in a pure state.

The time evolution is encoded in the system-environment time evolution operator U_{SE}; the basis of the environment is (as before) $\{|e_k\rangle\}$. Thus, the system density operator (the "system" subscripts will be dropped here) at any (later) time is given by

$$\begin{aligned} \rho' \;&= \text{Tr}_{\text{env}}\left(U_{\text{SE}}\,(\rho \otimes |e\rangle\langle e|)\;U^{\dagger}_{\text{SE}}\right) \;= \\ &= \sum_k \langle e_k|U_{\text{SE}}|e\rangle\,\rho\,\langle e|U^{\dagger}_{\text{SE}}|e_k\rangle \;= \\ &= \sum_k M_k\,\rho\,M_k^{\dagger} \qquad \text{with} \\ M_k \;&\equiv \langle e_k|U_{\text{SE}}|e\rangle \end{aligned}$$

Note that, with $|e_{(k)}\rangle$ an environment-only state and $U_{\rm SE}$ a universe operator, the M_k are now system-only operators. They are called "Kraus" operators. From their definition, one can define the following two properties:

1. M_k is a system operator. Thus, there are n^2 linear independent such operators, if n is the dimension of the system Hilbert space.

2. $$\sum_k M_k^\dagger M_k \;=\; \sum_k \langle e|U_{\rm SE}^\dagger|e_k\rangle\langle e_k|U_{\rm SE}|e\rangle \;=\; \langle e|U_{\rm SE}^\dagger U_{\rm SE}|e\rangle \;=\; \mathbf{1}_S.$$

The last operator denotes the unity in the system Hilbert space. The form

$$\rho' \;=\; \sum_k M_k\,\rho\,M_k^\dagger$$

is called the "Kraus representation" of a linear map. (Please note that this is a very shortened version of the whole formalism involving measurements, POVMs, Kraus operators. The beginning assumption of decoupling system and environment is also not necessary for the Kraus representation – it just simplifies the derivation of the Kraus operator properties.)

Obviously, the time evolution from $\rho(t)$ to $\rho(t+\delta t)$ is also such a linear map and the Kraus representation can be used for it. In particular:

$$\rho(t+\delta t) \;=\; \rho(t) + \dot\rho(t)\,\delta t \;=\; \sum_k M_k\,\rho\,M_k^\dagger. \tag{3.4}$$

This means that the RHS of Eq. (3.4) has to be a combination of unity and terms that are linear in δt. Without loss of generality, one can therefore say that either

$$M_k \;=\; \mathbf{1}_S + \mathcal{O}(\delta t)$$

or

$$M_k \;=\; \mathcal{O}(\sqrt{\delta t}).$$

Thus one can define:

$$\begin{aligned} M_0 &= \mathbf{1}_S + (K+iH)\delta t, \\ M_k &= L_k\sqrt{\delta t} \quad \text{for} \quad k \neq 0. \end{aligned}$$

In order for $K+iH$ to be the most general (system) operator, both K and H are Hermitian. This form can now be plugged into Eq. (3.4) and gives DW: Perhaps note that $\mathcal{O}(\delta t^2)$ terms are dropped?

$$\begin{aligned}\sum_k M_k\,\rho\,M_k^\dagger &= (1+(K+iH)\delta t)\rho(1+(K-iH)\delta t)) + \sum_{k\neq 0} L_k\rho L_k^\dagger \delta t \\ &= \rho(t) + \left[(K\rho+\rho K) + i\,[H,\rho] + \sum_{k\neq 0} L_k\rho L_k^\dagger\right]\delta t = \rho(t)+\dot\rho(t)\delta t \qquad (3.5)\end{aligned}$$

The quantity in square brackets is therefore the time derivative $\dot\rho(t)$.

Before continuing with the discussion of time evolution, one should verify that the properties of M_k are still valid:

$$\sum_k M_k^\dagger M_k \;=\; 1+(K+iH)+(K-iH)+\sum_{k\neq 0} L_k^\dagger L_k \;\overset{!}{=}\; 1$$

and thus Change + to a subscript

$$K \;=\; -\frac{1}{2}\sum_{k\neq 0} L+k^\dagger L_k.$$

Putting this together with Eq. (3.5), the full equation of motion reads

$$\dot\rho \;=\; i[H,\rho] + \frac{1}{2}\sum_{k\neq 0}(2L_k\rho L_k^\dagger - L_k^\dagger L_k\rho - \rho L_k^\dagger L_k) \qquad (3.6)$$

Comparing this equation with the correct dimensions and the von Neumann equation, one finds that the H in the equation above has to be replaced by $-H/\hbar$ for the Hamiltonian and that the L_k operators have to have a dimension of $1/\sqrt{\text{second}}$. With this, the full Master Equation becomes

$$\dot\rho \;=\; \frac{1}{i\hbar}\,[H,\rho] + \mathcal{L}[\rho], \qquad (3.7)$$

where

$$\mathcal{L}[\rho] \;\equiv\; \frac{1}{2}\sum_k \left(2L_k\,\rho\,L_k^\dagger - L_k^\dagger L_k\,\rho - \rho\,L_k^\dagger L_k\right)$$

for any set of system operators L_k with the correct dimension. This is the most general way to write out the time dependence for a density matrix.

3.2.3 Two-level master equation

As an example, one can try this out for a two-level system:

The possible system operators in this context are the Pauli matrices (or any combination of them). There are three, σ_z, σ_+, and σ_- (or, alternatively, σ_z, σ_x, and σ_y) – the fourth would be the unit operator which can be easily verified to give a zero contribution. The $\sigma_\pm$ terms are, in this context, also known as "jump operators."

σ_-: Here, $L_k = \sqrt{\gamma}\,|g\rangle\langle e|$, with some rate (i.e., quantity with dimension 1/second) γ. Thus one gets

$$2L_k\,\rho\,L_k^\dagger - L_k^\dagger L_k\,\rho - \rho\,L_k^\dagger L_k \;=\; 2|g\rangle\langle e|\rho|e\rangle\langle g| - |e\rangle\langle e|\rho - \rho|e\rangle\langle e|.$$

Thus, one can find

$$\dot{\rho}_{ee}\big|_\gamma \;=\; \frac{\gamma}{2}\langle e|\big(2|g\rangle\langle e|\rho|e\rangle\langle g| - |e\rangle\langle e|\rho - \rho|e\rangle\langle e|\big)|e\rangle \;=\; -\gamma\,\rho_{ee}$$

and similar for the other elements of ρ. With that,

$$\begin{aligned} \dot{\rho}_{ee}\big|_\gamma &= -\,\gamma\,\rho_{ee} \\ \dot{\rho}_{gg}\big|_\gamma &= +\,\gamma\,\rho_{ee} \\ \dot{\rho}_{eg}\big|_\gamma &= -\,\frac{\gamma}{2}\,\rho_{eg} \\ \dot{\rho}_{ge}\big|_\gamma &= -\,\frac{\gamma}{2}\,\rho_{ge}. \end{aligned}$$

Looking at the terms, one sees immediately that this describes the usual spontaneous emission term with decay rate γ (see Fig. 3.1a).

σ_+: Similarly, here, $L_k = \sqrt{\bar{\gamma}}\,|r\rangle\langle g|$, with some rate $\bar{\gamma}$. This leads to

$$\begin{aligned} \dot{\rho}_{ee}\big|_{\bar{\gamma}} &= +\,\gamma\,\rho_{gg} \\ \dot{\rho}_{gg}\big|_{\bar{\gamma}} &= -\,\gamma\,\rho_{gg} \\ \dot{\rho}_{eg}\big|_{\bar{\gamma}} &= -\,\frac{\bar{\gamma}}{2}\,\rho_{eg} \\ \dot{\rho}_{ge}\big|_{\bar{\gamma}} &= -\,\frac{\bar{\gamma}}{2}\,\rho_{ge}, \end{aligned}$$

i.e., exactly the opposite of the above decay term. This would be a "pump" (see Fig. 3.1b).

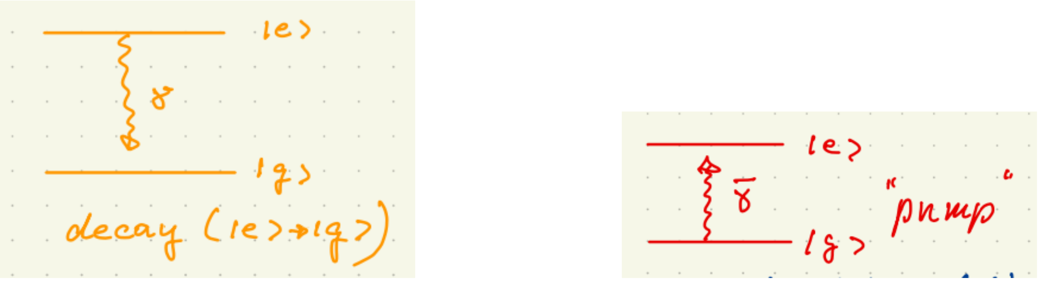


Figure 3.1: The effect of the σ_- (a) and σ_+ jump operators as decay and pump.

Note: without any extra pump, the two terms above with the effect of temperature would be

$$\begin{aligned} \gamma &\rightarrow (\bar{n}+1)\Gamma_0 \\ \bar{\gamma} &\rightarrow \bar{n}\Gamma_0, \end{aligned}$$

where $\bar{n}$ is the number of thermal photons (as determined by the Bose-Einstein or Boltzmann distribution).

σ_z: $L_k = \sqrt{\gamma_{\text{deph}}}\,(|e\rangle\langle e| - |g\rangle\langle g|)$ and thus

$$\begin{aligned} \dot{\rho}_{ee}\big|_{\gamma_{\text{deph}}} &= 0 \\ \dot{\rho}_{gg}\big|_{\gamma_{\text{deph}}} &= 0 \\ \dot{\rho}_{eg}\big|_{\gamma_{\text{deph}}} &= -\,\gamma_{\text{deph}}\,\rho_{eg} \\ \dot{\rho}_{ge}\big|_{\gamma_{\text{deph}}} &= -\,\gamma_{\text{deph}}\,\rho_{ge}. \end{aligned}$$

This type of decay is known as "dephasing": It does not affect the energy of the system, just the phase/coherence!

Literature for the derivation of the master equation with Kraus operators can be found by going to John Preskill's website and looking at chapter 3 of his "quantum information" lectore notes.

The full master equation or "Optical Bloch equations" for a two-level system, with

$$\frac{H}{\hbar} = -\delta|e\rangle\langle e| - \frac{\Omega_R}{2}|e\rangle\langle g| - \frac{\Omega_R^*}{2}|g\rangle\langle e|,$$

which gives

$$-i\left[\frac{H}{\hbar},\,\rho\right] \;=\; i\delta\,[|e\rangle\langle e|,\,\rho] + i\frac{\Omega_r}{2}\,[|e\rangle\langle g|,\,\rho] + i\frac{\Omega_R^*}{2}\,[|g\rangle\langle e|,\,\rho]$$

and thus

$$\begin{aligned}
\dot\rho_{ee} &= -\,\gamma\,\rho_{ee} + \frac{i}{2}\,(\Omega_R\,\rho_{ge} - \Omega_R^*\,\rho_{eg}) \qquad (3.8)\\
\dot\rho_{gg} &= -\,\dot\rho_{ee}, \qquad \text{or better } \rho_{ee}+\rho_{gg} \;=\; 1\\
\dot\rho_{eg} &= -\left(\frac{\gamma}{2}+\gamma_{\text{deph}}-i\delta\right)\,\rho_{eg} - \frac{i}{2}\Omega_R(\rho_{ee}-\rho_{gg})\\
\dot\rho_{ge} &= -\left(\frac{\gamma}{2}+\gamma_{\text{deph}}+i\delta\right)\,\rho_{eg} + \frac{i}{2}\Omega_R^*(\rho_{ee}-\rho_{gg})
\end{aligned}$$

3.3 Optical Bloch equations

As it should be, the form of the master equation in the last section is equivalent to the Bloch equations if one adds decay. The Bloch equations are the same as in Section 2.7. In that section, the equations were described in polar coordinates. Transforming back into cartesian coordinates gives the Bloch equations in their "original" form. Decays have been originally [1] added by hand. The equations then read

$$\begin{aligned}
\frac{\partial}{\partial t}\langle\sigma_x\rangle &= \delta\,\langle\sigma_y\rangle - \frac{\langle\sigma_x\rangle}{T_2}\\
\frac{\partial}{\partial t}\langle\sigma_y\rangle &= -\,\delta\,\langle\sigma_x\rangle - \frac{\langle\sigma_y\rangle}{T_2} - \Omega_R\,\langle\sigma_z\rangle\\
\frac{\partial}{\partial t}\langle\sigma_z\rangle &= -\,\frac{\langle\sigma_z\rangle - \langle\sigma_z^{\text{eq}}\rangle}{T_1} + \Omega_R\,\langle\sigma_y\rangle\,.
\end{aligned}$$

Here, $\langle\sigma_z^{\text{eq}}\rangle$ denotes the equilibrium population distribution. If one then compares the decay times T_1 and T_2 with the master equation terms, one finds that

$$T_1^{-1} \;=\; \gamma \qquad \text{and} \qquad T_2^{-1} \;=\; \gamma_{\text{deph}} + \frac{\gamma}{2}.$$

Nowadays, when people talk about "optical Bloch equations," they usually refer to the master equation system Eq. (3.8).

3.4 Saturation (Example of optical Bloch equations)

The equation system (3.8) can now easily be solved in the steady state, i.e., by setting all time derivatives equal to zero, $dot\rho_{ij} \ = \ 0$. With $\gamma_{\mathrm{deph}} = 0$, this leads to

$$\rho_{ee} \ = \ \frac{|\Omega_R|^2}{4} \frac{1}{\delta^2 + \left(\frac{\gamma}{2}\right)^2 + \frac{1}{2}|\Omega_R|^2}.$$

The rate of the scattered light/fluorescence is then $\gamma_{\mathrm{scatt}} \ = \ \gamma\rho_{ee}$. The following limiting cases exist:

low intensity: $|\Omega_R| \ll \gamma$

$$\rho_{ee} \ \approx \ \frac{|\Omega_R|^2}{4} \frac{1}{\delta^2 + \left(\frac{\gamma}{2}\right)^2} \ \leq \ \left|\frac{\Omega_r}{\gamma}\right|^2.$$

This confirms the earlier result obtained in the "low excitation" limit and the Lorentzian line shape of the fluorescent radiation.

high intensity: $|\Omega_R| \gg \gamma$

$$\rho_{ee} \ \approx \ \frac{1}{2} \frac{1}{1 + 2\frac{\delta^2}{|\Omega_R|^2}} \ \overset{\delta=0}{\rightarrow} \ \frac{1}{2}.$$

In this limit, the transition is "saturated." The "saturation parameter" is thus $s \ = \ \frac{|\Omega_R|^2}{\gamma^2}$.

This seemingly contradicts the solution of Rabi oscillations obtained earlier for the same limit. Note, however, that the Rabi oscillations are the (time-dependent) solution for strong driving. Here, the solution reflects the infinite time limit where the Rabi oscillations have died down. The exact dynamics in this case looks like the curve in Fig. 3.2.

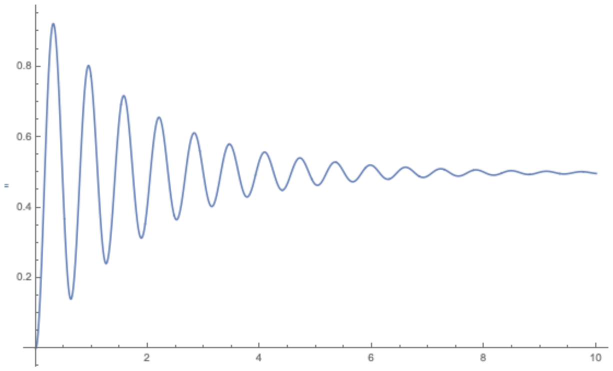


Figure 3.2: The time evolution of a two-level system with strong driving field. The excited state population (or relative scattering rate) is on the y-axis, time on the x-axis.

Chapter 4

Atoms

In this chapter, the assumption that there are only two levels which are coupled by a non-zero dipole moment is dropped and the exact level structures of one-electron atoms (and approximate for many-electron atoms) are derived, first non-relativistically and then relativistically.

4.1 Spectroscopic notation

Please note that this is somewhat out of order: The notation for atoms is introduced in this section before the explanation where the terms actually comes from. (This makes sense given that most people at this point have seen some treatment of the Bohr atom.) Thus, this section introduces some nomenclature.

What are the elements that will play a role in this chapter?

- Atoms are assumed to consist of a **nucleus** with charge Ze, which is surrounded by Z electrons with charge $-e$. The nucleus is assumed to be much heavier than the electrons. In addition, the derivations in this chapter are also valid for positive ions (i.e., the same model but less than Z electrons) if one introduces an additional scaling factor for the stronger effective Coulomb force. It does not work equally well for negative ions (i.e., more than Z eletrons) since even in the best of cases, additional electrons are bound only very weakly.

- Quantum numbers are unique identifiers for the particular states an electron can be in. For the Bohr atoms, the ones that are normally used are

  - the *principal* quantum number n, denoting the shell
  - the *orbital* quantum number ℓ, denoting the orbital angular momentum.
  - the *magnetic* quantum number m giving the projection of the angular momentum onto the main quantization axis (which can be an external magnetic field, hence the name).
  - the spin quantum number s.
  - Capital letters (L and S) denote the combined orbital and spin numbers for several atoms, and J is the combination of L and S.
  - the *nuclear* quantum number, which gives the spin of the nucleus.

- Atoms a designated in one of two ways: the one is the “**term**,” which is written as

  $$(n)^{2S+1}L_J,$$

  where S and J are written in their numerical form, whereas L is given by

  $$L \;=\; \begin{array}{cccccc} 0 & 1 & 2 & 3 & 4 & \ldots \\ \text{“P}'' & \text{“P}'' & \text{“D}'' & \text{“F}'' & \text{“G}'' & \end{array},$$

  where the letters (historically) were denoted for the appearance of the spectral lines of one-electron atoms: “sharp”,“principal”,“diffuse”,“fundamental”. (The higher orbitals are just named alphabetically from there.) The leading shell number n is given in parentheses because it is often left out. An example for a term would be $3^2S_{1/2}$, which means that the active electron is in the third shell ($n = 3$), has $S = 1/2$, $L = 0$, and $J = 1/2$.

- The other designation is the “**configuration**.” This consists just of the product of symbols $n\ell^k$ for k electrons in the $n\ell$ orbit, e.g., excited calcium would read $(1s^2 2s^2 2p^6 3s^2 3p^6 4s)3d$, which means two electrons in the $1s$ orbital, two in the $2s$, six in the $2p$, two in the $3s$, six in the $3p$, one in the $4s$ and one in the $3d$. Often, again, only the outer shell electrons are mentioned and the rest left out.

  Note that one configuration can result in several terms: as an example, the above calcium configuration could result in the terms ${}^1D_2$, ${}^3D_2$, or one of the ${}^3D_{1,2,3}$. This means that the two unpaired electrons could be either parallel ($S = 1$) or anti-parallel ($S = 0$), the total orbital angular momentum of those unpaired electrons is $L = 0 + 2 = 2$, and, in the case of $S = 1$, the L and S could add up to 1, 2, or 3.

- **Selection rules** denote the allowed ΔJ, ΔL and ΔS for any transition. ("Allowed" means typically a transition that coupled to an electric dipole moment.)

Note that the configuration often is not pure: if two configurations give the same term, often intera-atom electrostatic interaction mixes them. This is known as "configuration interaction" and results in level shits and line intensity changes.

4.2 The Bohr atom

The simplest atom (with one nucleus and one electron) in the non-relativistic approximation results from the Schrödinger equation for a Coulomb potential.

$$\frac{\hbar^2}{2\mu}\,\vec{\nabla}^2\psi - \frac{e^2}{4\pi\epsilon_0\,r}\,\psi \;=\; E\,\psi, \tag{4.1}$$

where the reduced mass is defined from the electron and nuclear masses

$$\mu \;=\; \frac{m_e\,m_{\rm nucl}}{m_e + m_{\rm nucl}} \;\leq\; m_e$$

Since this is obviously a system with spherical symmetry, one can easiest choose polar coordinates. As a reminder, the derivative operator then reads

$$\begin{aligned}
\vec{\nabla}^2 &= \frac{1}{r^2}\,\partial_r\,r^2\,\partial_r - \frac{1}{r^2}\,\hat{\vec{L}}^2 && \text{with}\\
\hat{\vec{L}}^2 &= -\,\frac{1}{\sin\theta}\,\partial_\theta\,\sin\theta\,\partial_\theta - \frac{1}{\sin^2\theta}\,\partial_\phi^2 && \text{and thus}\\
\hat{L}_\pm &= e^{\pm i\phi}\,(\pm\partial_\theta + i\,\cos\theta\,\partial_\phi) && \text{and}\\
\hat{L}_z &= -\,i\,\partial_\phi.
\end{aligned}$$

In order to solve this equation, separation of variables can be done. The first step is

$$\psi(r,\theta,\phi) = R(r);Y(\theta,\phi) \tag{4.2}$$

Plugging into Eq. (4.1), one gets:

$$\frac{1}{R}\partial_r r^2 \partial_r R - \frac{2\mu}{\hbar^2} r^2 (V-E) \;=\; \lambda \tag{4.3}$$

$$\hat{\vec{L}}^2 Y \;=\; \lambda Y \tag{4.4}$$

To work out the angular part, one can perform another separation of variables:

$$Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi) \tag{4.5}$$

which leads to:

$$\frac{\sin\theta}{\Theta}\partial_\theta \sin\theta \partial_\theta \Theta + \lambda \sin^2\theta \;=\; m^2 \tag{4.6}$$

$$\partial_\phi^2 \Phi = -m^2 \Phi, \tag{4.7}$$

where equation 4.7 could be easily solved with the periodic boundary condition $\Phi(\phi) \;=\; \Phi(\phi+2\pi)$:

$$\Phi = Ae^{im\phi} + Be^{-im\phi}, \qquad m \in \mathbb{Z}$$

Note that the m here is the *magnetic quantum number* that was mentioned in Sec. 4.1, since $\hat{L}_z\Phi = \hbar m \Phi$. With the commutator relations

$$[\hat{\vec{L}}^2, \hat{L}_z] \;=\; [\hat{\vec{L}}^2, \hat{L}_\pm] \;=\; 0$$

the states Y, $\hat{L}_z Y$, and $\hat{L}_\pm Y$ are eigenfunctions of $\hat{\vec{L}}^2$ with the same eigenvalue. In addition, since $\hat{L}_\pm \propto e^{\pm i\phi}$, it acts as a raising/lowering operator.

Another constraint is that m has to have a maximum:

$$m_{\max} \;\equiv\; \ell.$$

This is stated without proof here, but one can relate this to the harmonic oscillator cutoff condition. Eq. (4.4) is thus equivalent to

$$\hat{L}_+ Y_\ell \;=\; 0,$$

and subsequently solve for smaller m. This gives $Y \;=\; Y_{\ell m}(\theta,\phi)$ which are the spherical harmonics. Plugging into Eq. (4.4), yields:

$$\lambda = \ell(\ell+1)$$

ℓ is called the *orbital quantum number*. Because of the symmetry of the problem a similar argument can be made about $m_{\min} = -\ell$. One final remark for the angular wave function is that $|Y_{00}(\theta,\phi)|$ is a constant function, corresponding to a spherical orbit.

Next, move to the radial wave function where one starts with the substitutions:

$$\begin{aligned} P(r) &= rR(r) \\ \rho^2 &= \frac{2\mu|E|}{\hbar^2} r^2 \\ b &= \frac{e}{4\pi\epsilon_0}\sqrt{\frac{2\mu}{\hbar^2|E|}} \end{aligned}$$

leading to a radial function that is simpler in form :

$$\partial_\rho^2 P(\rho) - [\frac{\ell(\ell+1)}{\rho^2} - \frac{b}{\rho} \pm 1]\, P(\rho) = 0 \tag{4.8}$$

(The "+" sign is for negative E, i.e., bound states, the "-" for $E > 0$.) This gives a (dimensionless) 1D Schrödinger equation with an effective potential

$$V_{eff} = \frac{\ell(\ell+1)}{\rho^2} - \frac{b}{\rho}.$$

In Fig. 4.1 are two plots of the effective potential with $\ell = 0$ and $\ell = 1$. For $\ell = 0$ the potential goes to $-\infty$ at $r = 0$, indicating that the electron probability density is large near the center; for $\ell > 0$, the potential goes to infinity at $r = 0$, indicating that the electron probability density is 0 at the center. It is also easy to see that for both cases, there exist bound states.

Solving Eq. (4.8) is done using a series ansatz; thus one finds that b has to be an even integer for the solution not to diverge. Writing $b = 2n, n \in \mathbb{Z}$, one obtains an expression for the energy E:

$$E = -\frac{\mu(\frac{e^2}{4\pi\epsilon_0})^2}{2\hbar^2 n^2} \equiv -\frac{\mathrm{Ry}}{n^2} \tag{4.9}$$

Note that E only depends on n (for this reason, n is called the *principal quantum number*). For atom with Z protons (nuclei charge $= eZ$) but only

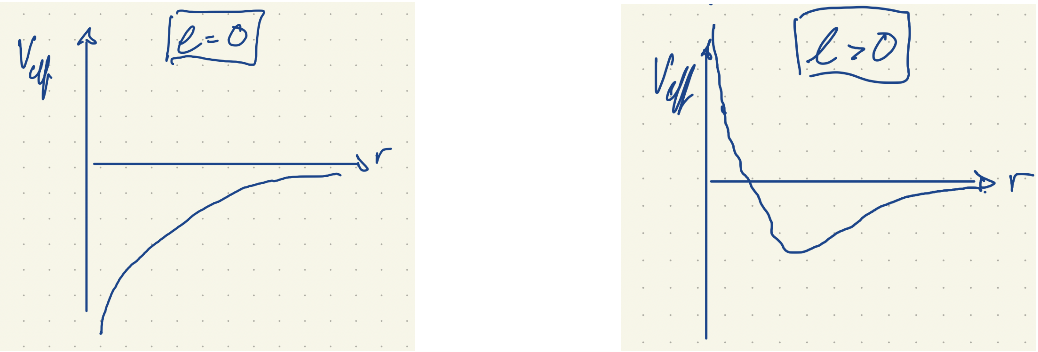


Figure 4.1: The effective potential of the radial equation for $\ell = 0$ suggests the main density of the electron at the origin ($r = 0$) while the potential barrier for $\ell > 0$ gives a density of zero at the origin.

one electron, one scales the energy by an extra factor of Z^2:

$$E_Z = -Z^2 \frac{\mathrm{Ry}}{n^2} \tag{4.10}$$

The final solution of the radial wave function for bound states is

$$\begin{gathered} R(\rho) \;\propto\; \rho^{n+1} e^{-\frac{\rho}{2}} L_{n-\ell-1}(\rho), \text{ with} \\ \int_0^\infty |R(r)|^2 r^2 dr = 1 \end{gathered}$$

where $L_i(\rho)$ is the Laguerre polynomial and the second line is the normalization.

The degeneracy for a given energy E comes from three sources:

1. l has n values (0, 1, ... n-1)
2. m has $2\ell + 1$ values ($-\ell$, $-\ell + 1$,... ℓ)
3. spin has 2 values (this is not included in the Schrödinger equation)

Therefore, each n has $2\sum_{\ell=0}^{n-1}(2\ell+1) = 2n^2$ degenerate wave functions. Note that the degeneracies in points 2 and 3 would be lifted by relativistic effects (Dirac equation), while the ℓ-degeneracy can only be lifted by including the vacuum fluctuations (the famous Lamb shift).

Remark: for $E > 0$, there would be a continuum of unbounded states, and there is no limit on b.

Finally some general properties of the wave function:

1. for fixed ℓ, small r, wave functions are independent of n except for a general scaling $n^{-3/2}$
2. for fixed n, changing ℓ only affects the wavefunction in short range (small r). For large r, the effect of potential barrier is negligible.
3. the size of the atom is $\langle r\rangle = \frac{1}{2}[3n^2 - \ell(\ell+1)]a$ with Bohr radius a, which leads to the n^2 scaling for the sizes of Rydberg atoms (atoms with high n).

4.3 Angular momentum

In both classical mechanics and quantum mechanics, we have:

$$\vec{J} = \vec{r} \times \vec{p}.$$

Only for quantum mechanics, the commutation relations (of $\vec{r}$ and $\vec{p}$ or, equivalently, of the angular momentum elements) lead to

$$\vec{J} \times \vec{J} = i\hbar\vec{J}. \tag{4.11}$$

This is equivalent to their eigenvalue solutions

$$\begin{cases} J^2|j, m_j\rangle = \hbar^2 j(j+1)|j, m_j\rangle \\ J_z|j, m_j\rangle = \hbar m_j|j, m_j\rangle \end{cases}$$

One can define raising and lowering operators ($J_\pm = J_x \pm iJ_y$) such that:

$$J_\pm|j, m_j\rangle = \hbar\sqrt{(j \mp m)(j \pm m + 1)}|j, m_j \pm 1\rangle$$

4.3.1 Angular momentum addition

Angular momentum can be added to give a total angular momentum – this might be, for example, angular momenta from several electrons or the combination of orbital and spin angular momenta.

$$\vec{J} \;=\; \vec{J}_1 + \vec{J}_2 \tag{4.12}$$

with commutation relations

$$\begin{aligned}[J^2, J_{1/2}^2] &= 0 \\ [\vec{J}, J_{1/2}^2] &= 0 \\ [J^2, \vec{J}_{1/2}] &\neq 0\end{aligned}$$

The last relation can be seen by writing $J^2 = J_1^2 + J_2^2 + 2\vec{J}_1 \cdot \vec{J}_2$. There are two sets of eigen-basis for the coupled angular momentum operators which are mutually exclusive:

1. the "uncoupled representation": $|j_1, m_1, j_2, m_2\rangle$. These are good quantum numbers in that they fully describe the system, but they are not eigenstates of J^2.
2. the "coupled representation": $|j, m, j_1, j_2\rangle$. These are also good quantum numbers, and they are eigenstates of J^2, J_z, J_1^2, J_2^2, but not for J_{1z} and J_{2z}.

Both representations are convenient in some scenarios and inconvenient in others, so the transformation between them is needed:

$$\begin{aligned}|j, m, j_1, j_2\rangle &= \sum_{m_1, m_2} |j_1, m_1, j_2, m_2\rangle \underbrace{\langle j_1, m_1, j_2, m_2 | j, m, j_1, j_2\rangle} \\ |j_1, m_1, j_2, m_2\rangle &= \sum_{j,m} |j, m, j_1, j_2\rangle \underbrace{\langle j, m, j_1, m_2 | j_1, m_1, j_2, j_2\rangle}\end{aligned}$$

where the expressions in the underbrace are the *Clebsch-Gordan coefficients.* The possible values of those coefficients are limited by the fact that they are only nonzero when $m_1 + m_2 = m$ and $|j_1 - j_2| \leq j \leq |j_1 + j_2|$ (conservation of angular momentum, which follows from Eq. (4.12)). Note that the dimension of the Hilbert space works out nicely, as

$$\sum_{j=|j_1-j_2|}^{|j_1+j_2|} (2j+1) = (2j_1+1)(2j_2+1)$$

4.4 Spin Orbit Coupling

Until this point, the spin of the atom has not been considered. Assuming now that the atom has spin $\vec{S}$, the atom's spin will unavoidably interact with its orbital angular momentum $\vec{L}$ because both operators are magnetic moments. The interaction will take on the general form:

$$H_{LS} = V_{LS}(r)\,\vec{L}\cdot\vec{S} \tag{4.13}$$

The full Hamiltonion $H + H_0 + H_{LS}$ does not commute with $\vec{L}$ or $\vec{S}$ individually, but it *does* commute with the total angular momentum operator $\vec{J}$:

$$\vec{J} = \vec{L} + \vec{S} \tag{4.14}$$

Using this definition, the expectation value of the $\vec{L}\cdot\vec{S}$ can be computed from the quantum numbers of $\vec{J}$, $\vec{L}$, and $\vec{S}$.

$$\begin{aligned}\langle\vec{L}\cdot\vec{S}\rangle &= \frac{1}{2}\langle\vec{J}^2 - \vec{L}^2 - \vec{S}^2\rangle \\ &= \frac{\hbar^2}{2}\Big(j(j+1) - l(l+1) - s(s+1)\Big)\end{aligned} \tag{4.15}$$

For the case of a single (spin-1/2) electron, there are only two possible values.

$$\langle\vec{L}\cdot\vec{S}\rangle = \frac{\hbar^2}{2}\begin{cases} l & \text{for } j = l + \frac{1}{2} \\ -(l+1) & \text{for } j = l - \frac{1}{2}\end{cases} \tag{4.16}$$

4.5 The Quantum Defect

For atoms with one outer-shell electron (e.g., the alkalis), it is a good approximation to use the Hydrogen potential: outside of the inner shells, the potential seen by the electron is the same as the Hydrogen (point-like) Coulomb potential. However, because the Hydrogenic wavefunctions have a finite probability density inside the inner shell of these atoms, the short range potential (for small r) will change.

$$V_{tot} = V_{Coulomb,H} + V_{sr} \tag{4.17}$$

Here, the subscript sr stands for "short range." In order for the short range potential to remain local to small r, it must decay faster than the Coulomb potential:

$$\lim_{r\to\infty} V_{sc}(r)\,r^2 = 0 \tag{4.18}$$

The energy eigenvalues E_n of this modified potential will follow the same rules ($E_n \propto n^{-2}$); however, n will differ. In fact, n will no longer be an integer, and its exact deviation must be measured experimentally.

$$E_n = -\frac{Z^2\text{Ry}}{(n-\delta_\ell)^2} \tag{4.19}$$

The deviation δ_l is known as the **quantum defect**. As suggested by the subscript, the quantum defect will not only depend on n, but also on the orbital angular momentum ℓ. In general, the quantum defect will be larger for atoms with larger atomic numbers and smaller for larger values of ℓ. The first trend follows from the increasing size of the short range potential; the second trend follows from the fact that Hydrogenic wavefunctions of large l tend to have smaller overlap with the inner shell.

	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	...
$n = 2$, Li	0.4	0.04	0	0	
$n = 3$, Na	1.35	0.85	0.01	0	
$n = 4$, K	2.19	1.71	0.25	0	
$n = 5$, Rb	3.13	2.66	1.34	0.01	
$n = 6$, Cs	4.06	3.58	2.46	0.02	
...					

4.6 The Dirac equation

The Schrödinger equation does not give the full picture – it is not Lorentz-invariant, and therefore, it cannot be correct. Consider the (relativistic) energy of a free particle:

$$E^2 = m^2c^4 + p^2c^2. \tag{4.20}$$

(Note that in order to account for external electric and magnetic fields, one should replace $E \to E - q\phi$, $\vec{p} \to \vec{p} - q\vec{A}$, where ϕ is the electric potential and $\vec{A}$ is the magnetic vector potential.) Making replacements $E \to i\hbar\partial_t$, $\vec{p} \to -i\hbar\vec{\nabla}$, one arrives at the **Klein-Gordon equation**:

$$\left(\frac{1}{c^2}\partial_t^2 - \nabla^2\right)\phi + \frac{m^2c^2}{\hbar^2}\phi = 0 \tag{4.21}$$

A positive aspect of this equation is that it yields the familiar plane wave solutions one would expect. However, one would also expect the solutions be normalized to a constant that does not change in time:

$$\frac{d}{dt}\int \phi^{*}\phi \, d^{3}x = \int \left(\dot{\phi}^{*}\phi + \phi^{*}\dot{\phi}\right) d^{3}x \;=\; 0$$

The solutions of the Klein-Gordon equation do *not* necessarily obey this, because it is a second-order differential equation and therefore requires initial conditions for both ϕ and $\dot{\phi}$, leading to the possibility of non-conservation in the above equation. (It turns out, however, that the Klein-Gordon equation is the correct description for spin-0 particles.)

In an effort to find an equation linear in E (and thus first-order in the time derivative), Dirac decided to take the "square root" of the Klein-Gordon equation, creating his famous **Dirac equation**. There are of course positive and negative solutions when taking the square root of something. For the case of the Dirac equation, this led to two **spinors**.

$$H = c\vec{\alpha} \cdot \vec{p} + \beta mc^{2} + V(r) \tag{4.22}$$

What about $\vec{\alpha}$ and β? When the Hamiltonian above is used in the time-independent Schrödinger equation ($H|\psi\rangle = E|\psi\rangle$) and enforce $E^{2} = m^{2}c^{4} + p^{2}c^{2}$, several constraints appear for $\vec{\alpha}$ and β:

$$\begin{aligned} \alpha_i\alpha_j + \alpha_j\alpha_i &= 2\delta_{ij}\mathbb{1} \\ \alpha_i\beta + \beta\alpha_i &= 0 \\ \beta^{2} &= \mathbb{1} \end{aligned} \tag{4.23}$$

Choosing the simplest representation:

$$\begin{aligned} \vec{\alpha} &= \begin{bmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{bmatrix} \\ \beta &= \begin{bmatrix} \mathbb{1}_{2x2} & 0 \\ 0 & \mathbb{1}_{2x2} \end{bmatrix} \end{aligned} \tag{4.24}$$

Note that it is possible to write the Dirac equation in a *Lorentz-invariant* form, renaming $\alpha_i \equiv \gamma_i$, $\beta \equiv \gamma_0$, in which case the form of the Dirac equation is simply:

$$i\hbar\gamma^{\mu}\partial_{\mu}\Psi - mc\Psi = 0 \tag{4.25}$$

The constraints on $\vec{\alpha}$ and β require at least four degrees of freedom to be solved. Solutions will therefore be four-vectors:

$$\Psi = \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{bmatrix} = \begin{bmatrix} \vec{\Psi}_+ \\ \vec{\Psi}_- \end{bmatrix} \tag{4.26}$$

The objects $\vec{\Psi}_\pm$ are the 2D **spinors** alluded to previously. In terms of spinors, the Dirac equation is given by two coupled equations:

$$\begin{aligned} \big(\vec{\sigma} \cdot \vec{p}\big)\vec{\Psi}_+ &= \frac{1}{c}\big(E + mc^2 - V(r)\big)\vec{\Psi}_- \\ \big(\vec{\sigma} \cdot \vec{p}\big)\vec{\Psi}_- &= \frac{1}{c}\big(E - mc^2 - V(r)\big)\vec{\Psi}_+ \end{aligned}$$

In the non-relativistic limit, notice that the difference $E - mc^2$ appearing in the second equation above will be very small (if it is assumed that $E > 0$).

$$\begin{aligned} E > 0: \quad & |E + mc^2 - V(r)| \gg |E - mc^2 - V(r)| \\ & |\vec{\Psi}_-| = \frac{c\langle \vec{\sigma} \cdot \vec{p} \rangle}{E - mc^s - V(r)} |\vec{\Psi}_+| \end{aligned} \tag{4.27}$$

For the non-relativistic limit, $|\vec{\sigma} \cdot \vec{p}| \approx mv$ and $E - mc^2 - V \approx \frac{1}{2}mv^2$. Making these substitutions:

$$\frac{|\vec{\Psi}_+|}{|\vec{\Psi}_-|} \approx \frac{2c}{v} \gg 1 \tag{4.28}$$

So, for $E > 0$, $|\vec{\Psi}_+| \gg |\vec{\Psi}_-|$. For the case of $E < 0$, the opposite will be true. This is the meaning behind the ± subscripts: for positive energy, the "positive energy" solution $\vec{\Psi}_+$ is most significant; for negative energy, the "negative energy" solution $\vec{\Psi}_-$ is most significant.

The interpretation of these negative-energy solutions (that don't exist in the Schrödinger atom) is the so-called *electron sea* - the vacuum consists of a "sea" of electrons that fill all energy levels up to $E = 0$; the solutions $\vec{\Psi}_-$ then describe holes in this sea – these are then the positrons.

4.6.1 Non-relativistic limit of the Dirac equation: Relativistic corrections

Since in the non-relativistic limit only the $\vec{\Psi}_+$ solutions are important we eliminate $\vec{\Psi}_-$ in Eq. (4.27) and arrive at

$$\big(\vec{\sigma}\cdot\vec{p}\big)\frac{c^2}{E+mc^2-V(r)}\big(\vec{\sigma}\cdot\vec{p}\big)\vec{\Psi}_+=\big(E-mc^2-V(r)\big)\vec{\Psi}_+$$

Defining $\mathcal{E}=E-mc^2$, the fraction appearing on the left side of the equation can be Taylor expanded in the non-relativistic limit:

$$-\frac{c^2}{2mc^2+\mathcal{E}-V(r)}\approx\frac{1}{2m}\Big(1-\frac{\mathcal{E}-V(r)}{2mc^2}\Big)$$

Pauli matrices obey the following property:

$$\big(\vec{\sigma}\cdot\vec{A}\big)\big(\vec{\sigma}\cdot\vec{B}\big)=\vec{A}\cdot\vec{B}+i\vec{\sigma}\cdot\big(\vec{A}\times\vec{B}\big)$$

Using the two expressions above leads to

$$\begin{aligned}\big(\vec{\sigma}\cdot\vec{p}\big)f(r)\big(\vec{\sigma}\cdot\vec{p}\big)&=f(r)\big(\vec{\sigma}\cdot\vec{p}\big)\big(\vec{\sigma}\cdot\vec{p}\big)-i\hbar\frac{f'(r)}{r}\big(\vec{\sigma}\cdot\vec{r}\big)\big(\vec{\sigma}\cdot\vec{p}\big)\\&=f(r)\vec{p}^2-i\hbar\frac{f'(r)}{r}\big(\vec{r}\cdot\vec{p}+i\vec{\sigma}\cdot(\vec{r}\times\vec{p})\big)\end{aligned}$$

where:

$$f(r)=\frac{1}{2m}\Big(1-\frac{\mathcal{E}-V(r)}{2mc^2}\Big).$$

Recognizing $\vec{r}\times\vec{p}=\vec{L}$, the quantity $\hbar\vec{\sigma}\equiv 2\vec{s}$ is defined, where $\vec{s}$ is called **spin**. Obviously, with and extra factor of $\hbar$ and $\frac{1}{2}$, the Pauli matrices satisfy the angular momentum commutation relations. For the simplest case of $\vec{\Psi}_+$ being a 2-spinor, this gives the spin-$\frac{1}{2}$-quality to an electron. Note that higher-dimensional operators can be used in Eq. (4.24). These will lead to particles with higher spin numbers. (This will be revisited in the group theory part of this class.) As for nomenclature: Mostly, small letters $(\vec{\ell},\vec{s})$ will be used strictly for single electrons; capital letters $(\vec{L},\vec{S})$ denote total orbital/spin angular momentum.

Putting the equations together one gets

$$\left[\left(1-\frac{\mathcal{E}-V(r)}{2mc^2}\right)\frac{p^2}{2m}-i\hbar\frac{1}{4m^2c^2}\,\frac{V(r)}{r}\,(\vec{r}\cdot\vec{p})+\frac{1}{2m^2c^2}\,\frac{V'(r)}{r}\,\vec{S}\cdot\vec{L}\right]\Psi_+ \;=$$
$$=\;[\mathcal{E}-V(r)]\;\Psi_+$$

with

$$\mathcal{E}-V(r)\approx\frac{p^2}{2m}.$$

Thus, the total Hamiltonian reads

$$\Longrightarrow \boxed{H \;=\; \frac{p^2}{2m}-\frac{p^4}{8m^2c^2}+V(r)+H_{LS}+H_D}$$

The first two terms of this equation are the two lowest terms of the kinetic energy, $\sqrt{p^2c^2+m^2c^4}-mc^2$. H_D is called the "Darwin term." It is important to note that $i\frac{V'}{r}\vec{r}\cdot\vec{p}$ is not Hermitian; this happens because the coupling between Ψ_+ and Ψ_- is neglected. Symmetrizing this term (first done by Darwin) gives

$$i\frac{V'}{r}\vec{r}\cdot\vec{p}\Psi \;\longrightarrow\; \frac{1}{2}\big(i\,\frac{V'}{r}\,\vec{r}\cdot\vec{p}-i\vec{p}\cdot\vec{r}\,\frac{V'}{r}\big)\,\Psi \;=\; -\hbar\,\Psi\,\vec{\nabla}^2\,V(r).$$

Thus, the complete Darwin term gives

$$\boxed{H_D \;=\; \frac{\hbar^2}{8m^2c^2}\,\vec{\nabla}^2\,V(r) \;=\; \frac{\pi\hbar^2Ze^2}{2m^2c^2(4\pi\epsilon_0)}\,\delta(\vec{r})},$$

where the Coulomb potential was substituted for the general potential in the first equality of H_D. Note that this term is only relevant for $\ell=0$ since the s-orbitals are the only ones with finite density at the origin. One accepted way to interpret this term is to estimate the uncertainty of $V(r)$, ΔV, using

$$\Delta V \;\approx\; \langle\delta r_i\rangle\,\langle\delta r_j\rangle\,\vec{\nabla}^2V \;\approx\; \lambda_c^2\,\vec{\nabla}^2V,$$

where it is assumed that the uncertainty in location of the potential (singularity) is given by the "Compton wavelength," $\lambda_c \;=\; \frac{\hbar}{mc}$ for λ_e the "Compton wavelength". Comparing the terms above shows that this estimate only neglects an extra factor of $\frac{1}{8}$.

The next term describes the spin-orbit coupling whose presence had been guessed in the previous section already. (Note that both spin and spin-orbit coupling do follow directly and automatically from the Dirac equation.)

$$\boxed{H_{\mathrm{LS}} \;=\; \frac{1}{2m^2c^2}\,\frac{V'}{r}\,\vec{L}\cdot\vec{S} \;=\; \frac{Ze^2}{2m^2c^2(4\pi\epsilon_0)}\,\frac{1}{r^3}\,\vec{L}\cdot\vec{S}}.$$

The energy of this term, i.e., the expectation value gives

$$E_{\text{spin-orbit}} \;=\; \frac{1}{2m^2c^2}\,\frac{Ze^2}{4\pi\epsilon_0}\,\langle\frac{1}{r^3}\rangle\,\langle\vec{L}\cdot\vec{S}\rangle$$

with

$$\langle\frac{1}{r^3}\rangle \;=\; \frac{1}{\ell(\ell+1/2)(\ell+1)}\,\frac{Z^3}{(n\,a_B)^3},$$

and

$$\langle\vec{L}\cdot\vec{S}\rangle \;=\; \frac{\hbar^2}{2}\begin{cases}\ell & \text{for}\quad j=\ell+\frac{1}{2}\\ -(\ell+1) & \text{for}\quad j=\ell-\frac{1}{2}\end{cases}.$$

The splitting between those two terms would give

$$\Delta\langle\vec{L}\cdot\vec{S}\rangle \;=\; \hbar^2(\ell+\frac{1}{2}).$$

This results in the spin-orbit coupling of

$$E_{\text{spin-orbit}} \;=\; \frac{\hbar^2}{4m^2c^2}\,\frac{e^2}{4\pi\epsilon_0}\,\frac{1}{\ell(\ell+1)}\,\frac{Z^3}{(n\,a_B)^3} \;=\; \frac{(Z\alpha)^2}{n^3\ell(\ell+1)}\,E_n$$

with the undisturbed (i.e., Bohr-model) energy E_n. The complete energy with relativistic corrections then reads

$$E_{nj} \;=\; E_n\left(1-\frac{(Z\alpha)^2}{2n^2}-\frac{(Z\alpha)^4}{2n^4}(\frac{n}{J+1/2}-\frac{3}{4})\right)$$

where the terms are now sorted by order of the fine structure constant α. Higher order terms are the "relativistic corrections" with the correction to the kinetic energy second and fine structure fourth order in α.

4.7 The Lamb Shift

Looking at the Dirac equation, the pairs $({}^2s_{1/2},{}^2P_{1/2}), ({}^2P_{3/2},{}^2D_{3/2}), ({}^2D_{5/2},{}^2F_{5/2}), ...$ are all (pairwise) degenerate. But measurement of the energy difference by Lamb and Retherford (1947) yielded the "Lamb Shift"

$$\delta_L \;=\; (E({}^2S_{1/2}) - E(2^2P_{1/2}))/\hbar \;\approx\; 1058\mathrm{MHz}.$$

The reason for this is the interaction of the atom with vacuum fluctuations of electromagnetic fields, i.e., quantum electrodynamic (or QED) corrections:

$$\langle E\rangle = 0,\ \langle E^2\rangle \neq 0$$

A brief derivation is as follows:

$$\Delta V = V(\vec{r}+\delta\vec{r}) - V(\vec{r}) \;=\; \delta\vec{r}\cdot\vec{\nabla}V + \frac{1}{2}(\delta\vec{r}\cdot\vec{\nabla})^2V + ...$$

For isotropic fluctuations:

$$\langle\delta\vec{r}\rangle_{vac} = 0$$

and

$$\langle(\delta\vec{r}\cdot\vec{\nabla})^2 \;=\; \frac{1}{3}\langle(\delta\vec{r})^2\rangle\vec{\nabla}^2.$$

Thus

$$\langle\Delta V\rangle = \frac{1}{6}\langle\delta\vec{r}^2\rangle_{vac}\langle\vec{\nabla}^2\frac{-e}{4\pi\epsilon_0 r}\rangle_{atom} \tag{4.29}$$

For the first factor it is assumed that the uncertainty in the position of the electron stems from its interaction with the electromagnetic field of the vacuum fluctuations:

$$m\,\ddot{\delta\vec{r}} \;=\; -eE_k \;\propto\; e^{i\nu t}$$

The relevant fluctuation frequencies ν have to be $\nu > \frac{\pi c}{a_B}$ for $\Delta r = a_B$, because of uncertainty $\Delta k{\cdot}\Delta r \leq 1/2$ for the electron. A reasonable maximum for the relevant ν is the the Compton freqency $\nu_c = c/\lambda_c$. With that the above solves to

$$\delta\vec{r} \;=\; \frac{e}{mc^2k^2}\,\mathcal{E}_k\big(\alpha_k e^{-i\nu t+i\vec{k}\delta\vec{r}} + c.c\big)$$

For quantization volume Ω_q this gives for the vacuum Rabi frequency with wavenumber k

$$\mathcal{E}_k \;=\; \sqrt{\frac{\hbar ck}{2\epsilon_0\Omega_q}}$$

and thus

$$\begin{aligned}
\langle\delta\vec{r}\rangle^2 &= \sum_k \big(\frac{e}{mc^2k^2}\big)^2 \frac{\hbar ck}{2\epsilon_0\Omega_q} \approx \\
&\approx 2\,\frac{\Omega_q}{(2\pi)^3}\,4\pi\int k^2dk\,\big(\frac{e}{mc^2k^2}\big)^2\,\frac{\hbar ck}{2\epsilon_0\Omega_q} = \\
&= \frac{1}{2\epsilon_0\pi^2}\,\frac{e^2}{\hbar c}\big(\frac{\hbar}{mc}\big)^2\int dk\,\frac{1}{k}
\end{aligned}$$

With the integration limits of this expression as discussed above, this leads to

$$\langle\delta\vec{r}^2\rangle \approx \frac{1}{2\epsilon_0\pi^2}\frac{e^2}{\hbar c}\big(\frac{\hbar}{mc}\big)^2\ln\frac{4\epsilon_0\hbar c}{e^2}.$$

In the second factor of Eq. (4.29) the second derivative of the Coulomb potential gives (again) a delta function of which the expectation value can directly be calculated:

$$-\frac{e^2}{4\pi\epsilon_0}(-4\pi)\langle\delta\vec{r}\rangle_{atom} = \frac{e^2}{\epsilon_0^2}|\Psi(0)|^2,$$

where, for the "basic" Lamb shift the $2S_{1/2}$ orbital is used and thus

$$|\Psi(0)|^2 = \frac{1}{8\pi\alpha_B^2}.$$

Putting both parts together yields

$$\langle\Delta V\rangle_{2S} = \frac{1}{6}\frac{e^2}{\epsilon_0}\frac{1}{8\pi a_B^3}\frac{1}{2\pi^2\epsilon_0}\frac{e^2}{\hbar c}\big(\frac{\hbar}{mc}\big)^2\ln\frac{4\epsilon_0\hbar c}{e^2} = \alpha^5mc^2\frac{1}{6\pi}\ln\frac{1}{\pi\alpha}\approx 1\text{ GHz}.$$

4.8 Effects of the nucleus

In previous sections, it was assumed that the nucleus was infinitely heavy and point-like. Real nuclei have finite mass (denoted M, m_n), angular momentum ($\vec{I}$), and a finite volume of charge, electric dipole moment, magnetic quadrupole moment, etc. (alternating electric and magnetic effects).

Now, one needs to consider total atomic angular momentum $\vec{F}$, given by

$$\vec{F} = \vec{J} + \vec{I} \tag{4.30}$$

where $\vec{J}$ is the total electronic angular momentum ($\vec{L}+\vec{S}$), and $\vec{I}$ is the total nuclear angular momentum. The nuclear angular momentum contribution is

Effect	Result	Observe via
finite mass	mass shift	isotope shift
finite volume	volume shift	isotope shift
magnetic dipole	hyperfine structure	hyperfine splitting
electric quadrupole	” ”	” ”
⋮		

typically much smaller than the electronic contribution (since the mass of the nucleus is large compared to electrons), so for many applications it can be neglected. However, nuclear angular momentum does play a very important role in determining selection rules.

4.8.1 Hyperfine Interaction

A good reference for this is section 1.4 in the textbook *Atomic physics: An exploration through problems and solutions* by Budker, Kimball, and DeMille.

The hyperfine correction Hamiltonian has a similar form to the fine structure corrections:

$$H_{hf} = -\vec{\mu_I} \cdot \vec{B_J} = ah\vec{I} \cdot \vec{J} \tag{4.31}$$

where $\vec{\mu_I}$ is the nuclear magnetic moment, $\vec{B_J}$ is the magnetic field due to the magnetic moment of the electrons, and a is some constant that we will calculate.

From an energy point of view, the hf splitting is small. The fine structure splitting is α^2, while the hf splitting goes as $\alpha^2 \frac{m_e}{m_n}$ (3 orders of magnitude smaller). Hyperfine states make are useful as (meta-) stable ground states (e.g. EIT (see HW 5), qubit states).

One can think of the nucleus as a charge cloud with angular momentum, which results in electric an magnetic moments (dipole, quadrupole, etc.). In principle, there could be an electric and magnetic moment for each of these, but there are additional limitations imposed by parity and time reversal symmetry. The result is that there is only a magnetic dipole moment, only an electric quadrupole moment, only a magnetic octopole moment, etc. In addition, a magnetic dipole only exists if I is non-0 (i.e. $I \geq 1/2$). This moment results in hyper-fine splitting only if $J \geq 1/2$. Similarly, electric quadrupole splitting requires $I, J \geq 1$.

We first need to define several new quantities:

$\vec{\mu}_s = -g_s \mu_0 \vec{S}/\hbar$	electron spin magnetic moment
$\vec{\mu}_l = -g_l \mu_0 \frac{\vec{L}}{\hbar}$	electron orbital magnetic moment
$\vec{\mu}_I = g_I \mu_N \frac{\vec{I}}{\hbar}$	nuclear magnetic moment
$\mu_0 = \frac{e\hbar}{2m_e} \approx 9.24 \times 10^{-24}$ J/T	Bohr magneton
$\mu_N = \frac{e\hbar}{2m_n} \approx 5.05 \times 10^{-27}$ J/T	nuclear magneton

Where g is the called the gyromagnetic ratio (or the Lande g-factor). Some important values of g are:

$g_s = 2$	electron (from the Dirac equation (see HW5))
$g_l = 1$	electronic orbital (matches classical eqn (μ = current × area))
$g_p = 5.586$	proton
$g_n = -3.826$	neutron

Generalizing to the total atomic angular momentum, we see that:

$$\begin{aligned}\vec{\mu}_F &= \vec{\mu}_I + \vec{\mu}_J \\ \vec{\mu}_s &= g_s \frac{q}{2m} \vec{J} \\ \vec{\mu}_I &= g_I \frac{q}{2m} \vec{I}\end{aligned}$$

Total angular momentum $\vec{F}$ is associated with quantum numbers F and M_F, these are good quantum numbers (they fully describe the system of the atom).

Now we are ready to calculate the value ah in Eqn. (4.31). Notice that $\vec{B}_J$ should be proportional to and parallel to $\vec{J}$, and $\vec{\mu}_I$ is proportional to $\vec{I}$, so we can say that

$$\vec{I} \cdot \vec{B}_J = \frac{(\vec{I} \cdot \vec{J})(\vec{J} \cdot \vec{B}_J)}{J^2} \tag{4.32}$$

By combining equations (4.32) and (4.31), one gets

$$ah = -\frac{\vec{\mu}_I}{\vec{I}} \cdot \frac{\vec{J} \cdot \vec{B}_J}{J^2} \tag{4.33}$$

Recall

$$\vec{J} = \vec{L} + \vec{S} \tag{4.34}$$

$$\vec{B_J} = \vec{B}_L + \vec{B}_S \tag{4.35}$$

By plugging these two formulas back into equation (4.33), we can calculate the energy ah. This is a somewhat tedious calculation that you can find written out for Hydrogen in *Atomic physics: An exploration through problems and solutions*, as well for the general case in the AMO lecture notes by Wolfgang Ketterle.

Electric quadrupole

Also part of the HF structure, the electric quadrupole moment can be calculated by

$$Q = \frac{1}{e}\int d^3r\rho(\vec{r})(3z^2 - r^2)$$

If $Q < 0$, the quadupole moment is called "oblate," if $Q > 0$ it is called "prolate." The total electric quadupole moment energy shift is on the order:

$$\begin{aligned} E^Q_{hf} &\propto \frac{Q}{a_B^2}\left\langle\frac{1}{r^3}\right\rangle \\ \Rightarrow \quad Q &\leq \left\langle r^2_{ml}\right\rangle \approx 10^{-24}cm^2 \end{aligned}$$

The full hyperfine shift is small compared to the fine structure shift:

$$\begin{aligned} \frac{E_{hf}}{E_{fs}} &\approx g_I\frac{m_e}{m_n}\frac{1}{Z} \approx 10^{-3} \\ \frac{E_{hf}}{\hbar} &\approx \frac{1}{(l+\frac{3}{4})^3}\text{ GHz.} \end{aligned}$$

4.8.2 Isotope effects

Mass effect for a single e^-: Starting with the energy calculated when one assumes that the mass of the nucleus is infinite ($E_{n,0}$), the total energy of the n^{th} shell including the finite mass of the nucleus (m_n) is

$$E_n = E_{n,0}\frac{m_n}{m_n + m_e} \approx E_{n,0}\left(1 - \frac{m_e}{m_n}\right)$$

When there are ≥ 2 electrons, there is an additional term that one must take into account. The shift is due to the change in the total kinetic energy of the center of mass of the atom:

$$\begin{aligned}\Delta E_{n,m_n} &= \frac{\vec{p}^2}{2m} \\ &= -\frac{m_e}{m_n}\left(\underbrace{\frac{1}{2m_e}\sum_i \vec{p}_i^2}_{\text{“normal shift”}} + \underbrace{\frac{1}{2m_e}\sum_{i\neq j}\vec{p}_i\cdot\vec{p}_j}_{\text{“specific shift”}}\right)\end{aligned}$$

where the index i is summed over all electrons, and the specific shift is zero in the case of a single electron. The result for the specific shift is:

$$\Delta E_{\text{spec}} = (1-2S)\frac{m_e}{m_n}\frac{3f_{ns,n'l}}{2}\,\hbar\,\omega_{ns,n'l}, \tag{4.36}$$

where $\omega_{ns,n'l}$ is the energy difference between a state n with orbital angular momentum 0 (an s orbital) and a state n' with orbital angular momentum ℓ. Note that ΔE_{spec} has a different sign for the singlet ($S=0$) and triplet ($S=1$) states. $f_{ns,n'l}$ is the "oscillator strength" between states n, s and n', l, given by:

$$f_{eg} = \frac{2m_e}{2\hbar}\sum_{\text{all hf states}} |\langle e|r|g\rangle|^2\,\omega_{eg} \tag{4.37}$$

(The oscillator strength will be defined briefly in the next chapter.) Note that the $\langle e|r|g\rangle$ term means that if the transition is not allowed, then $\Delta E_{\text{spec}} = 0$.

With all that, the isotope shift reads

$$\frac{\Delta E_{n,m_n+\Delta m_n} - E_{n,m_n}}{E_n} \approx \frac{m_e}{m_n}\frac{\Delta m_n}{m_n}. \tag{4.38}$$

4.8.3 Volume effect

Inside the nucleus, the potential is less deep, which means that the valence e^- with non-zero density inside the nucleus sees increased energy. The transition energy will thus be lowered if the effect is stronger for the lower state (which is the typical case). So the total effect depends on $\frac{d\delta}{dn}$ (quantum defect), Z, Z_{nucl}, and r_{nucl}.

Many more details about the calculations and exact numbers shown in this section can be found in the book be I. I. Sobelman, *Atomic Spectra and Radiative Transitions*.

Chapter 5

Atoms in DC fields

This chapter looks at how atoms behave in DC fields (magnetic or electric). Specifically, we will look at how the energy levels will split or shift when atoms are in these fields.

5.1 Atoms in DC magnetic fields

5.1.1 Coupling with individual angular momentum

Atoms interact with magnetic fields because atoms carry magnetic moment (comes from orbital circulation of electron, electron spin magnetic momentum, and nuclear spin magnetic moment). The interaction energy U of a magnetic moment $\vec{\mu}$ with external magnetic field $\vec{B}$ is given by:

$$U = -\vec{\mu} \cdot \vec{B}. \tag{5.1}$$

Therefore, to understand the interaction with the external magnetic field, one must first understand the magnetic moment. Here is a start with a brief review of the classical relation between magnetic moment and angular momentum.

The classical angular momentum is:

$$\vec{L} \;=\; \vec{r} \times \vec{p} = m(\vec{r} \times \vec{v}),$$

and the magnetic moment is:

$$\vec{\mu} \;=\; \frac{1}{2}\vec{r} \times \vec{i} \;=\; \frac{q}{2}\,(\vec{r} \times \vec{v}),$$

where $\vec{i}$ is the electric current and q is the charge carried by the particle. Therefore, the magnetic moment and the angular momentum satisfy the following classical relation:

$$\vec{\mu} = \frac{q}{2m}\vec{L}, \tag{5.2}$$

where the factor $\frac{q}{2m}$ is called *gyromagnetic ratio*, and this relation holds as long as the material has uniform charge-to-mass ratio.

Specifically, if one plugx the electron charge $q = -e$ into Eq. (5.2), this will give:

$$\vec{\mu} = -\frac{e\hbar}{2m_e}\frac{\vec{L}}{\hbar} = -\mu_B\frac{\vec{L}}{\hbar}, \tag{5.3}$$

where $\mu_B \equiv \frac{e\hbar}{2m_e}$ is the *Bohr magneton*, and its value is:

$$\mu_B = 9.274 \times 10^{-24}\text{J/T}. \tag{5.4}$$

Note that Eq. (5.3) only applies to the orbital motion of electrons (which is somewhat classical), and not to the intrinsic electronic spin. In fact, the Dirac equation formalism predicts that the spin magnetic field and spin angular momentum satisfy:

$$\vec{\mu}_S = -g_e\mu_B\frac{\vec{S}}{\hbar}, \tag{5.5}$$

where $g_e = 2$ is the *Landé g-factor* of the electron spin. One point worth noticing is that although the Dirac equation predicts the exact value $g_e = 2$, this value receives a QED correction in reality, which makes it slightly deviate from 2. The most accurate experimental measurements up to today shows:

$$\frac{g_e}{2} = 1.0011596521869(14) = 1 + \frac{\alpha}{2\pi} + O(\alpha^2), \tag{5.6}$$

where α is the fine structure constant.

The nuclear magnetic moment also has a similar expression, with the only difference that the characteristic magnetic moment is the *nuclear magneton* $\mu_N = \frac{e\hbar}{2m_p}$, where m_p is the mass of proton. The relations between magnetic moment and angular momentum is summarized below:

$$\begin{aligned} \vec{\mu}_L &= -g_L\mu_B\frac{\vec{L}}{\hbar} \qquad && g_L = 1 \\ \vec{\mu}_S &= -g_S\mu_B\frac{\vec{S}}{\hbar} \qquad && g_S \approx 2 \\ \vec{\mu}_I &= -g_I\mu_N\frac{\vec{I}}{\hbar} \qquad && g_I \text{ Complicated} \end{aligned} \tag{5.7}$$

Eq. (5.1) and Eq. (5.7) describe how individual angular momentum is coupled to the external magnetic field $\vec{B}$. The next few subsections describe what happens when these angular momenta (orbital, electron spin, nuclear spin) are coupled.

5.1.2 Weak magnetic field – Zeeman splitting without hyperfine structure

Recall that in atoms, angular momenta are coupled: first, $\vec{L}$ and $\vec{S}$ couple into $\vec{J}$ by spin-orbit coupling $\vec{L}\cdot\vec{S}$; this gives the fine structure; then $\vec{J}$ and $\vec{I}$ couple into $\vec{F}$ through $\vec{I}\cdot\vec{J}$ which gives the hyperfine structure. The classical picture of these couplings is that $\vec{L}$ and $\vec{S}$ are determined only up to a common rotation around the common axis $\vec{J}$, while $\vec{J}$ itself and $\vec{I}$ are determined up to rotation around their common axis $\vec{F}$ (with coupling between $\vec{I}$ and $\vec{J}$ is much weaker than coupling between $\vec{L}$ and $\vec{S}$: hyperfine structure lives on much lower energy scales than fine structure).

When the external magnetic field is weak enough (when coupling with the external magnetic field is much weaker than coupling between atomic angular momenta), the external magnetic field will not destroy the coupling between angular momenta described above. Therefore, F and m_F are good quantum numbers in this situation.

In the classical picture, what happens in this situation is that as $\vec{L}$ and $\vec{S}$ rotate around their common axis $\vec{J}$, their total magnetic moment $\vec{\mu}_L+\vec{\mu}_S$ also rotates around the common axis $\vec{J}$. The result of this rotation is that the component (of $\vec{\mu}_L+\vec{\mu}_S$) orthogonal to $\vec{J}$ is meaningless and thus does not interact with the external magnetic field. Therefore, the effective magnetic moment that interacts with the external magnetic field is the component parallel to $\vec{J}$. (This is similar in the coupling of $\vec{J}$ and $\vec{I}$; only the projection of magnetic moment on $\vec{F}$ direction is effective.)

In the previous paragraph, it was basically argued that the direction of the total effective magnetic moment is a good choice for quantization axis. What is its quantity? The first step is the coupling between $\vec{L}$ and $\vec{S}$, with projection on $\vec{J}$. For the projections of $\vec{\mu}_L$ and $\vec{\mu}_s$ onto the direction of $\vec{J}$ one finds

$$\mu_{L,J} \;=\; -g_L\,\frac{\mu_0\,|\vec{L}|}{\hbar}\,\frac{\vec{L}\cdot\vec{J}}{|\vec{L}||\vec{J}|} \quad\text{and}\quad \mu_{S,J} \;=\; -g_S\,\frac{\mu_0\,|\vec{S}|}{\hbar}\,\frac{\vec{S}\cdot\vec{J}}{|\vec{S}||\vec{J}|}.$$

This leads to

$$\vec{\mu}_J \;=\; -g_J\,\mu_0\,\frac{\vec{J}}{\hbar}$$

with

$$\begin{aligned} g_J &= -\frac{\hbar}{\mu_0}\,\frac{\mu_{L,J}+\mu_{S,J}}{|\vec{J}|} \\ &= \frac{g_L\,\vec{L}\cdot(\vec{L}+\vec{S})+g_S\,\vec{S}\cdot(\vec{L}+\vec{S})}{|\vec{J}^2|} \;= \\ &= 1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}, \end{aligned} \tag{5.8}$$

where $2\vec{L}\cdot\vec{S}=\vec{J}^2-\vec{L}^2-\vec{S}^2$ was used. Thus, the splitting is (using Eq. (5.1)):

$$\Delta E \;=\; (g_{j'}m_{j'}-g_{j''}m_{j''})\,\mu_0\,B$$

if the two levels of the transition are labeled j' and j'', respectively. This splitting is called *Zeeman splitting*, It is obvious that the smallest number of different level splittings happens (i.e., the same ΔE for all neighboring split levels) if $g_{j'}=g_{j''}$ or either $j'=0$ or $j''=0$. There are three split levels in this case if $\Delta m = mn_{j'}-m_{j''}=0,\pm 1$. In the general case, there are more levels.

5.1.3 Weak magnetic field and hyperfine structure

The complete Hamiltonian for the hyperfine and magnetic field couplings is now

$$H \;=\; a\,h\,\vec{I}\cdot\vec{J}-\vec{\mu}_J\cdot\vec{B}-\vec{\mu}_I\cdot\vec{B}, \tag{5.9}$$

where obviously

$$\vec{\mu}_J \;=\; -g_J\,\mu_0\frac{\vec{J}}{\hbar} \quad\text{and}\quad \vec{\mu}_I \;=\; -g_I\,\mu_N\frac{\vec{I}}{\hbar}.$$

If the field is weak enough (i.e., weaker than the $\vec{I}\cdot\vec{J}$ coupling), the magnetic field again can be treated as a perturbation, and F and m_F are good quantum numbers. Thus

$$H_B \;=\; -g_F\,(\vec{\mu}_J+\vec{\mu}_I)\cdot\vec{B} \;\approx\; -g_F\,\vec{\mu}_J\cdot\vec{B},$$

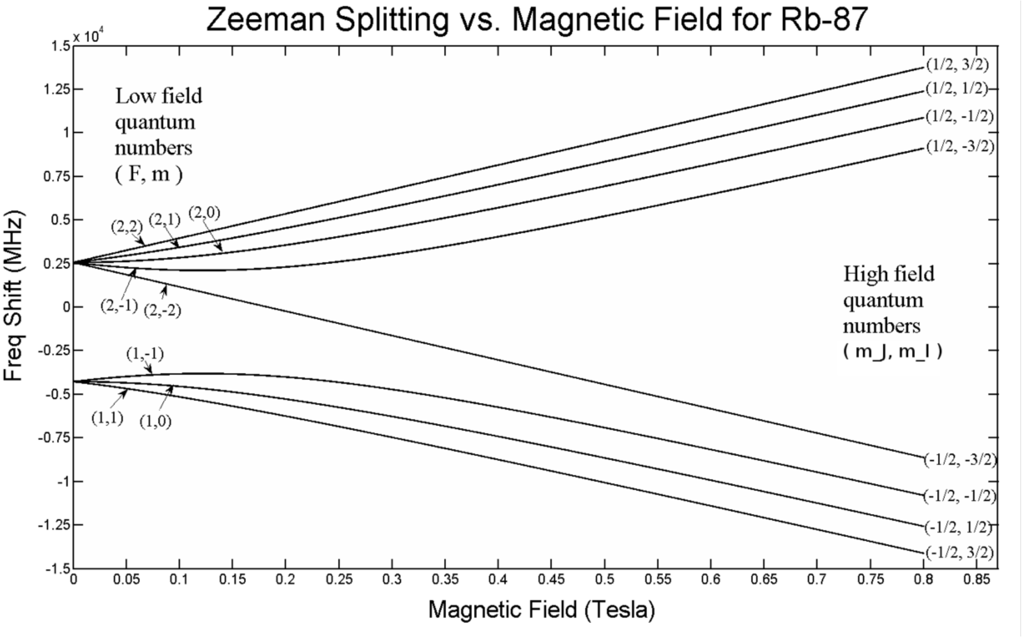


Figure 5.1: Zeeman splitting of ^{87}Rb.

where for the approximation one uses that the nuclear moment is much smaller than the electronic one (note that for $\vec{\mu}_J = \vec{J} = 0$ there is no hyperfine splitting to start with!). It is important to remember that nevertheless $\vec{I}$ and $\vec{J}$ couple into $\vec{F}$ first and only then to $\vec{B}$, i.e., the quantum numbers of $F, m_F, L, andS$ need to be used. Thus, the above logic of the coupling of the angular momenta is the same for the coupling between $\vec{I}$ and $\vec{J}$. The total Landé g-factor of the hyperfine state F is given by

$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)}. \tag{5.10}$$

(For an expression that uses only S, L, and I, see section writeup.)

This energy shift split the different m_F states, and the splitting is linear in B. An example is the low-B limit in Fig. 5.1 for ^{87}Rb.

5.1.4 Stronger magnetic field

When the coupling with the external magnetic field is strong compared to the coupling between $\vec{J}$ and $\vec{I}$, the picture is different. Now, the classical picture is that both $\vec{J}$ and $\vec{I}$ rotate independently around B because their coupling with the external magnetic field dominate the coupling between them. Because they interact independently with the magnetic field, the good quantum numbers are J, I, m_I, and m_J in this situation.

Thus the energy of Hamiltonian (5.9) reads

$$\langle H \rangle \; = \; a\, h\, m_I m_J + g_J m_J \mu_B B + g_I m_I \mu_N B. \tag{5.11}$$

This is the expression for the energy shift at large external magnetic field (stronger than the hyperfine coupling to break the coupling between $\vec{I}$ and $\vec{J}$, but weaker than the fine structure coupling to preserve the coupling between $\vec{L}$ and $\vec{S}$). The second term $g_J m_J \mu_B B$ is the largest term in this expression, therefore it determines the main "trend" of the splitting. The strong field Zeeman splitting can be seen at the high B end of Fig.5.1.

5.1.5 Paschen-Back effect

For a B-field that is strong enough to dominate even the $\vec{L}$-$\vec{S}$ coupling, both spin and orbital angular momentum couple seperately to the magnetic field, making L, S, m_L, m_S good quantum numbers. The logic is mostly the same as above. The only notable thing is that now the spin-degree of freedom can be entirely ignored for selection rules. (Reminder: Selection rules are dominated by parity – see next section.) Thus, Δj or ΔF along with Δm need to have allowed values. The spin itself (i.e., uncoupled from the orbital degree of freedom) does not have an influence on the parity; thus, with the Paschen-Back effect the spin degree of freedom has no influence on selection rules at all.

5.1.6 The General Solution

The general solution that applies for any B value can be found by direct diagonalization of $\hat{H}$ in Eq. (5.9). Thus, an analytic solution only exist for the case $I \leq 1/2$ or $J \leq 1/2$ (i.e. when there are at most two hyperfine states). The solution is called "Breit-Rabi formula." The diagram for the solution in a simple case can be seen in Fig. 5.1.

5.2 Atoms in DC electric fields

5.2.1 Consideration of parity

"Parity" is the effect that a system has under space inversion, $\hat{\vec{r}} \longrightarrow -\hat{\vec{r}}$. For this, one can define a partity operator $\hat{\pi}$

$$\hat{\pi}\hat{\vec{r}}\hat{\pi}^{\dagger} = -\hat{\vec{r}},$$

where also $\hat{\pi}^{\dagger} = \hat{\pi}$ is hermitian.

A look at the eigenfunctions of $\hat{\vec{r}}$ can illuminate some properties. (In the argument that follows, only the $\hat{x}$ coordinate is used – obviously, the argument is the same for $\hat{y}$ and $\hat{z}$.)

$$\hat{x}|\vec{r}\rangle = x|\vec{r}\rangle, \qquad \text{thus}$$

$$\hat{x}\,\hat{\pi}\,|\vec{r}\rangle = -\hat{\pi}\,\hat{x}\,|\vec{r}\rangle = -\hat{\pi}\,x\,|\vec{r}\rangle = -x\,\hat{\pi}\,|\vec{r}\rangle.$$

From this, one sees that $\hat{\pi}\,|\vec{r}\rangle$ is also an eigenfunction of $\hat{\vec{r}}$ with eigenvalue $-\vec{r}$. Obviously, using the space inversion operation twice will give the identity, or, in math speak

$$|\hat{\pi}^2| = 1 \quad \Rightarrow \quad \text{eigenvalues}\,\langle\hat{\pi} = \pm 1\rangle\,.$$

In a table, these are the operations and possibilities for the parity operator:

behavior	state $\|\alpha\rangle$	operator $\hat{A}$
"odd parity"	$\hat{\pi}\,\|\alpha\rangle = -\|\alpha\rangle$	$\hat{\pi}\,\hat{A}\,\hat{\pi} = -\hat{A}$
"even parity"	$\hat{\pi}\,\|\alpha\rangle = \|\alpha\rangle$	$\hat{\pi}\,\hat{A}\,\hat{\pi} = \hat{A}$

A look at the most basic physics vectors gives $\vec{r}$ and $\vec{p}$ as having odd parity; these are **polar** vectors (or just "vectors"). A different example is the angular momentum, $\vec{L} = \vec{r} \times \vec{p}$; this has even parity. Vectors with even parity are called **axial** vectors or "pseudo-vectors."

Back to the atomic wavefunctions: The spherical harmonics have the property

$$\hat{\pi}\,|Y_{\ell m}\rangle = (-1)^{\ell}\,|Y_{\ell m}\rangle,$$

i.e., they are odd or even depending on whether the quantum number ℓ is odd or even. Now one can revisit the question of *selection rules.*

$$\begin{aligned} \langle\alpha|\hat{A}|\beta\rangle &\neq 0 \quad \text{“allowed''} \\ &\qquad \text{(i.e., the transition from } |\beta\rangle \text{ to } |\alpha\rangle \text{ using coupling } \hat{A}\text{)} \\ \langle\alpha|\hat{A}|\beta\rangle &= 0 \quad \text{“forbidden''.} \end{aligned}$$

Here, $\hat{A}$ can be any coupling operator, e.g., $e\hat{\vec{r}}$. Thus, parity selection rules with

$$\hat{\pi}\,|\alpha\rangle \;=\; p_\alpha\,|\alpha\rangle, \quad \hat{\pi}\,|\beta\rangle \;=\; p_\beta\,|\beta\rangle, \qquad p_\alpha, p_\beta \;=\; \pm 1,$$

give in general

$$\langle\beta|\hat{\vec{r}}|\alpha\rangle \;=\; \underbrace{\langle\beta|\hat{\pi}}_{\langle\beta|\,p_\beta}\,\underbrace{\hat{\pi}\,\hat{\vec{r}}\,\hat{\pi}}_{-\hat{\vec{r}}}\,\underbrace{\hat{\pi}\,|\alpha\rangle}_{p_\alpha\,|\alpha\rangle} \;=;-p_\alpha\,p_\beta\,\langle\beta|\hat{\vec{r}}|\alpha\rangle.$$

Comparing the left and right end of those equations, one finds that allowed transitions (with the electric dipole operator as coupling) only exist for $p_\alpha = -p_\beta$, i.e., between states of opposite parity. Obviously, the same is true for any odd coupling operator, while for even coupling operators (such as the magnetic dipole operator) the two states have to have the same parity.

How does parity act on the Hamiltonian? Typically,

$$\boxed{\left[\hat{H}_0,\,\hat{\pi}\right] \;=\; 0}, \tag{5.12}$$

which takes into account that the undisturbed (e.g., atomic) Hamiltonian contains only even terms, such as $\vec{p}^2, \vec{r}^{-2n}, \frac{1}{|\vec{r}|}$, etc. Thus, the eigenfunctions of the undisturbed atomic Hamiltonians (the atomic “bare” states) with a given set of quantum numbers n, ℓ, and m are all odd or even! Any magnetic interaction does not change this, since angular momenta and the magnetic field operators all also are even.

5.2.2 Static DC electric field – Stark effect

The effect of a static electric field on the states and energies of atoms is easiest studied in perturbation theory. There are two cases, non-degenerate and degenerate states.

Non-degenerate energy levels

Without loss of generality, the electric field can be chosen with a polarization in the $\hat{z}$-direction, $\vec{e} = e\hat{z}$. Then the correction to the bare energy level E_n with eigenstate $|n\rangle$ reads

$$\Delta E_n^{(1)} \;=\; e\,E\,\langle n|\hat{z}|n\rangle \;=\; 0$$

to first order in E. Thus, one should look at the next, second, order:

$$\Delta E_n^{(2)} \;=\; (e\,E)^2 \sum_{m\neq n} \frac{|\langle n|\hat{z}|n\rangle|^2}{E_n - E_m},$$

which, in general, is nonzero. Because of the quadratic electric field dependence, this is called "quadratic Stark effect." The correction to state $|n\rangle$ is then (unnormalized)

$$|\tilde{n}'\rangle \;=\; |n\rangle + e\,E \sum_{m\neq n} \frac{|\langle n|\hat{z}|n\rangle|^2}{E_n - E_m}|m\rangle.$$

Please note that this means that $|n'\rangle$ is not an eigenfunction of the parity operator $\hat{\pi}$! If there are N electrons (instead of one), the same procedure applies, only that the single $\hat{z}$ operator is replaced by the sum $\sum_{i=1}^{N} \hat{z}_i$ at the locations of the electrons. In this case, one finds the *polarizability* α_d via the dipole element $\vec{d}$:

$$\vec{d} \;=\; -e\,\langle n'|\hat{z}|n'\rangle \;=\; 2e^2 \sum_{m\neq n} \frac{|\langle n|\hat{z}|n\rangle|^2}{E_n - E_m}\,E + \mathcal{O}(E^2) \;\equiv\; \alpha_d \vec{E} + \mathcal{O}(E^2).$$

Thus, effectively, the quadratic Stark effect reads

$$\boxed{\Delta E_n^{(2)} \;=\; -\frac{\alpha_d}{2}\,E^2}.$$

Degenerate energy levels

In the case of several degenerate levels, all of them have to be taken into account, which leads to a multi-dimensional problem, with, in general, $\Delta_n^{(1)} \neq$

0. As an example, it is useful to look at the (relatively simple) case of $n = 2$:

$$H \propto \begin{pmatrix} E_1 & 0 & 0 & e\,E\,\langle z\rangle_{14} & 0 \\ 0 & E_2 & 0 & 0 & 0 \\ 0 & 0 & E_2 & 0 & 0 \\ e\,E\,\langle z\rangle_{41} & 0 & 0 & E_2 & e\,E\,\langle z\rangle_{45} \\ 0 & 0 & 0 & e\,E\,\langle z\rangle_{54} & E_2 \end{pmatrix} \quad \begin{array}{c} \text{with the} \\ \text{line/column } c \\ \text{indices as} \end{array} \quad \begin{array}{r} |1,0,0\rangle \\ |2,1,1\rangle \\ |2,1,-1\rangle \\ |2,1,0\rangle \\ |2,0,0\rangle \end{array} .$$

where $\langle z\rangle_{ij} \equiv \langle (i)|\hat{z}|(j)\rangle$ and the quantum number triplets consist of n, ℓ, and m and E_1 and E_2 are the energies of the states with $n == 1, 2$. All of the non-diagonal elements that give zero matrix elements because of either parity or transitions of a different polarization are set to zero already (i.e., for $\hat{z}$-polarization one needs $\Delta m = 0$ and because of parity $\Delta\ell \neq \pm 1$ is forbidden). This matrix should now be diagonalized to produce the new eigenvalues and eigenstates. Note that these are no linear, to lead to the "linear Stark effect," which is also much stronger than the quadratic one, see Fig. 5.2 An example

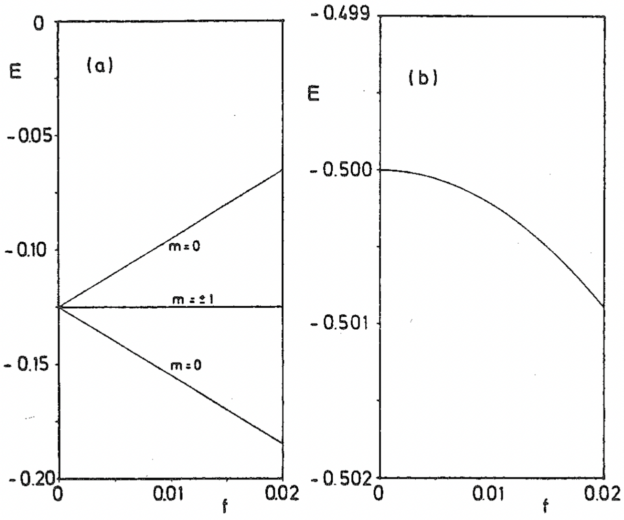


Fig. 3.15. (a) Splitting of the degenerate $n = 2$ level in hydrogen due to the linear Stark effect Problem 3.8). (b) Energy shift of the hydrogen ground state due to the quadratic Stark effect (3.235). f is the electric field strength in units of $E_0 \approx 5.142 \times 10^9$ V/cm (3.241), and the energies are in atomic units

Figure 5.2: Figure taken from H. Friedrich, *Theoretical Atomic Physics*, Springer. Note that the energy scale for the quadratic version is much smaller!

for an eigenstate in this case is $(|2,1,0\rangle \mp |2,0,0\rangle)/\sqrt{2}$ for $E = E_2 \pm e\,E\,|\,\langle\hat{z}\rangle_{45}\,|$, where $\langle\hat{z}\rangle_{45} = \langle 2,1,0|\hat{z}|2,0,0\rangle$. The resulting shift is obviously linear in the electric field. (If there is a different quantization axis than $\vec{E}$, this calculation becomes a bit more complicated, since in this case there will be more non-diagonal elements even for one single field polarization!)

5.2.3 Strong fields: Field ionization

With a really strong electric field, the interaction term cannot be treated as a perturbation any more. The main consequence is that there is a maximum in the potential in one dimension, which means that the electron, in principle, can tunnel out and away from the atom. Once the field is strong enough the barrier becomes both much lower and much thinner as in Fig. 5.3, the physics is dominated by ionization.

For simplicity (and without loss of generality), one can assume that the electric field lies, again, along the z-axis. Then, the 1D potential maximum (that is plotted in Fig. 5.3) will also be on the z-axis and one can perform a 1D calculation to estimate the effect.

The total potential is

$$U_{\mathrm{tot}} \;=\; U_{\mathrm{atom}} + U_{\mathrm{el}} \;=\; -\frac{Z\,e^2}{|z|} - eEz.$$

Thus, the maximum is found for

$$z \;=\; \sqrt{\frac{Z\,e}{4\pi\epsilon_0 E}}.$$

For the total energy to reach this maximum value $\langle H\rangle = U_{max}$, one finds for the field (i.e, the minimum field strength for ionization E_{ion})

$$E_{\mathrm{ion}} \;=\; \frac{\langle H\rangle^2}{4\,\tilde{e}^2\,Z} \;\approx\; \frac{3.2\cdot 10^8}{Z\,n^{*4}}\,\frac{\mathrm{V}}{\mathrm{cm}},$$

where with $n^* = n - \delta_{n\ell}$ the quantum defect is taken into account. Please note that this equation does not take into account that the energy values of the bound states also change, especially close to the potential maximum. Nevertheless, this estimate comes to about 20% of the true value.

The most interesting case of this consideration is in the realm of ultrafast pulses and table-top high-harmonic generation. The electrons can actually

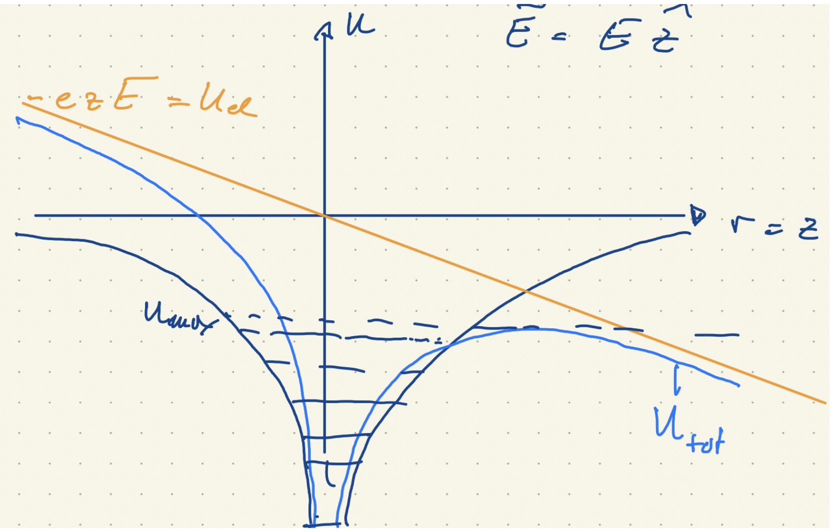


Figure 5.3: Effective potential (light blue) of atom in strong electric field. This potential has a maximum along one (i.e., the plotted) dimension, thus, electrons can tunnel out.

tunnel out very effectively especially if there is a quantized mode structure outside of the atomic potential well. This happens, for example, if one uses an AC electric field. Obviously, this means that, if the electron for example tunnels out to the right eventually the field will turn to attract the electron back to the atom and thus it recombines under emission of a photon. If this periodic motion of tunneling out and recombining is timed exactly such that it is all resonant with each other, the process will eventually produce extremely coherent photons that combine effectively to very, very short pulses.

5.2.4 Oscillating electric field

If the electric field is oscillating with a frequency ν (which does not have to be close to any resonance), the interaction Hamiltonian reads

$$H' = -d\,E\,\hat{z}\,\cos\nu t,$$

While there is not necessarily a transition induced in this case, the more interesting case is if there are two orm more states taken into account:

$$|\psi\rangle \;=\; \sum_n a_n\, e^{-i\omega_n t}\, |n\rangle,$$

with atomic eigenstates $|n\rangle$. Here, there is only a very short outline of the calculation (H. Friedrich's book or W. Ketterle's lecture notes provide details), but the equations of motion

$$\dot{a}_k \;=\; \frac{1}{i\hbar} \sum_n \langle k|H'|n\rangle\, a_n\, e^{i\omega_{kn} t}$$

can be solved and plugged into the form of the dipole moment

$$\vec{d} \;=\; \langle\psi|e\,\vec{r}|\psi\rangle.$$

Formally, this turns out to be a similar calculation as for the classical dipole moment treated in the beginning of class. The solution comes out to

$$d(\nu, t) \;=\; \alpha(\nu)\, E\, \cos\nu t$$

with the (AC) “polarizability”

$$\alpha(\nu) \;=\; \frac{2\,e^2}{\hbar} \sum_k \frac{\omega_{kg} \left|\langle k|\hat{\vec{r}}|g\rangle\right|^2}{\omega_{kg}^2 - \nu^2},$$

which assumes the polarizability of the atom in state $|g\rangle$.

Chapter 6

Atoms in electromagnetic fields

This chapter revisits topics that were covered in the beginning chapters, such as two level system, but with additional details taken into account such as multi-level structures including the coninuum states (i.e., the states above the ionization threshold) and the quantization of electromagnetic fields.

6.1 Spontaneous and Stimulated Emission

In 1917 Einstein had two questions:

1. How do **internal** states (kinetic and potential energy of electron) of atoms reach thermal equilibrium?
   → Led to the concept of spontaneous emission.

2. How do the **external** states (center of mass degrees of freedom) of atoms reach thermal equilibrium?
   → Led to the concept of photon recoil.

Einstein solved the first question by considering two level atoms and rate equations. For a two level atom with total number of electrons N:

$$N = N_e + N_g$$
$$\Delta E = E_e - E_g = \hbar\omega,$$

where N_g is the number of electrons in the ground state, N_e is the number of electrons in the excited state and ω is the resonant frequency of the atoms. He considered two probability distributions. The first was the Planck distribution:

$$\overline{n_{ph}} = \frac{1}{e^{\frac{\hbar\omega}{k_bT}} - 1} \tag{6.1}$$

which is the average number of (thermal) photons at frequency ω. This means that the energy density of the field in the window $d\omega$ is

$$\rho_E(\omega)\ d\omega = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\frac{\hbar\omega}{k_bT}} - 1}\ d\omega \tag{6.2}$$

The second distribution was the Boltzmann distribution which can be used to describe how the electron population (of independent states and for many independent atoms) is distributed over the internal states of the atoms:

$$\frac{N_e}{N_g} = \frac{g_g}{g_e} e^{-\frac{\hbar\omega}{k_bT}} \tag{6.3}$$

where $\frac{g_g}{g_e}$ is the ratio of the degeneracy of the states.

At this point, the idea was that the atoms and the fields had to exchange energy. Although at the time it was not clear how this worked microscopically, Einstein wrote a rate equation in attempt to describe this:

$$\dot{N}_e \ = \ -\dot{N}_g \ = \ -\rho_E(\omega)B_{eg}N_e + \rho_E(\omega)B_{ge}N_g$$

where B_{eg} is an undetermined rate that goes from e→ g and B_{ge} is an undetermined rate that goes from g→ e. in thermal equilibrium, these time derivatives are zero. However, by substituting in the equations (6.2) and (6.3) into the rate equation Einstein noticed a contradiction since B_{eg} and B_{ge} should not depend on temperature. This led him to believe that there should be an extra term that is independent of the energy density $\rho_E(\omega)$. By adding this extra term the rate equation in equilibrium becomes

$$\boxed{0 \ = \ -\rho_E(\omega)B_{eg}N_e + \rho_E(\omega)B_{ge}N_g - A_{eg}N_e}. \tag{6.4}$$

The rate A_{eg} is called the "**spontaneous emission rate**" since it is completely independent of the density of states of the field. Eq. (6.4) can be solved and gives

$$\boxed{\begin{array}{c} g_e B_{eg} = g_e B_{ge} \\ \dfrac{\hbar\omega^3}{\pi^2 c^3} B_{eg} = A_{eg} \\ \Updownarrow \\ \rho_E(\omega) B_{eg} = \overline{n_{ph}} A_{eg} \end{array}}$$

By using these relations the total emission and absorption rates:

$$\begin{aligned}
\text{emission} &\longrightarrow B_{ge}\rho_E(\omega) + A_{eg} = (\overline{n_{ph}} + 1)A_{eg} \\
\text{absorption} &\longrightarrow B_{eg}\rho_E(\omega) = \frac{g_e}{g_g}\overline{n_{ph}}A_{eg} \\
\frac{\text{absorption}}{\text{emission}} &= \frac{\overline{n_{ph}}}{\overline{n_{ph}} + 1} \qquad\qquad (\text{for } g_g = g_e)
\end{aligned}$$

The B_{eg}, B_{ge} and A_{eg} are known as the "**Einstein A and B coefficients**". The main result is that in order for the internal states to reach thermal equilibrium it is necessary to consider both the driving field and the spontaneous emission.

6.2 Quantum Theory of Absorption and Emission

6.2.1 Quantization of Electromagnetic Fields

To obtain a full quantum mechanical description of absorption and emission it is necessary to consider the quantization of the electromagnetic field.

Lets assume a single mode (one frequency) quantized field:

$$\hat{\vec{E}} = -ig(\hat{a}\ \hat{\vec{e}}\ e^{i(\vec{k}\cdot\vec{r}-\omega t)} - h.c.) \tag{6.5}$$

Note that when quantizing the electromagnetic field, the fields are now operators. In the right hand side of equation (6.5), $\hat{a}$ is the annihilation operator, $\hat{\vec{e}}$ is thie unit vector in the direction of the polarization of the field. The name and value of g will be discussed shortly.

Removing the explicit hat notation from the operators, the Hamiltonian for the electric field of a single frequency:

$$H_{\text{field}} = \hbar\omega(\hat{a}^\dagger\hat{a} + \frac{1}{2}) \tag{6.6}$$

This Hamiltonian is the one for an harmonic oscillator. (The details to make this comparison are left out here — they involve the energy of the electromagnetic field which includes quadratic terms in each, the electric and magnetic field, akin to the momentum and coordinate of the traditional harmonic oscillator.) The energy expectation value in vacuum is thus

$$\langle H_{\text{vacuum}} \rangle \; = \; \frac{1}{2}\hbar\omega. \tag{6.7}$$

To connect this with the classical energy in an electric field, recall that the classical energy is given by $\epsilon_0 E^2 V$ where V is the volume and E is the field strength. Plugging in the field in Eq. (6.6) and setting $\epsilon_0\, E^2 V = \langle H_{\text{vacuum}} \rangle$, one finds that g is the Rabi frequency of the vacuum field fluctuations and reads

$$\boxed{g = \sqrt{\frac{\hbar\omega}{2\epsilon_0 V}}}.$$

Note that the volume V is the quantization volume for the vacuum field, which is, more often than not, the volume of the universe or the volume of the box or cavity in which the experiment takes place. In many cases (e.g., the one of the Wigner-Weisskopf calculation below) it cancels out.

6.2.2 Electric field fnteraction with atom

Consider the interaction of the atom with the vacuum electric field:

$$U \; = \; -\vec{d}\cdot\vec{E} \; = \; -i\, e\, g\; \hat{\vec{r}} a \hat{\vec{e}}\; e^{-i\omega t} + h.c.. \tag{6.8}$$

Here the $e^{i(\vec{k}\cdot\vec{r})}$ has been ignored due to the "**dipole**" approximation. This assumes that the part that has a monopole, dipole, ect. is so small that you can treat the particle, in this case a dipole, as a point charge. Thus, it has a typical dipole radiation pattern but in terms of effective size it is zero i.e. $r \ll \frac{1}{k} \rightarrow e^{i(\vec{k}\cdot\vec{r})} \approx 1$.

Note that in equation (6.8) g plays the role of a Rabi frequency. Because of this g is mostly called the "**vacuum Rabi frequency**". The vacuum Rabi frequency is one of the most quantum properties since it assumes that both the atom and field are quantized and also takes into account vacuum fluctuations. And so even in vacuum there is a small coupling with the atom to the electromagnetic field and this is where spontaneous emission comes from.

Now consider an initial state $|i\rangle = |a, n\rangle$ and final state $|f\rangle = |b, n'\rangle$ where $|a\rangle$ and $|b\rangle$ correspond to two atomic levels in the rotating frame and $|n\rangle$ is a field eigenstate (where n is the photon number) of H_{field}, assuming the field polarization is in $\hat{z}$ direction

$$\langle f|U|i\rangle \;=\; -i\,e\,\langle b|\hat{z}|a\rangle\,g\,\langle n'|(\hat{a}\,e^{-i\omega t} - \hat{a}^{\dagger}e^{i\omega t})|n\rangle e^{-i\omega_{ba}t}$$

Here $\hat{a}$ and $\hat{a}^{\dagger}$ act on the states $|n\rangle$ the same way as the case for the harmonic oscillator:

$$\begin{aligned}\hat{a}|n\rangle &= \sqrt{n}|n-1\rangle\\ \hat{a}^{\dagger}|n\rangle &= \sqrt{n+1}|n+1\rangle.\end{aligned}$$

Thus,

$$\langle f|U|i\rangle \;=\; -i\,e\,\langle b|\hat{z}|a\rangle\,g\,(\sqrt{n}\;\delta_{n',n-1}e^{-i(\omega-\omega_{ba})} - \sqrt{n+1}\;\delta_{n',n+1}e^{-i(\omega+\omega_{ba})}).$$

For the case of absorption and emission:

$$\begin{aligned}\text{absorption: } &\omega_{ba} = \omega \qquad (|b\rangle = |e\rangle \text{ and } |a\rangle = |g\rangle)\\ &\longrightarrow n' = n-1\\ \text{emission: } &\omega_{ba} = -\omega \qquad (|b\rangle = |g\rangle \text{ and } |a\rangle = |e\rangle)\\ &\longrightarrow n' = n+1\end{aligned}$$

and the ratio of the probabilities,

$$\begin{aligned}&P = |\langle f|U|i\rangle|^2\\ \longrightarrow\;\; &\frac{P_{abs}}{P_{em}} = \frac{n}{n+1}\end{aligned} \tag{6.9}$$

Note that since n is the photon number, equation (6.9) is equivalent to equation (**??**) which was found using the Einstein A and B coefficients.

6.3 Oscillator Strength

It is possible to define a dimensionless quantity that defines how strong does the field couple to the atom. This is given by the "**oscillator strength**" which is defined by:

$$\boxed{f_{kj} \;=\; \frac{2m_e}{\hbar}\,\omega_{kj}\,|\langle k|z|j\rangle|^2} \qquad \text{(for } \hat{z} \text{ polarization)}$$

Thus the dipole moment of an atom in oscillating field of frequency ν can be rewritten in terms of the oscillator strength:

$$d_g = \sum_k f_{kg} \frac{e^2}{m({\omega_{kg}}^2 - \nu^2)} Ecos(\nu t) \tag{6.10}$$

Note that f_{kj} gives all of the atomic properties that interact with the field so it is a quantity that is completely independent of the field with the exception of looking at one particular polarization. The dipole moment, on the other hand, depends on properties of the field such as the frequency.

Thus the behaviour of an atom in an oscillating field is similar to the behavior of a classical damped harmonic oscillator. So an oscillating electric field mimics a classical oscillating dipole with the same frequency but with having an effective charge. The charge of the electron is e but note that by comparing the equation (6.10) with the result obtained by a classical dipole:

$$\boxed{q_k^2 = f_{kg} e^2} \tag{6.11}$$

where q_k is the effective charge of a classical dipole.

There is a sum rule for the oscillator strengths starting from a particular state $|g\rangle$ which is obtained by summing over all of the other state indices k. The resulting total strength is:

$$\boxed{\begin{aligned} \sum_k f_{kg} &= Z \quad (\#\text{ of } e^-\text{for one polarization}) \\ &= 3Z \quad (\text{for all three polarizations}) \end{aligned}} \begin{matrix}(6.12)\\(6.13)\end{matrix}$$

This is know as the "**Thomas–Reiche–Kuhn (TRK) sum rule**" which states that the total oscillator strength (for one polarization) is equal to the total number of electrons.

6.4 Bound to Continuum States

To treat problems involving bound states to continuum states, assume, like in the bound to bound state calculations, both the rotating frame as well as the rotating wave approximation. Taking these approximations results in the following Hamiltonian:

$$H = \hbar\sum_k \underbrace{(\omega_k - \nu)}_{-\delta_k} |k\rangle\langle k| - \hbar\sum_k \left(\frac{\Omega_k}{2}|k\rangle\langle 0| + |0\rangle\langle k|\frac{\Omega_k^*}{2}\right), \tag{6.14}$$

where ω_k is the transition frequency between the ground and kth continuum state, ν the field frequency, the detuning between the two frequencies is given as δ_k, and Ω_k the Rabi frequency which depends on the particular continuum state being considered. Here, the continuum states are taken as $|k\rangle$, and are defined as the states that have energy past the ionization energy (and are thus, no longer bound), while $|0\rangle$ is one of (the infinitely many) bound states, typically the ground state. Given that the continuum states do not spontaneously decay, the Schrödinger equation is enough to mathematically describe these transitions. Take:

$$\begin{aligned} \dot{c}_0 &= i\sum_k \frac{\Omega_k^*}{2} c_k, \\ \dot{c}_k &= i\delta_k c_k + i\frac{\Omega_k}{2} c_0, \end{aligned} \tag{6.15}$$

where $c_0(0) = 1$ given that the ground state is entirely occupied before the transition occurs. Integrating $\dot{c}_k$ and plugging it into the first equation above gives

$$\dot{c}_0 = -\sum_k |\frac{\Omega_k}{2}|^2 \int_0^t dt'\, c_0(t')\, e^{-i\delta_k(t'-t)}. \tag{6.16}$$

In order to solve this integral, note that because of the $e^{-i\delta_k(t'-t)}$ term, the strongest contribution comes when $t = t'$. Thus, take $c_0(t) \approx c_0(t')$, and to solve the integral, introduce the value ϵ such that $\epsilon \to 0$ like a decay rate. Then,

$$\lim_{\epsilon\to 0+} \int_0^t dt' e^{-i(\delta_k + i\epsilon)(t'-t)} = \lim_{\epsilon\to 0+} \frac{1 - e^{(i\delta_k - \epsilon)t}}{\delta_k + i\epsilon}. \tag{6.17}$$

Taking the limit for long times $t \to \infty$,

$$\lim_{\epsilon\to 0+} \frac{i}{\delta_k + i\epsilon} = \pi\,\delta(\delta_k) + i\mathcal{P}\,\frac{1}{\delta_k}, \tag{6.18}$$

where $\mathcal{P}$ denotes the principal value to account for the singularity encountered when the denominator goes to 0. Putting this all together, an expres-

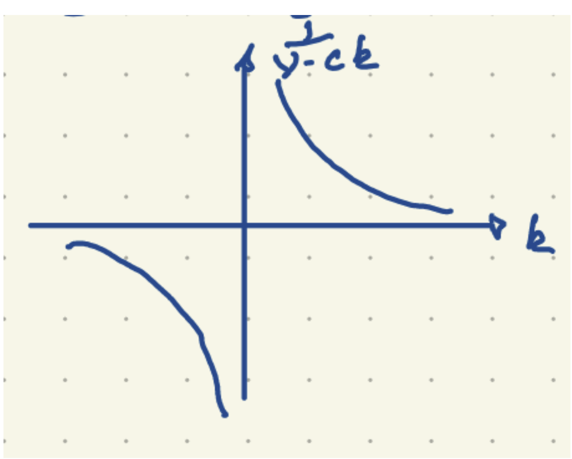


Figure 6.1: The principal value of this function is defined at all points except for the singularity.

sion for $c_0(t)$ can be obtained:

$$\begin{aligned} c_0(t) &= \underbrace{c_0(0)}_{1}\, e^{\frac{\gamma}{2}t}\, e^{i\Delta t}, \qquad \text{with} \qquad (6.19)\\ \gamma &= 2\pi \sum_k |\frac{\Omega_k}{2}|^2\, \delta(\nu - ck), \qquad \text{and}\\ \Delta &= \sum_k |\frac{\Omega_k}{2}|^2\, \mathcal{P}\frac{1}{\nu - ck}. \end{aligned}$$

Here, γ is the "decay" into the continuum states and is non-zero only above the ionization threshold. Δ is a shift that is present below the ionization threshold and mostly cancels out above it, and is thus always present for bound-to-bound transitions (especially if the excited state is close to the ionization threshold). This is elucidated in Fig. 6.1, where in the plot, integrating along the k-axis far beyond the singularity results in a larger cancellation between the curves.

6.5 Spontaneous Emission

The procedure for derivation of the value of the spontaneous emissing constant γ has been famously derived by Wigner and Weisskopf. The idea is outlined here. Spontaneous emission can be described by first starting in some excited state, $|e,0\rangle$ where the 0 indicates that there is no photon, and ending in the ground state $|g,1_k\rangle$ where one photon is emitted into mode k. (The photon frequency is open here, but can be expected, because of energy conservation, to be close to the atomic transition frequency.) This process can now be described by the Hamiltonian of a two-level system but taking into account *all* modes of the vacuum field:

$$H = \hbar\omega|e\rangle\langle e| + \sum_k \hbar ck(a_k^\dagger a_k + \frac{1}{2}) - \hbar\sum_k \left(g_k|e\rangle\langle g|a_k + g_k^*|g\rangle\langle e|a_k^\dagger\right). \tag{6.20}$$

The relevant state space is taken as $|\xi\rangle = |e,0\rangle + \sum_k |g,1_k\rangle$, and an effective Hamiltonian can be defined as

$$H_{\text{eff}} = |\xi\rangle\langle\xi|H|\xi\rangle\langle\xi|, \tag{6.21}$$

which projects the original Hamiltonian into the relevant state space, limiting the relevant Hilbert space, such that

$$H_{\text{eff}} = \hbar\omega|e,0\rangle\langle e,0| + \sum_k \hbar ck|g,1_k\rangle\langle g,1_k| - \hbar\sum_k \left(g_k|e,0\rangle\langle g,1_k| + \text{h.c.}\right). \tag{6.22}$$

In the rotating frame H_{eff} is the same as Eq. (6.14) with $|e,0\rangle \to |0\rangle$ and $|g,1_k\rangle \to |k\rangle$ (note that the roles of ground and excited states are reversed here). The shift is now the Lamb shift which describes coupling to the vacuum fluctuations of the electromagnetic field, while γ describes the spontaneous decay between the two levels $|e\rangle$ and $|g\rangle$. Note that this takes place for all possible polarizations; in particular, each mode $\vec{k}$ has two polarizations α (i.e., the directions perpendicular to $\vec{k}$). If one changes the sum over k in Eqs. (6.19) to an integral and remembers that spontaneous emission is spherically symmetric (in free space), it is obvious that the polarization direction is independent of azimuthal angle ϕ and can be projected onto the polar direction such that

$$\sum_\alpha |g_{k,\alpha}|^2 = |g_k|^2 \sin\theta^2$$

and thus one finally finds

$$\begin{aligned}
\gamma &= 2\pi \sum_{k,\alpha} |g_{k,\alpha}|^2 \, \delta(ck-\omega) \qquad (6.23)\\
&= 2\pi \sum_{\alpha} \frac{V}{(2\pi)^3} \int k^2 dk \int d\phi \int d\theta \, \sin\theta \, |g_{k,\alpha}|^2 \, \delta(ck-\omega)\\
&= 2\pi \frac{V}{(2\pi)^3} 2\pi \int k^2 dk \int d\theta \, \sin^3\theta \, \delta(ck-\omega)\\
&= \frac{16\pi^2}{3} \frac{V}{(2\pi)^3} \left(\frac{\omega}{c}\right)^2 \frac{1}{c} \underbrace{\left|g_{k=\frac{\omega}{c}}\right|^2}_{\frac{|\wp|^2\omega}{2\hbar\epsilon_0 V}},
\end{aligned}$$

and thus the full functional form of the spontaneous emission constant is given by

$$\boxed{\gamma \;=\; \frac{\omega^3 |\wp|^2}{3\epsilon_0 \pi \hbar c^3}}. \tag{6.24}$$

This is the Einstein A coefficient, where $\wp$ is the dipole matrix element. This explains why the decay is strong for high frequencies: $\gamma \propto \omega^3$ and for strongly allowed transitions, $\gamma \propto |\wp|^2$.

6.6 Higher Order Radiation Processes

Define the interaction Hamiltonian for the dipole interaction,

$$\langle b|H|a\rangle = -\frac{e}{mc} \langle b|\vec{p}\cdot\vec{A}(\vec{r})|a\rangle, \tag{6.25}$$

where if a magnetic field and electric field are defined as $\vec{B} = -ikA\hat{y}$, $\vec{E} = ikA\hat{z}$, with a vector potential in the $\hat{z}$ direction, then the Hamiltonian is proportional to $\hat{p}\cdot\hat{z}e^{\vec{k}\cdot\vec{x}}$, which describes a wave propagating in the $\hat{x}$ direction, while being polarized in the $\hat{z}$ direction. In the dipole approximation, $e^{i\vec{k}\cdot\vec{x}} \approx 1$, whereas this term can be Taylor expanded such that

$$\begin{aligned}
e^{ikx} &= 1 + ikx - \frac{1}{2}(kx)^2 + \cdots ,\\
\langle b|H|a\rangle &= H(E1) + H(B1) + H(E2) + \cdots ,
\end{aligned}$$

where $H(E1)$, the electric dipole term, is associated with 1, $H(B1)$ and $H(E2)$, the magnetic dipole and electric quadrupole terms respectively are related to ikx, where higher order terms in the expansion of the exponential term and the Hamiltonian expectation value continue to match. Given that

$$\begin{aligned} H(B1) &= B \cdot \langle b|\mu_0 \vec{L}|a\rangle, \\ H(E2) &= \frac{ie\omega}{2c} E \cdot \langle b|xz|a\rangle, \end{aligned}$$

for the magnetic dipole and electric quadrupole terms, respectively, it can be seen that in atomic units, $\mu_0, \frac{1}{c} \propto \alpha$. As a result, given that the rate is proportional to the above terms squared, the magnetic dipole and electric quadrupole transitions are a factor of α^2 weaker (about four orders of magnitude), and are thus counted as "forbidden" transitions.

6.7 Selection Rules and the Wigner-Eckart Theorem

For the E1 transition between states b and a (or any other transition), the Wigner-Eckart theorem allows us to considerably simplify the exact calculation of coupling elements, due to symmetry. Take the E1 transition from $|a\rangle$ to $|b\rangle$, for example:

$$\langle b, j_b, m_b|\hat{\vec{r}}|a, j_a, m_a\rangle. \tag{6.26}$$

For any spherical tensor, T (for example, for $T_{lm} \propto Y_{lm}$, the spherical harmonics, the Wigner-Eckart theorem results in:

$$\langle j, m|T_{kg}|j', m'\rangle = \langle j, m, k, g||j', m'\rangle\langle j|||T_k|||j'\rangle, \tag{6.27}$$

where the first term is simply a Clebsch-Gordan coefficient, and the second term keeps only its first quantum number dependence. Essentially, all m, m' pairs of this transition differ only by some calculable numerical factor which is given by ratios of the Clebsch-Gordan coefficients. The proof, which is not stated here, can be constructed by utilizing the spherical symmetry of the problem, and noting that the m, m' elements are related by rotations.

Take the E1 transition as an example for $L = 1$ using spherical harmonics such that

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta, \qquad Y_{1,\pm1} = \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}. \tag{6.28}$$

Then, define

$$r_0 = r\cos\theta = \frac{4\pi}{3} r Y_{10}, \qquad r_\pm = \frac{4\pi}{3} r Y_{1,\pm 1}. \tag{6.29}$$

Using the Wigner Eckart theorem then results in

$$\langle b, j_b, m_b | r_m | a, j_a, m_a \rangle = \langle b, j_n | r | a, j_a \rangle \langle j_b, m_b | T_{1m} | j_a, m_a \rangle, \tag{6.30}$$

where $rT_{1m} \equiv r_m$ is defined. In the above equation, the first term is related only to the radial coordinate, r and is dominated by parity selection rules. The second term is dependent on the angles (θ and ϕ), and can be easily calculated from the Wigner-Eckart theorem using the Clebsch-Gordan coefficients. The second term gives

$$j_b - j_a = \pm 1, 0, \; m_b - m_a = \pm 1, 0, \tag{6.31}$$

with $j_a = j_b = 0$ being forbidden. If it turns out that $\vec{L}, \vec{S}$ are good quantum numbers instead of $\vec{j}$, then $\Delta L = \pm 1, 0$, $\Delta m_l = \pm 1, 0$ with $\Delta S = 0,$, $\Delta m_s = 0$ where for a single electron, $\Delta l \neq 0$. Another example is given in figure 6.2. This particular example is only complicated when it comes to calculating $\langle j' = 1 | T | j = 0 \rangle, \langle j' = 1 | T | j = 1 \rangle, \langle j' = 0 | T | j = 1 \rangle$, where the rest of the calculation is just via finding the right Clebsch-Gordan coefficients. For higher order transitions, similar logic is applied, for example, finding that $\Delta J = \pm 2, \pm 1, 0$ with $\Delta m_j = \pm 2, \pm 1, 0$.

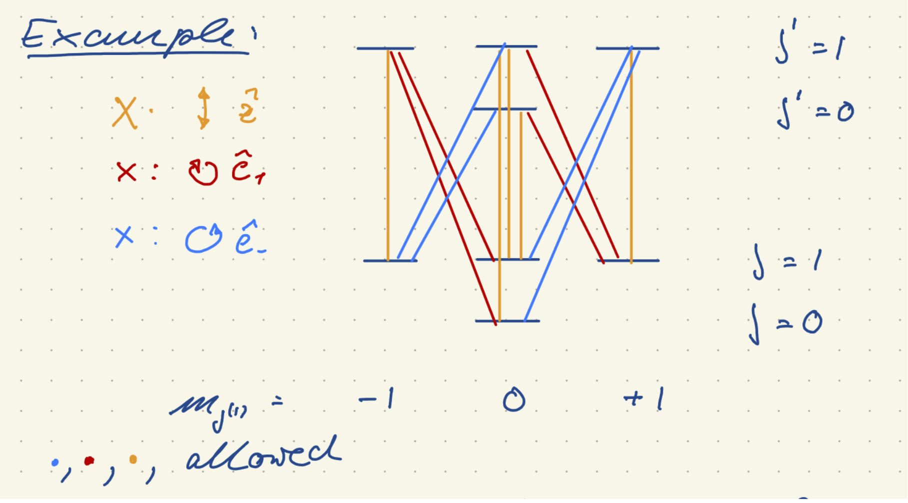


Figure 6.2: An example of the main ($j \rightarrow j'$) transitions and the "sub-transitions" for different m, m'. Note that the different colors refer to different polarizations of the light.

Chapter 7

Line Shapes

7.1 Recap and motivation

Even in a completely coherent two-level system, the decay rate of the state will still lead to lifetime broadening, resulting in a finite width of the transition. In addition to lifetime broadening, many other factors may also affect the line width, some of which will be covered here.

Recall that the ideal line shape for measurement is a Rabi transition. In this case, the probability for a transition is given by:

$$P = \frac{\Omega^2}{\Omega^2 + \delta^2} \sin^2 \frac{\sqrt{\Omega^2 + \delta^2}}{2} t$$

Although this is what we aspire to, we must also deal with various broadenings.

7.1.1 General Approach

In what follows, a general method of approaching broadening will be given. Let V be some potential that couples $|a\rangle$ and $|b\rangle$, and let $\omega_0 = \omega_b - \omega_a$. Let the wavefunction be given by $|\psi\rangle = a|a\rangle + b|b\rangle$. The equations of motions for a and b are then:

$$\begin{aligned} i\dot{a} &= \langle a|V|b\rangle e^{-i\omega_0 t} b \\ i\dot{b} &= \langle b|V|a\rangle e^{i\omega_0 t} a \end{aligned}$$

Without loss of generality, assume that $a(0) = 1$. The aim of this calculation is to find the rate from $|a\rangle$ to $|b\rangle$:

$$W_{ba} : \text{rate } |a\rangle \text{ to } |b\rangle \equiv \frac{d}{dt}|b(t)|^2 \tag{7.1}$$

First order perturbation theory can then be used to solve for W_{ba} if the interaction is weak enough. This entails the approximation that $a(t) \approx a(0) = 1$, so the population of the starting state changes very little. Note that this approximation usually makes sense considering the fact that various line broadening effects limit the time over which the measurement is useful. Thus, in most cases, the starting state population does not change much over the time span of the measurement. Then,

$$\begin{aligned} W_{ba} &= \int_0^t dt' \underbrace{\langle a|V(t)|b\rangle\langle b|V(t')|a\rangle}_{G_{ba}(t,t')=G_{ba}(t-t')} e^{-i\omega_0(t-t')} + c.c. \\ &= \int_{-\infty}^t d\tau\, G_{ba}(\tau)e^{-i\omega_0\tau} \end{aligned} \tag{7.2}$$

Note that taking the Green's function $G_{ba}(t,t')$ to be of the form $G_{ba}(t-t') \equiv G_{ba}(\tau)$ is an assumption: it is true in steady-state cases and approximately true in most other cases because typically the function changes much slower with t than with τ. (This gives the same short-time ($t << \frac{1}{\Omega}$) monochromatic limit as the case of Rabi oscillations.) Note that the above formulation has made some assumptions that may not necessarily hold in a completely general case.

7.2 Homogeneous and Inhomogeneous Broadening

"Homogeneous line broadening" means that all atoms (or other radiators) in the system have identical line shape functions. Examples include the natural lineshape (i.e., lifetime broadening) and pressure broadening. The lineshape of homoegenous broadening is typically a Lorentzian.

"Inhomogeneous broadening" indicates that each atom has a slightly different micro-environment. The most important example of this is Doppler

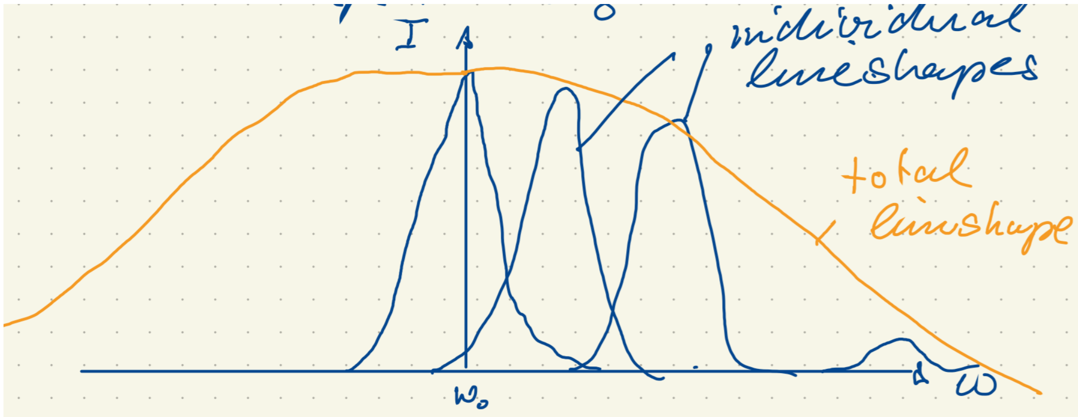


Figure 7.1: An example of a Doppler broadened lineshape as an average over the lineshapes of individual atoms.

broadening, in which each atom has a slightly different velocity and thus sees a different Doppler shift. The total lineshape is then an average over lineshapes of individual atoms, as shown in Fig. 7.1. Orders of magnitude can separate the widths of the blue lines and yellow lines. The lineshape associated with inhomogeneous broadening is typically a Gaussian.

7.3 Examples

7.3.1 Natural Linewidth

In the case of natural linewidth:

$$G_{ba}(\tau) = \frac{|\wp|^2}{4} e^{-\Gamma/2\tau} e^{i\omega\tau}$$

Where $\Gamma = \gamma_b + \gamma_a$ if both levels decay. Then,

$$W_{ba} = \frac{|\wp|^2}{2} \frac{\Gamma/2}{(\Gamma/2)^2 + \delta^2} \tag{7.3}$$

Note that this is the limit of $\Omega \to 0$, and it is a Lorentzian.

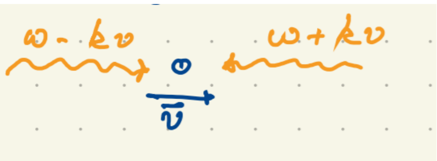


Figure 7.2: A schematic depiction of the Doppler shift of ω of the electric field seen by an atom moving at velocity $\vec{v}$.

7.3.2 Doppler Broadening

The Doppler shift of an atom with velocity $\vec{v}$ and resonance frequency ω_0 is given by:

$$\omega' = \omega_0 + \vec{k} \cdot \vec{v} \tag{7.4}$$

This is depicted schematically in Fig. 7.2.

From Fig. 7.2, the following relation is seen:

$$\frac{\Delta\omega}{\omega_0} = \frac{v}{c} \tag{7.5}$$

In order to calculate the overall lineshape, an average over all the atoms must be performed. To do this, note that the velocity varies across the ensemble of atoms, with the typical velocity distribution given by the Maxwell-Boltzmann distribution. So, the fraction of atoms with velocity between v and $v + dv$ is given by:

$$f(v)dv = \frac{1}{\sqrt{\pi}\alpha} e^{-\frac{v^2}{\alpha^2}} \tag{7.6}$$

This is the Maxwell-Boltzmann distribution, where $\alpha = \sqrt{\frac{2kT}{M}}$ is the most probable velocity and depends on temperature T and the atomic mass M.

When Eq. (7.6) and Eq. (7.5) are put together, this yields:

$$\boxed{g_{\text{Doppler}}(\omega') = \frac{c}{\sqrt{\pi}\alpha\omega_0} e^{-(\frac{c\Delta\omega}{\alpha\omega_0})^2}} \tag{7.7}$$

The function g is called "spectral density" or "form factor." The FWHM of g_{Doppler} is $\Delta\omega = 2\sqrt{\ln 2}\frac{\alpha\omega_0}{2} = 2\frac{\ln 2}{\alpha}k$. For example, for Hydrogen at room temperature, $\alpha \approx 2230 m/s$, and $\frac{\Delta\omega_{Doppler}}{2\pi} \approx 6$ GHz for a wavelength of $\lambda = 600 nm$. The spectral density reflects the Gaussian lineshape, as typical for inhomogenous broadening.

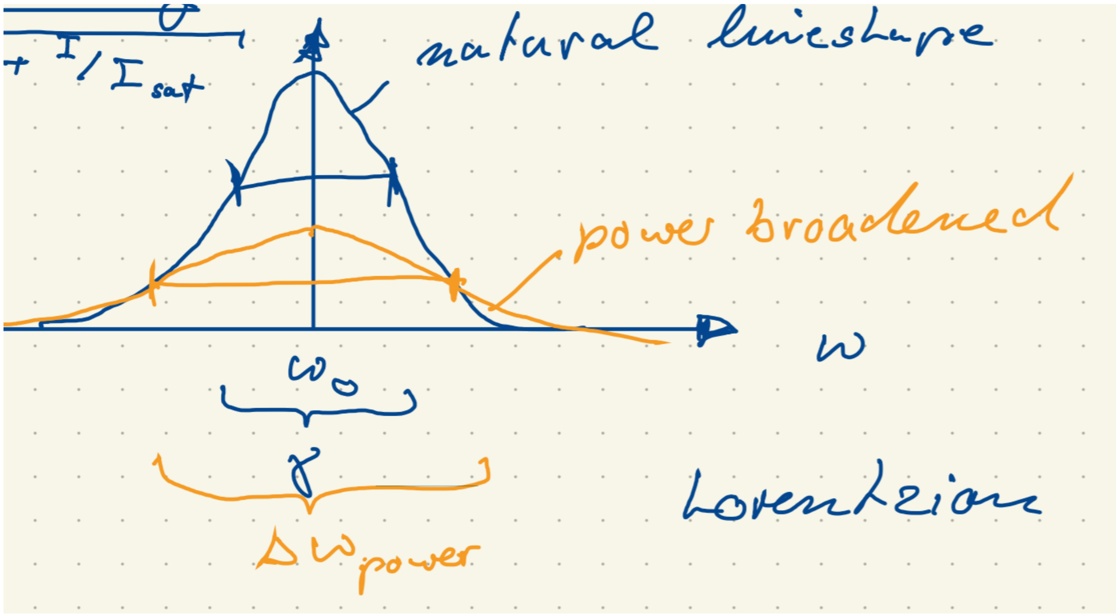


Figure 7.3: An example of a power broadened linewidth.

7.3.3 Power Broadening

As this concept has been covered previously in a different context, only the results will be cited here. The power broadened lineshape is given by:

$$\Delta\omega_{power} = \Gamma\sqrt{1 + I/I_{sat}} \tag{7.8}$$

I is intensity, and I_{sat} is saturation intensity. An example of a power-broadened lineshape is given Fig. 7.3. Typically, Doppler broadening is many orders of magnitude larger than the natural linewidth, but the power broadened linewidth is only somewhere between two to ten times larger than the natural linewidth. This is Lorentzian, as expected of homogeneous broadening.

7.3.4 Pressure Broadening

Pressure broadening typically arises from the fact that there are many atoms or particles which can collide elastically with each other. Thus, nothing changes inside the atom due to the collision, but the relative velocities of the atoms will be affected. The motion is then governed by diffusion. As collisions are assumed here to lead to loss of coherence, the collision time is equivalent to the correlation/coherence time T_2. The pressure broadening is given by:

$$\Delta\omega_{pressure} = \frac{1}{\pi T_2} \tag{7.9}$$

The lineshape is Lorentzian because diffusion affects all atoms equally.

7.3.5 Dicke Narrowing

Unlike the case above, some elastic collisions don't disturb the coherence of the atoms. For example, this is the case with buffer gases like Helium. In this scenario, Doppler broadening is limited as collisions with the buffer gas effectively slow the atoms down.

Again, the atoms are governed by diffusion:

$$\begin{aligned}
P(z, z', t) &\equiv \text{probability}[(z, 0) \rightarrow (z', t)] \\
P(z, z', t) &= \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{(z-z')^2}{4Dt}} \\
G_{ba} &= \frac{|\wp|^2}{4} \overline{e^{ik(z-z')}} \\
&= \frac{|\wp|^2}{4\sqrt{4\pi Dt}} \int ds e^{\frac{-s^2}{4Dt}} e^{iks} \\
&= \frac{|\wp|^2}{4} e^{-k^2 Dt}
\end{aligned}$$

Using the Green's function to calculate W_{ba}:

$$W_{ba} = \frac{|\wp|^2}{2} \frac{k^2 D}{(k^2 D)^2 + \delta^2} \tag{7.10}$$

This is a Lorentzian, and $\Delta\omega_{Dicke} = 2k^2 D$. For an ideal gas, $D = \frac{\alpha l}{3}$, where l is the mean free path. Subsituting this into $\Delta\omega_{Dicke}$ yields:

$$\Delta\omega_{Dicke} 2\frac{2\pi}{\lambda} k \frac{\alpha l}{3} = \frac{2\pi}{3\sqrt{2\ln 2}} \frac{l}{\lambda} \Delta\omega_{Doppler}$$

Note that if $l \ll \lambda$, there can be considerable narrowing compared to $\Delta\omega_{Doppler}$.

7.3.6 Transit-time Broadening

This occurs when atoms transit through an interaction region such as a laser bean during a time window τ. In this case, the calculation is given by:

$$\begin{aligned}
\overline{E(\nu)} &= \frac{E_0}{2}\int_{-\tau/2}^{\tau/2} d\tau (e^{i\omega_0 t} + e^{-i\omega_0 t})e^{-i\nu t} \\
&= E_0 \frac{\sin(\frac{\omega_0 \cdot \nu}{2}\tau)}{\omega_0 \cdot \nu} \\
&\implies g_{\text{transit}}(\delta) = \frac{2}{\pi\tau}\frac{\sin^2(\delta/2\tau)}{\delta^2} && (7.11) \\
&\implies \Delta\omega_{\text{transit}} \approx \frac{5.6}{\tau} && (7.12)
\end{aligned}$$

For example, for $v = 500 m/s$ and a laser beam width of $1mm$, $\tau \approx 2 \times 10^{-6}s$, so $\Delta\omega_{transit} \approx 2.8MHz$.

7.4 Mitigation of broadening

Often, it is easy, or at least possible to employ line narrowing techniques. Among the most common techniques is to measure longer if possible (most linewidths depend inversely on the square root of the measuring time). In addition, for low-noise situation, one can "split the line," i.e., determine the line maximum to considerably higher accuracy than the pure concept of the linewidth suggests.

This brief section mentions some concepts that are central to the discussion of line forms.

7.4.1 Definition of "life times"

In a typical experimental context, three types of life time are discussed.

- T_1 is the population life time, i.e., the inverse of the natural linewidth γ.
- T_2 is the coherence life time, i.e., the inverse of the decay rate of the non-diagonal density matrix elements, in the ideal case. It is often much longer than T_2^* ("tee-two-star"), the actual measured decoherence time. More often than not, T_2 and T_2^* are the homogeneous and

inhomogeneous coherence times, and techniques like spin echo can effectively lengthen T_2^* to T_2.

Note that the shortest of the three life times is dominant and effectively determines the linewidth.

7.4.2 Inhomogeneous broadening

Inhomogeneous broadening can typically relatively easily be treated by selecting out certain atoms or groups of atoms. For example, Doppler broadening can be mitigated by measuring perpendicularly to an atomic beam or by so-called "hole burning," a technique where the combination of two lasers depletes atoms of only one velocity group. Another possibility is spin echo: Here, the diffusion of turning spins after a pulse is reversed by sending the reverse of the pulse, thus effectively inverting time. In general the understanding is that there is always something that can be done to narrow an imhomogeneously broadened line if one is willing to invest some work.

7.4.3 Homogeneous broadening

There are not typically methods that can be easily employed to narrow homogeneously broadened lines. Thus, more often than not, trying to increase the measuring time is the best option.

7.4.4 Ramsey interferometry

Effectively lengthening the accessible measuring time without adding to the noise is the goal of Ramsey interferometry. Here is a brief outline of the idea of this technique.

As a recap, the transition probability into the excited state is

$$P(t) \;=\; \frac{\Omega^2}{\Delta^2+\Omega^2}\sin^2\frac{\sqrt{\delta^2+\Omega^2}}{2}t,$$

with Rabi frequency Ω and detuning Δ. (This is the ideal case where the decay on the relevant time scale can be neglected.) The linewidth of this expression determines the measuring precision with the measuring time for a

π-pulse (that transfers the maximum amount of population into the excited state)

$$\tau = \frac{\pi}{\sqrt{\Delta^2 + \Omega^2}}.$$

With these expressions, it is obvious that the linewidth is, ideally Ω. Making Ω very small leads to a long τ. Obviously, how long τ can be is limited by the coherence in the system, and often the main source of decoherence is during the interaction with the laser. Thus, ideally one would like to increase the time (i) beyond $1/\Omega$ and (ii) for a situation where the atoms don't interact with anything.

Ramsey's idea was to split the π-pulse into two $\frac{\pi}{2}$-pulses and let the atoms evolve freely (for a time T) in between (see Fig. 7.4. Then one finds that for $\Delta \to 0$, the excited state population probability

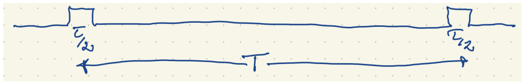


Figure 7.4: Ramsey pulse sequence with π-pulse time τ and free evolution time T.

$$P(t) \propto \cos^2 \frac{\Delta\omega\, T}{2},$$

that is, the fringe width is now $\Delta\omega = \frac{2\pi}{T}$. And T is limited now only by the (native) decoherence! (See the Cs fountain clock example in chapter 2, Fig. 2.8).

Chapter 8

Many-Electron Atoms

While in previous chapters, often the behaviour of many electrons in an atom vs. the single atom in hydrogen was mentioned, there was an important piece missing: the electrons have a strong (Coulomb) interaction between each other, which rescales the energy and dictates which orbitals (i.e., eigenfunctions) in the atom are occupied in which order (see "Hund's rules").

8.1 Helium

Helium is the simplest example for an atom with more than one electron. Assuming, for the moment, an infinitely heavy nucleus, the Hamiltonian for helium reads

$$H \;=\; \sum_{i=1}^{2} \underbrace{\left(\frac{\hbar^2}{2m}\vec{\nabla}_i^2 - \frac{2\tilde{e}}{r_i}\right)}_{H_i} + \underbrace{\frac{\tilde{e}}{r_{12}}}_{V} \,,$$

with $H_i$the single-electron (hydrogen-like) Hamiltonian of electron i, r_i the distance between nucleus and electron i and r_{12} the distance between the two electrons, determining the interaction term V.

8.1.1 Ground state

In the ground state, both electrons occupy the same orbital ($1s^2$). The unperturbed wavefunction is then determined via

$$\begin{aligned}(H_1 + H_2)|\Psi\rangle &= E^{(0)}|\Psi\rangle \\ \text{where} \quad |\Psi\rangle_{1s^2} &= |\psi_1\rangle \otimes |\psi_2\rangle \qquad (Z=2) \\ E^{(0)} &= 2E_1(Z=2) \;\approx\; -109\text{eV}.\end{aligned}$$

Adding in V as (first-order) perturbation to $\Psi^{(0)}_{1s^2} = \frac{1}{4\pi} R_{1s}(r_1)\, R_{1s}(r_2)$ leads to

$$\langle V\rangle \;=\; \langle \Psi_{1s^2}|V|\Psi_{1s^2}\rangle \;\approx\; 34\text{eV},$$

which leads to the perturbed ground state energy in helium of $E^{(1)}(1s^2) \approx$ -75 eV. For the ionization energies of helium, this would mean

$$\begin{aligned}\text{He}^+ \;&\rightarrow\; \text{He}^{++} \;:\approx\; 54.5\text{eV} \quad (=\; 109\text{eV}/2), \\ \text{which leaves for He} \;&\rightarrow\; \text{He}^{+} \;:\approx\; 21\text{eV}\end{aligned}$$

Obviously, perturbation theory is not extremely accurate here, since 34 eV is not that much smaller than 75 eV. Typically, the next approach is to use variational theory with the same ansatz, which leads to the much more accurate helium ground state energy of -79 eV.

8.1.2 Excited state

For the excited states, the electrons typically are in different orbitals (e.g., $1s$ and $n\ell$). The same logic as above gives for the unperturbed wavefunctions

$$\begin{aligned}\psi_{1s}(r_1) &= \frac{1}{\sqrt{4\pi}} R_{1s}(r_1), \\ \psi_{n\ell} &= Y_{\ell m}(\theta_2,\phi_2)\, R_{n\ell}(r_2).\end{aligned}$$

Thus

$$\Psi \;=\; \begin{Bmatrix} \psi_{1s}(1)\,\psi_{n\ell}(2) \quad \text{or} \\ \psi_{n\ell}(1)\,\psi_{1s}(2) \end{Bmatrix} \qquad \text{“exchange degeneracy''}$$

The symmetry behind this (i.e., symmetry under electron exchange) leads to further thoughts. Start by defining a two-particle exchange operator $\hat{P}$:

$$\hat{P}_{12}\, f(\vec{r}_1,\vec{r}_2) \;\equiv\; f(\vec{r}_2,\vec{r}_1) \;=\; \pm f(\vec{r}_1,\vec{r}_2),$$

where the second equal sign comes from the fact that two exchanges must result in the same function as the original one. If the Hamiltonian is symmetric und two-particle exchange, $[H, \hat{P}_{12}] = 0$, the eigenfunctions of H can be chosen such that they are also eigenfunctions of $\hat{P}_{12}$, i.e.,

$$\Psi^{\pm} \;=\; \frac{1}{\sqrt{2}} \left(\psi_{1s}(1)\, \psi_{n\ell}(2) \pm \psi_{n\ell}(1)\, \psi_{1s}(2) \right).$$

If one now takes the perturbation V into account, one finds

$$\langle V \rangle^{\pm} \;=\; J \pm K,$$

where

$$\begin{aligned} J &= \langle (1,2)|V|(1,2)\rangle \;=\; \langle (2,1)|V|(2,1)\rangle \\ K &= \langle (1,2)|V|(2,1)\rangle \;=\; \langle (2,1)|V|(1,2)\rangle. \end{aligned}$$

To give an order of magnitude of these terms, for $n = 2, \ell = p$ one finds $J \approx -2.8 \cdot 10^{-2}$ eV and $K \approx 0.25$ eV. This is much smaller than the ground state perturbation (because of the much smaller overlap of the wavefunctions), but also note that the splitting K is much bigger than the shift J.

8.1.3 Spin eigenfunctions

Electrons are fermions, thus the total wavefunction, including spin, has to be antisymmetric! Thus for the ground state

$$\begin{aligned} &\Psi^{\text{space}}_{1s^2} \text{ is symmetric, \quad thus} \\ &\Psi^{\text{spin}}_{\text{g.s.}} \text{ is antisymmetric!} \end{aligned}$$

Similar, in the excited state

$$\begin{array}{lccc} \Psi^{\text{space}}_{1s^2} & \text{is } \underbrace{\text{symmetric}} & \text{or} & \underbrace{\text{antisymmetric}} \\ \Psi^{\text{spin}}_{\text{g.s.}} & \text{is antisymmetric} & \text{or} & \text{symmetric} \end{array}$$

More formally, for symmetric (S) and antisymmetric (A) wave functions,

$$\Psi^{\text{total}} \;=\; \Psi^{\text{space}} \cdot \Psi^{\text{spin}} \;=\; \begin{cases} \Psi^{\text{space}}_{S} \cdot \Psi^{\text{spin}}_{A} & \text{or} \\ \Psi^{\text{space}}_{A} \cdot \Psi^{\text{spin}}_{S}. \end{cases}$$

Here, of the spin functions (of two electrons of spin-$\frac{1}{2}$):

$$\Psi^{\text{spin}} \;\in\; \{ |\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle \},$$

the symmetric ones have spin quantum number $S = 1$ with $M_S = 0, \pm 1$, thus, the *triplet state* consists of

$$\Psi_S^{\text{spin}} \;=\; |\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right),$$

whereas for the antisymmetric *singlet state* $S = 0, M_S = 0$,

$$\Psi_A^{\text{spin}} \;=\; \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right).$$

8.2 Many-electron systems (with nucleus)

The full formulation for a general N electron atom requires considering the nucleus as well. For an atom with a nucleus of charge Z, the Hamiltonian is given by

$$H_{N,Z} = \frac{p_{nuc}2}{2m_{nuc}} + \sum_{i=1}^{N}\left(\frac{p_i^2}{2m_i} - \frac{\tilde{e}Z}{|\vec{r}_i - \vec{r}_{nuc}|}\right) + \frac{1}{2}\sum_{i\neq j}\frac{\tilde{e}}{|\vec{r}_i - \vec{r}_j|} \tag{8.1}$$

These terms represent the momentum of the nucleus, the momentum of the individual electrons, the interaction bewteen the electrons and the nucleus, and the interaction of the electrons with each other. We want to be able to separate external degrees of freedom (coordinates of the center-of-mass) and internal degrees of freedom (coordinates of individual particles relative to the COM). In the COM frame, we make the following substitutions:

$$\begin{aligned}
M &= m_{nuc} + \sum_i^N m_i && \text{(total mass)} \\
\vec{R} &= \frac{1}{M} \sum \left(m_{el} \sum_i \vec{r}_{i,el} + m_{nuc} \vec{r}_{nuc} \right) && \text{(COM)} \\
\vec{r}_i &= \vec{r}_{i,el} - \vec{r}_{COM} \\
\vec{P} &= \frac{\hbar}{i} \vec{\nabla}_R \\
\vec{p}_i &= \frac{\hbar}{i} \vec{\nabla}_i \\
\vec{P}_{nuc} &= \frac{m_{nucl}}{M} \vec{P} + \sum_i \vec{p}_i \\
\vec{p}_{i,el} &= \frac{m_{el}}{M} \vec{P} + \vec{p}_i
\end{aligned}$$

Plugging in these values allows to rewrite the total kinetic energy as:

$$\frac{\vec{p}_{nuc}^2}{2m_{nuc}} + \sum_i^N \frac{\vec{p}_{i,el}^2}{2m_{i,el}} = \frac{\vec{P}^2}{2M} + \sum_i \frac{\vec{p}_i^2}{2\mu} + \underbrace{\frac{1}{m_{nuc}} \sum_{i<j} \vec{p}_i \cdot \vec{p}_j}_{\text{“mass polarization”}} \tag{8.2}$$

The mass polarization term is usually neglected. (See chapter 4 for description of this term.) One can now rewrite the total Hamiltonian in COM coordinates, and separate the internal and external degrees of freedom. The level structure only depends on the internal degrees of freedom, so we can set aside the part describing the COM motion and only consider the total Hamiltonian for the internal degrees of freedom:

$$H = \sum_i^N \frac{\vec{p}_i^2}{2\mu} + \sum_i^N V_i + \sum_{i<j} W_{ij} \tag{8.3}$$

where we have defined two interaction terms

$$V_i = -\frac{\tilde{e} Z}{r_i} \qquad \text{the interactions of electrons with the nucleus}$$

$$W_{ij} = \frac{\tilde{e}}{r_{ij}} \qquad \text{the interactions between electrons.}$$

8.2.1 The Pauli principle and the Slater determinant

The general wave functions for N electrons depend on:

- spatial coordinates $\vec{r}_i$, and
- spin coordinates m_{si}.

We can combine them together as a single set of coordinates $x_i = \{\vec{r}_i, m_{si}\}$.

There are two important ideas to remember when constructing the many body wavefunction:

First, electrons are **indistinguishable**. This means that the Hamiltonian commutes with the "permutation operator" P. P acting on the N particle wave function ψ permutes the coordinates of ψ:

$$P\psi(x_1, ..., x_N) = \psi(x_{P(1)}, x_{P(2)}, ..., x_{P(N)}) \ .$$

Any general permutation operator P can be built up from the two particle exchange operators ("swaps") introduced in the previous section. An exchange operator P_{ij} acts on ψ by exchanging the coordinates of particles i and j:

$$\begin{aligned} P_{ij}\psi(x_1, ..., x_i, ..., x_j, ..., x_N) &= \psi(x_1, ..., x_i, ..., x_j, ..., x_N) \\ &= \pm\psi(x_1, ..., x_i, ..., x_j, ..., x_N) \end{aligned} \tag{8.4}$$

If the sign in equation (8.4) is "+", then the particles are bosons (wavefunction is symmetric), if it is "−", then the particles are fermions (the wavefunction is antisymmetric).

This leads to the second idea: for fermions, the wavefunction changes sign under odd permutations (it is antisymmetric under particle exchange), but for bosons it does not (it is symmetric under particle exchange). Even though there are typically multiple ways to decompose a general permutation P into two particle "swaps", the number of swaps for a given P will be either always even or always odd. An odd number of swaps will result in a sign change when P acts on an antisymmetric wavefunction:

$$P\psi \rightarrow (-1)^P\psi$$

where

$$(-1)^P = \begin{cases} +1 & \text{if } P \text{ is even} \\ -1 & \text{if } P \text{ is odd} \ . \end{cases}$$

So for fermions, $P\Psi = (-1)^P\Psi$ (Ψ is antisymmetric), and for Bosons, $P\Psi = \Psi$ (Ψ is symmetric).

Now, one can construct an antisymmetric many-body wavefunction using the "antisymmetrization operator"

$$\hat{A} = \underbrace{\frac{1}{\sqrt{N!}}}_{\text{normalization}} \sum_P (-1)^P P \tag{8.5}$$

Where the sum is over all $N!$ possible permutations (P) of N electrons. Acting with $\hat{A}$ on a wavefunction of N electrons will produce a wavefunction that is antisymmetric.

Proof:

$$\begin{aligned}
P\hat{A}\psi &= \frac{1}{\sqrt{N!}} \sum_Q (-1)^Q PQ\psi \\
&= \frac{1}{\sqrt{N!}} \sum_{PQ} (-1)^P (-1)^{PQ} PQ\psi \\
&= (-1)^P \frac{1}{\sqrt{N!}} \sum_R (-1)^R R\psi \qquad\qquad (\text{where } R \equiv PQ) \\
&= (-1)^P \hat{A}\psi.
\end{aligned}$$

Starting with a wavefunction Ψ_0 that is a product of individual particle wavefunctions ψ_i, one gets

$$\Psi_0(x_1, ..., x_N) = \prod_i^N \psi_i(x_i) \tag{8.6}$$

Ψ_0 is not an eigenfunction of the permutation operator. In order to find the real fermionic wavefunction (Ψ_f), we need to apply $\hat{A}$:

$$\begin{aligned}
\Psi_f(x_1, ..., x_N) &= \hat{A}\Psi_0 &(8.7)\\
&= \frac{1}{\sqrt{N!}} \underbrace{\det(a_{ij})}_{\text{“Slater determinant”}} &(8.8)
\end{aligned}$$

where $a_{ij} \equiv \psi_i(x_j)$ for single-particle wavefunctions.

Slater determinant

This antisymmetrized wavefunction is called “Slater determinant,” Properties that arise from the Slater determinant:

- If any two ψ_i are equal then $\Psi_f = 0$. This is the **Pauli principle: no two fermions can occupy the same single-particle state.** More generally, $\Psi_f = 0$ if any of the single-particle states are linearly dependent.

- Ψ_f is invariant under elementary replacement (i.e. elementary replacements of rows (or columns) in the matrix does not change the determinant): $\psi_i \to \psi_i + \sum_{i \neq j} c_j \psi_j$. So the **Slater determinant Ψ_f is not determined by a particular set of ψ_i, but by the subspace they span.**

8.2.2 Scalar products and expectation values

How to calculate scalar products and expectation values using the full wavefunctions/Slater determinants? Recall that

$$\langle \vec{x} | \Psi \rangle \equiv \Psi(\vec{x}) = \Psi(x1, ..., x_N).$$

The scalar product between two many-body states is

$$\langle \Phi | \Psi \rangle = \det \langle \phi_j | \psi_i \rangle \tag{8.9}$$

Proof:

$$\begin{aligned} \langle \Phi | \Psi \rangle &= \int d^N x \frac{1}{N!} \sum_{P,Q} (-1)^{PQ} \, \phi_i^*(x_{P(i)}) \, \psi_j(x_{Q(j)}) \\ &= \frac{1}{N!} \sum_{P,Q} (-1)^{PQ} \sum_k \langle \phi_{P^{-1}(k)} | \psi_{Q^{-1}(k)} \rangle \\ &= \det \langle \phi_j | \psi_i \rangle . \end{aligned}$$

The generalized expectation value of the interactions terms is calculated similarly via

$$\langle \Phi | \sum_{i=1}^{N} V_i | \Psi \rangle = \langle \Phi | \Psi \rangle \sum_{i,j} \langle \phi_i | \sum_k V_k | \psi_j \rangle B_{ji} \tag{8.10}$$

$$\langle \Phi | \sum_{i<j} W_{ij} | \Psi \rangle = \langle \Phi | \Psi \rangle \sum_{i,j,k,l} \langle \phi_i \psi_j | \sum W | \psi_k \psi_l \rangle (B_{ki} B_{lj} - B_{kj} B_{li}) \tag{8.11}$$

with $B_{ij}^{-1} = \langle \phi_i | \psi_j \rangle$.

Properties:

As expected, the wavefunctions are normalized so that

$$\langle \Psi | \Psi \rangle = 1 \qquad\qquad \text{if } \psi_i \text{ are orthonormal.}$$

We also have that

$$\langle \Phi | \Psi \rangle \neq 0 \tag{8.12}$$

iff the same single particle states are occupied for Φ and Ψ.

For $\{\psi_i\}$, $\{\phi_i\}$ orthonormal, we use equation (8.10) to show that

$$\langle \Psi | \sum_i V_| \Psi \rangle = \sum_i \langle \psi_i | V_i | \psi_i \rangle$$

and thus

$$\langle \Phi | \sum V | \Psi \rangle \neq 0$$

only if *at most* one ψ_i = "ψ_{hole}" is replaced in Φ by ϕ_j = "ϕ_{particle}" that is occupied in ψ_i. In this case, Φ is called a "one-particle-one-hole" excitation $\Phi_{p.h.}$ of Φ and

$$\langle \Psi_{p.h.} | \sum V | \Psi \rangle = \langle \psi_p | V | \psi_h \rangle. \tag{8.13}$$

Similarly, for W, we have "two-particle-two-hole" excitations

$$\begin{aligned} \langle \Phi | \sum_{i<j} W_{ij} | \Psi \rangle &= \langle \Phi_{p1,p2;h1,h2} | \sum_{i<j} W_{ij} | \Psi \rangle \qquad (8.14) \\ &= \langle \psi_{p1} \psi_{p2} | W_{12} | \psi_{k1} \psi_{k2} \rangle - \langle \psi_{p1} \psi_{p2} | W_{12} | \psi_{k2} \psi_{k1} \rangle. \end{aligned}$$

8.3 Hund's Rules

The framework developed in the last few sections can be boiled down to a concise set of rules for describing the orbital filling of many-electron atoms. These rules are known as *Hund's Rules* and are responsible for the structure of the periodic table. They are as follows:

1. In any given subshell (i.e. for a given n and L), the state with the largest S has the lowest energy.

2. Within a shell (i.e. for a given n) and for the same S, the state with highest L has the lowest energy.

In the preceding, n refers to the principal quantum number while capital S and L refer to the total spin and orbital angular momenta of the (potentially many) electrons respectively. The intuition behind these rules is that Coulomb repulsion between the electrons leads to lower energy states when the electrons and further apart from one another, which occurs for states with higher S and lower L. An important note is that the first rule gives a bigger energy difference than the second.

8.3.1 The Example of Carbon

As a simple example of Hund's rules which will motivate further study, consider a carbon atom with the configuration: $1s^2 2s^2 2p^2$. The level scheme is given in the figure below.

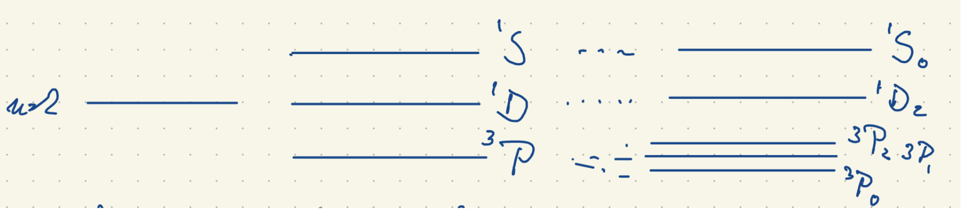


Figure 8.1: Schematic energy level diagram for carbon.

In order to understand the qualitative structure of this level scheme, first consider all the states which could in principle be allowed based on angular momentum considerations alone. For two electrons in the outermost shell the allowed values of L and S are:

- $|l_1 - l_2| \leq L \leq |l_1 + l_2| \Rightarrow$ (for p shell $l_1 = l_2 = 1$): $0 \leq L \leq 2$.
- $|s_1 - s_2| \leq S \leq |s_1 + s_2| \Rightarrow (s_1 = s_2 = 1/2) : 0 \leq S \leq 1$.

Therefore $L = \{0, 1, 2\}, S = \{0, 1\}$ and, in principle, the allowed states are: ${}^1S_0, {}^3S_1, {}^1P_1, {}^3P_0, {}^3P_1, {}^3P_2, {}^1D_2, {}^3D_1, {}^3D_2, {}^3D_3$.

However, since both electrons are in the $n = 2$ shell, the spin wavefunction must be antisymmetric under exchange in order to preserve proper Fermi statistics. The behaviors of the states associated with each quantum number are given below:

- $S : S = 0$ (odd); $S = 1$ (even).
- $L : S, D$ (even); P (odd).

Therefore the only allowed states consistent with spin statistics are: ${}^1S_0, {}^3S_1$, ${}^1D_2, {}^3P_0, {}^3P_1, {}^3P_2$. Hund's first rule then says that the $S = 3$ states have the lowest energy while Hund's second rule says that the D state has lower energy than the S state. This reproduces the L-splitting in Figure 8.1.

8.3.2 Hund's "Third" Rule

To determine the level scheme amongst states with the same L but different J (e.g. the different ${}^3P$ states of carbon above) we introduce a third rule (sometimes informally referred to as Hund's third rule). In principle this is determined on a case-by-case basis but, in practice, the following generalization is useful. There are two cases:

- *"Regular ordering"*: for up to half-filled subshells, the state with the highest total J has the highest energy after applying Hund's rules.
- *"Inverted ordering"*: the opposite ordering applies for subshells which are greater than half-full.

8.3.3 Justification of Hund's Rules

Some qualitative reasoning for the three rules discussed above is the following:

1. Electron repulsion leads to subshells (e.g. p_x, p_y, p_z) being singly occupied before pairing up. Additionally, all electrons are in the same spin state (if possible) as this configuration leads to more effective screening and thus lower energy.
2. States with higher L have larger distances between electrons, leading to lower energy (this can easily be verified by inspection of orbital diagrams).
3. Recall that $\langle H_{spin-orbit} \rangle = \zeta \langle \mathbf{L} \cdot \mathbf{S} \rangle$ for some proportionality constant ζ. Thus, $E_{j+1} - E_j|_{equal L,S} = \zeta(j+1)$ where:
    - $\zeta > 0$ for regular ordering $\Rightarrow$ subshells ruled by electrons.

- $\zeta < 0$ for inverted ordering $\Rightarrow$ subshells ruled by holes.

In general, atoms possess an **electron-hole symmetry**: electrons in empty subshells have the same effect as holes in full subshells (e.g. the pairs $(p^1, p^5), (p^2, p^4), (d^1, d^9), (d^2, d^8)$, etc. each have the same configuration).

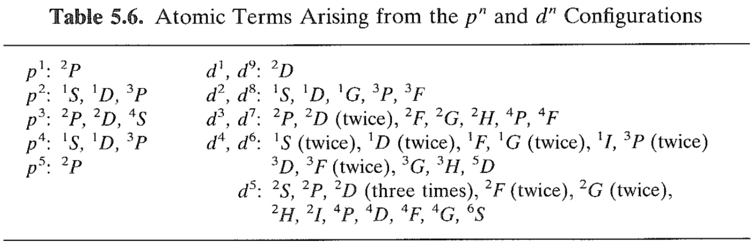


Table 5.6. Atomic Terms Arising from the p^n and d^n Configurations

p^1: ^2P	d^1, d^9: ^2D
p^2: ^1S, ^1D, ^3P	d^2, d^8: ^1S, ^1D, ^1G, ^3P, ^3F
p^3: ^2P, ^2D, ^4S	d^3, d^7: ^2P, ^2D (twice), ^2F, ^2G, ^2H, ^4P, ^4F
p^4: ^1S, ^1D, ^3P	d^4, d^6: ^1S (twice), ^1D (twice), ^1F, ^1G (twice), ^1I, ^3P (twice) ^3D, ^3F (twice), ^3G, ^3H, ^5D
p^5: ^2P	d^5: ^2S, ^2P, ^2D (three times), ^2F (twice), ^2G (twice), ^2H, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S

Figure 8.2: Example of electron-hole symmetry in atomic electron configurations. (Credit: P. Bernath, "Spectra of Atoms and Molecules")

Chapter 9

Symmetry

9.1 Introduction

Symmetry plays an important role in many systems in AMO physics. In addition to atoms, some examples are:

- molecular orbitals
- artificial atoms
    - quantum dots
    - Josephson junctions
    - color centers (NV centers, silicon-vacancy centers)

The goal of this chapter is to explain why these systems behave the way they do and to determine the selection rules based on symmetry principles. Of course, the selection rules for atomic systems can also be understood as a consequence of symmetry principles. The symmetries responsible for the atomic selection rules are:

- Parity: $\Delta l, \Delta j = \text{odd}$.
- Spherical symmetry: $\Delta l = \pm 1; \Delta j = \pm 1, 0; \Delta m_l, \Delta m_j = \pm 1, 0$

In general the selection rules will be different for systems without spherical symmetry.

Note that a **symmetry** is defined as an operation R that commutes with the Hamiltonian: $[H, R] = 0$.

9.2 Time-Reversal Symmetry

Define the time-reversal operator as:

$$\hat{T} : t \rightarrow -t \tag{9.1}$$

Note that while closed systems (in QED) are time-reversal symmetric, open systems described by nonunitary evolution are not. Many operators can be classified based on their behavior under time-reversal:

- <u>even:</u> $\vec{r}, \ddot{\vec{r}}, E, V(\propto r^{\alpha}), \vec{F}, \vec{d}, ...$
- <u>odd:</u> $\dot{\vec{r}}, \vec{L}, \vec{L}, \vec{B}, ...$

Many operators behave oppositely under time-reversal as they do under parity. Time-reversal can also act on a wavefunction governed by the Schrödinger equation:

$$\hat{T}\psi(t) = \hat{T}\psi(0)e^{-iHt/\hbar} = \psi(0)e^{iHt/\hbar} = \psi^*(t). \tag{9.2}$$

The time-reversal operator has several important properties:

1. $[\hat{T}, H] = 0$
2. Anti-linearity: $\hat{T}i = -i\hat{T} \Rightarrow \hat{T}a = a^*\hat{T}$
3. $\hat{T}\psi(t) = \psi^*(t)\hat{T}$
4. <u>without spin:</u> $\hat{T}$ is the complex conjugate operator, $\hat{K} \Rightarrow \hat{T}^2 = 1$
   <u>with spin:</u> $\hat{T} = \hat{K}\sigma_y \Rightarrow \hat{T}^2 = -1$

The consequences of these properties are as follows:

- $\hat{T}$ and $\hat{K}$ are anti-unitary
- <u>Kramer's theorem:</u> for $\hat{T}^2 = -1$ (i.e. with spin) there must be at least a 2D irreducible representation. In physics, this means that there must be at least 2 degenerate eigenstates (this follows from the fact that $[\hat{T}, H] = 0$ so the time-reversed state must be an eigenstate–however it cannot be the same eigenstate because $\hat{T}\psi \neq \psi$).

- The electric field cannnot split states with $\pm|m|$. This follows from the fact that E is even under $\hat{T}$ whereas angular momentum is odd, and the energy must be invariant.

- An intrinsic (i.e. not induced) electric dipole moment (EDM) violates both time-reversal and parity symmetry.

  The proof of the last statement is as follows. Consider a particle (e.g. an electron) with total angular momentum $\vec{J}$ and assume it has an intrinsic dipole moment $\vec{d}$. $\vec{d}$ must be parallel to $\vec{J}$ because all components of $\vec{d}$ perpendicular to $\vec{J}$ average out and $\vec{J}$ is the only preferred direction. In other words: $\vec{d} = \beta\,\vec{J}$, where $\beta \in \mathbb{C}$. $\vec{J}$ changes under $\hat{T}$ but not under $\hat{P}$, whereas $\vec{d}$ changes under $\hat{P}$ but not under $\hat{T}$. Therefore:

  $$\vec{d} \,=\, \beta\,\vec{J} \xrightarrow{\hat{T} \text{ or } \hat{P}} -\beta\,\vec{J} \;\Rightarrow\; \vec{d} \,=\, 0$$

  As a result, there cannot be intrinsic electric dipole moments if the universe is time-reversal and parity symmetric.

9.3 Discrete groups and basics

Some questions that come up in the context of symmetry in AMO:

- What are the possible single- or many-particle states?

- What degeneracies exist?

- What couplings or selection rules are there?

In terms of group theory and quantum mechanics that becomes

- What symmetries leave H invariant?
  The group of these symmetry operations is called the “group of the Schrödinger Equation”

- This group can be expressed in terms of matrices, known as “representations.”

- These matrices act on the eigenstates or “basis functions.”

- The dimension of the degenerate eigenspaces is then the same as the dimensions of the so-called *irreducible representations.*

What follows is a very brief introduction to the most central elements of group theory. This is worked out much more complete in regular group theory books such as Ref. [4], Ref. [3], or Ref. [2].

9.3.1 Groups and Subgroups

A group is a set $G = \{g_i\}$ with the following rules:

1. $g_i, g_j \in G \quad \Longrightarrow \quad g_i \cdot g_j \in G$, where $g_i \cdot g_j$ denotes the "product" or "addition" of the two elements; for symmetry operations this means that first g_j is applied, then g_i.
2. $(g_i \cdot g_j) \cdot g_k \; = \; g_i \cdot (g_j \cdot g_k)$ (associative law)
3. $\exists e \in G$ such that $g_i \cdot e \; = \; e \cdot g_i \; = \; g_i \quad \forall g_i \in G$ (existence of a unity element)
4. $\exists g_i^{-1} \in G$ such that $g_i^{-1} \cdot g_i = g_i \cdot g_1^{-1} = e$
5. If $g_i \cdot g_j \; = \; g_j \cdot g_i \quad \forall g_i, g_j \in G$, then G is called "Abelian."

A *subgroup* S is a subset of G such that S is itself a group.

9.3.2 Representations

- Call $\Gamma(g_i)$ the (matrix) representation of $g_i \in G$:

$$g_i \cdot g_j = g_k \Longrightarrow \Gamma(g_i) \cdot \Gamma(g_j) = \Gamma(g_k)$$

$$\Gamma(e) = \mathbb{1}$$

- Define the "similarity transformation" for any S as

$$\Gamma'(g_i) = S^{-1}\Gamma(g_i)S$$

$$\Longrightarrow \Gamma'(g_i) \cdot \Gamma'(g_j) \; = \; \Gamma'(g_i \cdot g_j)$$

- Γ is called "reducible" if $\exists\, M$ such that for $M^{-1}\Gamma(g_i)M \quad \forall g_i \in G$, Γ' is a block matrix with more than one block.

$$\Gamma'_{\text{reducible}} \;=\; \sum a_i \Gamma^{(i)} \;\overset{\text{e.g.}}{=}\; \begin{pmatrix} \boxed{\Gamma^{(1)}} & & & \\ & \boxed{\Gamma^{(1)}} & & \\ & & \boxed{\Gamma^{(2)}} & \\ & & & \ddots \end{pmatrix} \text{ for } a_1 = 2, a_2 = 1, \ldots$$

  If a representation is not reducible, it is *irreducible*.

- Any Γ with $\det \Gamma \neq 0$ is similar to a unitary Γ.

- Irreducible representations obey an orthogonality relation:

$$\boxed{\sum_{g\in G} \Gamma^{(i)}(g)^*_{\mu\nu}\, \Gamma^{(j)}(g)_{\alpha\beta} \;=\; \frac{h}{l_i}\, \delta_{ij}\, \delta_{\mu\nu}\, \delta_{\alpha\beta}}$$

  for h the order of G, l_i the dimension of $\Gamma^{(i)}$, and $\Gamma^{(i)}, \Gamma^{(j)}$ are irreducible representations of G.

$$\boxed{\sum_{i\in\text{irr. reps.}} l_i^2 = h}$$

9.3.3 Classes

- g_i and g_j are called "conjugate" if $g\, g_i\, g^{-1} \;=\; g_j$ for some $g \in G$.

- The set of all group elements conjugate to g_i is called the "class" of g_i.

- For an Abelian group, all elements are in their own class.

9.3.4 Characters

The *character* is defined as

$$\chi^{(i)}(g) \;\equiv\; \operatorname{Tr}\Gamma^{(i)}(g)$$

for any representation. It is straightforward to prove that the character is invariant under similarity transformations and that all elements in a class have the same character.

The version of the orthogonality relation for characters is

$$\sum_{g \in G} \chi^{(i)}(g)^* \chi^{(i)}(g) \;=\; h\,\delta_{ij}$$

or, in a somewhat shorter way

$$\boxed{\sum_{k \in \text{classes}} \chi^{(i)}(\mathcal{C}_k)^* \chi^{(j)}(\mathcal{C}_k)\, N_k \;=\; h\,\delta_{ij}},$$

where $\mathcal{C}_k$ denotes any element in class k and N_k is the size of (i.e., the number of elements in) that class. From this, one learns about the possible number of classes/irreducible representations:

$$\boxed{\#\text{irreducible reps.} \;=\; \#\text{classes}}$$

The orthogonality relation can also be used to reduce representations Γ with $\text{Tr}\;\Gamma = \chi$ into their irreducible parts:

$$a_i \;=\; \frac{1}{h} \sum_k N_k\, \chi^{(i)}(\mathcal{C}_k)^*\, \chi(\mathcal{C}_k,$$

to give

$$\Gamma \;=\; \sum_i a_i \Gamma^{(i)}.$$

(Note the equal sign here already implies that there is likely a similarity transformation involved. Since similarity transformations don't change anything of importance, these are usually just implied.)

9.3.5 Basis Functions

Suppose G is the group of the Schrödinger equation. Then each $g \in G$ has an associated 3D rotation with rotation matrix $R = \Gamma(g)$ as an isomorphic representation.

$$\vec{r}' \;=\; R\,\vec{r}.$$

The group operation using group element g on any function of $\vec{r}$ is then defined

$$\boxed{P_g\, f(\vec{r}) \;\equiv\; f(R^{-1}\vec{r})}.$$

As a simple example, the rotation by 90 degrees around $\hat{x}$ is described via

$$x' = x,\ y' = z,\ z' = -y$$

and thus

$$R_g = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}.$$

For the function f this results in

$$P_g\, f(x, y, z) \;=\; f(R^{-1}\vec{r}) \;=\; f(x, -z, y).$$

What is the effect on the eigenfunctions of the Hamiltonian? Since this is the group of the Schrödinger Equation, by definition one has $[H, P_g] = 0$. Thus, with the eigenfunctions $H|\psi_m\rangle = E_m|\psi_m\rangle$ one knows that $P_g|\psi_m\rangle$ is also an eigenfunction with the same energy. Thus, given one eigenfunction $\psi_m^{(k)}$, one can generate other $\psi_m^{(l)}$ with all P_g! If this produces all possible $\psi_m^{(k)}$, degeneracy is said to be "normal." Otherwise, the degeneracy is "accidental," since it is, in this case, not caused by symmetry. As examples for this,the np_x, np_y, and np_z orbitals have normal degeneracy; for the np, ns orbitals, it's accidental. (Note that this accidental degeneracy is found to be lifted in the Dirac equation!)

In what follows, assume degeneracies are all normal. Then obviously, acting with g on one eigenfunction in the eigenspace must produce a superposition of all the eigenfunctions in this space:

$$P_g\, \psi_m^{(k)} \;=\; \sum_{\nu=1}^{\ell_m} \psi_m^{(\nu)}\, \Gamma^{(m)}(g)_{\nu\mu}$$

where ℓ_m is the degeneracy of E_m; $\Gamma^{(m)}$ is then an ℓ_m-dimensional irreducible representation. If the $\psi_m^{(\nu)}$ form an orthonormal basis, $\Gamma^{(m)}$ is unitary: The set of ℓ_m degenerate eigenfunctions $\psi^{(\nu)}$ for eigenvalue E_m form basis functions for ℓ_m-dimensional irreducible representation $\Gamma^{(m)}$ of the Schrödinger group.

A trivial extension of this says that a different set $\psi_m^{(\nu)'}$ of a similar $\Gamma^{(m)'} = S^{-1}\,\Gamma^{(m)} S$ has the same properties. Thus, they span the same space, using an equivalent irreducible representation.

Properties:

- m and μ, ν (row, column indices of $\Gamma^{(m)}$) are good quantum numbers.

- The dimension of irreducible representations gives all possible (normal) degeneracies.
- All eigenfunctions with different m, μ, ν are orthogonal.
- A perturbation H' lifts degeneracy iff it changes the symmetry group and dimension of the irreducible representation.

Some definitions of language: one says

- $\psi_m^{(\nu)}$ "transforms" according to $\Gamma^{(m)}$ or
- $\psi_m^{(\nu)}$ "belongs" to $\Gamma^{(m)}$ or
- the $\psi_m^{(\nu)}$ "generate" $\Gamma^{(m)}$.

How to form basis functions?

Basis functions in this section are now denoted by $\phi_n(\nu)$ if the belong to irreducible representation $\Gamma^{(n)}$. Remember:

$$P_g\,\phi_m^{(\nu)} \;=\; \sum_{k=1}^{l_m} \phi_m^{(k)}\,\Gamma^{(m)}(g)_{\mu\nu}.$$

Multiply from the left with $\sum_{g\in G}\Gamma^{(m)^*}(g)_{\mu'\nu'}$ to find the orthogonality relation

$$\sum_{g\in G}\Gamma^{(m)^*}(g)_{\mu'\nu'}\,P_g\,\phi_{m'}^{(\nu)} \;=\; \frac{h}{l_m}\,\delta_{mm'}\,\delta_{\mu\mu'}\,\delta_{\nu\nu'}\,\phi_m^{(\mu)}.$$

With this, one can define

$$\mathcal{P}_{\mu\nu}^{(m)} \;=\; \frac{h}{l_m}\sum_{g\in G}\Gamma^{(m)}(g)^*_{\mu'\nu'}\,P_g.$$

Thus, $\mathcal{P}_{\mu\nu}^{(m)}\phi_m^{(\eta)} = 0$ unless $\eta = \nu$. If $\eta = \nu$, then $\mathcal{P}_{\mu\nu}^{(m)}\,\phi_m^{(\nu)} \;=\; \phi_m^{(\mu)}$. With this, $\mathcal{P}_{\nu\nu}^{(m)}$ is a projector onto $\phi_m^{(\nu)}$. This now serves to find basis functions of $\Gamma^{(n)}$ via

$$\mathcal{P}_{\nu\nu}^{(m)}F \;=\; f_m^{(\nu)} \;\propto\; \phi_m^{(\nu)},$$

where F is any function. (If one wants to make sure that the resulting functions are also eigenstates of the Hamiltonian, F should be itself a solution of the Schrödinger Equation.) Then $\mathcal{P}^{(m)}_{\mu\nu}$ (with $\mu \neq \nu$) yields all "partners" (different $\phi^{(\nu)}_m$ belonging to the same irreducible representation). This can be simplified partially if one uses characters instead:

$$\mathcal{P}^{(m)} \left(\equiv \sum_{\kappa=1}^{l_m} \mathcal{P}^{(m)}_{\kappa\kappa} \right) \; = \; \frac{l_m}{h} \sum_{g \in G} \chi^{(m)}(g)\, P_g$$

projects onto the eigenspace of $\Gamma^{(m)}$ with eigenvalue E_m:

$$\mathcal{P}^{(m)}\, F \; = \; f^{(m)}(\propto \mathrm{span}(\phi^{(\nu)}_m))$$

An example of this procedure can be seen in the following simple case: take the group of mirror symmetry along the $\hat{x}$-axis: $G = \{e, \sigma_x\}$. With an order of 2, this group obviously has two classes, and thus two irreducible representations:

	e	σ_x
$\Gamma^{(1)}$	1	1
$\Gamma^{(2)}$	1	-1

Thus, using the character projection operator above, one gets

$$\begin{aligned} \mathcal{P}^{(1)} &= \frac{\ell}{h}\sum_{g\in G}\chi^{(1)}(g)\,P_g &&= \frac{1}{2}(P_e + P_{\sigma_x}) \quad \text{and} \\ \mathcal{P}^{(2)} &= \frac{\ell}{h}\sum_{g\in G}\chi^{(2)}(g)\,P_g &&= \frac{1}{2}(P_e - P_{\sigma_x}). \end{aligned}$$

Using this on any function on a three-dimensional coordinate, $F(x, y, z)$, one finds

$$f^{(1)/(2)}(x, y, z) = \frac{1}{2}\big(F(x, y, z) \pm F(-x, y, z)\big)$$

While these functions are automatically orthogonal, they still need to be normalized. Also, if one wants basis functions that are, at the same time, eigenfunctions of a Hamiltonian, the starting function (F) should be itself already a solution of the Schrödinger equation.

9.4 Representations and characters of continuous (rotation) groups

All the observations of the previous sections in principle apply if the group is continuous, except that it is of infinite order. This means, if one keeps in mind the relation $\sum \ell^2 = h$, that there are also an infinite amount of classes/irreducible representations without an a priori limit to their dimensions. While a full treatment of continuous groups would include the idea of Lie algebras, this chapter will limit itself to the cases that are important for AMO physics, i.e., continuous rotation symmetries. In this case, one can use the knowledge acquired from solving the Schrödinger equation for hydrogen to, in principle get to the full picture backwards, starting with basis functions, via characters and irreducible representations.

9.4.1 Cyclic groups

In order to get started in a simple an intuitive manner, one should take a step back and look at the particular (finite) type of groups that are *cyclic* groups. These are defined by just one basis elements, e.g., a, that, used again and again, will eventually give the unity again. Thus,

$$G_{\text{cyclic}} \;=\; \{a, a^2, \dots a^n = e\}$$

for a cyclic group of order n. Examples of such groups can be found where a is a rotation (around one axis) by 90^o (for order 4) or the modulus of a prime number p (for order p). Obviously, cyclic groups are Abelian and thus possess only n 1D irreducible representation and n classes. Thus:

$$\Gamma^n(a) \;=\; \Gamma(a^n) \;=\; \Gamma(e) \;=1 \;\Longrightarrow \Gamma(a)^{(p)} \;=\; \chi^{(p)}(a) \;=\; e^{2\pi i\frac{p}{n}}$$

for any $p = 1, 2, \dots, n$. This finding can be directly applied to give the **Bloch theorem**, where particles (e.g., electrons are in a periodic potential of h periods of length a. (In real geometry, this would have to be either ring-formed or periodic boundary conditions. For a very large potential, such as in a crystal, this theorem is, however, approximately true in any case.) Here one has (again)

$$P_a\,\psi(x) \;=\; \psi(x+a) \;=\; \Gamma(a)\,\psi(x) \;=\; e^{ika}\psi_k(x),$$

where $k = \frac{2\pi p}{L}$ for length L, and thus

$$\psi_k(x) \;=\; u_k(x)\,e^{ikx}, \quad \text{where} \quad u_k(x+a) \;=\; u_k(x).$$

9.4.2 Infinite rotation in 2D

Cylinder symmetry (i.e., infinite rotational symmetry in 2D) is, with the above definitions, and infinite-order cyclic group. Thus one can write immediately

$$\Gamma^{(m)}(\phi) \;=\; e^{im\phi} \;=\; \chi^{(m)}(\phi)$$

and

$$\psi_m(r,\theta,\phi) \;=\; f(r,\theta)\,e^{im\phi}.$$

Since a rotation by π and by $-\pi$ has to yield the same result:

$$\Gamma^{(m)}(\pi) \;=\; \Gamma^{(m)}(-\pi) \;\Longrightarrow\; e^{im\pi} \;=\; e^{-im\pi}.$$

From that, one can see that m is an integer! This means that, despite the fact that this is a continuous group, there are infinite but countable classes and characters/representations.

9.4.3 3D proper rotation group $SO(3)$

The group of proper rotations in 3D, ($SO(3)$ or $O^+(3)$) is not Abelian, but many of the findings in the previous paragraphs apply also here.

An obvious isomorphic representation of this group is the set of (orthogonal) 3D rotation matrices. They can be parametrized, for example, using Euler angles. One way to write this is

$$R(\alpha,\beta,\gamma) \;=\; R_z(\alpha)\,R_y(\beta)\,R_z(\gamma),$$

where $R_z(\phi)$ means rotation by ϕ around z:

$$R_z(\phi) \;=\; \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \text{etc.}$$

Because of the three degrees of freedom of a 3D rotation, this is called a "three-parameter group."

Basis functions

Earlier calculations found that a full set of basis functions of a spherically symmetric problem are provided by the spherical harmonics. With that, any rotation of a spherical harmonic results in the superposition of others with the same ℓ value (rotations are here parametrized again via the Euler angles):

$$P_R(\alpha,\beta,\gamma)\,Y_{\ell m}(\theta,\phi) \;=\; \sum_{m'=-\ell}^{\ell} Y_{\ell m'}(\theta,\phi)\,D^{(\ell)}_{m'm}(\alpha,\beta,\gamma),$$

where the coefficients build a $2\ell+1$-dimensional irreducible representation. (These famous representations can be calculated by just doing the rotations indicated above. They can also be found in tables.) The "D" comes from the German word for representation, "Darstellung," and was introduced by Wigner.

Classes

Rotations by the same angle – no matter the rotation axis – are members of the same class. The proof is simple; remembering the original definition the similarity relation of members of class:

$$R_{z'}(\phi) \;=\; R(z \to z')\, R_z(\phi)\, R^{-1}(z \to z').$$

Characters

The character of the representation $D^{(\ell)}(\phi)$ is

$$\chi^{(\ell)}(\phi) \;=\; \frac{\sin(\ell + \frac{1}{2})\phi}{\sin\frac{\phi}{2}}.$$

For proof, look at rotation of the axes by $-\alpha$ about $\hat{z}$;

$$P_\alpha\, Y_{\ell m}(\theta,\phi) \;\equiv\; Y_{\ell m}(\theta, \phi - \alpha) \;=\; e^{im\alpha}\, Y_{\ell m}(\theta,\phi),$$

which results in the diagonal form of the representation

$$D^{(\ell)}(\alpha) \;=\; \begin{pmatrix} e^{-i\ell\alpha} & 0 & \cdots & & \\ 0 & e^{-i(\ell-1)\alpha} & \cdots & & \\ & & & \cdots & \\ & & & & e^{i\ell\alpha} \end{pmatrix},$$

thus giving a character of $\chi^{(\ell)}(\alpha) = \sum e^{im\alpha}$, which gives the expression above.

These turn out to be the only (odd-dimensional) irreducible representations of $SO(3)$. (As a sketch of a proof, remember that characters obey an orthogonality relation and that this means that any new $\chi(\alpha)$ would thus also have to be orthogonal to $\chi^{(\ell)}(\alpha) - \chi^{(\ell-1)}(\alpha) \;=\; 2\cos\ell\alpha$. Thus, $\chi(\alpha)$ needs to be orthogonal to all cosine-Fourier series. Rotation by α and $-\alpha$, however, are in the same class and have thus the same character. They are thus an even function of α and as such could be written as a cosine-Fourier series. Thus, they can never be orthogonal to all cosine-Fourier series!)

9.4.4 Spin, $SU(2)$, and double groups

One might now ask the question whether there are even-dimensional representations for $SO(3)$, which would then need a half-integer angular quantum number. The character definition for such a case (with half-integer j) still makes sense:

$$\chi^{(j)}(\alpha) \;=\; \frac{\sin(j+\frac{1}{2})\alpha}{\sin\frac{\alpha}{2}}.$$

The problem is that the spherical harmonics exist only for integer ℓ! As a solution, (re-)introduce the spin-plus-angular momentum eigenfunctions one gets from solving the Dirac equation as basis functions – they are spherically symmetric but also contain spin. With the same logic as above one finds that the superpositions

$$P_R\,|j,m\rangle \;=\; \sum_{m=-j}^{j} |j,m'\rangle\, D^{(j)}_{m'm}$$

introduce $2j+1$-dimensional irreducible representations with the characters above. There is, compared to the $SO(3)$-basis functions, however, a wrinkle: a change of the system by 2π results in

$$\chi^{(j)}(\alpha+2\pi) \;=\; \frac{\sin(j+\frac{1}{2})(\alpha+2\pi)}{\sin\frac{\alpha+2\pi}{2}} \;=\; (-1)^{2j}\chi^{(j)}(\alpha),$$

that is, the half-integer j version of these representations takes the Hilbert space into itself only with a 4π rotation, but not with a 2π one!

This can be remedied by defining a new group element (in $SO(3)$), r with $r^2 = e$. Thus, as compared to $SO(3)$, there are double as many group members, i.e., for $G = \{e, g_2, \ldots, g_h\}$ the **double group** is $G' = \{e, g_1, g_2, \ldots, g_h, r, rg_1, \ldots, rg_h\}$. It turns out that the group that has both even- and odd-dimensional representations $D^{(j)}$, $SU(2)$, is the double group of $SO(3)$!

Before proving this, a brief side remark: While, for finite groups, double groups have double the order, the same is not necessarily true for classes. One example where the number of classes is O (the class of proper transformations of cubic symmetry) vs. its double group O' which contains also the improper transformations (i.e., inversions/mirroring). (Please look up in group theory book if interested in more details!)

How does the mapping between $SO(3)$ and $SU(2)$ work? (And why is is called thus?) As for the naming: $O(3)$ is the group of 3D $\underline{o}$rthogonal matrices, the "S" stands for "special" and denotes the "proper" part. By the same logic, $SU(2)$ is the group of unitary 2D matrices with a determinant of +1.

In order to find the mapping one has to show (i) that the three coordinates x, y, z can equally generally be transformed by a orthogonal 3D real matrix as by a unitary complex 2D one and (ii) that there are indeed two elements in $SU(2)$ for each one in $SO(3)$. In order to do this, one needs to find a mapping of the 3D coordinate vector into the 2D complex space. This can be done the following way: Assume a 2D traceless Hermitian matrix. This can be written as

$$X = \begin{pmatrix} z & x+iy \\ x-iy & -z \end{pmatrix}.$$

Obviously, the most general such matrix spans the same space as the usual 3D coordinate matrix, with all possible real values for x, y, z. In addition, the most general way to write a 2D U with $\det U = 1$ is

$$U = e^{i\frac{\vec{\sigma}\cdot\vec{\phi}}{2}} = \cos\frac{\phi}{2}\mathbf{1} + i\vec{\sigma}\cdot\vec{\phi}\,\sin\frac{\phi}{2},$$

where $\vec{\phi}$ has the angle as the absolute value and the axis as the direction, while $\vec{\sigma}$ is the vector of Pauli matrices. It can be easily shown that the rotation of the coordinate vector $\vec{r}' = R^T\vec{r}R$ can also be written in the complex way as $X' = U^\dagger X U$. But this makes it also clear that both U and $-U$ map onto the same rotation R! For example,

$$U_z(2\pi) = \begin{pmatrix} e^{-i\pi} & 0 \\ 0 & e^{i\pi} \end{pmatrix} = -\mathbf{1}.$$

9.5 Combination of groups for AMO

Some of the most important questions come up when various different symmetries come together. This is interesting from the point of view how to simplify things if the symmetries have nothing to do with each other (e.g., concern entirely different dimensions) which gives the concept of *product groups* or how the physical properties change if the symmetries in a system are lowered, e.g., by putting an atom inside a crystal field or switching on an electric field around an NV center.

9.5.1 Direct product groups

Often, the complete symmetry of a system can be broken up into distinct sets of operations that commute with each other, such as, for example, in a

Hydrogen molecule, (i) exchange symmetry of the two protons, (ii) exchange symmetry of the two electrons, and (3) rotating the molecule as a whole around some symmetry axis or point. Obviously, either of the operations in set (i), (ii), or (iii) can be done entirely independent of the the other. The total group can then be written as a "direct product group":

$$\begin{aligned} G_1 &= \{e, a_2, \ldots, a_{h_1}\}, \quad G_2 = \{e, b_2, \ldots, b_{h_2}\}, \text{ then} \\ G' &= \{e, a_2, \ldots, b_2, \ldots, a_2 b_2, a_3 b_2, \ldots\}, \end{aligned}$$

where G' obviously has order $h' = h_1 \cdot h_2$. The representations can easiest also be written as direct products

$$\Gamma_{1,ij}\, \Gamma_{2,kl} \;\equiv\; (\Gamma_1 \times \Gamma_2)_{ijkl}.$$

The characters in this case also just multiply

$$\chi'(ab) \;=\; \chi_1(a)\, \chi_2(b).$$

An example for such a system is if one defines G_1 as the symmetry group of a 2D equilateral triangle $D_3 = \{e, c_{120}, c_{240}, \sigma_0, \sigma_{120}, \sigma_{240}\}$ in the xy-plane with two rotation and three mirror image symmetries. This has the following character table

D_3	e	$2\ C_3$	3σ
$\Gamma^{(1)}$	1	1	1
$\Gamma^{(2)}$	1	1	-1
$\Gamma^{(3)}$	2	-1	0

and G_2 consists of the mirror symmetry along the z-axis $\mathcal{S} = \{e, \sigma_h\}$ with

$\mathcal{S}$	σ_h	
$\Gamma^{(1)}$	1	1
$\Gamma^{(2)}$	1	-1

The direct product group has then the following character table

D_3	e	$2\ C_3$	3σ	σ_h	$2\ \sigma_h C_3$	$3\sigma_h\sigma$
$\Gamma^{(1)}$	1	1	1	1	1	1
$\Gamma^{(2)}$	1	1	-1	1	1	-1
$\Gamma^{(3)}$	2	-1	0	2	-1	0
$\Gamma^{(4)}$	1	1	1	-1	-1	-1
$\Gamma^{(5)}$	1	1	-1	-1	-1	1
$\Gamma^{(6)}$	2	-1	0	-2	1	0

9.5.2 Direct product representation

Despite the similar name, this is rather different from the previous section. Here the question is "what is the resulting representation of the product of two representations within a group?" This would be relevant, e.g., if one looks at the resulting representation that a two-electron wavefunction belongs to in He. The single-electron representations are given by the usual $\Gamma^{(i)}$ and $\gamma^{(j)}$ (e.g., the $D^{(i)}$ of the spherical group). The question is then what the resulting "direct product representation," $\Gamma^{(i)} \otimes \Gamma^{(j)}$ is. The characters just multiply, $\chi = \chi^{(i)}\,\chi^{(j)}$. With the help of the orthogonality relation of the characters, one can find which irreducible representations the resulting representation is made up of:

$$\begin{aligned} \Gamma \;=\; \Gamma^{(i)} \otimes \Gamma^{(j)} \;&=\; \sum_{k \text{ irr.}} a_{ijk}\, \Gamma^{(k)} \\ \chi \;&=\; \sum_{k} a_{ijk}\, \chi^{(k)}, \end{aligned}$$

where, similar as before,

$$\begin{aligned} a_{ijk} \;&=\; \frac{1}{h} \sum_{g \in G} \chi^{(i)}(g)\, \chi^{(j)}(g)\, \chi^{(k)}(g)^* \\ &=\; \frac{1}{h} \sum_{k \text{ (classes)}} N_k\, \chi^{(i)}(\mathcal{C}_k)\, \chi^{(j)}(\mathcal{C}_k)\, \chi^{(k)}(\mathcal{C}_k)^* \end{aligned}$$

9.5.3 Interlude: some nomenclature for point groups

This brief section introduces some of the most used notations for groups, classes, and irreducible representations.

The 32 groups of possible 3D crystal symmetry are called *point groups*. They are divided basically into two types, those with one main symmetry axis, and those with more; all of the latter are either based on the tetrahedral ("T") or cubic ("O") symmetry. The possible classes in the point groups are

- C_j denotes a j-fold rotational symmetry about the principal axis
- C_j' or C_j'' denote a j-fold rotational symmetry about another axis
- σ (with various subscripts) denotes a reflection

- i denotes inversion.

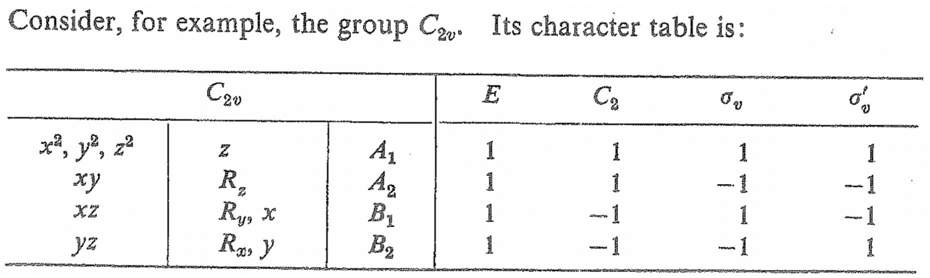
The classification of the irreducible representations are

- A for a one-dimensional irreducible representation if $\chi(C_j) = 1$;
- B for a one-dimensional irreducible representation if $\chi(C_j) = -1$;
- E for a two-dimensional irreducible representation;
- T for a three-dimensional irreducible representation.

There are no higher-dimensional irreducible representations for the point groups. These level denominations are, e.g., used in NV centers.

Basis functions in group tables

The symmetry of the basis functions in group tables are given as linear and quadratic and combinations functions of the coordinates, e.g., $x, y, z, x^2, \ldots, x^2 + y^2, \ldots xy, \ldots$ or R_x, R_y, R_z, i.e., the axial (i.e., even under inversion) version of the coordinates and their combinations. An example of a typical character table is given in Fig. 9.1



Consider, for example, the group C_{2v}. Its character table is:

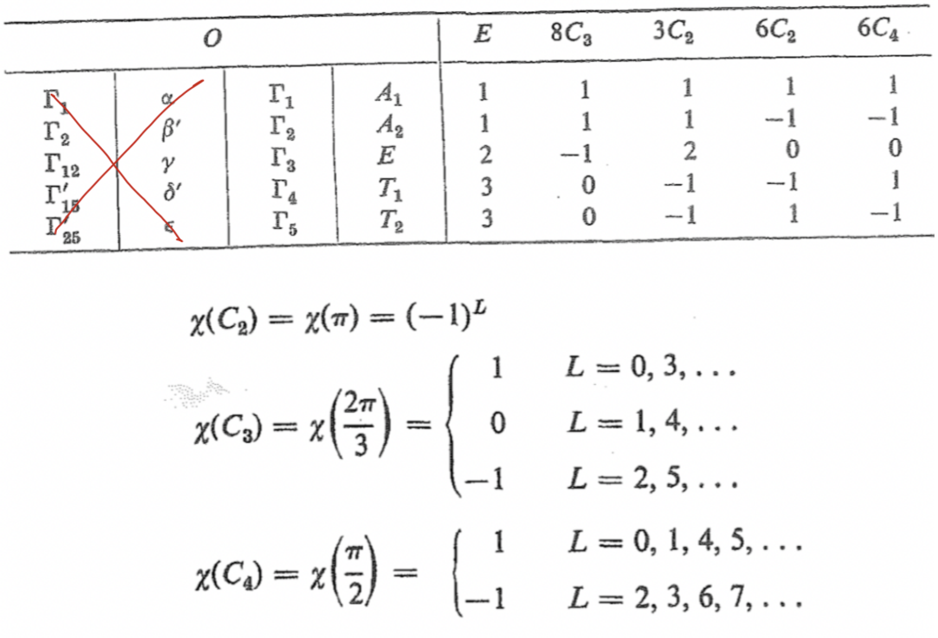
C_{2v}			E	C_2	σ_v	σ'_v
x^2, y^2, z^2	z	A_1	1	1	1	1
xy	R_z	A_2	1	1	−1	−1
xz	R_y, x	B_1	1	−1	1	−1
yz	R_x, y	B_2	1	−1	−1	1

Figure 9.1: Character table example (from Tinkham, [4]). This group, the group with a rotation around the principal (z-) axis and vertical mirror symmetry, has four one-dimensional irreducible representations that have basis functions transforming like the functions of x, z given on the left side of the table.

9.6 Crystal field splitting

What is the effect of lowering the symmetry? What, for example, happens to an atom's eigenstates when the atom is placed into a crystal (such as diamond impurties/color centers)?

The answer is given easiest by employing an example: assume that an atom (with native spherical symmetries and therefore having eigenstates belonging to the $D^{(j)}$ with integer j) is placed into an environment with symmetry O, i.e., consisting of the proper rotations in 3D of a cube. The order h of O is 24 (see character table in Fig. 9.2). The irreducible representations in the original (spherical) symmetry can now be broken up into irreducible representations of the new (O) symmetry (see Fig. 9.3). In particular, this tells into how many manifolds (degeneracies) one (spherical) manifold breaks into.



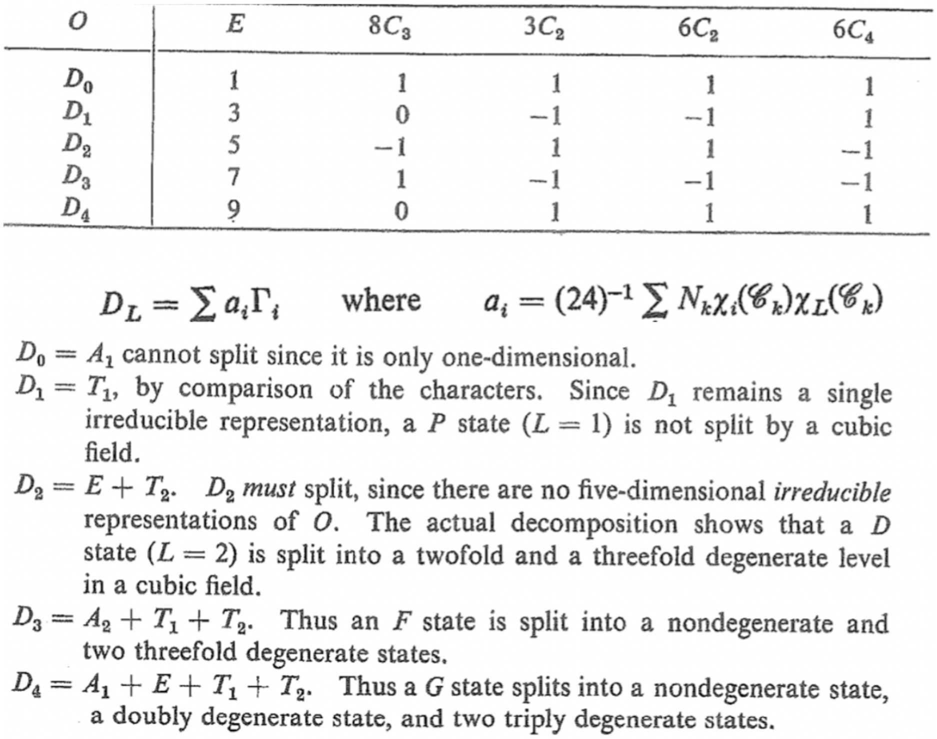
O				E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
~~Γ_1~~	~~α~~	Γ_1	A_1	1	1	1	1	1
~~Γ_2~~	~~β'~~	Γ_2	A_2	1	1	1	-1	-1
~~Γ_{12}~~	~~γ~~	Γ_3	E	2	-1	2	0	0
~~Γ'_{15}~~	~~δ'~~	Γ_4	T_1	3	0	-1	-1	1
~~Γ'_{25}~~	~~ϵ~~	Γ_5	T_2	3	0	-1	1	-1

$$\chi(C_2) = \chi(\pi) = (-1)^L$$

$$\chi(C_3) = \chi\left(\frac{2\pi}{3}\right) = \begin{cases} 1 & L = 0, 3, \ldots \\ 0 & L = 1, 4, \ldots \\ -1 & L = 2, 5, \ldots \end{cases}$$

$$\chi(C_4) = \chi\left(\frac{\pi}{2}\right) = \begin{cases} 1 & L = 0, 1, 4, 5, \ldots \\ -1 & L = 2, 3, 6, 7, \ldots \end{cases}$$

Figure 9.2: Upper part: character table for group O. (The crossed-out part is somewhat outdated nomenclature.) Lower part: Calculation of characters for the $D^{(L)}$ for certain O-relevant rotation angles.(From Tinkham [4]



O	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
D_0	1	1	1	1	1
D_1	3	0	-1	-1	1
D_2	5	-1	1	1	-1
D_3	7	1	-1	-1	-1
D_4	9	0	1	1	1

$$D_L = \sum a_i \Gamma_i \qquad \text{where} \qquad a_i = (24)^{-1} \sum N_k \chi_i(\mathscr{C}_k)\chi_L(\mathscr{C}_k)$$

$D_0 = A_1$ cannot split since it is only one-dimensional.

$D_1 = T_1$, by comparison of the characters. Since D_1 remains a single irreducible representation, a P state ($L = 1$) is not split by a cubic field.

$D_2 = E + T_2$. D_2 *must* split, since there are no five-dimensional *irreducible* representations of O. The actual decomposition shows that a D state ($L = 2$) is split into a twofold and a threefold degenerate level in a cubic field.

$D_3 = A_2 + T_1 + T_2$. Thus an F state is split into a nondegenerate and two threefold degenerate states.

$D_4 = A_1 + E + T_1 + T_2$. Thus a G state splits into a nondegenerate state, a doubly degenerate state, and two triply degenerate states.

Figure 9.3: Upper part: table that gives the characters of the spherical irreducible representations for the operations in O. Lower part: Irreducible representations of $D^{(i)}$ in O symmetry. (From Tinkham [4])

9.7 Matrix elements & selection rules

The Hamiltonian H is (by definition) invariant under all $g \in G$, where G is the group of the Schrödinger Equation. Thus, H belongs (always) to A_1 (the 1D group where every character is 1). Assume that basis functions ϕ_m and ϕ_n belong to $\Gamma^{(m)}, \Gamma^{(n)}$. Thus,

$$\langle \phi_n^{(\nu)} | H | \phi_m^{(\kappa)} \rangle \ \propto \ \delta_{nm}.$$

The question is what happens with a perturbation V, which could be, for example, a coupling field which has a different symmetry. In particular, when

$$\langle \phi_n^{(\nu)} | V | \phi_m^{(\kappa)} \rangle \ \neq \ 0,$$

i.e., when is a transition not forbidden for coupling V? Assume V belongs to Γ_V (which can be any of the irreducible representations of the symmetry group). Then $V|\phi_m^{(\kappa)}\rangle$ belongs to $\Gamma_V \otimes \Gamma^{(m)}$ with

$$\Gamma_V \otimes \Gamma^{(m)} \ = \ \sum_k a_{V,mk} \, \Gamma^{(k)}.$$

Thus,

$$\langle \phi_n^{(\nu)} | V | \phi_m^{(\kappa)} \rangle \ = \ 0 \quad \text{iff} \quad a_{V,mn} \ = \ 0.$$

This constitutes the most general formulation of (symmetry-based) selection rules.

Chapter 10

Atomlike systems

Why do we use atoms? Atoms are controllable, coherent, and they are indistinguighable. This makes them useful for many applications, including qubits, systems with an engineered quantum level response functions, metrology (atomic clocks) and more.

What about other systems? There are molecules, artificial atoms (such as quantum dots, color centers in diamond or similar, and nanocircuits (e.g., superconducting circuits/qubits), all of which sport properties that are not attainable with atoms.

10.1 Artificial atoms

The terms "artificial atom" typically is given to any systems that has similar properties to atoms, such as discrete energy levels, a structure that allows to use two levels as a two-level systems (without any other levels interfering too much). In addition, these systems can be constructed/engineered and manipulated in specific ways.

Why is there interest in such systems? The goal is to be able to completely freely engineer systems properties such as transition frequencies, system size, coupling strengths, etc, and do this, ideally, on a chip or similarly self-contained unit.

There are basically two types of artificial atoms:

1. **Confined electrons:** If particles (e.g., electrons) are confined to very small spaces, their (quantum mechanical energy) levels are discrete. As an example, look at a quantum dot of GaAs in a matrix of InGaAs.

This is effectively a zero-dimension confinement whose band-structure can roughly (in one dimension) be depicted as in Fig. 10.1. There are a number of quantum dot pictures (from various sources) at the end of this section (10.4,10.5) which include quantum dots whose confinement is created differently (see figure captions). The question is how well these structures work as atoms. While typical quantum dots in one system have close frequencies, their energy spread is typically many orders of magnitude wider than in atoms, due to their inhomogeneous sizes. As was seen in the previous chapter, level degeneracies and coupling selectivity arises from symmetry. Quantum dots are not typically very symmetric; as a consequence, there are basically no selection rules. There is, however, the typical spin-1/2 degeneracy.

2. **Color centers** are defects in crystals, in particular in diamond (which is otherwise colorless). The most typical examples in active physics research are NV^- centers (negatively charged nitrogen vacancy centers, consisting of an N replacing a C and a resulting vacancy in a neigboring lattice site) and SiV centers (where two neighboring C are replaced by one Si, which sits in the middle of the two vacancies). See Fig. 10.2 for a depiction of NV^- and its level scheme, and Fig. 10.3 for a depiction of SiV. Both centers can be seen as single atoms that a priori inherit the O_h symmetry of the diamond lattice. The symmetry breaking along the center axis splits some levels, e.g., the $m = 0$ versus $m = \pm 1$ levels of the NV level diagram. Note that the remaining symmetry of the SiV is somewhat higher than for NV, since SiV has in addition reflection symmetry along the center axis. The resulting better selectrion rules contribute to the fact that SiV have overall better coherence properties. In general, color centers are typically defects of confined, typically unpaired electrons or holes with the overall symmetry of the lattice (and potentially single axes as lower-symmetry perturbations). They are called "color centers" because they, other than the lattice that supports them, have discrete energy levels and thus a color.

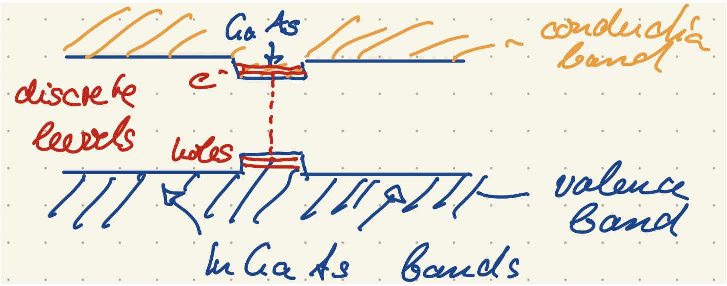


Figure 10.1: Qualitative band structure diagram in coordinate space of InGaAs with an embedded GaAs quantum dot in the middle. The narrower band gap allows for discrete levels in the GaAs conduction and valence bands close to the band gap. If electrons are excited in GaAs from the valence to the conduction band with a frequency slightly below the InGaAs bandgap, the electrons occupy discrete levels in the conduction band, leaving holes in discrete levels in the valence band.

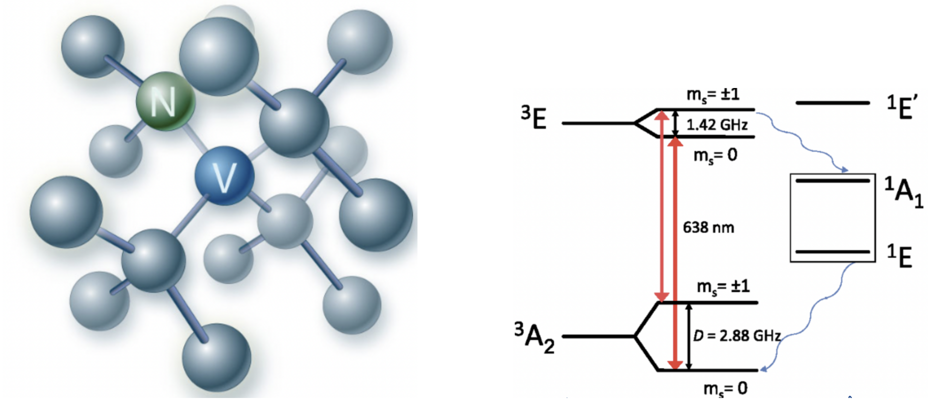


Figure 10.2: (left) Structure of NV center. The NV axis breaks the symmetry of the diamond lattice. (right) Level scheme of the NV^- center. The levels are named using the irreducible representations of the diamond's O_h group, the perturbation can be seen, e.g., in the splitting between the different m levels.

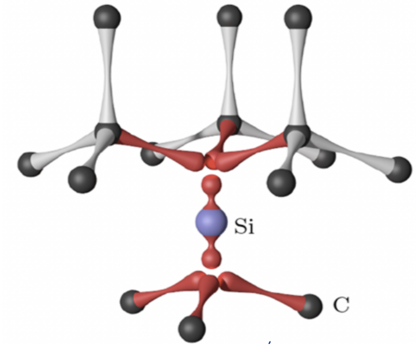


Figure 10.3: Structure of a SiV center. The center breaks the symmetry of the diamond lattice, which can be seen as a perturbation in the level scheme (which is not shown in this text). Figure source internet...)

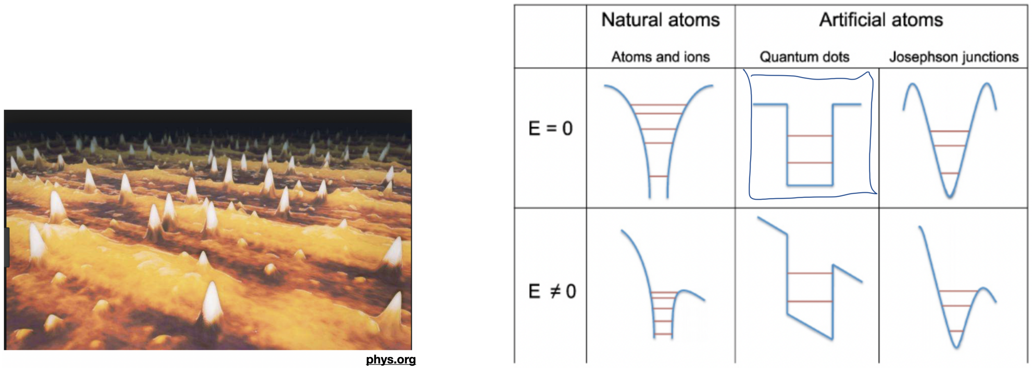


Figure 10.4: (left) Microscopic picture of typical quantum dots on semiconductor surface. (right) Table of stylized potentials that electrons typically see in different situations.

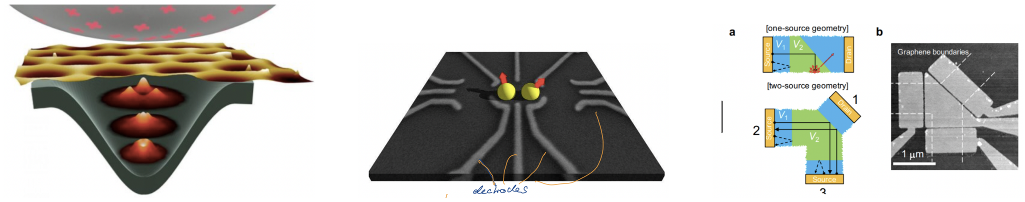


Figure 10.5: (left) The charged tip of a scanning tunneling microscope and an additional magnetic field lead to localized stable electron states in graphene. (Credit: Nils Freitag, RWTH Aachen) (middle) Electrodes on a semiconductor surface create a localized potential well for two electrons.(Credit: C. Marcus group, Science 30, 2005) (right) Similar to middle picture, but on graphene.

10.2 Brief introduction to molecules

10.2.1 Basic principles (hydrogen)

Why do molecules exist? Look at the simplest example, the H_2^+ molecular ion, consisting of two protons (i.e., two nuclei) and one electron. Even this would be already a sizeable challenge to solve exactly, being a three-body problem. Instead, for a good analytic approximation one uses the knowledge garnered from atoms. The notable difference from atoms is that for molecules the geometric setup of the nuclei also plays a role. In this simple case, this means that the energy and eigenfunctions of H_2^+ depends on R, the distance between the nuclei, as in Fig. 10.6.

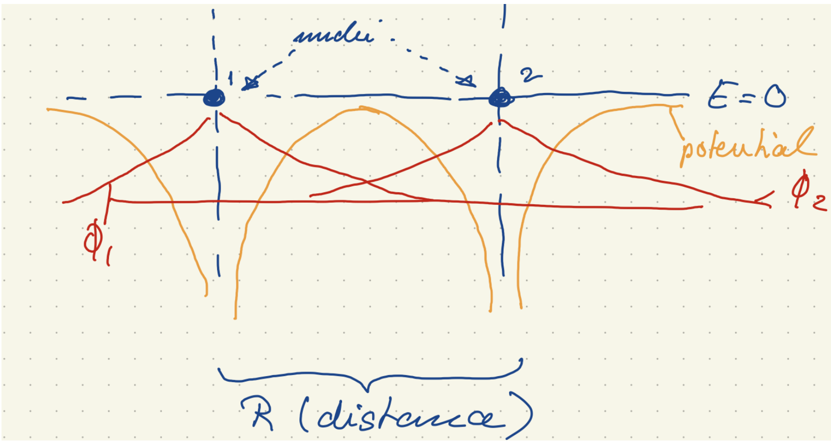


Figure 10.6: Geometry (blue) and potential (yellow) of the H_2^+ molecule along with the undisturbed ground state wavefunctions ϕ_1 and ϕ_2 of the respective atoms (red). The easiest approximation to molecular wavefunctions is to build superpositions of the atomic orbitals.

As a first approximation, one can make an ansatz that consists of a superposition of the atomic wavefunctions:

$$\Phi \;=\; c_1\,\phi_1 + c_2\,\phi_2,$$

where ϕ_1 and ϕ_2 denote the atomic wavefunctions belonging to nucleus 1 or 2. This can be used as a variational ansatz such as to minimize the total energy E:

$$E \;=\; \frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle} \;\overset{!}{=}\; \text{minimum as function of } R$$

This easy calculation results in

$$\frac{\partial E}{\partial c_1} \;=\; \frac{\partial E}{\partial c_2} \;=\; 0$$

or

$$\begin{vmatrix} H_{11} - E & H_{12} - E\,S \\ H_{21} - E\,S & H_{22} - E \end{vmatrix} \;=\; 0,$$

where $H_{ij} = \langle\phi_i|H|\phi_j\rangle$ and $S = \langle\phi_1|\phi_2\rangle$. This results in the two solutions for H_2^+

$$E_\pm \;=\; \frac{H_{11} \pm H_{12}}{1 \pm S} \qquad \Rightarrow \qquad \Phi_\pm \;=\; \frac{\phi_1 \pm \phi_2}{\sqrt{2(1 \pm S)}}$$

The result is depicted in Fig. 10.7. Note that E_- is the higher energy, fitting with the intuition that the wavefunction with a node is the higher-lying one.

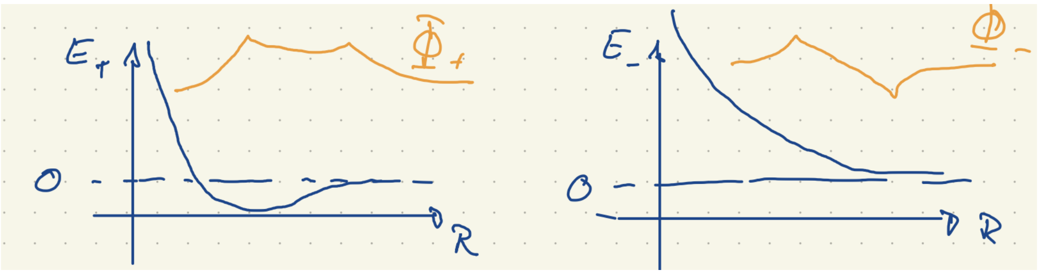


Figure 10.7: Distance-dependent energies of the H_2^+ molecular ion with qualitative depiction of the resulting wavefunctions. (left) Lowest energy with finite electron density everywhere between the nuclei. In fact, the higher electron density between the positively charged nuclei lowers the overall energy as compared to the atomic wavefunctions (normalized to zero energy), thus making the molecular state Φ_+ the preferred state. (right) The higher energy belongs to the so-called "anit-bonding" state with vanishing electron density at one plane between the nuclei.

As can be seen from the energies $E_\pm$ in Fig. 10.7, the symmetric ("bonding") state has an energy minimum and thus supports bound states.

Two obvious things to be learned from this simple case:

- Higher electron density between the nuclei lowers overall energy.
- The total wavefunction is more spread out than a single atom wavefunction, making the molecule bigger than a (comparable) atom.

The transition from the hydrogen molecular ion (with one electron) to the neutral H_2 molecule is qualitatively similar to the transition from hydrogen to helium – both consist of similar setups, but now two electrons need to be accommodated.

If both electrons are in their (bound) ground state, the spin wavefunction is antisymmetric, $\Psi^{\text{spin}} = \Psi_A^{\text{spin}} = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$. The energy of H_2 is somewhat shifted from twice the energy of H_2^+, similar to He to twice H, with a similar order of magnitude to the energy splitting, cf. Fig. 10.8.

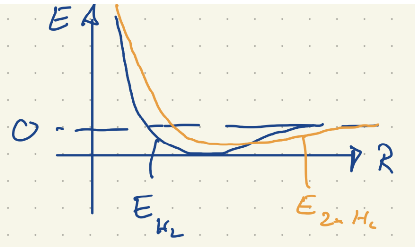


Figure 10.8: The R-dependent molecular energy of the hydrogen molecule (blue) vs twice the energy of the hydrogen molecular ion (yellow).

In general, how do molecular orbitals look? Note that the main molecular axis is by convention defined to be the z direction. They basically can just be seen to add up from the atomic orbitals. Examples can be found in Figs. 10.9 and 10.10.

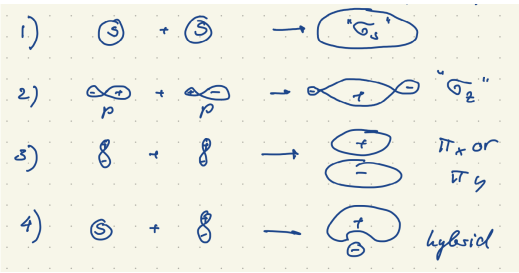


Figure 10.9: A couple of examples of molecular orbitals made as superpositions of atomic orbitals.

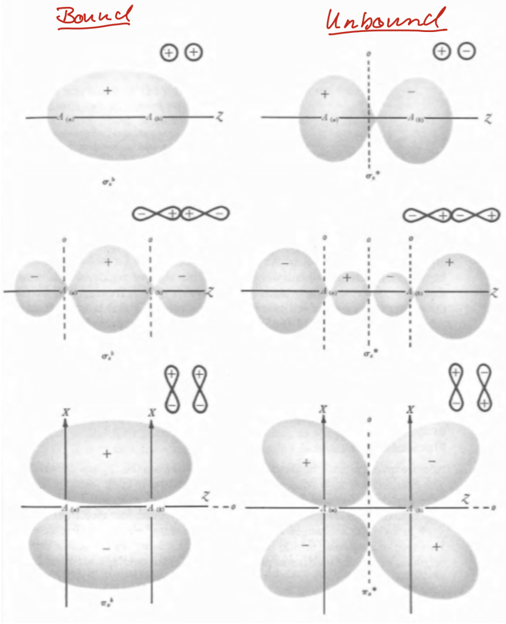


Figure 10.10: Similar to previous figure - from *Gray, Chemical Bonds.*

10.2.2 Quantum numbers

Quantum numbers in molecules have to be handled differently from atoms because of lack of symmetry, even for single-electron states.

- **Principal quantum numbers:** This is a more complicated issue than it looks like in the beginning. With the LCAO theory put forward above, electronic energy levels are a superposition of the (at least) two atomic orbitals they are made up of. Obviously, those two (or more) could stem from different atomic principal quantum numbers n_1 and n_2. In addition, the fact that molecular electronic orbits have a distance dependent value (see, e.g., Fig. 10.7 and Fig. **??**) can result in overlapping energy levels. Thus, in practice the electronic orbits are sorted by energy. The nomenclature typically is such that “X” denotes the ground state, “A” the first excited state, “B” the second, and so on, up the alphabet.

- **Angular quantum number:** The ℓ number in atoms does not work for molecules, because it is based on the (spherically symmetric) spherical harmonics that are the basis functions for atoms. Thus, for cylindrically symmetric molecules (one symmetry axis, such as, e.g., for diatomic molecules), the projection of the angular momentum on the principal axis is used instead, and greek letters are used. Thus, one would get for

	single electrons	many electrons
atoms:	$\ell = 0, 1, 2 \dots$	$L = 0, 1, 2, \dots$
	i.e., $\ell \to s, p, d, \dots$	i.e., $L \to S, P, D, \dots$
molecules:	projection onto $\hat{z}$ (= quantization) axis	
	$\lambda = 0, 1, 2, \dots$	$\Lambda = 0, 1, 2, \dots$
	i.e., $\lambda \to \sigma, \pi, \delta, \dots$	$\Lambda \to \Sigma, \Pi, \Delta, \dots$

The angular momentum around the remaining axis is mostly dominated by the rotation of the nuclei around each other, which is covered below.

- **Selection rules:** To the first approximation, the selection rules follow the same principles for angular quantum numbers, but do take the rotational quantum number (see below) into account as well.

10.2.3 Vibrational states

The states bound by the energy curve are the vibrational states of the molecule, cf. Fig. 10.11.

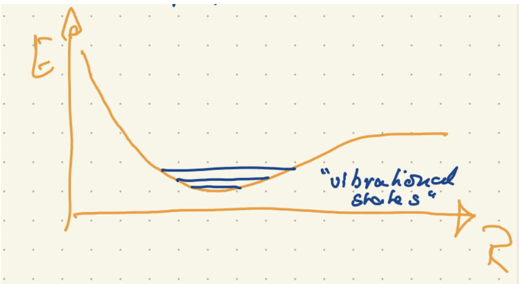


Figure 10.11: Distance-dependent energy curve of molecules with the quantum states bound by the potential. These are the vibrational states of the molecule.

These don't look like harmonic oscillator states by chance: the two or more (charged) nuclei vibrate around their equilibrium position. For low energies, the potential curve is in most cases approximately a parabola. Note that the vibrational states are closer in energy for higher-lying states in the same electronic potential. For diatomic molecules, there is only one vibrational mode, while for polyatomic molecules there is a number of modes that depend on the particular geometry of the nuclei.

Selection rules for electric or magnetic transitions between vibrational modes exist not in all cases. For diatomic molecules, vibrations don't change the parity, thus there are no (purely) vibrational transitions. For polyatomic molecules, this depends on the symmetry. Note that, nevertheless, most molecular spectra used to recognize molecules are done as infrared spectra between vibrational states in practice! Vibrational energy differences are typically in the infrared range.

10.2.4 Rotational states

Any rotation around an axis that is not a cylindrical symmetry axis will give a number of rotational states. Obviously, these are angular momentum states and their quantum number will couple to the other angular momentum quantum numbers in the system. The easiest comparison of rotational states is if one compares the electronic angular momentum states in atoms with the nuclear rotational states in molecules (see Fig. 10.12).

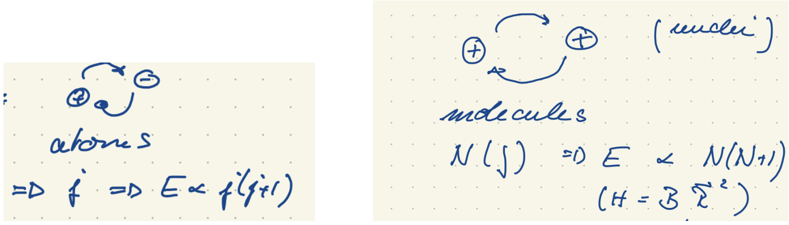


Figure 10.12: (left) Angular momentum given by rotations of electrons relative to the nucleus, resulting in an angular momentum quantum number j and energy $E \propto j(j+1)$. (right) Angular momentum given by rotations of nuclei around each other, resulting in a rotational quantum number N and energy $E = B\,N(N+1)$. The rotational Hamiltonian is here $H = B\vec{R}^2$, B is the "rotational constant."

Subsequent rotational levels alternate in parity (similar to the atomic angular momentum states); thus, selection rules apply and transitions are allowed, with typical nearest-level energies ranging between microwaves and IR.

A typical molecular energy diagram is given in Fig. 10.13, with vibrational quantum numbers v and total angular momentum quantum numbers J (these contain both rotational and electronic angular momentum).

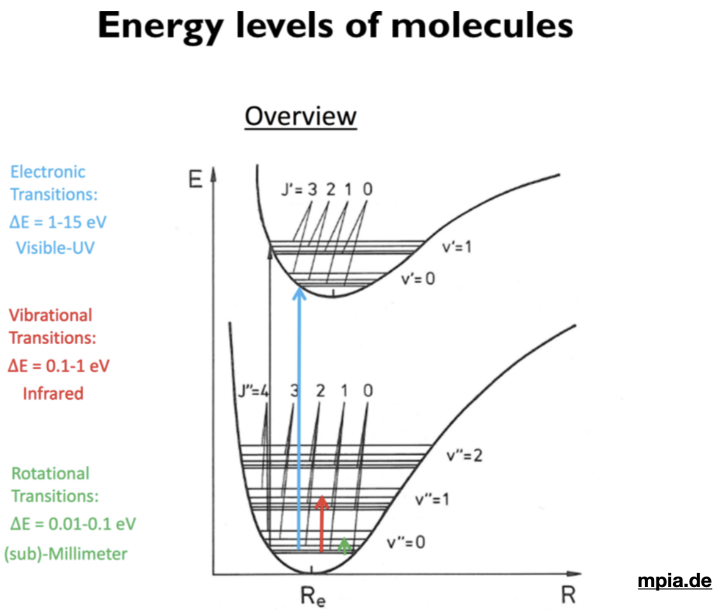


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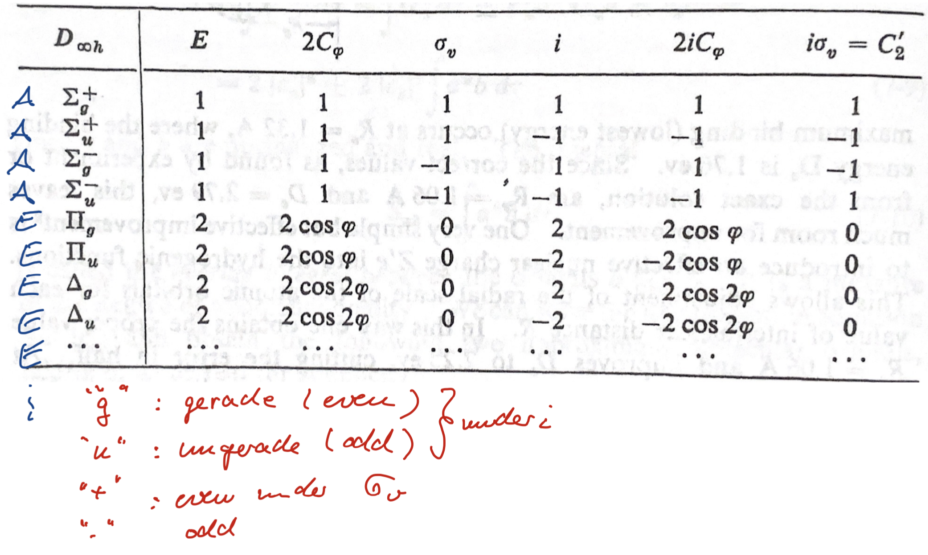
Figure 10.13: Electronic, vibrational, and rotational level structure of molecules, as a function of nuclear distance. Typical electronic transition frequencies are comparable to atomic electronic transitions, vibrational transitions are in the infrared, rotational ones typically sub-millimeter.

10.3 Examples of molecules by symmetry

10.3.1 Homonuclear diatomic molecules

This simplest class of molecules, consisting of two equal atoms, has symmetry $D_{\infty h}$. This means that it has one rotational axis with full cylindrical symmetry and a reflection symmetry along the same axis, thus including elements of the type $e, C_\infty, \sigma_v, i, \ldots$ see table in 10.14.



	$D_{\infty h}$	E	$2C_\varphi$	σ_v	i	$2iC_\varphi$	$i\sigma_v = C_2'$
A	Σ_g^+	1	1	1	1	1	1
A	Σ_u^+	1	1	1	-1	-1	-1
A	Σ_g^-	1	1	-1	1	1	-1
A	Σ_u^-	1	1	-1	-1	-1	1
E	Π_g	2	$2\cos\varphi$	0	2	$2\cos\varphi$	0
E	Π_u	2	$2\cos\varphi$	0	-2	$-2\cos\varphi$	0
E	Δ_g	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
E	Δ_u	2	$2\cos 2\varphi$	0	-2	$-2\cos 2\varphi$	0
E	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$

i

"g" : gerade (even) } under i
"u" : ungerade (odd) }
"+" : even under σ_v
"-" odd

Figure 10.14: Group table for $D_{\infty h}$, from Tinkham [4].

Note that the irreducible representations of this class are only one- or two-dimensional!

In a simple case like this, one can still find somewhat of an analogue to the principal quantum number in atoms. For two atoms, there are two limits: (a) name the n of both atoms separately, and (b) use the n of the combined atoms. As an example, in H_2^+, the bound ground state would be designated (a) "$\sigma_g\, 1s$" or (b) "$1s\,\sigma_g$," cf. the "correlation diagram" in Fig. 10.15. For the first excited state of H_2^+, i.e., the unbound state consisting of the two $1s$ atomic orbitals, this would give (a) "$\sigma_u\, 1s$" or (b) "$2p\,\sigma_u$." As a brief explanation, here the "$1s$" in (a) is relative to each separate nucleus while the "$2p$" in (b) comes from the combined symmetry of the level and the fact that this is, effectively, the second electronic level. In the correlation diagram of Fig. 10.15, it depends on the particular molecule, where exactly on the smooth transition between the two limiting cases (a) and (b) the truth lies.

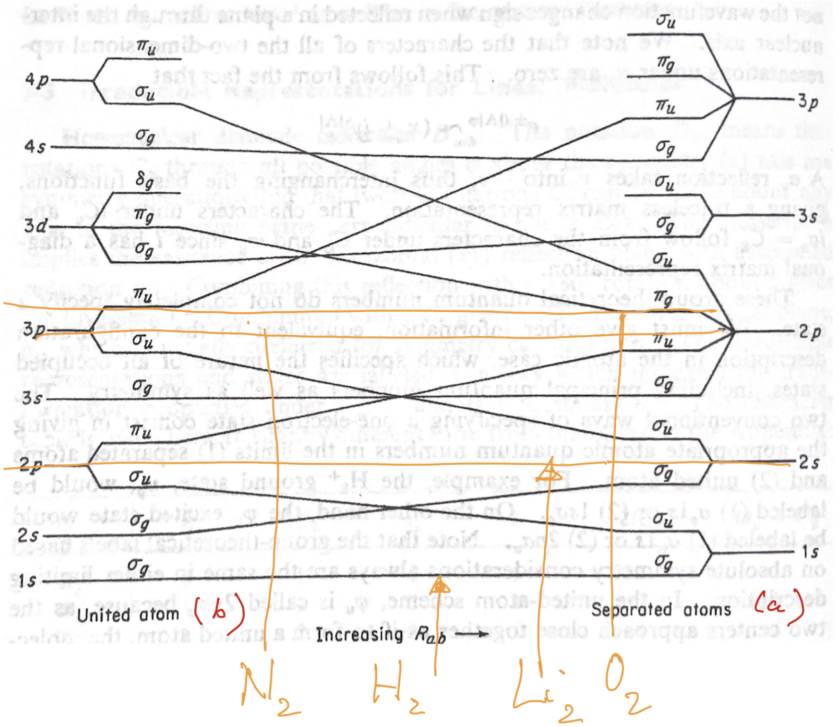


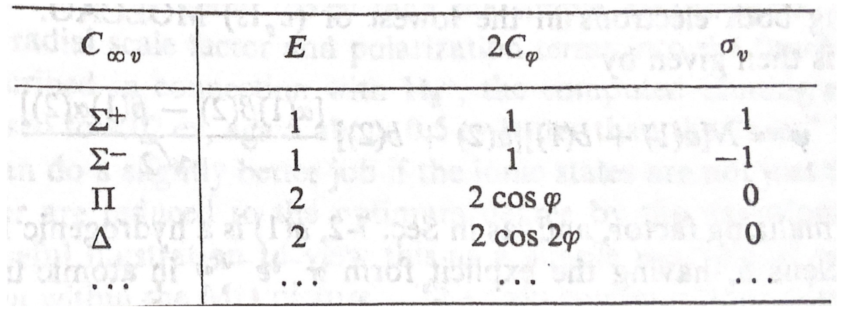
Figure 10.15: Correlation diagram with "separated atom" and "united atom" limiting cases. The respective equilibrium distance R_{ab} depends on the particular molecule.

In the next example of H_2, the ground state spins must be opposed/the spin state antisymmetric, since the electrons are both in the symmetric ground state ((a) $\sigma_g\,1s$ or (b) $1s\,\sigma_g$). Thus, $\Lambda = \lambda_1 + \lambda_2 = 0$ and the term denomination is $^1\Sigma{*}{+}_g$, i.e., it is a singlet state with zero angular momentum in the gerade/+ representation. (The "+" sign comes from the fact that the orbital, i.e., the left uppermost in Fig. 10.10, has reflection symmetry along all axes.

In a slightly more complex example, O_2 has a total of 16 electrons. In the ground state, one sees that all orbitals up to $\pi_u\,2p/3p\,\sigma_u$ are filled with the first 14 of those. This will leave two electrons in $\pi_g\,2p$ $(3p\,\pi_u)$, i.e., a half-filled π-orbital. By Hund's first rule (which is true also for molecules!), the spins for the lowest energy state line up in parallel, $S = 1$ (i.e., giving a symmetric (triplet) spin function). This leaves an antisymmetric electronic function, thus, the angular momenta of the two electrons are opposite and thus $\Lambda = 0$. The term for the oxygen molecule ground state is thus ${}^3\Sigma_g^-$. (The g is inherited from the π_g, i.e., the separated atom picture is more accurate in this case. The "-" comes from the fact that the wavefunction changes sign under σ_v (because both electrons are in a π orbital).

10.3.2 Diatomic heteronuclear molecules

The symmetry group in this case lacks the i element of the homonuclear case, thus giving $C_{\infty v}$ with a group table in Fig. 10.16.



$C_{\infty v}$	E	$2C_\varphi$	σ_v
Σ^+	1	1	1
Σ^-	1	1	-1
Π	2	$2\cos\varphi$	0
Δ	2	$2\cos 2\varphi$	0
...	...	...	...

Figure 10.16: Group table for $C_{\infty v}$, the symmetry of heteronuclear diatomic molecules.

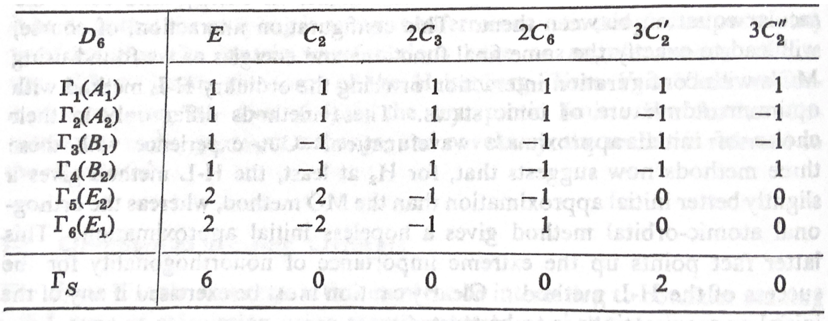
Because there is no inversion, there is no parity and thus no g and u representations. The representations are $\Sigma^\pm$ (1D) and one 2D representation for each Π, Δ, etc.

10.3.3 Connection of molecular spatial symmetry and basis functions

This section looks at a somewhat more complicated molecule, benzene. This has two goals:

1. Introduce how symmetry can help to estimate the basis functions with no more knowledge about the molecule than that is has six carbon atoms in a hexagonal arrangement and one p-like orbital per carbon atom singly occupied. (Of the other three outer electrons two bind to the neighboring carbon and one to the neighboring hydrogen.)
2. Introduce Hückel theory - the theory of building aromatic molecular ring orbitals in LCAO.

The symmetry of the hexagonal geometry is D_{6h}. For simplicity, the σ_h-reflection is left out of the following discussion, so D_6 (Fig. 10.17) is assumed in what follows.



D_6	E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$
$\Gamma_1(A_1)$	1	1	1	1	1	1
$\Gamma_2(A_2)$	1	1	1	1	−1	−1
$\Gamma_3(B_1)$	1	−1	1	−1	1	−1
$\Gamma_4(B_2)$	1	−1	1	−1	−1	1
$\Gamma_5(E_2)$	2	2	−1	−1	0	0
$\Gamma_6(E_1)$	2	−2	−1	1	0	0
Γ_S	6	0	0	0	2	0

Γ_S : permutation representation of 6 points

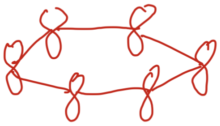


Figure 10.17: Character table of irreducible representations of D_6 and the character of the 6-permutation (reducible) representation. From Tinkham [4].

This uses the projection method for finding basis functions but starts with knowledge that all six C electrons will have to be used in a symmetric manner, which means the combination of basis functions belongs to the permutation representation of six particles Γ_S. (This representation just gives all possible permutations of six particles, and thus trivially is six-dimensional and only has a non-zero character for the identity element: $\chi(e) = 6$, $\chi(g \neq e) = 0$.) From the character table one immediately finds that the reduction of Γ_S gives

$$\Gamma_S \;=\; \Gamma_1 + \Gamma_3 + \Gamma_5 + \Gamma_6$$

of which the former two are 1D, the latter two 2D. This gives exactly a six-dimensional space, with two pairs of degenerate functions. From the character table one can now make the following ansatz (with normalization) starting with the single-C orbitals which are, for simplicity, called $a, b, \ldots$ here and where S denotes the overlap integral of neighboring atom orbitals.

$$\begin{aligned}
\Psi_1(\Gamma_1) &= \frac{a+b+c+d+e+f}{\sqrt{6(1+2S)}} \\
\Psi_2(\Gamma_3) &= \frac{a-b+c-d+e-f}{\sqrt{6(1-2S)}} \\
\Psi_3(\Gamma_5) &= \frac{a-b+d-e}{\sqrt{4(1-S)}} \\
\Psi_4(\Gamma_5) &= \frac{a+b-2c+d+e-2f}{\sqrt{16(1-S)}} \\
\Psi_5(\Gamma_6) &= \frac{a+b-d-e}{\sqrt{4(1-S)}} \\
\Psi_6(\Gamma_6) &= \frac{a-b-2c-d+e+2f}{\sqrt{16(1-S)}}.
\end{aligned}$$

The respective energies can be built from

$$\begin{aligned}
Q &\equiv \langle a|H|a\rangle = \langle b|H|b\rangle = \ldots \\
\beta &\equiv \langle a|H|b\rangle = \langle b|H|c\rangle = \ldots
\end{aligned}$$

which then results in

$$\begin{aligned}
E(\Gamma_1) &= \langle \Psi_1|H|\Psi_1\rangle = \frac{Q+2\beta}{1+2S} \\
E(\Gamma_3) &= \frac{Q-2\beta}{1-2S} \\
E(\Gamma_5) &= \frac{Q-\beta}{1-S} \\
E(\Gamma_6) &= \frac{Q+\beta}{1+S}.
\end{aligned}$$

The energies and wavefunctions are depicted in Fig. 10.18

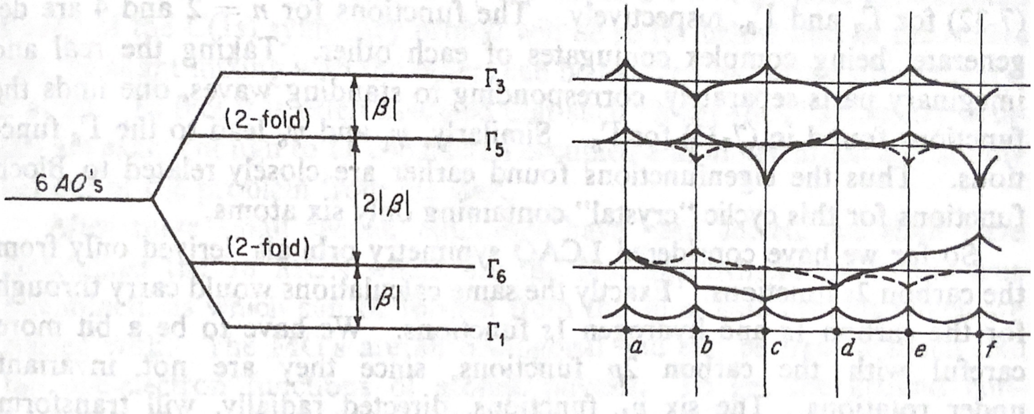


Fig. 7-7. *Molecular-orbital energy-level scheme for benzene, with overlap integrals neglected. The form of the MO is also shown schematically in each case, a* 1*s atomic orbital being used for simplicity. In case of degeneracy, the two functions are distinguished by solid and dashed curves.*

Figure 10.18: From Tinkham [4].

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