THE UNIVERSITY OF
SYDNEY

School of Physics

PHYS 3015/3039/3042/3043/3044
First Semester 2015

Quantum Physics Module
Dr. Michael Schmidt
michael.schmidt@sydney.edu.au

©School of Physics, University of Sydney 2015

The course is based on the textbook Quantum Mechanics by David H. McIntyre. References to the book are denoted by M: x.y, where x.y is the chapter number. These notes are a modified version of the 2014 lecture notes of Associate Professor Brian James.

Contents

1   Review of Basic Concepts in Quantum Physics

Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle \tag{1.1}$$

The time dependence can be analytically solved for a time-independent Hamiltonian

$$|\Psi(t)\rangle = e^{-i\hat{H}(t-t_0)/\hbar} |\Psi_0\rangle \tag{1.2}$$

with the quantum state at time t_0 defined as $|\Psi(t_0)\rangle \equiv |\Psi_0\rangle$. It remains to solve the time-independent Schrödinger equation in terms of its eigenstates $|E\rangle = \varphi_E(x)$

$$\hat{H}\varphi_E(x) = E\varphi_E(x) , \tag{1.3}$$

i.e. find the eigenstates of the Hamiltonian $\hat{H}$ and determine their respective energies.

   The Hamiltonian is obtained from the Hamiltonian in classical physics by changing to operators. In classical mechanics the Hamiltonian determines the energy of a system and it can be generally written as the sum of kinetic (T) and potential (V) energy

$$H = T + V \quad \Rightarrow \quad \hat{H} = \hat{T} + \hat{V} . \tag{1.4}$$

Concretely, we will define the position and momentum operators as follows

$$\hat{x} \equiv x \qquad\qquad \hat{p} \equiv -i\hbar \frac{\mathrm{d}}{\mathrm{d}x} \tag{1.5}$$

The two operators satisfy the commutation relation[1]

$$[\hat{p}, \hat{x}] = -i\hbar \tag{1.8}$$

For a point particle within a potential V, the classical Hamiltonian is given by

$$H = \frac{p^2}{2m} + V(x) \quad \Rightarrow \quad \hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) \tag{1.9}$$

Energy eigenvalue equation is a differential equation

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \varphi_E(x) = e\varphi_E(x) . \tag{1.10}$$

---

[1]It can be easily derived by applying the commutator to an arbitrary wave function

$$[\hat{p}, \hat{x}]\psi(x) = [-i\hbar \frac{\mathrm{d}}{\mathrm{d}x}, x]\psi(x) = -i\hbar \left(\frac{\mathrm{d}}{\mathrm{d}x} x\psi(x) - x\frac{\mathrm{d}}{\mathrm{d}x}\psi(x) \right) \tag{1.6}$$

$$= -i\hbar \left(1 + x\frac{\mathrm{d}}{\mathrm{d}x}\psi(x) - x\frac{\mathrm{d}}{\mathrm{d}x}\psi(x) \right) = -i\hbar\psi(x) \tag{1.7}$$

The generalisation to more dimensions is straightforward. In three dimensions with, the Hamiltonian reads

$$\hat{H} = \frac{\hat{p}_1^2 + \hat{p}_2^2 \hat{p}_3^2}{2m} + V(\hat{x}_1, \hat{x}_2, \hat{x}_3) \tag{1.11}$$

$$= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) + V(x_1, x_2, x_3) \tag{1.12}$$

and the commutation relations between the momentum operators $\hat{p}_i$ and the position operators $\hat{x}_j$ are given by[2]

$$[\hat{p}_i, \hat{x}_j] = -i\hbar\delta_{ij} . \tag{1.14}$$

1.1 Relation between quantum state vector and wave function

Previously we used the quantum state vector $|\psi\rangle$ and its projections onto the spin eigenstates $\langle\pm|\psi\rangle$. These are the probability amplitudes for $|\psi\rangle$ to be measured in a particular spin eigenstate. Using the projections onto spin eigenstates, the quantum state vector can be written as

$$|\psi\rangle = \begin{pmatrix} \langle+|\psi\rangle \\ \langle-|\psi\rangle \end{pmatrix} . \tag{1.15}$$

The corresponding probabilities to measure a quantum state in a given spin state is given by

$$\mathcal{P}_\pm = |\langle\pm|\psi\rangle|^2 . \tag{1.16}$$

In a similar way we can define the projections onto the energy eigenstates $\langle E_i|\psi\rangle$ and the projections onto the position eigenstates $\langle x|\psi\rangle$. Experiment tells us that the physical observable x is not quantised and all values are allowed. In this case, the column vector representation is inconvenient and the most convenient representation is the wave function

$$\psi(x) = \langle x|\psi\rangle . \tag{1.17}$$

The corresponding probability density function is

$$\mathcal{P}(x) = |\psi(x)|^2 . \tag{1.18}$$

The sum over discrete probabilities is changed to an integral and the normalisation condition becomes

$$1 = \int \mathcal{P}(x)dx = \int \psi(x)^*\psi(x)dx \tag{1.19}$$

and the probability to detect the quantum state in the interval $a < x < b$ is

$$\mathcal{P}_{a<x<b}(x) = \int_a^b \mathcal{P}(x)dx . \tag{1.20}$$

---

[2]The Kronecker-delta δ_{ij} is defined as

$$\delta_{ij} \equiv \begin{cases} 1 & \text{for } i = j \\ 0 & \text{otherwise} \end{cases} . \tag{1.13}$$

Generally the probability to find a quantum state $\langle\psi|$ in state $\langle\varphi|$ is given by

$$\langle\varphi|\psi\rangle = \int \varphi^*(x)\psi(x)dx \ . \tag{1.21}$$

Finally, an expectation value of an operator $\hat{A}$ is given by

$$\left\langle\hat{A}\right\rangle = \left\langle\psi|\hat{A}|\psi\right\rangle = \int \psi^*(x)A(x)\psi(x)dx \ . \tag{1.22}$$

Summarising the correspondence between the bra-ket formalism and the wave function formalism:

$$|\psi\rangle \leftrightarrow \psi(x) \qquad \langle\psi| \leftrightarrow \psi^*(x) \qquad \langle|\rangle \leftrightarrow \int dx \qquad \hat{A} \leftrightarrow A(x) \tag{1.23}$$

After recapitulating the basic notions of quantum mechanics, we apply them to simple one-dimensional quantum mechanical systems.

1.2   Orthogonality and Completeness

Eigenstates of any hermitean operator are orthogonal

$$\langle n|m\rangle = \delta_{nm} \qquad\qquad \int \varphi_n(x)^*\varphi_m(x) = \delta_{nm} \tag{1.24}$$

and form a complete basis, i.e. any wave function can be expressed as a superposition

$$\psi(x) = \sum_n c_n\varphi_n(x) \tag{1.25}$$

The prime example is the Hamiltonian, i.e. the energy eigenstates form a complete orthonormal basis

$$\langle E_n|E_m\rangle = \delta_{nm} \qquad\qquad \sum_n |E_n\rangle\langle E_n| = 1 \tag{1.26}$$

1.3   Infinite square well

The potential of an infinitely deep potential well of size L is given by

$$V(x) = \begin{cases} \infty, & x < 0 \\ 0 & 0 < x < L \\ \infty, & x > L \ . \end{cases} \tag{1.27}$$

We solve the time-independent Schrödinger equation (1.10) in the three different regions separately. Outside the box the potential energy is infinite and thus the only solution is $\varphi_E(x) \equiv 0$. Inside the box the potential energy is zero and it can be rewritten as

$$\left(\frac{d^2}{dx^2} + \frac{2mE}{\hbar^2}\right)\varphi_E(x) = 0 \ . \tag{1.28}$$

It is a linear second order ordinary differential equation (ODE) with constant coefficients and can be solved using the ansatz

$$\varphi_E(x) = Ae^{ikx} \ . \tag{1.29}$$

The characteristic equation is given by

$$- k^2 + \frac{2mE}{\hbar^2} = 0 \tag{1.30}$$

and the general solution inside the box is the linear superposition of the different possible solutions

$$\varphi_E(x) = Ae^{ikx} + Be^{-ikx} \tag{1.31}$$

with $k = \sqrt{2mE}/\hbar$ and A, B two complex numbers, which are determined by the boundary conditions and the normalisation. The general solution is thus given by

$$\varphi_E(x) = \begin{cases} 0, & x < 0 \\ Ae^{ikx} + Be^{-ikx} & 0 < x < L \\ 0, & x > L . \end{cases} \tag{1.32}$$

We have to require that the solution is continuous everywhere, i.e.

$$\varphi_E(0) = \varphi_E(L) = 0 \Rightarrow A + B = 0 \quad \text{and} \quad Ae^{ikL} + Be^{-ikL} = 0 . \tag{1.33}$$

Hence there is a discrete set of solutions of the form

$$\varphi_n(x) = A' \sin(k_n x) \quad \text{with} \quad k_n = n\frac{\pi}{L}, n = 1, 2, 3, \ldots \tag{1.34}$$

with energies

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} . \tag{1.35}$$

The constant A' is fixed by correctly normalising the wave function

$$1 = \int_0^L dx |A'|^2 \sin^2(k_n x) dx \tag{1.36}$$

and the correctly normalised energy eigenstates are

$$\varphi_n(x) = \frac{2}{L} \sin(\frac{n\pi x}{L}), \quad n = 1, 2, 3, \ldots \tag{1.37}$$

1.4 Inversion symmetry and parity

Inspection of the wave functions for the states of a particle in an infinite well show that, with respect to the middle of the well, the wave functions are alternately symmetric (n=1,3,5,...) or antisymmetric (n=2,4,6,...). This is even clearer if we change the x-axis origin to the middle of the well, and place the walls at $x = \pm a$ so that the width of the well is $2a$, and the wave functions become

$$\varphi_n(x) = \sqrt{\frac{1}{a}} \cos \frac{n\pi x}{2a} \qquad n = 1, 3, 5, \ldots \varphi_n(x) = \sqrt{\frac{1}{a}} \sin \frac{n\pi x}{2a} \qquad n = 2, 4, 6, \ldots \tag{1.38}$$

Clearly state with odd n, are symmetric with respect to inversion ($x \to -x$); those with even n are antisymmetric. Symmetric states where $\varphi_n(-x) = +\varphi_n(x)$ are said to have positive parity; antisymmetric states where $\varphi_n(-x) = -\varphi_n(x)$ are said to have negative parity. We will see later that allowed transitions can only occur between states of opposite parity.

1.5 Finite square well

If the sides of the well are not infinite, so that the potential well of width $2a$ is defined by[3]

$$V(x) = \begin{cases} V_0, & x < -a \\ 0 & -a < x < a \\ V_0, & x > a . \end{cases} \tag{1.39}$$

Inside the box the Schrödinger equation is the same as for the infinitely deep potential well. Outside the box the Schrödinger equation can be rewritten as

$$\left(\frac{d^2}{dx^2} - \frac{2m(V_0 - E)}{\hbar^2} \right) \varphi_E(x) = 0 . \tag{1.40}$$

Assuming a bound state with $0 < E < V_0$ we can similarly make an ansatz $\varphi_E(x) = Ae^{qx}$ and obtain the general solutions with

$$q^2 = \frac{2m(V_0 - E)}{\hbar^2} \tag{1.41}$$

and the general solution is given by

$$\varphi_E(x) = \begin{cases} Ae^{qx} + Be^{-qx}, & x < -a \\ Ce^{ikx} + De^{-ikx} & -a < x < a \\ Ee^{qx} + Fe^{-qx}, & x > a \end{cases} \tag{1.42}$$

In order to interpret the wave function, we have to normalise it, this automatically forces $B = E = 0$. Furthermore demanding that the solution is

1. continuous

2. and continuously differentiable ($\frac{d\varphi_E(x)}{dx}$ being differentiable) [if $V_0 \neq \infty$]

everywhere fixes three of the other coefficients. The last coefficient is fixed by the normalisation condition.

Because of the finite height of the barriers, the particle can tunnel into the region beyond the edges of the well, where on physical grounds we would expect the wave functions to decay with distance beyond the edge of the well. Within the well, where the particle is free, we expect the wave functions to be sinusoidal as in the case of the infinite well. The solution of the energy eigenvalue equation in this case is not trivial (in fact it can be solved by numerical means only). For solutions to be physically acceptable, the wave functions must approach zero with distance away from the well, and be continuous and smooth across the boundaries (i.e. $\varphi_E(x)$ and $d\varphi_E(x)/dx$ are continuous at the walls of the well). Such solutions occur for discrete values of E only.

As the equation can be solved by numerical means only, it is not possible to write down a formula for the energy levels. However, as expected, the energies approach those of the infinite case as $V_0 \to \infty$. Figure 1 is a reproduction of Figure 5.18 from McIntyre showing energy levels for an infinite square well and finite square well of the same width. Note that for the finite square well the wave function penetrates the walls of the well, beyond which it decays, and that its value and gradient are continuous across the well boundary, as required. In the case of the infinite well the wave function vanishes at the walls of the well and in this limit the gradient is discontinuous at the edge of the well.

---

[3]The width of the well is given as L for the infinite case and $2a$ for the finite case in order to be consistent with the notation used by McIntyre
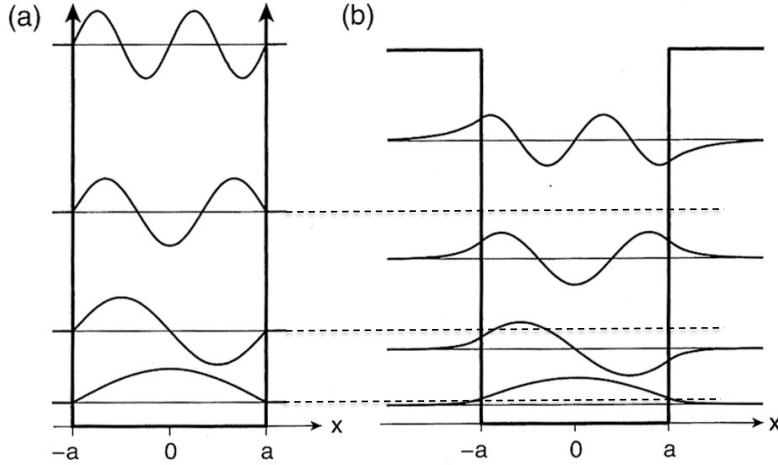
Figure 1: Energy levels and wave functions for (a) an infinite square well of width $2a$ and (b) a finite square well of width $2a$. Note that as the finite well has reduced confinement, the energy levels are lower than those for an infinite well of the same width. Based on figure 5.18 of *Quantum Mechanics* by D.H. McIntyre.

1.6 Harmonic oscillator

The last 1D example which we are studying is the harmonic oscillator. A particle with mass m is subject to a restoring force $-kx$, where x is the displacement from the equilibrium position. The potential energy of the particle is

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2 \tag{1.43}$$

where $\omega = \sqrt{k/m}$ is the angular oscillation frequency. Hence the time-independent Schrödinger equation is given by

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right)\varphi_E(x) = E\varphi_E(x) \ . \tag{1.44}$$

The solution of this equation involves a well studied special function, the Hermite polynomial, such that the normalised wave functions can be written as

$$\varphi_E(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}H_n(\xi)e^{-\xi^2/2} \quad \text{with } \xi = \sqrt{\frac{m\omega}{\hbar}}x \text{ and } n = 0, 1, 2, 3, \ldots \tag{1.45}$$

where H_n is a Hermite polynomial of order n.

$$H_0(x) = 1, \qquad H_1(x) = 2x, \qquad H_2(x) = 4x^2 - 2 \qquad H_3(x) = 8x^3 - 12x \tag{1.46}$$

The corresponding energy eigenvalues are given by

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad n = 0, 1, 2, 3, \ldots \tag{1.47}$$

Note that the lowest energy level is not zero as it would be for a classical harmonic oscillator, but $\frac{1}{2}\hbar\omega$. It is known as the zero point energy. Figure 2 shows wave functions and probability densities for the first four energy levels of a harmonic oscillator.

9
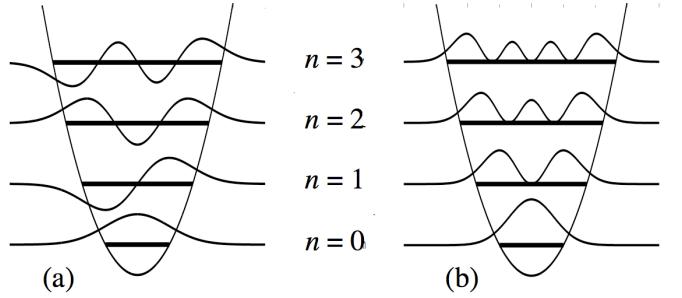
Figure 2: (a) Wave functions and (b) the probability density for the first four energy levels of a harmonic oscillator.

1.7 Application: molecular vibrational energy levels

The two nuclei of a diatomic molecule can vibrate about their equilibrium separation. For sufficiently small amplitude vibrations the motion can be treated as a harmonic oscillation in a parabolic potential. The quantised energy levels would then be given by

$$E_n = (n + \frac{1}{2})\hbar\omega_0 = (n + \frac{1}{2})h\nu_0 \qquad \text{where} \quad n = 0, 1, 2, 3, \ldots \qquad (1.48)$$
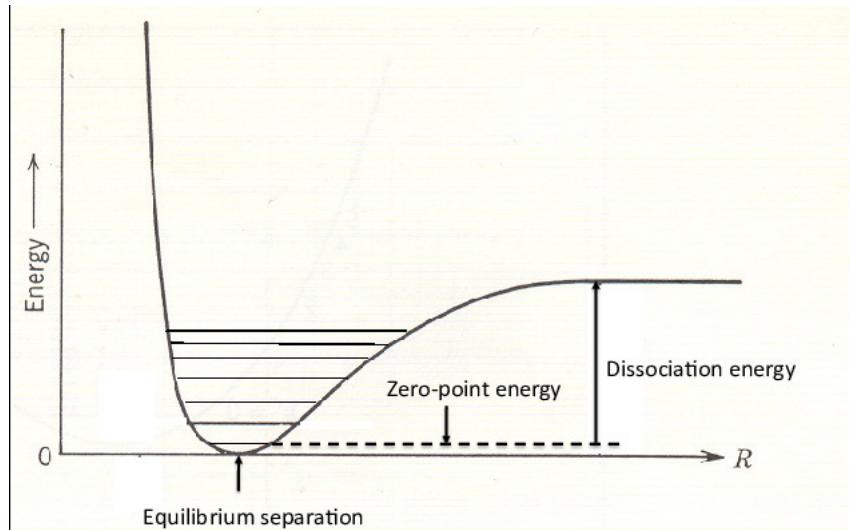
Figure 3: Potential curve for a typical diatomic molecule showing vibrational energy levels. At lower levels where the potential approximates a parabola the energy levels are almost equally spaced. At higher levels where the potential profile becomes wider than a parabola, the spacing decreases.

and $\nu_0 = \omega_0/2\pi$ is the classical vibration frequency (in Hz). Transitions between adjacent vibrational energy levels are in the infrared part of the electromagnetic spectrum.[4] Figure 3 shows a typical

---

[4]In fact transitions for which $|\Delta n| > 1$ are much more unlikely than those for which $|\Delta n| = 1$, and are called *forbidden transitions*. The condition $|\Delta n| = 1$ is called a *selection rule* and transitions which satisfy this condition are said to be

potential curve (energy as a function of nuclear separation) for a diatomic molecule. At low energy levels, where a parabolic approximation to the potential curve is a good fit, the actual energy levels are equally spaced, but at higher levels where the parabolic approximation is a poorer fit the spacing between levels gradually decreases.

1.8   For discussion in lectures

- Zero-point energy

- Molecular vibrational spectra

---

allowed transition. For more on these concepts see Appendix C.

2   Quantum Physics of Central Potentials

One of the main goals of this course is to solve the hydrogen atom. It is a two-body problem in 3 dimensions, with a positively charged proton and a negatively charged electron. They interaction via Coulomb interaction which is described by the Coulomb potential

$$V(|\mathbf{r_1} - \mathbf{r_2}|) = -\frac{Ze^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} = -\frac{Z\alpha\hbar c}{|\mathbf{r}_1 - \mathbf{r}_2|} \ . \tag{2.1}$$

It is a *central potential*, which only depends on the relative distance between the two particles.

2.1   Separation of Variables

We will actually solve the slightly more general problem of an arbitrary two-body system with a *central potential*. It is described by the Hamiltonian

$$\hat{H}_{sys} = \frac{\hat{\mathbf{p}}_1^2}{2m_1} + \frac{\hat{\mathbf{p}}_2^2}{2m_2} + V(|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|) \ , \tag{2.2}$$

where m_i, $\hat{\mathbf{p}}_i$, and $\hat{\mathbf{r}}_i$ are the mass, momentum and position of particle i.

Similarly to classical mechanics, the Hamiltonian can be separated in the Hamiltonian of the centre of mass motion and the relative motion about the centre. We define the centre of mass coordinate

$$\hat{\mathbf{R}} = \frac{m_1\hat{\mathbf{r}}_1 + m_2\hat{\mathbf{r}}_2}{m_1 + m_2} \tag{2.3}$$

and the relative position vector

$$\hat{\mathbf{r}} = \hat{\mathbf{r}}_2 - \hat{\mathbf{r}}_1 \ . \tag{2.4}$$

Similarly we define the momentum in the centre of mass frame

$$\hat{\mathbf{P}} = \hat{\mathbf{p}}_1 + \hat{\mathbf{p}}_2 \tag{2.5}$$

and the relative velocity in term of the relative momentum $\hat{\mathbf{p}}_{rel}$

$$\frac{\hat{\mathbf{p}}_{rel}}{\mu} = \frac{\hat{\mathbf{p}}_2}{m_2} - \frac{\hat{\mathbf{p}}_1}{m_1} \tag{2.6}$$

with the *reduced mass*

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \ . \tag{2.7}$$

Rewriting the Hamiltonian in these new coordinates, it separates in a Hamiltonian describing the centre of mass motion and the relative motion, $\hat{H} = \hat{H}_{CM} + \hat{H}_{rel}$ with

$$\hat{H}_{CM} = \frac{\hat{\mathbf{P}}^2}{2M} \tag{2.8}$$

$$\hat{H}_{rel} = \frac{\hat{\mathbf{p}}_{rel}^2}{2\mu} + V(r) \tag{2.9}$$

and $M = m_1 + m_2$. It is a valid assumption that the quantum state also separates

$$\psi_{sys}(\mathbf{R}, \mathbf{r}) = \psi_{CM}(\mathbf{R})\psi_{rel}(\mathbf{r}) \,, \tag{2.10}$$

because the potential does *not* depend on the centre of mass coordinate $\hat{\mathbf{R}}$ and did not depend on it previously, but it only depends on the relative coordinate $\hat{\mathbf{r}}$. Explicitly we can show using the Schrödinger equation

$$E\psi_{sys}(\mathbf{R}, \mathbf{r}) = \hat{H}\psi_{sys}(\mathbf{R}, \mathbf{r}) \tag{2.11}$$

$$= \left(\hat{H}_{CM} + \hat{H}_{rel}\right)\psi_{CM}(\mathbf{R})\psi_{rel}(\mathbf{r}) \tag{2.12}$$

$$= \left(\psi_{rel}(\mathbf{r})\hat{H}_{CM}\psi_{CM}(\mathbf{R}) + \psi_{CM}(\mathbf{R})\hat{H}_{rel}\psi_{rel}(\mathbf{r})\right) \tag{2.13}$$

$$\tag{2.14}$$

We divide by ψ_{sys}

$$E = \psi_{CM}^{-1}(\mathbf{R})\hat{H}_{CM}\psi_{CM}(\mathbf{R}) + \psi_{rel}^{-1}(\mathbf{r})\hat{H}_{rel}\psi_{rel}(\mathbf{r}) \tag{2.15}$$

and bringing one of the ratios to the other side of the equation

$$E - \psi_{CM}^{-1}(\mathbf{R})\hat{H}_{CM}\psi_{CM}(\mathbf{R}) = \psi_{rel}^{-1}(\mathbf{r})\hat{H}_{rel}\psi_{rel}(\mathbf{r}) \,, \tag{2.16}$$

we see that the left-hand side of the equation is independent of $\mathbf{r}$ and the right-hand side independent of $\mathbf{R}$. Hence both of them have to be constant, which we denote by E_{rel}, the energy of the subsystem of the relative coordinate. Thus we can write

$$\hat{H}_{CM}\psi_{CM}(\mathbf{R}) = E_{CM}\psi_{CM}(\mathbf{R}) \tag{2.17}$$

$$\hat{H}_{rel}\psi_{rel}(\mathbf{r}) = E_{rel}\psi_{rel}(\mathbf{r}) \tag{2.18}$$

where $E_{CM} = E - E_{rel}$ is the energy of for the subsystem describing the centre of mass coordinates.

2.2 Solution to the Center of Mass equation

The Hamiltonian for the centre of mass motion is given by

$$\hat{H}_{CM} = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right) \tag{2.19}$$

with $\mathbf{R} = (X, Y, Z)^T$. It corresponds to the Hamiltonian of a free particle in three dimensions, which can be solved in terms of free particle eigenstates

$$\psi_{CM}(X, Y, Z) = \frac{1}{(2\pi\hbar)^{3/2}}e^{i(P_X X + P_Y Y + P_Z Z)/\hbar)} = \frac{1}{(2\pi\hbar)^{3/2}}e^{i\mathbf{P}\cdot\mathbf{R}/\hbar} \tag{2.20}$$

with $\mathbf{P} = (P_X, P_y, P_z)^T$. The energy eigenvalues are given by

$$E_{CM} = \frac{1}{2M}\left(P_X^2 + P_Y^2 + P_Z^2\right) \,. \tag{2.21}$$

Note that the momentum $\mathbf{P}$ is not discrete, but a continuous variable. Using Eq. (1.2), the time-dependent wave-function is then given by

$$\psi_{CM}(t, X, Y, Z) = \frac{1}{(2\pi\hbar)^{3/2}}e^{-i(Et - \mathbf{P}\cdot\mathbf{R})/\hbar} \,, \tag{2.22}$$

where we set $t_0 = 0$. The solution are plane waves travelling forward with phase velocity $|\mathbf{v_{ph}}| = E/|\mathbf{P}|$ and group velocity $\mathbf{v_g} = \nabla_{\mathbf{p}} E$. The average momentum is given by the expectation value of the momentum operator

$$\left\langle \hat{P} \right\rangle = \int d^3x \psi^*_{CM}(X, Y, Z) \left(-i\hbar\nabla\right) \psi_{CM}(X, Y, Z) = \mathbf{P} \,. \tag{2.23}$$

Lecture 3 M: 7.3

2.3 Classical Angular Momentum

In classical mechanics, the angular momentum is conserved for central forces, like the Coulomb potential in the hydrogen atom

$$\frac{d\mathbf{L}}{dt} = \frac{d\mathbf{r} \times \mathbf{p}}{dt} \tag{2.24}$$

$$= \mathbf{v} \times \mathbf{p} + \mathbf{r} \times \mathbf{F} \tag{2.25}$$

$$= -\mathbf{r} \times \nabla V(r) \tag{2.26}$$

$$= -\mathbf{r} \times V'(r)\frac{\mathbf{r}}{r} = 0 \,. \tag{2.27}$$

We will make use of that fact to simplify the eigenvalue equation for the relative motion of the hydrogen atom.

2.4 Angular momentum

We are already familiar with the fact that an electron has intrinsic angular momentum, usually called *spin.* This is a property of the electron, just like its mass or charge. An electron in an atom, however, can also have angular momentum due to its motion, usually called *orbital angular moment.* Before considering orbital angular momentum, let us summarise what we know about electron spin.

2.4.1 Spin

An electron has spin characterised by a spin quantum number $s = 1/2$ and magnetic quantum numbers $m_s = \pm 1/2$, with spin magnitude and component values quantised according to

$$\mathbf{S}^2 = s(s+1)\hbar^2 = \frac{3}{4}\hbar \qquad [\,\text{or } |\mathbf{S}| = \sqrt{s(s+1)}\hbar = \sqrt{3}\hbar/2\,] \tag{2.28}$$

$$S_z = m_s\hbar = \pm\tfrac{1}{2}\hbar \tag{2.29}$$

In the S_z representation the spin eigenstates $|sm_s\rangle$ are

$$|+\rangle = \left|\tfrac{1}{2}, \tfrac{1}{2}\right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{2.30}$$

$$|-\rangle = \left|\tfrac{1}{2}, -\tfrac{1}{2}\right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{2.31}$$

The various spin operators are given by

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar}{2}\sigma_1 \qquad (2.32)$$

$$\hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{\hbar}{2}\sigma_2 \qquad (2.33)$$

$$\hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{2}\sigma_3 \qquad (2.34)$$

$$\hat{S}^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad (2.35)$$

where σ_i denotes the three Pauli spin matrices. The vector model for spin in Figure 4 conveniently summarises the quantisation properties for spin. It is straightforward to show[5]

$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z \qquad (2.36)$$

$$[\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x \qquad (2.37)$$

$$[\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y \qquad (2.38)$$

$$[\hat{\mathbf{S}}^2, \hat{S}_x] = [\hat{\mathbf{S}}^2, \hat{S}_y] = [\hat{\mathbf{S}}^2, \hat{S}_z] = 0 . \qquad (2.39)$$
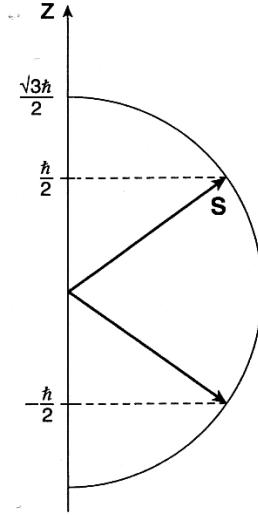
Figure 4: The vector model for electron spin.

2.4.2 Orbital angular momentum

The angular momentum of a particle is given by $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. As the momentum operator in the position representation is given by

---

[5]The three spin operators form the Lie algebra of SU(2) and the square of the vector of spin operators, $\hat{\mathbf{S}}^2$ is called Casimir operator, which commutes with all three spin operators. The Casimir operator plus any of the three spin operators form the maximal commuting set of operators and can be used to classify quantum states with angular momentum.

$$\hat{\mathbf{p}} = -i\hbar \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) = -i\hbar \nabla \tag{2.40}$$

the operator for angular momentum is therefore

$$\hat{\mathbf{L}} = \mathbf{r} \times (-i\hbar \nabla) \tag{2.41}$$

The operators for the components and the magnitude of angular momentum are

- Cartesian coordinates

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \tag{2.42}$$

$$\hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \tag{2.43}$$

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \tag{2.44}$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{2.45}$$

- Spherical polar coordinates (see Figure 26) in Sec. E)

$$\hat{L}_x = i\hbar \left(\sin\phi \frac{\partial}{\partial \theta} + \cot\theta \cos\phi \frac{\partial}{\partial \phi} \right) \tag{2.46}$$

$$\hat{L}_y = i\hbar \left(-\cos\phi \frac{\partial}{\partial \theta} + \cot\theta \sin\phi \frac{\partial}{\partial \phi} \right) \tag{2.47}$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \tag{2.48}$$

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \tag{2.49}$$

It is straightforward to show that the commutation relations for the angular momentum components are

$$\left[\hat{L}_x, \hat{L}_y \right] = i\hbar \hat{L}_z \tag{2.50}$$

$$\left[\hat{L}_y, \hat{L}_z \right] = i\hbar \hat{L}_x \tag{2.51}$$

$$\left[\hat{L}_z, \hat{L}_x \right] = i\hbar \hat{L}_y \tag{2.52}$$

With a little more algebraic manipulation (see McIntyre, p211), it is possible to show that $\hat{L}^2$ commutes with each of the component operators:

$$\left[\hat{L}^2, \hat{L}_x \right] = 0 \tag{2.53}$$

$$\left[\hat{L}^2, \hat{L}_y \right] = 0 \tag{2.54}$$

$$\left[\hat{L}^2, \hat{L}_z \right] = 0 \tag{2.55}$$

We note that these are the same commutation relations satisfied by spin angular momentum. By analogy, therefore we can conclude it is possible to find states that are simultaneously eigenstates of $\hat{L}^2$ and one of the component operators, which according to convention we choose to be $\hat{L}_z$. Recalling that the spin eigenvalue equations are

$$\hat{S}^2 \left| s m_s \right\rangle = s(s+1)\hbar^2 \left| s m_s \right\rangle \tag{2.56}$$
$$\hat{S}_z \left| s m_s \right\rangle = m_s \hbar \left| s m_s \right\rangle \tag{2.57}$$

where $m_s = s, s-1, \ldots, -s$, the equivalent equations for orbital angular momentum will be

$$\hat{L}^2 \left| l m_l \right\rangle = l(l+1)\hbar^2 \left| l m_l \right\rangle \tag{2.58}$$
$$\hat{L}_z \left| l m_l \right\rangle = m_l \hbar \left| l m_l \right\rangle \tag{2.59}$$

where $m_l = l, l-1, \ldots, -l$.

Although we are mostly concerned with spin $\frac{1}{2}$ systems, the spin quantum number s can in principle be half integer or integer. In contrast we will see soon that the orbital angular quantum number l can only be an integer; for the moment we will assume that this is the case.

In order to simplify the notation we will often drop the hat when writing operators, i.e. denote operators by A instead of $\hat{A}$.

2.5   The vector model for orbital angular momentum

The quantisation of angular momentum can be summarised by the vector model which shows the possible orientations of the angular momentum vector. The fact that the vector is limited to having a discrete number of orientations with respect to the z axis is referred to as *space quantisation*. Figure 5 depicts the vector model of angular momentum for $l = 3$, for which $|\mathbf{L}| = 2\sqrt{3}\hbar$ and $L_z = (3, 2, 1, 0, -1, -2, -3)\hbar$.
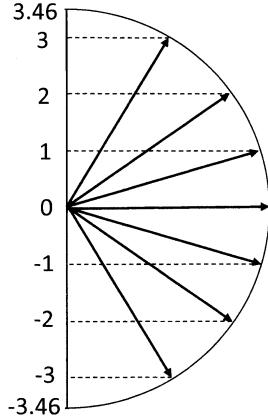

Figure 5: The vector model of angular momentum for $l = 3$. Angular momentum values are given in units of $\hbar$.

2.6 Application: molecular rotational energy levels

The moment of inertia of a diatomic molecule about its centre of mass is

$$I = \mu R_0^2 \tag{2.60}$$

where μ is the reduced mass of the molecule and R_0 is the nuclear separation. The energy associated with rotation can be expressed in terms of the angular momentum L as

$$E_{rot} = \frac{L^2}{2I} \tag{2.61}$$

Noting that angular momentum is quantised according to $L^2 = l(l+1)\hbar^2$, where l is an integer quantum number, leads to quantised rotational energy levels given by

$$E_{rot} = \frac{\hbar^2}{2I}l(l+1) \quad \text{where} \quad l = 0, 1, 2, 3, \ldots \tag{2.62}$$

2.6.1 Rotational spectra

The selection rule[6] for allowed transitions is : $\Delta l = \pm 1$. Therefore,

$$h\nu = \frac{hc}{\lambda} = hc\sigma = E_{l+1} - E_l = \frac{\hbar^2}{I}(l+1) \tag{2.63}$$

where $\sigma = 1/\lambda$ is the wave number.[7] Rotational spectra are in the far infrared and microwave regions between of the electromagnetic spectrum ($\lambda \sim 0.1$ mm - 10 mm)[8]. Only molecules with a permanent dipole moment will have a pure rotational spectrum. Thus molecules with identical nuclei (e.g. H_2, C_2) do not have pure rotational spectra.

2.6.2 Vibrational-rotational spectra

There will be rotational levels associated with each vibrational level. Thus a transition between vibrational states may also involve a change in rotational state, and we speak more generally of *vibrational-rotational* spectra for which the selection rules are: $\Delta l = \pm 1$ and $\Delta n = \pm 1$. Vibrational-rotational spectra are typically in the *infrared*. As molecules are predominantly in the ground vibrational levels at room temperature, vibrational-rotational spectra are usually observed as absorption spectra.

Example

For absorption transitions between vibrational levels n and $n + 1$, there are two groups of absorption lines corresponding to $\Delta l = \pm 1$. A small amount of algebra yields the following:

$$h\nu = h\nu_0 \pm \frac{\hbar^2}{I}l \quad l = 1, 2, 3, \ldots \tag{2.64}$$

---

[6]Selection rules are the result of conservation of angular momentum when a photon is emitted or absorbed. In most cases they are expressed in terms of the change in quantum numbers between the initial and final states. Transitions that satisfy selection rules are refereed to as *allowed* transitions. Transitions that do not satisfy selection rules are called *forbidden* transition. They can still occur but at much lower transition rates. For more on this topic see Appendix C.

[7]For vibrational-rotational spectra, wave number is often used instead of either wavelength or frequency. Although the SI unit is m^{-1}, cm^{-1} is commonly used. The symbol $\bar{\nu}$ is often used in older texts.

[8]The terms *sub-millimetre wave* and *millimetre wave* are also used to describe a region of the electromagnetic spectrum between the far-infrared and microwave regions.

Thus the lines are in two groups on either side of ν_0, with equal spacing of

$$\Delta\nu = \frac{\hbar}{2\pi I} \tag{2.65}$$

Note that there is no line at ν_0. Measurement of the spacing between lines allows the moment of inertia of the molecule to be calculated. Figure 6 shows the rotational-vibrational absorption spectrum of HBr. The spacing between the absorption lines is slightly non-uniform due to increase of the inter-atomic separation (i.e. stretching of the bond) with increasing angular momentum (i.e. with increasing value of the quantum number l).
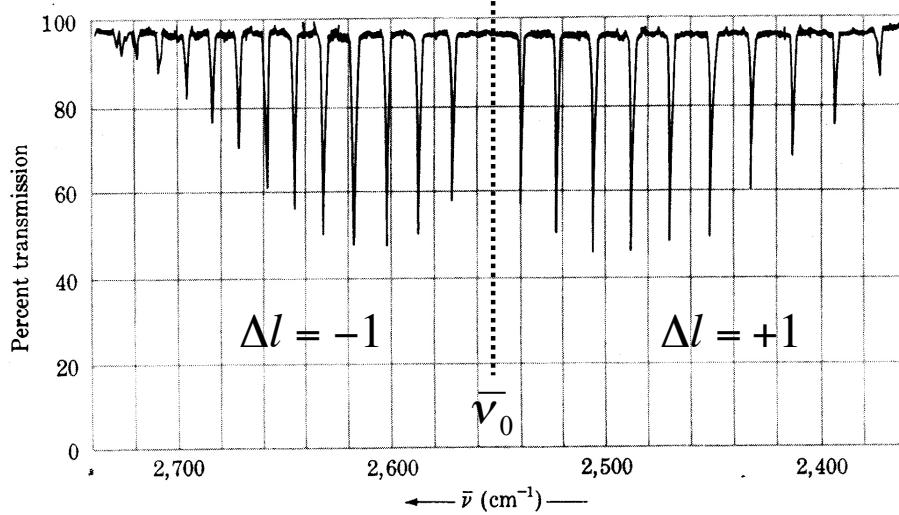
Figure 6: The vibrational-rotational absorption spectrum for HBr. (based on Figure 8-5, *Basic Principles of Spectroscopy*, R. Chang, McGraw-Hill, New York, 1971)

Lecture 4 M: 7.4-6; Read 7.4

2.7   The Hamiltonian of a spherically symmetric potential

We now move on to the energy eigenvalue equation of the relative motion for a spherically symmetric potential, Eq. 2.9 and Eq. 2.18. Its energy eigenvalue equation can be written as

$$\left(-\frac{\hbar^2\nabla^2}{2\mu^2} + V(r)\right)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi) \tag{2.66}$$

As it is spherically symmetric, it is convenient to express the Laplace operator in terms of spherical coordinates, which is given in Eq. (E.3). Noting that the θ and ϕ parts are proportional to the $\hat{L}^2$ operator (Equation 2.49), the Hamiltonian of the relative motion can be written as

$$H_{rel} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\mathbf{L}^2}{\hbar^2 r^2}\right] + V(r) \, . \tag{2.67}$$

As the angular part of H is completely contained in $\mathbf{L}^2$, it is obvious that

$$[H, \mathbf{L}^2] = [H, L_z] = 0 \tag{2.68}$$

19

and thus the magnitude of the orbital angular momentum and L_z are good quantum numbers.

The energy eigenvalue equation can be written as

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\hat{L}^2\right]\varphi_E(r,\theta,\phi) + V(r)\varphi_E(r,\theta,\phi) = E\varphi_E(r,\theta,\phi) \qquad (2.69)$$

2.8 Separation of variables of radial and spherical part

The solutions of this partial differential equation (PDE) will be $\varphi_E(r,\theta,\phi)$, wave functions for the energy eigenstates. As each term of the PDE involves derivatives of only one independent variable, it can be solved using the *separation of variables* technique. We begin by letting

$$\varphi(r,\theta,\phi) = R(r)Y(\theta,\phi) \qquad (2.70)$$

and substituting into Equation 2.69. The resulting equation is then divided through by $R(r)Y(\theta,\phi)$ and the result can be rearranged to give:

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) - \frac{2\mu}{\hbar^2}(E - V(r))r^2 = \frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\hat{L}^2Y(\theta,\phi) \qquad (2.71)$$

Note that the left-hand side is a function of r only while the right-hand side is a function of θ and ϕ only. The two sides can be equal for all values of the independent variables only if they are equal to a constant, A. We have therefore an ODE involving r (which we will deal with shortly) and a PDE involving θ and ϕ:

$$\hat{L}^2Y(\theta,\phi) = A\hbar^2Y(\theta,\phi) \qquad (2.72)$$

2.9 Angular momentum eigenfunctions

Writing $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$, another stage of separation, with the introduction of another constant B, leads to two ODEs, one for each of the independent variables θ, ϕ:

$$\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) - B\frac{1}{\sin^2\theta}\right]\Theta(\theta) = -A\Theta(\theta) \qquad (2.73)$$

$$\frac{d^2\Phi(\phi)}{d\phi^2} = -B\Phi(\phi) \qquad (2.74)$$

The solution to Equation 2.74 is

$$\Phi(\phi) \propto e^{-i\sqrt{B}\phi} \qquad (2.75)$$

It follows that

$$\hat{L}_zY(\theta,\phi) = -i\sqrt{B}Y(\theta,\phi) \qquad (2.76)$$

Comparing equations 2.72 and 2.76 with equations 2.58 and 2.59 we can make the following identifications:

$$A = l(l+1) \qquad (2.77)$$
$$B = m_l^2 \qquad (2.78)$$

and

$$|lm_l\rangle \propto Y(\theta, \phi) \tag{2.79}$$

As wave function represent physical reality, they must be single valued, so $\Phi(\phi + 2\pi) = \Phi(\phi)$, which requires that m_l be an integer, and by implication that l is also an integer.

To summarise, the θ and ϕ functions are the solutions, respectively, to the equations

$$\left[\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta} \right) - m_l^2 \frac{1}{\sin^2\theta} \right] \Theta(\theta) = -l(l+1)\Theta(\theta) \tag{2.80}$$

$$\frac{d^2\Phi(\phi)}{d\phi^2} = -m_l^2 \Phi(\phi) \tag{2.81}$$

where l is an integer and $m_l = l, l-1, \ldots, -l$. The solutions of the θ equation are called an associated Legendre functions, and the solution to the ϕ equation is an exponential function. The orbital angular momentum wave functions are product of these, and when appropriately normalised are called spherical harmonics:

$$|lm_l\rangle = Y_l^{m_l}(\theta, \phi) \tag{2.82}$$

where the dependence on l and m_l is explicitly indicated by subscript and superscript respectively; the normalisation condition is

$$\int_0^{2\pi} \int_0^\pi |Y_l^{m_l}|^2 \sin\theta d\theta d\phi = 1 \tag{2.83}$$

The spherical harmonics can be expressed in terms of *associated Legendre polynomials*

$$Y_l^m(\theta, \phi) = (-1)^{(m+|m|)/2} \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos\theta) e^{im\phi} \tag{2.84}$$

The sign convention leads to

$$Y_l^{-m}(\theta, \phi) = (-1)^m Y_l^{m*}(\theta, \phi) \tag{2.85}$$

Several spherical harmonics are shown in Table 1.

The spherical harmonics form a complete basis of smooth (wave) functions on a sphere and satisfy the following orthonormality condition

$$\langle l_1 m_1 | l_2 m_2 \rangle = \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi Y_{l_1}^{m_1*}(\theta, \phi) Y_{l_2}^{m_2}(\theta, \phi) = \delta_{l_1 l_2} \delta_{m_1 m_2} \tag{2.86}$$

and the completeness relation

$$\psi(\theta, \phi) = \sum_{l=0}^\infty \sum_{m=-l}^l c_{lm} Y_l^m(\theta, \phi) \tag{2.87}$$

where the coefficients are the projections of the smooth (wave) function onto the $|lm\rangle$ eigenstates

$$c_{lm} = \langle lm | \psi \rangle = \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi Y_l^{m*}(\theta, \phi) \psi(\theta, \phi) \tag{2.88}$$

21

l	m_l	$Y_l^{m_l}(\theta, \phi)$			parity: $(-1)^l$
0	0	Y_0^0	=	$\sqrt{\frac{1}{4\pi}}$	+1
1	0	Y_1^0	=	$\sqrt{\frac{3}{4\pi}}\cos\theta$	-1
	± 1	$Y_1^{\pm 1}$	=	$\mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$	-1
2	0	Y_2^0	=	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$	+1
	± 1	$Y_2^{\pm 1}$	=	$\mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi}$	+1
	± 2	$Y_2^{\pm 2}$	=	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm i2\phi}$	+1

Table 1: Several spherical harmonics. More can be found in Table 7.3 of *Quantum Mechanics* by D.H. McIntyre, p238.

2.10   Inversion symmetry: parity of spherical harmonics

In three dimensions, inversion corresponds to, $\mathbf{r} \to -\mathbf{r}$. In terms of Cartesian coordinates inversion corresponds to $x \to -x; y \to -y; z \to -z$. In terms of spherical polar coordinates inversion corresponds to

$$r \;\to\; r \tag{2.89}$$
$$\theta \;\to\; \pi - \theta \tag{2.90}$$
$$\phi \;\to\; \phi + \pi \tag{2.91}$$

The hydrogen wave functions either remain unchanged (*even* parity), or change sign (*odd* parity) under inversion[9]. The parity is determined by the value of $(-1)^l$: $+1$ for even parity; -1 for odd parity. It follows that if l is even, parity is even; if l is odd, parity is odd.

The parity of a wave functions depends on the inversion property of the θ, ϕ part, i.e. the spherical harmonic. Noting that for the inversion indicated above,

$$e^{im\phi} \;\to\; (-1)^m e^{im\phi} \tag{2.92}$$
$$\cos\theta \;\to\; -\cos\theta \tag{2.93}$$
$$P_l(\cos\theta) \;\to\; P_l(-\cos\theta) = (-1)^l P_l(\cos\theta) \tag{2.94}$$
$$P_l^m(\cos\theta) \;\to\; P_l^m(-\cos\theta) = (-1)^{l+m} P_l^m(\cos\theta) \tag{2.95}$$
$$Y_l^m(\theta, \phi) \;\to\; (-1)^l Y_l^m(\theta, \phi) . \tag{2.96}$$

Lecture 5   Quiz

2.11   Visualization of Spherical Harmonics

The standard convention is to label the spherical harmonics, sometimes denoted orbitals, with a letter corresponding to the orbital angular momentum quantum number l.

$$l = 0,\ 1,\ 2,\ 3,\ 4,\ 5, \ldots \tag{2.97}$$
$$= s,\ p,\ d,\ f,\ g,\ h, \ldots \tag{2.98}$$

---

[9]The usefulness of this symmetry of the hydrogen wave functions will become apparent later.

(a) $l = 0$(s), $m = 0$

(b) $l = 1$ (p), $m = 0, \pm 1$

(c) $l = 2$ (d), $m = 0, \pm 1, \pm 2$
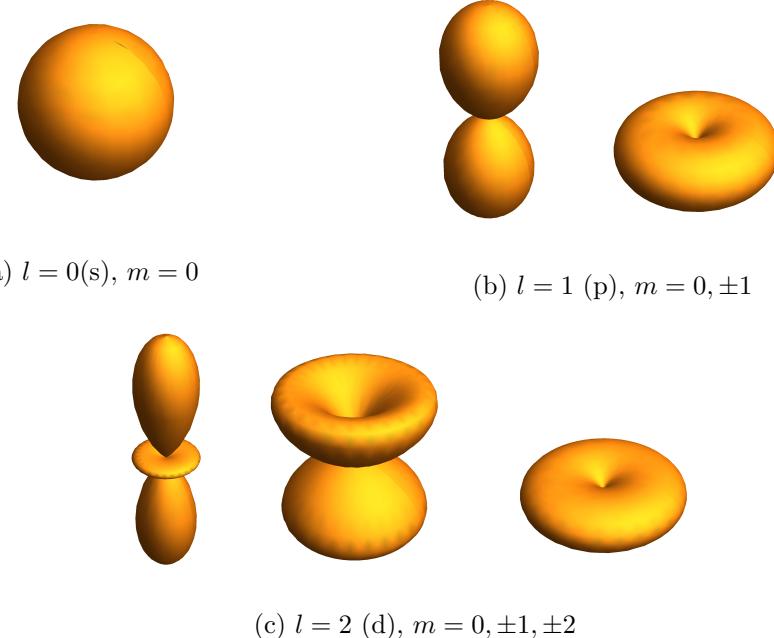
Figure 7: Spherical Harmonics

The spherical harmonics are complex valued functions depending on two variables and hence difficult to plot. We thus show the probability density $|Y_l^m(\theta, \phi)|^2$ in Fig. 7.

2.12 Summary

Let us briefly recapitulate the main steps towards the solution of two particles in a central potential before applying it to the hydrogen atom.

1. We started with the Hamiltonian, Eq. (2.2)

$$\hat{H}_{sys} = \frac{\hat{\mathbf{p}}_1^2}{2m_1} + \frac{\hat{\mathbf{p}}_2^2}{2m_2} + V(|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|) , \tag{2.99}$$

and chose a more convenient coordinate system going to centre of mass and relative coordinates.

2. The centre of mass energy eigenvalue was straightforward to solve in terms of a free-particle wave function (See Eq. (2.20)).

$$\psi_{CM}(\mathbf{R}) = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\mathbf{P} \cdot \mathbf{R}/\hbar} \tag{2.100}$$

3. The Hamiltonian of the relative motion is given by Eq. (2.9)

$$\hat{H}_{rel} = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \tag{2.101}$$

with the reduced mass μ. We then studied orbital angular momentum and showed in Eq. (2.67) that the Hamiltonian can be written as

$$\hat{H}_{rel} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\mathbf{L}^2}{\hbar^2 r^2}\right] + V(r) \tag{2.102}$$

and the wave function can thus be further separated in a radial and an angular part

$$\varphi(r,\theta,\phi) = R(r)Y(\theta,\phi) \ . \tag{2.103}$$

The solution of the angular part led us to spherical harmonics $Y_l^m(\theta,\phi)$ with discrete values for l and $m = -l, -l+1, \ldots, l-1, l$.

4. We are left with the energy eigenvalue equation for the radial component $R(r)$, which can be obtained from Eq. (2.67) by replacing $\hat{L}^2$ with its eigenvalue $l(l+1)\hbar^2$

$$\left[-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + V(r) + l(l+1)\frac{\hbar^2}{2\mu r^2}\right]R(r) = ER(r) \tag{2.104}$$

where $l = 0, 1, 2, \ldots$. Note that the energy eigenvalue equation resembles a one-dimensional eigenvalue equation with an *effective potential*

$$V_{eff}(r) = V(r) + l(l+1)\frac{\hbar^2}{2\mu r^2} \ , \tag{2.105}$$

where the second term is called the *centrifugal barrier*.

3 Hydrogen Atom

After our discussion of a general central potential in the last section, we now study the hydrogen atom and apply our general result for the radial eigenvalue equation in Eq.(2.104) to the hydrogen atom. The potential $V(r)$ is given by Coulomb potential defined in Equation 2.1 with $Z = 1$

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} = \frac{-\alpha\hbar c}{r} \ . \tag{3.1}$$

3.1 Solution of the radial equation

We will outline the solution to the radial equation. We first rewrite Eq. (2.104) in terms of dimensionless quantities

$$\rho = \frac{r}{a} \ . \tag{3.2}$$

and obtain

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[\frac{2\mu a^2}{\hbar^2}E + \frac{\mu e^2}{4\pi\epsilon_0 \hbar^2}\frac{2a}{\rho} - \frac{l(l+1)}{\rho^2} \right] R = 0 \ . \tag{3.3}$$

Thus the characteristic length and energy scales are given by

$$\frac{a}{\hbar c} \equiv \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2 \hbar c} = \frac{1}{\alpha\mu c^2} \tag{3.4}$$

$$-\gamma^2 \equiv \frac{E}{\left(\frac{\hbar^2}{2\mu a^2} \right)} = 2\mu c^2 E \left(\frac{a}{\hbar c} \right)^2 \tag{3.5}$$

and the energy eigenvalue equation reads

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[-\gamma^2 + \frac{2}{\rho} - \frac{l(l+1)}{\rho^2} \right] R = 0 \ . \tag{3.6}$$

Lecture 6 M: 8.1-2; Read: M: 8.1-2

3.1.1 Asymptotic Solution

We first look at the two limiting cases for small and large ρ. In the limit of large $\rho \to \infty$ we can neglect all terms proportional to ρ^{-1} and ρ^{-2} and Eq. (3.6) becomes

$$\frac{d^2 R}{d\rho^2} - \gamma^2 R = 0 \ . \tag{3.7}$$

There are two possible solutions $R(\rho) = e^{\pm\gamma\rho}$. The requirement that the probability should be normalized to 1 only allows

$$R(\rho) \sim e^{-\gamma\rho} \tag{3.8}$$

for large ρ. In the limit of small ρ we can neglect $-\gamma^2 + 2/\rho$ vs. the centrifugal barrier term $l(l+1)/\rho^2$ and study

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2}R = 0 \ . \tag{3.9}$$

This equation can be solved by a polynomial ansatz $R \sim \rho^q$ with the characteristic equation

$$0 = q(q-1) + 2q - l(l+1) = q(q+1) - l(l+1) \ . \tag{3.10}$$

There are two solutions $q = l$ and $q = -l - 1$. We can again discard the solution with negative q because it diverges for $\rho \to 0$. In order to obtain the full solution of the radial eigenvalue equation, we will look for solutions with

$$R(\rho) = \rho^l e^{-\gamma \rho} H(\rho) \tag{3.11}$$

with some arbitrary function H.

3.1.2 Series solution

Our ansatz leads to the following equation for H

$$\rho \frac{d^2 H}{d\rho^2} + 2(l + 1 - \gamma\rho)\frac{dH}{d\rho} + 2(1 - \gamma - \gamma l)H(\rho) = 0 \ . \tag{3.12}$$

This equation can be solved by a power series, which is generally possible if the solutions are smooth

$$H(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \ . \tag{3.13}$$

Inserting it in Eq. (3.12) and comparing the coefficients for each power of ρ, we obtain a recursion relation

$$c_{j+1} = \frac{2\gamma(1 + j + l) - 2}{(j+1)(j+2l+2)} c_j \overset{j \to \infty}{\longrightarrow} \frac{2\gamma}{j} c_j \ . \tag{3.14}$$

For large ρ, the function $H(\rho)$ behaves like

$$H(\rho) \sim \sum_j \frac{1}{j!}(2\gamma\rho)^j = e^{2\gamma\rho} \tag{3.15}$$

and thus diverges for $\rho \to \infty$. Thus the series has to be finite and there is a $j_{\max}$ such that $c_j = 0$ for $j > j_{max}$,

$$2\gamma(1 + j_{max} + l) - 2 = 0 \tag{3.16}$$

and we define the new *principal quantum number*

$$n = j_{max} + l + 1 = \frac{1}{\gamma} \ . \tag{3.17}$$

As j_{max} and l are non-negative we find that n is a positive integer $n = 1, 2, 3, \ldots$. Turning the argument around, for a given n, the angular momentum quantum number has to satisfy

$$0 \le l = n - j_{max} - 1 \le n - 1 \ . \tag{3.18}$$

The energy of the different quantum states does not depend on l or m_l and is given by

$$E_n = -\frac{1}{2n^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{\mu}{\hbar^2} = -\frac{\alpha^2 \mu c^2}{2}\frac{1}{n^2} \tag{3.19}$$

26

$$R_{10}(r) = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$$

$$R_{20}(r) = 2 \left(\frac{Z}{2a_0} \right)^{3/2} \left[1 - \frac{Zr}{2a_0} \right] e^{-Zr/2a_0}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0}$$

Table 2: Several radial wave functions. More can be found in Table 8.1 of *Quantum Mechanics* by D.H. McIntyre, p262.

and the radial solutions are

$$R_{nl}(r) = - \left\{ \left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} e^{-Zr/na_0} \left(\frac{2Zr}{na_0} \right)^l L_{n+l}^{2l+1}(2Zr/na_0) \qquad (3.20)$$

where L are polynomials (called *associated Laguerre polynomials*) and a_0 is the Bohr radius. These radial functions are normalised according to the condition

$$\int_0^\infty r^2 dr |R_{nl}(r)|^2 = 1 \qquad (3.21)$$

allowing us to identify

$$P(r) = r^2 |R_{nl}(r)|^2 \qquad (3.22)$$

as the *radial probability density*. Examples of low order radial wave functions are given Table 2.

Lecture 7 M: 8.3-6

3.2   Hydrogen Energy Levels

The hydrogen energy levels are given by Eq. (3.19)

$$E_n = -\frac{\alpha^2 \mu c^2}{2} \frac{1}{n^2} \quad \text{for } n = 1, 2, 3, \dots . \qquad (3.23)$$

where we again make use of the *fine structure constant*

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137} \qquad \text{(at low energy)} . \qquad (3.24)$$

The energy levels are negative and the zero energy is defined as the energy when the electron and the nucleus are infinitely separated. The generalization to different atoms with Z protons is straightforward

$$E_n = -\frac{Z^2 \alpha^2 \mu c^2}{2} \frac{1}{n^2} . \qquad (3.25)$$

The reduced mass of the hydrogen atom is given by

$$\mu = \frac{m_e m_p}{m_e + m_p} \approx m_e = 511\text{keV}/c^2 \qquad (3.26)$$

and the energy levels are numerically given by

$$E_n = -\frac{1}{n^2}13.6\text{eV} = -\frac{1}{n^2}\text{Ryd} \tag{3.27}$$

where we defined the unit of one Rydberg, Ryd= 13.6eV.

The other characteristic quantity is the *Bohr radius*

$$a_0 = \frac{\hbar c}{\alpha \mu c^2} = 0.0529\text{nm} = 0.529\text{Å} \tag{3.28}$$

3.3 Degeneracy

A state of a hydrogen-like atom is characterised by three *quantum numbers*: n, l, m_l. The energy of a state depends, however, upon the value of n only (Equation 3.19). For a given value of n, the quantum number l can have the values $n-1, n-2, \ldots, 0$ and for each l there are $2l+1$ possible values of m_l: $l, l-1, l-2, \ldots, -(l-1), -l$.

The number of states with the same energy is therefore

$$\sum_{l=0}^{n-1}(2l+1) = n^2 \tag{3.29}$$

Thus energy levels are *degenerate* with a *degeneracy* of n^2. When we take into account the two possible spin states for the electron ($|+\rangle$ and $|-\rangle$) there are $2n^2$ different quantum states which have the same energy E_n. We will see soon that this is only approximately true, as may of these "degenerate" levels differ in energy by small amounts (called *fine structure*).

3.4 Emission Spectrum

The hydrogen spectrum is characterised by the energy differences between the different energy levels

$$\Delta E_{fi} = |E_f - E_i| = \frac{\alpha^2 \mu c^2}{2}\left|\frac{1}{n_i^2} - \frac{1}{n_f^2}\right| . \tag{3.30}$$

The energy of the photon which is emitted or absorbed in a transitions between these energy levels is given by

$$E_\gamma = \hbar\omega = hf = \frac{hc}{\lambda} = \Delta E_{fi} . \tag{3.31}$$

The different spectral lines fall into different bands with closely spaced lines depending on the final energy level. See Fig. 8. Transitions to the ground state constitute the *Lyman series*, where the transition from the second energy level to the ground state is denoted as *Lyman-α*, the one from the 3rd energy level to the ground state *Lyman-β*, etc. The series from higher levels down to $n = 2$ are denoted *Balmer series* and the ones to the third level *Paschen series*.

Lecture 8 Quiz; M: 8.3-6

Not all transitions are allowed, the probability for a transition between two energy levels is given by the matrix element

$$\langle n_f l_f m_f | H_{int} | n_i l_i m_i \rangle \tag{3.32}$$
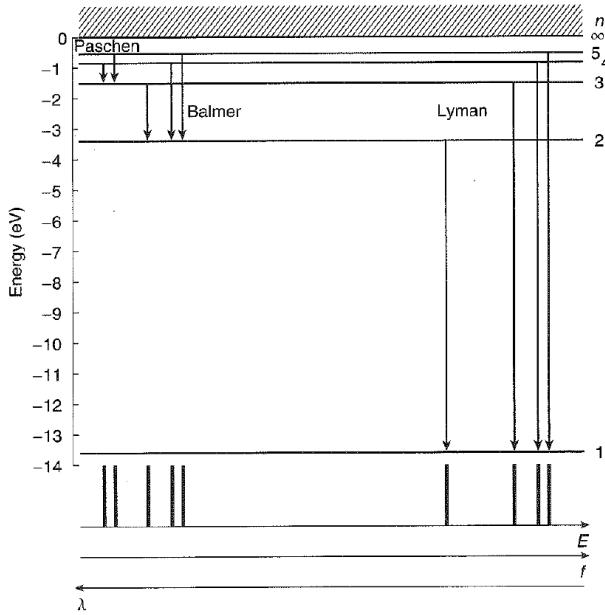
FIGURE 8.2   Hydrogen energy levels and emission spectrum.

Figure 8: Hydrogen energy levels and emission spectrum

where H_{int} is some Hamiltonian which describes the interaction leading to the transition. The interaction Hamiltonian of an electric dipole interaction can describe the interaction of atoms with light, like lasers. It is given by

$$H_{int} = -\mathbf{d} \cdot \mathbf{E} \tag{3.33}$$

where $\mathbf{E}$ is the electric field and $\mathbf{d} = -e\mathbf{r}$ is the atom's dipole moment. In this way absorption and emission of light can be described.

The *selection rules* for emission or absorption of photons in an atom are given by

$$\Delta l = l_f - l_i = \pm 1 \tag{3.34}$$

$$\Delta m = m_f - m_i = 0, \pm 1 \ . \tag{3.35}$$

See Sec. C for an explanation, why only $\Delta l = \pm 1$ is allowed.

3.5   Full hydrogen wave functions

The full normalised hydrogen wave functions are the product of a (normalised) radial function and a (normalised) spherical harmonic,

$$|nlm_l\rangle = \psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r)Y_l^{m_l}(\theta, \phi) \tag{3.36}$$

Wave functions for several low hydrogen levels are given in Table 3.

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}$$

$$\psi_{200}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\left[1-\frac{Zr}{2a_0}\right]e^{-Zr/2a_0}$$

$$\psi_{210}(r,\theta,\phi) = \frac{1}{2\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta$$

$$\psi_{21\pm1}(r,\theta,\phi) = \mp\frac{1}{2\sqrt{2\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}\sin\theta e^{\pm i\phi}$$

Table 3: Full wave functions for several low hydrogen levels. More can be found in Table 8.2 of *Quantum Mechanics* by D.H. McIntyre, p264.

3.6 Radial Probability Density

Looking at the full wave function, we can again recover the radial probability density by integrating over the angular part of the probability density

$$P(r) = \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi r^2 |R_{nl}(r)Y_l^m(\theta,\phi)|^2 = r^2|R_{nl}(r)|^2 \tag{3.37}$$

where we used the orthonormality of the spherical harmonics, which yields the same result as Eq. (3.22).

The value of r for which the *radial probability density* is a maximum i.e. the value of r for which[10]

$$\frac{d}{dr}(r^2[R_{nl}(r)]^2) = 0 \tag{3.38}$$

The *average radial position* is given by the expectation value of r, given by

$$\langle r \rangle = \int_0^\infty r^3 dr [R_{nl}(r)]^2 \tag{3.39}$$

3.7 Superposition

If an atom is in energy level n will it necessarily be in one of the $2n^2$ states with this energy? The answer is no - it will be in a random superposition of all states with that same energy. If an experiment is designed to measure the component of angular momentum in a particular direction, a value for that component will be obtained indicating that the atom is then in the state corresponding to that particular value of m_l. The act of measurement is said to cause the wave function to "collapse" from the random superposition to one with a definite value of m_l. This scenario is known as the Copenhagen interpretation of quantum mechanics.

---

[10]Of course there may be more than one maximum, and this condition will also give positions of minima.

4 Transition probability

Spontaneous emission is the most familiar process involving radiation and atoms: an atom in an excited state $|2\rangle$ undergoes a transition to a lower energy state $|1\rangle$ by emitting a photon. The frequency of the radiation emitted ν_{21} is given by

$$h\nu_{21} = E_2 - E_1 \tag{4.1}$$

Such a transition is characterised by a transition probability, A_{21}, which is the probability per unit time of an atom in state $|2\rangle$ undergoing the transition to state $|1\rangle$. If the excited state density is N_2, then the spontaneous emission power per unit volume is

$$P_{21} = N_2 A_{21} h\nu_{21} \tag{4.2}$$

4.1 Radiative lifetime

As a result of spontaneous emission, the population N_2 of the upper level $|2\rangle$ as a function of time is governed by the equation

$$\frac{dN_2}{dt} = -A_{21}N_2 \tag{4.3}$$

for which the solution is

$$N_2(t) = N_2(0)e^{-A_{21}t} \tag{4.4}$$

where $N_2(0)$ is the population at $t = 0$. Thus the upper level decays due to emission of radiation with a lifetime given by

$$\tau_{21} = \frac{1}{A_{21}} \tag{4.5}$$

For example, the transition probabilities and radiative lifetimes for the first few lines of the Balmer series are given in Table 4.[11]

line	λ (nm)	A_{21} (s^{-1})	τ_{21} (ns)
H$_\alpha$ ($n = 3 \to 2$)	656	4.41×10^7	23
H$_\beta$ ($n = 4 \to 2$)	486	8.42×10^6	119
H$_\gamma$ ($n = 5 \to 2$)	434	2.53×10^6	395
H$_\delta$ ($n = 6 \to 2$)	410	9.73×10^5	1030

Table 4: Transition probabilities and upper level lifetimes for the first 4 lines of the hydrogen Balmer series

---

[11]These values are for *allowed* transitions, in contrast to *forbidden* transitions for which values of A_{21} are many orders of magnitude lower. We will soon see what determines whether a transition is allowed or forbidden.

Note that if transitions to more than one lower energy level are possible the radiative lifetime of the excited state will be determined by the sum of the relevant transition rates,

$$\tau_2 = \frac{1}{\Sigma A_{2i}} \tag{4.6}$$

4.2 Absorption and stimulated emission

Absorption and stimulated emission differ from spontaneous emission in that they occur only in the presence of radiation at the transition frequency ν_{21}, and their transition rates are dependent upon the intensity of the radiation (See Figure 9). These processes are characterised by the coefficients B_{12} (absorption) and B_{21} (stimulated emission), where the corresponding transition rates are given by $B_{12}\rho(\nu)$ and $B_{21}\rho(\nu)$, where $\rho(\nu)$ is the energy density of the radiation at the transition frequency $\nu_{21} = (E_2 - E_1)/h$.
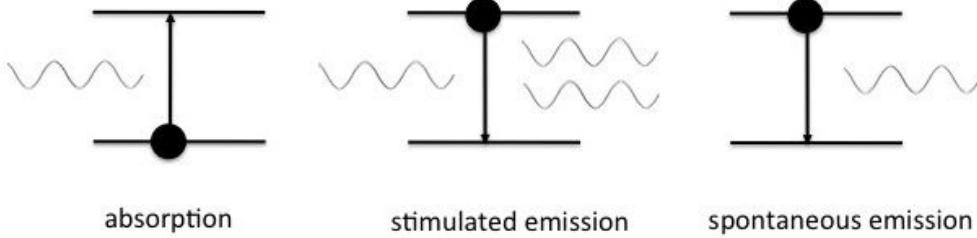
Figure 9: (a) absorption; (b) stimulated emission; (c) spontaneous emission

The coefficients A_{21}, B_{21} and B_{12} are known as Einstein coefficients. They are related via the Einstein relations, which are given by

$$\frac{B_{12}}{B_{21}} = 1 \tag{4.7}$$

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3} . \tag{4.8}$$

As eigenfunctions contain all the information we can know about a state, it is to be expected that the Einstein coefficients will depend upon the eigenfunctions of the upper and lower levels. This will be discussed in a later section. Note however that we need find this relationship for only one of the coefficients and the other two can be found using the Einstein relations. The derivation of the Einstein relations is given in Appendix D.

4.3 Allowed & forbidden transitions: selection rules

Transitions are called *allowed* or *forbidden* depending on whether or not they satisfy *selection rules*. Selections rules are conditions on the change in quantum numbers between the two levels in question, and are a consequence of the conservation of angular momentum during emission or absorption of a photon. If the section rules are obeyed the transition is allowed; if not, the transition is forbidden. For more details on this topic see Appendix C.

Allowed transitions typically have transition probabilities $\sim 10^{-7}$–10^{-8} s^{-1}. For forbidden transitions, transition probabilities are usually many orders of magnitude smaller.

The selection rules for transitions between hydrogen states, characterised by the quantum numbers are n, l, m_l as discussed in the last section, are

$$\Delta l = \pm 1 \qquad\qquad\qquad \Delta m_l = 0, \pm 1 \qquad\qquad (4.9)$$

with no restriction on Δn. Forbidden transitions are not necessarily unimportant. For example, our knowledge of the distribution of atomic hydrogen in our and nearby galaxies, is based on emission from a forbidden transition in hydrogen, the 21cm line in hydrogen, which we will discuss in one of the following sections. In this case, intensities are measurable as the large amount of neutral hydrogen compensates for the very low transition probability.

4.4   Metastable levels

If a state has no allowed transitions to lower levels, the lifetime of that state will be much longer than would be the case if there were one or more allowed transitions to lower levels. Such states are called metastable states. In discharges, for example, the populations of such states can build up to levels comparable to that of the ground state.[12] We shall see later that metastable states play a crucial role in the population inversion mechanism of the He-Ne laser.

---

[12] Electron-atom collisions still provide a means of transition between states and ultimately limit how large the metastable state population becomes.

5 Quantum harmonic oscillator

The harmonic oscillator is described by the potential in Eq. 1.43 and thus its Hamiltonian is given by

$$H = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \ . \tag{5.1}$$

In order to simplify our following discussion, we define the variable

$$\xi = \sqrt{\frac{m\omega}{\hbar}}x \qquad\qquad \frac{d}{d\xi} = \sqrt{\frac{\hbar}{m\omega}}\frac{d}{dx} \tag{5.2}$$

and can rewrite our Hamiltonian as follows

$$H = \frac{1}{2}\hbar\omega\left(-\frac{d^2}{d\xi^2} + \xi^2\right) \tag{5.3}$$

In the next step we want to factorize the Hamiltonian in analogy to the identity

$$u^2 - v^2 = (u - v)(u + v) \ . \tag{5.4}$$

Hence we form two new operators as linear combination of the old ones

$$a = \frac{1}{\sqrt{2}}\left(\xi + \frac{d}{d\xi}\right) = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + i\frac{\hat{p}}{m\omega}\right) \tag{5.5}$$

$$a^\dagger = \frac{1}{\sqrt{2}}\left(\xi - \frac{d}{d\xi}\right) = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - i\frac{\hat{p}}{m\omega}\right) \ . \tag{5.6}$$

The operators satisfy the following commutation relation

$$[a, a^\dagger] = 1 \ . \tag{5.7}$$

Looking at the product of the two operators

$$a^\dagger a = \frac{1}{\sqrt{2}}\left(\xi - \frac{d}{d\xi}\right)\frac{1}{\sqrt{2}}\left(\xi + \frac{d}{d\xi}\right) \tag{5.8}$$

$$= \frac{1}{2}\left(\xi^2 - \frac{d^2}{d\xi^2} + \xi\frac{d}{d\xi} - \frac{d}{d\xi}\xi\right) \tag{5.9}$$

$$= \frac{1}{2}\left(\xi^2 - \frac{d^2}{d\xi^2} + [\xi, \frac{d}{d\xi}]\right) \tag{5.10}$$

$$= \frac{1}{2}\left(\xi^2 - \frac{d^2}{d\xi^2} - 1\right) \tag{5.11}$$

we observe that we almost obtain the result which we wanted to obtain. Hence, the Hamiltonian can be rewritten as

$$H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) \ . \tag{5.12}$$

Before interpreting the operators $\hat{a}$ and $\hat{a}^\dagger$ physically, we have to show two more commutation relations:

$$[H, a] = Ha - aH \tag{5.13}$$

$$= \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) a - a\hbar\omega \left(a^\dagger a + \frac{1}{2} \right) \tag{5.14}$$

$$= \hbar\omega \left(a^\dagger a a - a a^\dagger a \right) \tag{5.15}$$

$$= \hbar\omega \left(a^\dagger a a - \left(a^\dagger a + [a, a^\dagger] \right) a \right) \tag{5.16}$$

$$= -\hbar\omega a \tag{5.17}$$

and similarly for the operator $a^\dagger$

$$[H, a^\dagger] = Ha^\dagger - a^\dagger H \tag{5.18}$$

$$= \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) a^\dagger - a^\dagger \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) \tag{5.19}$$

$$= \hbar\omega \left(a^\dagger a a^\dagger - a^\dagger a^\dagger a \right) \tag{5.20}$$

$$= \hbar\omega \left(a^\dagger a a^\dagger - a^\dagger \left(a a^\dagger + [a^\dagger, a] \right) \right) \tag{5.21}$$

$$= +\hbar\omega a^\dagger . \tag{5.22}$$

Now given an energy eigenstate $|E\rangle$ with a given energy E, we can calculate the energy eigenvalue of the states $a|E\rangle$ and $a^\dagger|E\rangle$ as follows

$$H(a|E\rangle) = Ha|E\rangle \tag{5.23}$$

$$= (aH + [H, a])|E\rangle \tag{5.24}$$

$$= (aE - \hbar\omega a)|E\rangle \tag{5.25}$$

$$= (E - \hbar\omega)(a|E\rangle) \tag{5.26}$$

and

$$H(a^\dagger|E\rangle) = \left(a^\dagger H + [H, a^\dagger] \right)|E\rangle \tag{5.27}$$

$$= \left(a^\dagger E + \hbar\omega a^\dagger \right)|E\rangle \tag{5.28}$$

$$= (E + \hbar\omega)(a^\dagger|E\rangle) . \tag{5.29}$$

Hence the states $a|E\rangle$, $a^\dagger|E\rangle$ are also energy eigenstates with energies $E \pm \hbar\omega$, respectively. The operators a and $a^\dagger$ transform a state with energy E into a state with energy $E \pm \hbar\omega$. They are denoted *ladder operators*, more specifically $a^\dagger$ is denoted *raising operator* and a *lowering operator*.

Next we have to find the lowest energy eigenstate. Classically we observe that there is a minimum energy of the harmonic oscillator. Hence there has to be a lowest energy eigenstate

$$a|E_{lowest}\rangle = 0 . \tag{5.30}$$

This is called the ladder termination condition. The energy of this lowest energy eigenstate is given by

$$H \left| E_{lowest} \right\rangle = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) \left| E_{lowest} \right\rangle = \frac{1}{2}\hbar\omega \left| E_{lowest} \right\rangle \tag{5.31}$$

and we recovered the *zero point energy*. It is related to the fact that the ladder operators a and $a^\dagger$ do not commute. The energy of the state $|n\rangle$ is given by

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) , \tag{5.32}$$

because applying the raising operator $a^\dagger$ n times increases the energy with respect to the ground state by $n \times \hbar\omega$. In addition to the ladder operators it is convenient to introduce the *number operator*,

$$\hat{N} = \hat{a}^\dagger \hat{a} , \tag{5.33}$$

which counts the energy quanta. It fulfills the following eigenvalue equation

$$\hat{N} \left| n \right\rangle = n \left| n \right\rangle , \tag{5.34}$$

where the n in $|n\rangle$ denotes the number of energy quanta. We can rewrite the Hamiltonian as

$$\hat{H} = \hbar\omega \left(\hat{N} + \frac{1}{2} \right) . \tag{5.35}$$

The wave function of the ground state $\phi_0(\xi)$ can be determined from the ladder termination condition in Eq. 5.30

$$0 = a\phi_0(\xi) = \frac{1}{\sqrt{2}} \left(\xi + \frac{d}{d\xi} \right) \phi_0(\xi) . \tag{5.36}$$

It is an ODE, which can be solved using standard techniques

$$\phi_0(\xi) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\xi^2/2} . \tag{5.37}$$

All other energy eigenstates can be constructed from the lowest energy eigenstate using the raising operator. By demanding that all states $|n\rangle$ are properly normalized,

$$\langle n|n \rangle = 1 , \tag{5.38}$$

it is possible to show that the raising and lowering operators act on a state $|n\rangle$

$$a \left| n \right\rangle = \sqrt{n} \left| n - 1 \right\rangle \tag{5.39}$$

$$a^\dagger \left| n \right\rangle = \sqrt{n+1} \left| n + 1 \right\rangle . \tag{5.40}$$

Thus we can write the state $|n\rangle$ as follows

$$\left| n \right\rangle \equiv \frac{1}{\sqrt{n!}} \left(a^\dagger \right)^n \left| 0 \right\rangle , \tag{5.41}$$

where we denoted the lowest energy eigenstate by $|0\rangle$. The factor $1/\sqrt{n!}$ ensures that the states are correctly normalized.

6 Perturbation Theory

Most of the times we can not solve problems in quantum physics exactly, like for the hydrogen atom and the harmonic oscillator. Thus we have to develop a technique to approximately solve problems. Suppose we know the exact energy eigenvalues and eigenstates for a Hamiltonian $\hat{H}_0$: E_n^0 and $\left|n^0\right\rangle$ respectively. We can obtain approximate solutions for the perturbed Hamiltonian $\hat{H}_0 + \hat{H}'$ provided the effects of the extra term are small.

We have to separately discuss the case of quantum states with degenerate energies. In the following section we will focus on non-degenerate energies and only briefly comment on the case with with degenerate energies.

6.1 Non-degenerate Perturbation Theory

We write our Hamiltonian as a sum

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}' \ , \tag{6.1}$$

where we introduced a parameter λ to keep track of the size of the perturbation. The energy eigenvalue equation is given by

$$E_n\left|n\right\rangle = \hat{H}\left|n\right\rangle = \hat{H}_0\left|n\right\rangle + \lambda\hat{H}'\left|n\right\rangle \ . \tag{6.2}$$

We can expect that the eigenstates and eigenvalues will change by small amounts only. Thus we can systematically expand the eigenstates $\left|n\right\rangle$ and eigenvalues E_n around the eigenstates $\left|n^{(0)}\right\rangle$ and eigenvalues $E_n^{(0)}$ of the Hamiltonian $\hat{H}_0$.

$$\left|n\right\rangle \ = \ \left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \lambda^2\left|n^{(2)}\right\rangle + \ldots \tag{6.3}$$

$$E_n \ = \ E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots \ , \tag{6.4}$$

where

$$E_n^{(0)}\left|n^{(0)}\right\rangle = \hat{H}_0\left|n^{(0)}\right\rangle \ . \tag{6.5}$$

Writing down the eigenvalue equation for the perturbed situation,

$$\left(\hat{H}_0 + \lambda\hat{H}'\right)\left(\left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \ldots\right) \ = \ \left(E_n^{(0)} + \lambda E_n^{(1)} + \ldots\right)\left(\left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \ldots\right) \tag{6.6}$$

Collecting all terms of order λ^0, we find Eq. (6.5). At order λ^1, we find the equation which determines the leading correction due to the Hamiltonian $\hat{H}'$

$$\hat{H}_0\left|n^{(1)}\right\rangle + \hat{H}'\left|n^{(0)}\right\rangle = E_n^{(0)}\left|n^{(1)}\right\rangle + E_n^{(1)}\left|n^{(0)}\right\rangle \tag{6.7}$$

Lecture 11 Quiz

As the eigenstates of the Hamiltonian $\hat{H}_0$ form a complete set of states $\{\left|m^{(0)}\right\rangle\}$, i.e. a basis, we can express the state $\left|n^{(1)}\right\rangle$ in terms of the $\left|m^{(0)}\right\rangle$

$$\left|n^{(1)}\right\rangle = \sum_m a_m\left|m^{(0)}\right\rangle \tag{6.8}$$

and thus

$$\sum_m E_m^{(0)} a_m\left|m^{(0)}\right\rangle + \hat{H}'\left|n^{(0)}\right\rangle = E_n^{(0)}\sum_m a_m\left|m^{(0)}\right\rangle + E_n^{(1)}\left|n^{(0)}\right\rangle \ . \tag{6.9}$$

Multiplying Eq. (6.9) by $\langle n^{(0)}|$, we find

$$E_n^{(1)} = \left\langle n^{(0)}|\hat{H}'|n^{(0)}\right\rangle \tag{6.10}$$

That is, the change in the energy of an eigenstate due to the perturbation is equal to the expectation value of the perturbation with respect to that eigenstate. We can use this result from perturbation theory to find the effects on energy levels of an atom of interactions associated with angular momentum which were left out of the operator in Schrödinger's equation. It can also be used to find the effects on energy levels due to external electric and magnetic fields.

On the other hand, if we multiply Eq. (6.9) by an arbitrary eigenstate $\left|p^{(0)}\right\rangle$ unequal to $\left|n^{(0)}\right\rangle$ of the Hamiltonian $\hat{H}_0$, we can determine the coefficients in the expansion (6.8)

$$a_m = \frac{\left\langle m^{(0)}|\hat{H}'|n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \ . \tag{6.11}$$

Note that we did not determine a_n, the correction in direction $\left|n^{(0)}\right\rangle$. It is not determined by Eq. (6.8), but the condition that the perturbed state $|n\rangle$ is correctly normalised, $\langle n|n\rangle = 1$. To this order in perturbation theory, we find $a_n = 0$. Hence the approximate eigenstate $|n\rangle$ to the energy $E_n = E_n^{(0)} + E_n^{(1)}$ is given by

$$|n\rangle = \left|n^{(0)}\right\rangle + \sum_{m \neq n} a_m \left|m^{(0)}\right\rangle \ . \tag{6.12}$$

Above we have considered the first order corrections to the energy and wave function when a system is perturbed. The theory can, of course, be extended to higher order corrections. Intuitively, if the perturbation is *small* we expect $E_n^{(1)} \ll E_n^{(0)}$ and that $\left|n^{(0)}\right\rangle$ is the dominant term in the perturbed wave function.

This procedure can be be continued to an arbitrary order in λ, i.e. the perturbation $\hat{H}'$.

6.2   Degenerate Perturbation Theory

The theory outlined above applies to non-degenerate eigenstates. For degenerate eigenstates the theory is more complicated and we will not discuss it during this lecture course, but only state that for degenerate energy eigenvalues, one has to consider the whole degenerate subspace and *diagonalize the perturbation Hamiltonian $\hat{H}'$ in the degenerate subspace.* In practice, one has to determine the matrix elements of the perturbation Hamiltonian in the degenerate subspace spanned by $\{|n\rangle\}$, $H'_{mn} = \left\langle m|\hat{H}'|n\right\rangle$ and diagonalize this matrix.

The effect of the perturbation may be different for the various degenerate eigenstates and generally lifts the degeneracy. Thus a common effect of a perturbation is to 'remove the degeneracy', partially or completely.

7 Magnetic moments, gyromagnetic ratio, ESR, NMR

An electron has magnetic dipole moments associated with both its orbital and spin angular momenta. For orbital motion we can find the relationship between magnetic moment and orbital angular momentum by considering an electron in a circular orbit of radius r. The angular momentum is given by

$$L = mvr \tag{7.1}$$

The motion of the electron constitutes a current loop of area πr^2. The charge e completing an orbit in a time $2\pi r/v$ corresponds to an equivalent current of $I = ev/(2\pi r)$. The magnetic moment of the current loop is, therefore:

$$\mu_l = IA = \frac{ev}{2\pi r}\pi r^2 = \frac{e}{2m}L = \frac{\mu_B}{\hbar}L \tag{7.2}$$

where $\mu_B = e\hbar/2m = 9.27\times 10^{-24}$ amp m^2 is the *Bohr magneton*. In terms of vectors this relationship is

$$\boldsymbol{\mu}_l = -\frac{g_l \mu_B}{\hbar}\mathbf{L} \tag{7.3}$$

where g_l, the gyromagnetic ratio, is equal to unity.

As you are aware, the electron also have a magnetic moment associated with its spin, with a similar relationship,

$$\boldsymbol{\mu}_s = -\frac{g_e \mu_B}{\hbar}\mathbf{S} \tag{7.4}$$

where the gyromagnetic ratio in this case is an intrinsic property of the electron and has a value very close to 2.[13] As $|\mathbf{L}|/\hbar \sim 1$ and $|\mathbf{S}|/\hbar \sim 1$, for both orbital angular momentum and spin $\mu \sim \mu_B$.

We note for future reference that the proton also has an intrinsic magnetic moment,

$$\boldsymbol{\mu}_p = \frac{g_p \mu_N}{\hbar}\mathbf{I} \tag{7.5}$$

where $\mathbf{I}$ is the spin angular momentum of the proton ($I = 1/2$), $\mu_N = (m_e/m_p)\mu_B = 5.05\times 10^{-27}$ JT^{-1} is the nuclear magneton, and $g_p = 5.585$. The neutron also has spin of $I = 1/2$ and a gyromagnetic ratio of $g_n = -3.826$.[14]

Lecture 12 M: 12.1-2; Read: 12.1-2

7.1 Electron spin resonance (ESR)

A free electron in a magnetic field has two energy levels due to the two possible orientations of its spin, and hence of its magnetic moment, with respect to the magnetic field. The energies of the levels are given by

$$E = -\boldsymbol{\mu_s}.\mathbf{B} = g_e\frac{\mu_B}{\hbar}\mathbf{S}\cdot\mathbf{B} = g_e\frac{\mu_B}{\hbar}S_z B = g_e\mu_B m_s B \approx \pm\mu_B B \tag{7.6}$$

---

[13]We will see later that $g_e = 2.00232\ldots$

[14]It may surprise you that the chargeless neutron has a magnetic moment. Like the proton, the neutron consist of three quarks: their charges add to zero, but their magnetic moments do not cancel.

since $m_s = \pm 1/2$, and $g_e \approx 2$.

Radiation that satisfies the condition

$$hv = 2\mu_B B \tag{7.7}$$

will cause transitions in both directions between the two levels. This is called *electron spin resonance* (ESR). Electrons which are effectively free can be found in radicals.[15] In contrast to molecules where electrons usually have paired electron spins, radicals are characterised by unpaired electrons. For a field of 1 tesla, $v = 28$ GHz (microwave); for a field of 1 mT $v = 28$ MHz (radiofrequency). The width of the resonance depends upon the internal magnetic field distribution, which depends upon the atomic environment of the electron; thus ESR spectra provide information about molecular structure in situations where there is unpaired electron spin to act as a probe.

7.2   Nuclear magnetic resonance (NMR)

As noted earlier, protons have spin $I = 1/2$ and as a consequence they also have a magnetic moment given by

$$\boldsymbol{\mu_p} = g_p \frac{\mu_N}{\hbar} \mathbf{I} \tag{7.8}$$

In a magnetic field the proton spin has two orientations such that the components of the spin parallel to $\mathbf{B}$ are $m_I \hbar$ where $m_I = \pm 1/2$. The energies of the two states are therefore given by

$$E = -\boldsymbol{\mu_p} . \mathbf{B} = -g_p \frac{\mu_N}{\hbar} \mathbf{I} \cdot \mathbf{B} = -g_p \frac{\mu_N}{\hbar} I_z B = -g_p \mu_N m_I B = \mp 2.79 \mu_N B \tag{7.9}$$

Nuclear magnetic resonance occurs when electromagnetic radiation causes transitions between these two levels. The condition for NMR in hydrogen is, therefore,

$$hv = 5.58 \mu_N B \tag{7.10}$$

For magnetic fields of around 1 tesla, the resonance frequency is in the radiofrequency range (42.5 MHz).[16] Hydrogen atoms in different chemical environments are subject to different internal magnetic fields, producing resonances at slightly different frequencies. Thus NMR in hydrogen is particularly useful for studies of the structure of organic molecules. It is also the basis of the medical imaging technique Magnetic Resonance Imaging (MRI) which produces images where the image contrast is determined by proton density or various relaxation times. As these vary with the chemical environment of the protons, MRI produces images with good contrast between different soft tissues.

7.3   Fine and hyperfine structure

The energy levels obtained by solving the energy eigenvalue equation for a Coulomb potential agree with those given by Bohr's theory. We have seen, however, that the levels are degenerate: there are two or more different quantum states corresponding to each energy level. However, the electron experiences a magnetic field due to its motion relative to the nucleus, and as a result there will be additional energy associated with its magnetic moment in this magnetic field. The additional energy

---

[15]Ionising radiation can rupture molecules to produce radicals. The use of ESR to detect enhanced radical content is the basis of a dating technique for artefacts that have been exposed to environmental ionising radiation. When applied to tooth enamel ESR can be used to measure human exposure to ionising radiation after the event.

[16]As $\mu_B \sim 10^3 \mu_N$, for a given magnetic field the resonant frequency for ESR is about $1000 \times$ that for NMR.

can vary among the degenerate states so that some of the degeneracy is removed. The resulting different energy levels are referred to as the *fine structure* of the hydrogen energy levels.[17]

A similar, but much smaller effect occurs due to the magnetic field of the magnetic moment of the hydrogen nucleus. The resulting different energy levels in this case are referred to as *hyperfine structure*. To begin, we will look at the hyperfine structure of the ground state of hydrogen.

---

[17]The term *fine structure* is also used to refer to the splitting of spectral lines into several closely-spaced lines as a consequence of the fine structure of the energy levels.

8 Fine structure, spin-orbit coupling, Dirac theory, Lamb shift

The Schroedinger equation is non-relativistic, i.e. it applies for small velocities $v \ll c$. Relating the Bohr energy (i.e. the energy levels of the H-atom) to the kinetic energy of an electron, we obtain

$$\frac{1}{2}\alpha mc^2 \sim \frac{1}{2}mv^2 \quad \Rightarrow \quad \alpha \sim \frac{v}{c} = \frac{p}{mc} \; . \tag{8.1}$$

As $\alpha = 1/137$ is small we find that the non-relativistic treatment of the hydrogen atom is justified, but relativistic corrections will play a role in precision studies. They contribute to the *fine structure* of the hydrogen energy levels. We can identify three contributions to the fine structure of the H levels:

1. relativistic correction

2. spin-orbit coupling

3. Lamb shift (contributes to fine structure, but not of relativistic origin)

The first two contributions are of similar order of magnitude and strictly speaking are not really independent corrections. In 1928 Dirac deduced the relativistic equation for a electron in a Coulomb field in a way that included the effect of the electron spin. This comprehensive relativistic treatment incorporates the first two corrections in the list above. We will consider here simplified estimates of the corrections (detailed treatments are given in McIntyre §12.2).

8.1 Relativistic correction to H energy levels

The total energy (kinetic + rest) for a relativistic particle is given by

$$E = \sqrt{m^2c^4 + p^2c^2} = mc^2\sqrt{1 + \left(\frac{p}{mc}\right)^2} \tag{8.2}$$

If the relativistic effect is small (as it is in this case), we can expand this equation to give

$$E = mc^2 \left[1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 + \cdots\right] \tag{8.3}$$

Subtracting the rest mass energy we obtain for the kinetic energy up to the first order relativistic correction,

$$\frac{p^2}{2m} - \frac{1}{8}\left(\frac{p}{mc}\right)^4 mc^2 \tag{8.4}$$

We can make a rough estimate of the relative magnitude of the first order relativistic correction to the ground state energy ($n = 1$) using $p/(mc) \sim \alpha$ and ignoring numerical factors

$$\frac{1}{8}\left(\frac{p}{mc}\right)^4 mc^2 \cdot \frac{1}{|E_1|} \sim \alpha^4 mc^2 \frac{1}{\alpha^2 mc^2} \sim \alpha^2 \sim 10^{-4} \tag{8.5}$$
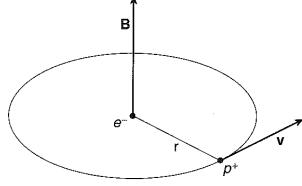
Figure 10: Proton rotating around electron. (Taken from McIntyre pg. 389)

8.2 Spin-orbit coupling correction to H energy levels

In order to understand the spin-orbit coupling, we will first consider the classical problem of a proton orbiting an electron as shown in Fig. 10. The magnetic field induced at the centre of the loop is given by Biot-Savart law

$$B = \frac{\mu_0 I}{2r} \tag{8.6}$$

with the current $I = ev/2\pi r$, where v denotes the speed of the proton, which can be related to the angular momentum of the electron (by considering the electron moving around the proton)

$$L = m_e v r \quad \Rightarrow \quad v = \frac{L}{m_e r} \ . \tag{8.7}$$

Hence the magnetic field at the centre of the loop is given by

$$B = \frac{\mu_0}{2r} \frac{eL}{2\pi m r^2} = \frac{e}{4\pi \epsilon_0 m_e c^2 r^3} L \ . \tag{8.8}$$

As the magnetic field B and the angular momentum point in the same direction, we can write it as a vectorial equation

$$\mathbf{B} = \frac{e}{4\pi \epsilon_0 m_e c^2 r^3} \mathbf{L} \ . \tag{8.9}$$

Hence the energy of the spin magnetic moment of the electron in the magnetic field of the proton is given by

$$\Delta E = -\mu_{\mathbf{s}} \cdot \mathbf{B} \tag{8.10}$$

with $\mu_{\mathbf{s}} = -\frac{g_e \mu_B}{\hbar} \mathbf{S}$. Thus the energy is given by

$$\Delta E = g_e \frac{\mu_B}{\hbar} \mathbf{S} \cdot \mathbf{B} = \frac{e^2}{4\pi \epsilon_0 m_e^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L} \tag{8.11}$$

and the corresponding Hamiltonian in quantum physics

$$\hat{H}_{so} = \frac{e^2}{4\pi \epsilon_0 m_e^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L} \ , \tag{8.12}$$

This term couples the spin $\mathbf{S}$ to the orbital angular momentum $\mathbf{L}$.

The z-component of the spin and the orbital angular momentum do not commute with $\hat{H}_{so}$, i.e. $[\hat{H}_{so}, \hat{L}_z] \neq 0$, and thus are not preserved. They are no longer good quantum numbers which can be used to describe the system.

However, the total angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{8.13}$$

is a constant of the motion and commutes with the Hamiltonian.
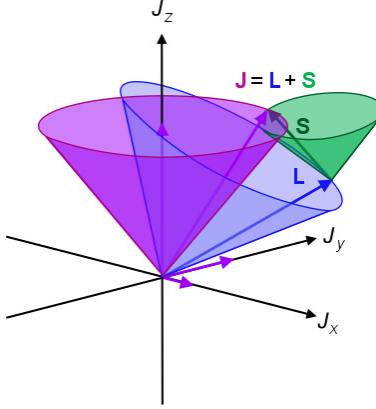
Figure 11: LS coupling (taken from Wikipedia)

Lecture 13 M: 12.2,11.1-2; 5-7 simplified; Read: M: 11.1-2

Thus we expect the state of an atom to be characterised by its value of total angular momentum. See Fig. 11 for an illustration of the addition of spin and orbital angular momentum. As is the case for any angular momentum in quantum mechanics, $\mathbf{J}$ is quantised according to

$$J^2 = j(j+1)\hbar^2 \tag{8.14}$$
$$J_z = m_j\hbar \tag{8.15}$$

where $m_j = j, j-1, \ldots, -j$.

$\mathbf{L}$ and $\mathbf{S}$ always add to give $\mathbf{J}$. As the magnetic field of $\mathbf{L}$ will induce a torque

$$\tau = \mu \times \mathbf{B} \tag{8.16}$$

on the spin $\mathbf{S}$, $\mathbf{S}$ will precess and vice versa. In summary, both $\mathbf{L}$ and $\mathbf{S}$ must be precessing about $\mathbf{J}$. As a result their magnitudes remain constant but *not* their z components. It follows that when the interaction between the orbital and spin angular momenta is taken into account, a stationary state of the hydrogen atom is characterised by the quantum numbers n, l, s, j, m_j. Such states are referred to as *coupled states*, represented in ket notation as[18]

$$|nljm_j\rangle \tag{8.17}$$

in contrast to the uncoupled states $|nlsm_lm_s\rangle$. Given that $\mathbf{J} = \mathbf{L} + \mathbf{S}$ and $s = \frac{1}{2}$, the possible values of j are

$$j = l + 1/2, \; l - 1/2 \tag{8.18}$$

except if $l = 0$ in which case $j = 1/2$ only.

We can use

$$\mathbf{J}^2 = (\mathbf{L} + \mathbf{S})^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L} \cdot \mathbf{S} \tag{8.19}$$

to rewrite

$$\hat{H}_{so} = \frac{e^2}{8\pi\epsilon_0 m_e^2 c^2 r^3} \left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right) . \tag{8.20}$$

---

[18]We do not include the quantum number s as it is 1/2 for all states

44

Thus the energy correction depends upon the quantum numbers j, l and s. If we take $r \sim a_0$ and $\mathbf{L.S} \sim \hbar^2$, a small amount of algebra shows that

$$\Delta E/E_1 \sim \alpha^2 \sim 10^{-4} \tag{8.21}$$

Therefore the relative shifts in energy levels due to spin-orbit interaction are of the order $\alpha^2 \sim 10^{-4}$. As the shifts vary with quantum number, not all the states with the same n will have the same energy, i.e. the spin-orbit interaction will *remove* some of the degeneracy.

8.3 Dirac's relativistic theory

We saw above that the relativistic and spin-orbit corrections to the hydrogen energy levels are of order α^2. Strictly speaking, the spin-orbit correction is also a relativistic correction as it depends upon the magnetic field experienced by the moving electron (the internal magnetic field $\mathbf{B} \to 0$ as $v/c \to 0$).

The complete relativistic treatment of the hydrogen atom, incorporating the spin of the electron was done by Dirac[19] in 1928 (for more detail see Appendix B). His theory gives the fine structure energy levels for hydrogen, and also a value of 2 for g_e. The resulting energy levels are

$$E_{nj} = -\frac{\alpha^2 \mu c^2}{2n^2}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right] \tag{8.22}$$

Thus we see that the energy levels depend upon the quantum numbers j and n but not l. The degeneracy of these levels is equal to the number of different m_j values for a given j (which is $2j+1$) summed over the relevant l values.

8.4 Spectroscopic notation

The electron configuration for a particular state of hydrogen is given by nx where the letter x represents the value of l where $x = s, p, d, f, g, \ldots$ corresponds to $l = 0, 1, 2, 3, 4, \ldots$. The *spectroscopic notation* for a state has the form

$$n^{2s+1}X_j \tag{8.23}$$

where X indicates the value of l: $S, P, D, F, G, \ldots$ correspond to $l = 0, 1, 2, 3, 4, \ldots$

The ground state of hydrogen has an electron configuration of $1s$ and its spectroscopic notation is $1^2S_{1/2}$. The configuration $2p$ corresponds to two states $2^2P_{1/2}$ and $2^2P_{3/2}$. For hydrogen the superscript is always 2; this indicates that there are two values of j for each value of l (except $l = 0$, for which there is only one value).[20]

8.5 The Lamb shift

Although Dirac's theory indicates that the $2^2S_{1/2}$ and $2^2P_{1/2}$ states have the same energy, an experiment by Lamb and Retherford in 1947 confirmed speculation that these states do differ in energy, by an amount now known as the *Lamb shift* and equal to 4.37462×10^{-6} eV (1057.77 MHz), which is about one tenth of the fine structure splitting between the Dirac fine structure levels $2^2P_{3/2}$ and

---

[19]See the recent biography: Graham Farmelo, *The Strangest Man: The Hidden Life of Paul Dirac, Quantum Genius*, Faber & Faber, London 2009.

[20]Without the n value, spectroscopic notation can also used for multielectron atoms, where the quantum numbers now refer to angular momenta of all the electrons.
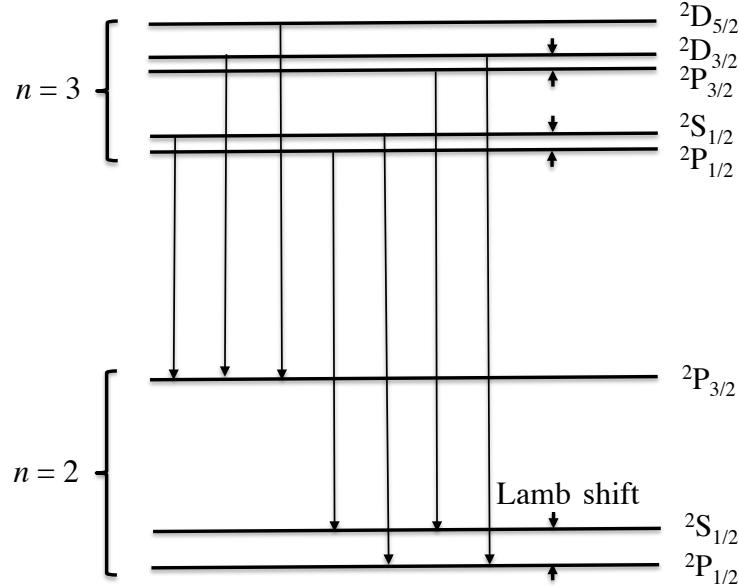
Figure 12: Fine structure of the $n = 2, 3$ hydrogen levels. The spacing between the fine structure levels is greatly exaggerated compared to the spacing between principal levels. The allowed transitions between $n = 3$ and $n = 2$, i.e. the fine structure H_α line, are also shown

$2^2 P_{1/2}$. This experiment was an important stimulus to the development of quantum electrodynamics (QED), which explains the Lamb shift in terms of the effect on the electron of the zero point energy of the quantised electromagnetic field.[21] QED also leads to a value for g_e ($= 2.00232$) slightly different from the Dirac value (2).

In his Nobel Prize lecture, Lamb quoted the following qualitative picture of the level shift.

> The fluctuating zero-point electric field of the quantized vacuum acts on an electron bound in a hydrogen atom. As a result, the electron is caused to move about its unperturbed position in a rapid and highly erratic manner. The point electron effectively becomes a sphere of a radius almost 10^{-12} cm. Such an electron in a hydrogen atom is not so strongly attracted to the nucleus at short distances as would be a point electron. States of zero orbital angular momentum like $2^2 S_{1/2}$ are therefore raised in energy relative to other states like $2^2 P_{1/2}$ in which the electron has a smaller probability of being found near the nucleus.

The final picture then is that for each unique combination of the quantum numbers n, l, j there is a distinct energy level with a degeneracy of $2j + 1$. For a given n the sublevels are close together with separations of the order of 10^{-4} of the separation between levels with different values of n. This fine structure of the energy levels means that the spectral lines resulting from the transitions between states of different n consist of several closely spaced lines. The fine structure of the $n = 2$ and $n = 3$ hydrogen levels and the transitions between them, which are the closely spaced components of the H_α transition, are shown in Figure 12.

---

[21] The 1955 Nobel Prize for Physics was divided equally between Willis Eugene Lamb (Stanford University) *for his discoveries concerning the fine structure of the hydrogen spectrum* and Polykarp Kusch (Columbia University) *for his precision determination of the magnetic moment of the electron.*

9 Hyperfine structure; Addition of angular momenta

9.1 Hyperfine structure

An electron in the ground state of hydrogen ($n = 1$) has zero orbital angular momentum ($l = 0$). The total angular momentum of the electron is due, therefore, to its spin only. There will be energy associated with the interaction between the magnetic moments $\mu_\mathbf{e}$ of the electron and nucleus (proton) $\mu_\mathbf{p}$.

$$\hat{H}'_{hf,1s} = \frac{2}{3}\mu_0 \frac{g_e \mu_B g_p \mu_N}{\hbar^2} \delta(\mathbf{r})\mathbf{S} \cdot \mathbf{I} \tag{9.1}$$

with the spin $\mathbf{S}$ ($\mathbf{I}$) of the electron (proton). Each magnetic moment will experience a torque due to the magnetic field of the other. There is no external torque on the atom, which in classical mechanics would mean that the total angular momentum of the system is conserved. The corresponding statement in quantum mechanics is that the system is characterised by a quantised value of total angular momentum. If we use the symbol $\mathbf{F}$ for the total angular momentum we have

$$\mathbf{F} = \mathbf{S} + \mathbf{I} \tag{9.2}$$

where, using the usual quantisation rules for angular momenta,

$$\mathbf{F}^2 = F(F+1)\hbar^2 \tag{9.3}$$
$$F_z = M_F \hbar \quad \text{where } M_F = F, F-1, \ldots, -F \tag{9.4}$$

where F is the quantum number associated with total angular momentum of the atom.

Using the coupled basis with the total spin F, we obtain for the correction to the energy of the $1s$ ($n = 1$, $l = 0$) state (Note that there is no orbital angular momentum (thus $j = \frac{1}{2}$) and we can use the uncoupled basis for spin and orbital angular momentum) due to hyperfine splitting

$$E_{hf,1s} = \left\langle nlm_l FISM_F | \hat{H}'_{hf,1s} | nlm_l FISM_F \right\rangle \tag{9.5}$$

$$= \left\langle nlm_l FISM_F | \frac{2}{3}\mu_0 \frac{g_e \mu_B g_p \mu_N}{\hbar^2} \delta(\mathbf{r})\mathbf{S} \cdot \mathbf{I} | nlm_l FISM_F \right\rangle \tag{9.6}$$

$$= \left\langle nlm_l FISM_F | \frac{2}{6}\mu_0 \frac{g_e \mu_B g_p \mu_N}{\hbar^2} (F^2 - S^2 - I^2)\delta(\mathbf{r}) | nlm_l FISM_F \right\rangle \tag{9.7}$$

$$= \frac{2}{6}\mu_0 g_e \mu_B g_p \mu_N (F(F+1) - S(S+1) - I(I+1)) |\psi_{nlm_l}(0)|^2 , \tag{9.8}$$

with the square of the spatial wave function $|\psi_{nlm_L}(0)|^2 \equiv \langle nlm_l | \delta(\mathbf{r}) | nlm_l \rangle$ evaluated at the origin (the position of the nucleus), i.e. the hyperfine splitting is proportional to the probability of the electron to be in the nucleus.

9.2 Addition of angular momenta

What is the value for F? The simplest way to answer this is to consider the component values,

$$F_z = S_z + I_z \quad \text{hence} \tag{9.9}$$
$$M_F = m_s + m_I \tag{9.10}$$

As m_s and m_I both have values of $\pm\frac{1}{2}$ the possible values of M_F are

$$\frac{1}{2} + \frac{1}{2} = 1; \quad \frac{1}{2} - \frac{1}{2} = 0; \quad -\frac{1}{2} + \frac{1}{2} = 0; \quad -\frac{1}{2} - \frac{1}{2} = -1 \tag{9.11}$$

Grouping these results as $(1, 0, -1)$ and 0, we can see that they constitute all the M_F values of $F = 1$ and $F = 0$ respectively. Thus the spin angular momenta of the electron and proton can add in two possible ways: one gives $F = 1$ i.e. $\frac{1}{2} + \frac{1}{2}$, and the other $F = 0$ i.e. $\frac{1}{2} - \frac{1}{2}$. We are seeing here a particular case of the addition of two arbitrary angular momenta. In general the total angular momentum J of a coupled state $|j_1 m_{j_1}\rangle |j_2 m_{j_2}\rangle$ can take values

$$J = j_1 + j_2, j_1 + j_2 - 1, \ldots, |j_1 - j_2| \tag{9.12}$$

and its z-component m_J is directly given by the sum of the z-components of the two coupled states

$$m_J = m_{j_1} + m_{j_2} \tag{9.13}$$

(a)   (b)
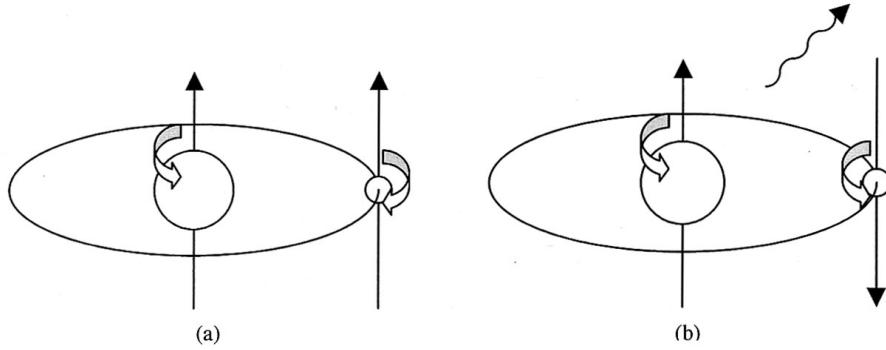
Figure 13: The spin-flip' transition between the hyperfine levels of the hydrogen ground state that leads to emission at 21 cm (1420 HHz).

The $F = 1$ (upper) state corresponds to "parallel spins"; the $F = 0$ (lower) state to "anti-parallel spins". As a consequence the transition between these two states is often called a "spin flip" transition. The difference in energy between these states corresponds to 1420 MHz or in terms of wavelength, 21 cm. Emission on this line has allowed radio telescopes to map the neutral hydrogen distributions in the Milky Way galaxy and other nearby galaxies. Note that as $l = 0$ for both upper and lower levels of this transition, it does not satisfy the selection rule $\Delta l = \pm 1$, and is therefore a forbidden transition. Its transition probability is 2.9×10^{-15} s^{-1}, corresponding to a lifetime of 1.1×10^7 years[22].

---

[22]Compare this with the allowed H$_\alpha$ transition, for which $A = 4.4 \times 10^8$ s^{-1} and $\tau = 23$ ns.

10   Identical particles, symmetry requirements, fermions and bosons

We now turn our attention to the helium atom. The two electrons are identical and as their wave functions will, in general, overlap it is not possible to distinguish one electron from the other. The wave functions which describe the helium atom must be consistent with the fact that *identical particles* are *indistinguishable*. To see the consequences of this suppose the wave function $\psi(\mathbf{r_1}, \mathbf{r_2})$ represents a quantum system consisting of two identical particles whose positions are specified by $\mathbf{r_1}$ and $\mathbf{r_2}$. If we exchange the particles the system is now described by the wave function $\psi(\mathbf{r_2}, \mathbf{r_1})$. As the particles are identical there can be no change in the physical reality of the system. Therefore, it must be true that

$$|\psi(\mathbf{r_1}, \mathbf{r_2})|^2 \equiv |\psi(\mathbf{r_2}, \mathbf{r_1})|^2 \tag{10.1}$$

From this we can conclude that

$$\psi(\mathbf{r_2}, \mathbf{r_1}) = \pm\psi(\mathbf{r_1}, \mathbf{r_2}) \tag{10.2}$$

i.e. the wave function must be either symmetric or antisymmetric with respect to interchange of the particles. This requirement is a consequence of the indistinguishability of the particles. We will begin our discussion of helium by considering first the description of the possible spin states for a system of two spin-$\frac{1}{2}$ particles.

10.1   Two spin-$\frac{1}{2}$ particles

We can represent the two particle state by the ket $|s_1 s_2 m_1 m_2\rangle$. As the state of each electron is indicated separately, we refer to this representations as using an *uncoupled* basis. However, as s_1 and s_2 are always equal to $\frac{1}{2}$, we need only indicate the signs of the m_s values $\pm\frac{1}{2}$. Therefore, possible configurations of the two particle system are,

$$|++\rangle, \ |+-\rangle, \ |-+\rangle, \ |--\rangle \tag{10.3}$$

The first and last of these are clearly symmetric, but the middle two are neither symmetric nor antisymmetric. Note also that for these four states the total magnetic quantum numbers will be $M_S = m_{s_1} + m_{s_2} = 1, 0, 0$ and -1 respectively.

We can form symmetric and antisymmetric superposition states from $|+-\rangle$ and $|-+\rangle$ as follows,[23]

$$\text{symmetric}: \qquad \frac{1}{\sqrt{2}}[|+-\rangle + |-+\rangle] \tag{10.4}$$

$$\text{antisymmetric}: \qquad \frac{1}{\sqrt{2}}[(|+-\rangle - |-+\rangle] \tag{10.5}$$

We now have three symmetric states (with $M_S = 1, 0, -1$) and one antisymmetric state (with $M_S = 0$). The former are called *triplet* states, the latter a *singlet* state. This is not unexpected since adding the individual spin angular momenta ($s = \frac{1}{2}$ in each case) we obtain total spin quantum numbers $S = 1$ ($M_S = 1, 0, -1$) and $S = 0$ ($M_S = 0$).

---

[23]If each ket is normalised,the $1/\sqrt{2}$ factor ensures that the linear combination is also normalised.

We can represent the three symmetric and one antisymmetric states in terms of total spin quantum numbers (called coupled basis states) $|S M_S\rangle$ as follows

$$|1\,1\rangle = |{+}{+}\rangle \tag{10.6}$$

$$|1\,0\rangle = \frac{1}{\sqrt{2}}[|{+}{-}\rangle + |{-}{+}\rangle] \tag{10.7}$$

$$|1-1\rangle = |{-}{-}\rangle \tag{10.8}$$

$$|0\,0\rangle = \frac{1}{\sqrt{2}}[(|{+}{-}\rangle - |{-}{+}\rangle] \,. \tag{10.9}$$

The state $|1 M_S\rangle$ is denoted triplet state and the state $|00\rangle$ singlet state. We can summarise the symmetries associated with exchange of particles by introducing an *exchange operator*, P_{12},

$$P_{12}\,|1 M_S\rangle = +\,|1 M_S\rangle \tag{10.10}$$

$$P_{12}\,|00\rangle = -\,|00\rangle \tag{10.11}$$

To complete the description of the helium atom we need to include the spatial part of the wave function $|\psi_{spatial}\rangle$, such that the complete wave function is given by

$$|\psi\rangle = |\psi_{spatial}\rangle\,|\psi_{spin}\rangle \tag{10.12}$$

We now consider the effect of symmetry requirements on the complete wave function.

10.2 Symmetric or antisymmetric?

As we have seen, the fact that particles are identical requires that systems of the particles be described by symmetric or antisymmetric wave functions, but does not specify which. It is however a fact of nature that particles can be divided into two groups:

bosons: particles with integer spin that have *symmetric* wave functions.

fermions: particles with half-integer spin that have *antisymmetric* wave functions.

As electrons, with spin $\frac{1}{2}$, are fermions[24] the states of helium must be antisymmetric. As helium states are the product of a spatial and spin part, as shown in Equation 10.12, antisymmetry may be achieved in two ways:

$$\left|\psi_{helium}^{SA}\right\rangle = \left|\psi_{spatial}^{S}\right\rangle\left|\psi_{spin}^{A}\right\rangle \tag{10.13}$$

$$\left|\psi_{helium}^{AS}\right\rangle = \left|\psi_{spatial}^{A}\right\rangle\left|\psi_{spin}^{S}\right\rangle \tag{10.14}$$

10.3 Two identical particles in one dimension

We can gain some insight into systems of two identical particles by considering a simple one-dimensional system, an infinite square well of width L ($x = 0 \to L$), which contains two non-interacting particles

---

[24]Protons and neutrons, both with spin $\frac{1}{2}$ are also fermions; photons with spin 1 are bosons, as is the Higgs boson with spin 0; atoms may be bosons or fermions depending the total spin of their composite particles: for example the hydrogen atom is a boson, $j = \frac{1}{2}, I = \frac{1}{2} \to F = 1, 0$.

with spin $\frac{1}{2}$. Suppose one particle is in energy eigenstate φ_{n_a} (energy: E_{n_a}) and the other in energy eigenstate φ_{n_b} (energy: E_{n_b}). Note that the combined states

$$\varphi_{n_a}(x_1)\varphi_{n_b}(x_2) \quad \text{and} \quad \varphi_{n_a}(x_2)\varphi_{n_b}(x_1) \tag{10.15}$$

both have the same energy $(E_{n_a} + E_{n_b})$ but neither satisfies either the symmetric or antisymmetric requirement. However we can form linear combinations which do:

$$\left|\psi_{space}^S\right\rangle = \psi_{n_a n_b}^S(x_1, x_2) = \frac{1}{\sqrt{2}}[\varphi_{n_a}(x_1)\varphi_{n_b}(x_2) + \varphi_{n_a}(x_2)\varphi_{n_b}(x_1)] \tag{10.16}$$

$$\left|\psi_{space}^A\right\rangle = \psi_{n_a n_b}^A(x_1, x_2) = \frac{1}{\sqrt{2}}[\varphi_{n_a}(x_1)\varphi_{n_b}(x_2) - \varphi_{n_a}(x_2)\varphi_{n_b}(x_1)] \tag{10.17}$$

Specific example: ground state

If both particles are in the ground state i.e. $n_a = n_b = 1$, it is obvious that $\left|\psi_{space}^A\right\rangle$ is identically zero, so the ground state can only be the product of a symmetric spatial function and an antisymmetric spin function:

$$\left|\psi_{11}^S\right\rangle |00\rangle \tag{10.18}$$

For an infinite well where the energy eigenfunctions are given by

$$|n\rangle = \varphi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \tag{10.19}$$

the probability density function $|\psi_{11}^S(x_1, x_2)|^2$ is shown in Figure 14.
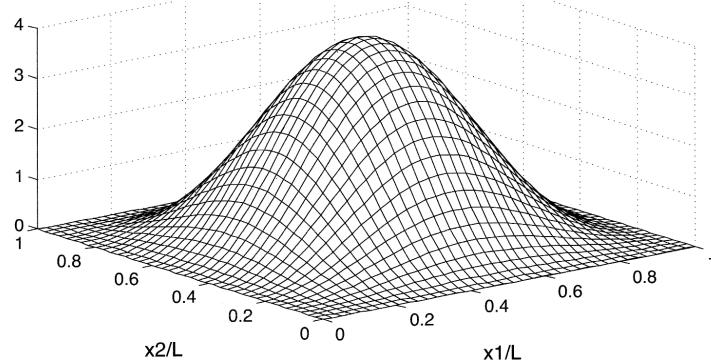
Figure 14: Probability density distribution for the ground state

Lecture 15 M:13.3-5

Specific example: excited state

Suppose one electron is in the ground state and the other in the first excited state. The wave functions for these states are, respectively

$$\varphi_1(x) = \sqrt{2/L}\sin(\pi x/L) \tag{10.20}$$
$$\varphi_2(x) = \sqrt{2/L}\sin(2\pi x/L) \tag{10.21}$$

We now form the symmetric and antisymmetric spatial functions,

$$\psi_{12}^S(x_1, x_2) = \frac{1}{\sqrt{2}}[\varphi_1(x_1)\varphi_2(x_2) + \varphi_2(x_1)\varphi_1(x_2)] \tag{10.22}$$

$$\psi_{12}^A(x_1, x_2) = \frac{1}{\sqrt{2}}[\varphi_1(x_1)\varphi_2(x_2) - \varphi_2(x_1)\varphi_1(x_2)] \tag{10.23}$$

The probability density functions $|\psi_{12}^S(x_1, x_2)|^2$ and $|\psi_{12}^A(x_1, x_2)|^2$ are shown in Fig. 15. We can see that, on average, the particles are closer together for the symmetric combination than for the antisymmetric combination. This effect is called the *exchange interaction.*[25] We can quantify this by calculating the average distance between the two particles $\langle (x_1 - x_2)^2 \rangle$. In our specific example, we find

$$\sqrt{\langle (x_1 - x_2)^2 \rangle} = \begin{cases} 0.20L & \text{symmetric wave function} \\ 0.32L & \text{distinguishable particles} \\ 0.41L & \text{antisymmetric wave function} \end{cases} . \tag{10.24}$$

See McIntyre Sec. 3.2.4 for more details.

(a) symmetric excited state

(b) antisymmetric excited state
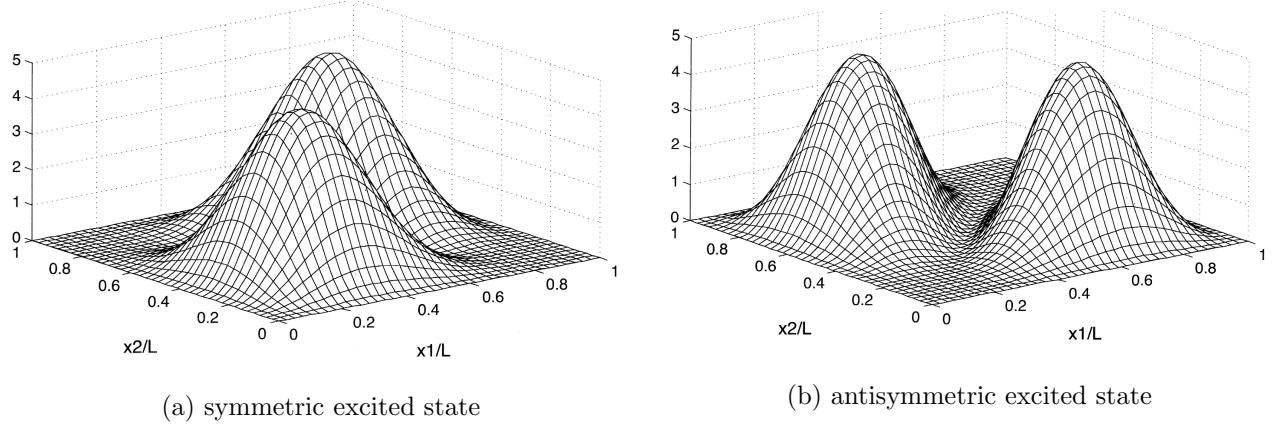
Figure 15: Probability density distributions

10.4 Interacting Particles

So far we did not consider any interactions between the identical particles. However, in interesting realistic situations, e.g. the two electrons in a helium atom, there are interactions betweent the identical particles. Let us assume that the interaction only depends on the particle separation

$$\hat{H}' = V_{int}(x_1 - x_2) \tag{10.25}$$

and that it can be treated in perturbation theory. Hence the correction to the energy of the state $\left| \psi^{(0)} \right\rangle$ is described by

$$E^{(1)} = \left\langle \psi^{(0)} | \hat{H}' | \psi^{(0} \right\rangle . \tag{10.26}$$

---

[25]The effect is also often said to be the result of an exchange force, but we need to realise that this can only be an apparent force. It is a purely quantum consequence of the symmetry requirements and not related to any of the fundamental force interactions.

As we argued previously the quantum state is a product of the spin and spatial part of the wave function, i.e.

$$E^{(1)} = \left\langle \psi_{spatial} | \hat{H}' | \psi_{spatial} \right\rangle \left\langle \psi_{spin} | \psi_{spin} \right\rangle . \tag{10.27}$$

The spatial part of the ground state wave function has to be symmetric irrespective of the spin of the particles. Hence we find

$$E_{11}^{(1)} = \left\langle \psi_{11}^S | \hat{H}' | \psi_{11}^S \right\rangle = \int dx_1 dx_2 \varphi_1^*(x_1) \varphi_2^*(x_2) V_{int}(x_1 - x_2) \varphi_1(x_1) \varphi_2(x_2) \equiv J_{11} . \tag{10.28}$$

In case of the first excited state, the spatial part of the wave function can be either symmetric of antisymmetric. Defining the *direct integral* J_{nm} and the *exchange integral* K_{nm}

$$J_{nm} \equiv \int dx_1 dx_2 \varphi_n^*(x_1) \varphi_m^*(x_2) V_{int}(x_1 - x_2) \varphi_n(x_1) \varphi_m(x_2) \tag{10.29}$$

$$K_{nm} \equiv \int dx_1 dx_2 \varphi_n^*(x_1) \varphi_m^*(x_2) V_{int}(x_1 - x_2) \varphi_n(x_2) \varphi_m(x_1) , \tag{10.30}$$

we find for bosons

$$E_{12}^{(1)} = J_{12} + K_{12} \tag{10.31}$$

and for fermions

$$E_{12}^{(1)} = J_{12} \pm K_{12} \tag{10.32}$$

with a $+$ $(-)$ sign for a (anti-)symmetric spatial wave function.

We now apply these concepts to the helium atom.

10.5 Helium atom

The Hamiltonian operator for the relative motion of a helium atom is

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{10.33}$$

where $r_{12} = |\mathbf{r_1} - \mathbf{r_2}|$. The last term is due to the electrostatic interaction between the two electrons and is not a small correction to the non-interacting Hamiltonian.

Suppose we initially ignore the interaction term. In this case each electron has energy levels equal to those of a "hydrogen atom with $Z = 2$". Thus the zeroth order energy of the helium atom will be

$$E_{n_a,n_b}^{(0)} = -4Ryd \left(\frac{1}{n_a^2} + \frac{1}{n_b^2} \right) . \tag{10.34}$$

One of the electrons in helium is always in the ground state. The state with two electrons in the excited state has energy $E_{22}^{(0)} = -2Ryd$, which is larger than the ground state energy of singly-ionised helium $E_{1\infty} = -4Ryd$. Hence the state with two excited electrons has a very short lifetime.

The interaction between the electrons will correspond to an increase in the energy. As this depends upon the relative distance between the electrons it will depend upon the electron probability distributions of each electron, which themselves depend upon their n and l quantum numbers. We will follow McIntyre and call this increase
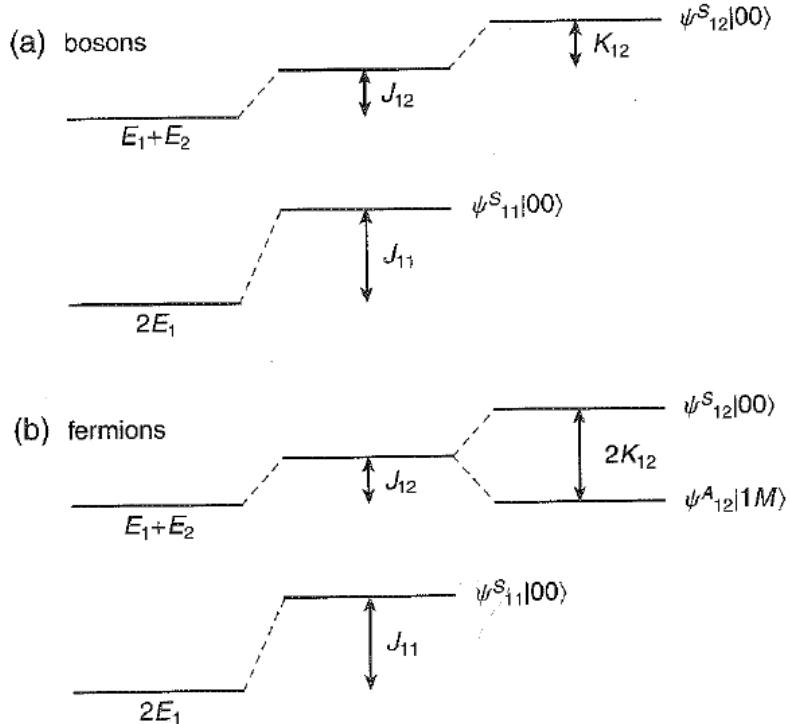
Figure 16: Energies and state vectors for the ground and first excited states of two identical paritcles (taken from McIntyre Sec. 13.3 pg 426)

$$J_{n_a l_a, n_b l_b} \tag{10.35}$$

Noting that each state specified by $n_a l_a, n_b l_b$ consists of a singlet ($S = 0$) and three triplet states ($S = 1$), we now take account of the exchange interaction, which leads to the average distance between the electrons in the singlet state being less than that for triplet states. Because of the electron-electron electrostatic interaction this means that the singlet state energy will be higher than that of the triplet states. Again following McIntyre we designate the energy change due to the exchange interaction as ("+" refers to the singlet state; "−" refers to the triplet state),

$$\pm K_{n_a l_a, n_b l_b} \tag{10.36}$$

10.5.1 Ground state of helium

For both electrons $n = 1$, $l = 0$ and $m_l = 0$ with an electron configuration $1s^2$. As we have seen for the 1D examples, it follows that $\psi_{space}^A = 0$, i.e. there is no triplet state: the ground state of helium consists of a singlet state only.

10.5.2 First excited state of helium

One electron remains in its ground state ($n = 1$, $l = 0$), the other in the first excited state ($n = 2$, $l = 1, 0$) with corresponding electron configurations $1s2s$ and $1s2p$. The effects of electron interaction and the exchange interaction on the energy levels are summarised in Figure 17.
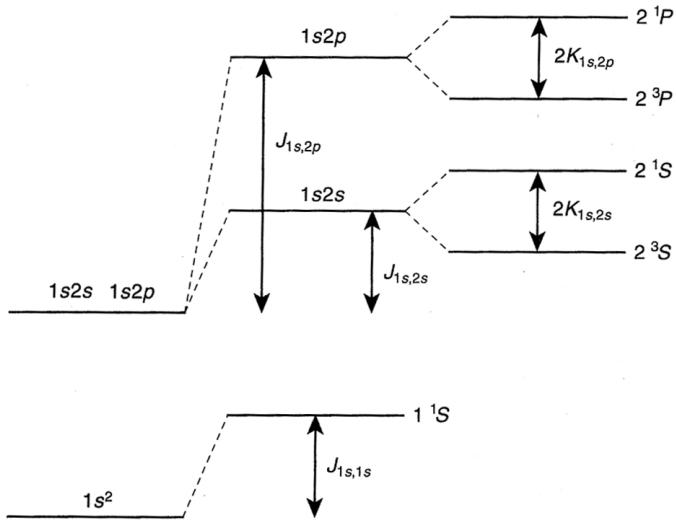
Figure 17: The effect of the electron-electron interaction and the exchange interaction on helium energy levels. Reproduced from Figure 13.9, McIntyre p432.

10.5.3   Spin-orbit coupling in helium

When spin-orbit coupling is taken into account we find the the triplet states have different energies. This is discussed further in Section 11.2.

10.6   Pauli exclusion principle

Consider the possibility of the two electrons in a helium atom having the same set of quantum numbers, i.e. of being in the same quantum state. As the m_s values are the same, the spin wave function must be symmetric, and therefore the spatial wave function must be antisymmetric, ψ_{space}^A. However if the quantum numbers n, l, and m_l are the same $\psi_{space}^A = 0$, and as a result the total wave function vanishes. It follows that it is impossible for the two electrons to be in the same quantum state. This is in fact a statement of the *Pauli Exclusion Principle*. More generally, for a multielectron atom, this principle states that no two electrons can be in the same quantum state i.e. the same set of values for their quantum numbers.

The fact that the ground state of helium consists of a singlet state only is an example of the Pauli exclusion principle. As both electrons have $n = 1$, $l = 0$ and $m_l = 0$, they must have different values of m_s: one $+\frac{1}{2}$, the other $-\frac{1}{2}$. The only possible value of M_S is therefore zero. It follows that S can only be zero, i.e. the ground state can only be a singlet state.

The Pauli Exclusion Principle is a consequence of the fact that electrons are fermions. There is no equivalent principle for a system of bosons: e.g. a laser is a system of bosons (photons) all in the same quantum state; Bose-Einstein condensation involves placing a collection of atoms with integer spin (i.e. bosons) into the same quantum state.

55

10.7   Bose-Einstein condensation

Hydrogen atoms in their ground state are bosons as they have integer spin: the proton has spin $I = 1/2$, the electron has spin $s = 1/2$, so the total spin quantum number is $F = 0, 1$. For atoms at temperature T, the de Broglie wavelength is given by

$$\lambda = \frac{h}{p} \sim \frac{h}{mv_{th}} \sim \left(\frac{h^2}{3mkT} \right)^{1/2} \tag{10.37}$$

where the root mean square speed has been used for v_{th}. If the atoms are cooled until λ is greater than the inter-atom spacing the wave functions of the atoms will overlap and the collection of atoms must be treated as a single quantum system of indistinguishable bosons.

When this situation is reached by cooling the atoms, the atoms undergo a quantum mechanical phase transition and form a *Bose-Einstein condensate*: a coherent cloud of atoms all occupying the same quantum state; they *can* occupy the same quantum state because they are bosons.

Experiments since 1995 have achieved Bose-Einstein condensation with different atoms[26]. For hydrogen, temperatures $\sim \mu$K are required. Atoms in the gaseous state can be trapped and cooled to such temperatures using the techniques of laser cooling[27].

---

[26]See "The Theory of Bose-Einstein Condensation of Dilute Gases", K. Burnett, M. Edwards and C.W. Clark, *Phys. Today*, **52** 37 (Dec 1999)

[27] See "Cooling and Trapping Atoms", W.D. Phillips and H.J. Metcalf, *Sci. Am.* **256** 36 (Mar 1987)

11   Multielectron atoms

Consider an atom with atomic number Z: the nuclear charge is $+Ze$ and there are Z electrons. According to the Pauli exclusion principle, each quantum state can contain one electron only. For the moment we will ignore spin-orbit coupling and specify a quantum state by the quantum numbers n, l, s, m_l and m_s. Each value of n specifies a *shell*; each value of l specifies a *subshell*. Taking account of the two possible values for m_s ($\pm\frac{1}{2}$), each full subshell contains $2(2l+1)$ electrons and each shell contains $2n^2$ electrons, as summarised in Table 5.

shell	subshells	$2n^2$
$n=1$	$l=0$; two $2s$ electrons	2
$n=2$	$l=0$; two $2s$ electrons	8
	$l=1$; six $2p$ electrons	
$n=3$	$l=0$; two $2s$ electrons	18
	$l=1$; six $2p$ electrons	
	$l=2$; ten $2d$ electrons	
$\vdots$	$\vdots$	$\vdots$

Table 5: Shell and subshell structure for a multielectron atom

The total angular momentum of a full subshell is zero as it contains electrons with all possible values of m_l ($l, l-1, \ldots, -l$) and m_s ($\pm\frac{1}{2}$) the sum of which is clearly zero. As the component value of the total angular momentum can only have the value of zero, the total angular momentum itself must be zero. It follows that the total angular momentum of a multielectron atom will be due to only those electrons in unfilled subshells. We will look at a simple multielectron example: alkali atoms.

11.1   Alkali atoms

The ground state of an alkali atom has one electron in an s state with all lower energy electrons in full subshells. This s electron is called the optically active electron as the emission spectrum of the atoms is almost entirely due to excitation of this electron and its subsequent radiative decay, while the electrons in full subshells remain unexcited. For example. the ground state electron configuration for sodium ($Z=11$) is $1s^2 2s^2 2p^6 3s$; the first excited configuration is $1s^2 2s^2 2p^6 3p$.

As the total angular momentum of a full subshell is zero, the total angular momentum of the electrons in an alkali atom is due to the optically active electron only. Unlike the electron in the hydrogen atom, however, this electron does not experience a Coulomb potential, as the Coulomb potential of the nucleus is modified due the the combined effect of all the other electrons. Thus the energy levels depend upon the values of the quantum number l, as well as n and j. [28]

When spin-orbit coupling is taken into account the states are characterised by the quantum numbers n, l, j, m_j; the energy levels correspond to each unique combination of n, l, j, and their degeneracy is $2j+1$, the number of different values for m_j. The selection rules for allowed transitions are:

---

[28] If the Lamb shift is ignored, it is only for a Coulomb potential that energy levels do not depend upon the quantum number l. Irrespective of the functional form of $V(r)$ however, the θ and ϕ equations are the same. Thus for multielectron atoms we can describe electron configurations using the same notation as used for for hydrogen, e.g.$1s$,$2s$,$2p$, etc.

$$\Delta l \;\; = \;\; \pm 1 \tag{11.1}$$
$$\Delta j \;\; = \;\; 0, \pm 1 \tag{11.2}$$

Example

The ground state of sodium has an electron configuration $1s^2 2s^2 2p^6 3s$, for which the spectroscopic notation is $^2S_{1/2}$. For the first excited state the electron configuration is $1s^2 2s^2 2p^6 3p$, for which there are two states with spectroscopic notations of $^2P_{3/2}$ and $^2P_{1/2}$, as shown in Figure 18. These two excited states have different energies (values of n and l are the same but j values are different), and transitions from both of them to the $^2S_{1/2}$ ground state are allowed - they satisfy the selection rules. The resulting two closely spaced spectral lines are the yellow doublet which is responsible for the strong yellow light from sodium lamps.
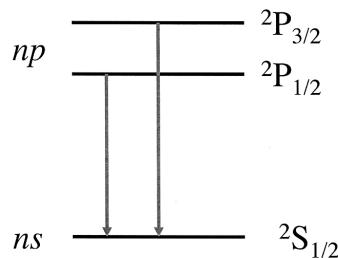

Figure 18: The energy levels of the sodium corresponding to the ground and first excited electron configurations. The two allowed transitions shown are the well-known yellow doublet of sodium: $\lambda = 589.0$ and 589.6 nm

11.2 The helium atom

Helium, with two electrons, is another simple example of a multielectron atom. Its ground state configuration is $1s^2$ and exited states usually involve only one excited electron: $1snl$. As we have seen, adding the spin of the electrons leads to either $S = 0$, a singlet state, or $S = 1$, a triplet state. If we now add the orbital angular momenta, noting that $l = 0$ for the $1s$ electron, we find that L is equal to the value of l for the excited electron. We then obtain total angular momentum values J by adding total spin and total orbital angular momenta.

For example, consider the $1s3d$ excited state of helium ($s_1 = 1/2, l_1 = 0; s_2 = 1/2, l_2 = 2$). Combining spins gives $S = 0, 1$; combining orbital angular momenta gives $L = 2$. This results in a singlet state with $J = 2$ ($^1D_2$), and a triplet state with $J = 3, 2, 1$ ($^3D_{3,2,1}$). When spin-orbit interaction is taken into account, singlet states remain single energy levels, while triplet states split into three different energy levels corresponding to the three values of J. This is illustrated in Figure 19. The selection rule

$$\Delta S = 0 \tag{11.3}$$

means that allowed transitions occur are only between singlet states or between triplet states, i.e. a transition between a singlet and a triplet state is forbidden.
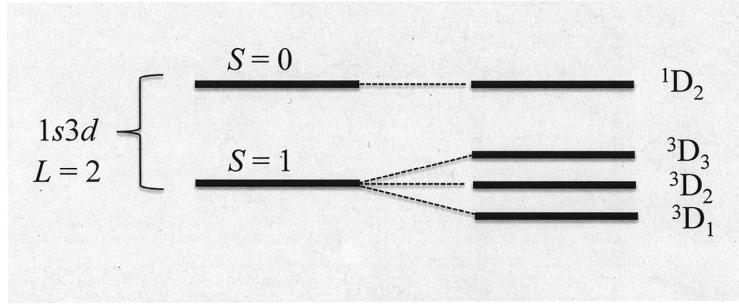
Figure 19: The energy levels of helium corresponding to the excited electron configuration $1s3d$.

11.3 LS coupling

The determination of the total angular momentum of helium states is an example of LS coupling.[29] It is applicable for atoms of small or intermediate atomic number where the spin-orbit interaction is weaker than the interactions between the spin and orbital angular momenta themselves. Thus to determine the total angular momentum we first add the spin angular momenta of the electrons to get a total spin angular momentum, and similarly add the orbital angular momenta of all the electrons to get the total orbital angular momentum[30]

$$\mathbf{S} = \mathbf{S_1} + \mathbf{S_2} + \mathbf{S_3} + \ldots \tag{11.4}$$
$$\mathbf{L} = \mathbf{L_1} + \mathbf{L_2} + \mathbf{L_3} + \ldots \tag{11.5}$$

The total angular momentum is then given by

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{11.6}$$

11.3.1 Selection rules for LS coupling

For the energy levels resulting from LS coupling allowed transitions obey the following rules.

- Only one electron undergoes a transition between sublevels

- For this electron $\Delta l = \pm 1$

- The changes in S, L and J must satisfy

$$\Delta S = 0 \tag{11.7}$$
$$\Delta L = \pm 1 \tag{11.8}$$
$$\Delta J = 0, \pm 1 \quad \text{but not } J = 0 \rightarrow J = 0 \tag{11.9}$$

Returning again to helium, Figure 20 is an energy level diagram for helium with singlet and triplet levels grouped separately, and it shows allowed transitions. Due to the $\Delta S = 0$ selection rule there

---

[29]Also called Russell-Saunders coupling.

[30]For high Z atoms a better description is given by the jj coupling scheme: for each electron the spin and orbital angular momenta are added to get a total angular momentum j. These are then added to obtain the total angular momentum J for the atom.

is no allowed transition from the lowest triplet state to the only lower state, which is a singlet state (this transition would also violate the $\Delta L = \pm 1$ selection rule). Also there is no allowed transition from the first excited singlet state: a transition to the lower singlet state would violate $\Delta L = \pm 1$ and a transition to the lower triplet state would also violate $\Delta S = 0$. The lowest singlet and triplet states of helium are, therefore, *metastable states*.
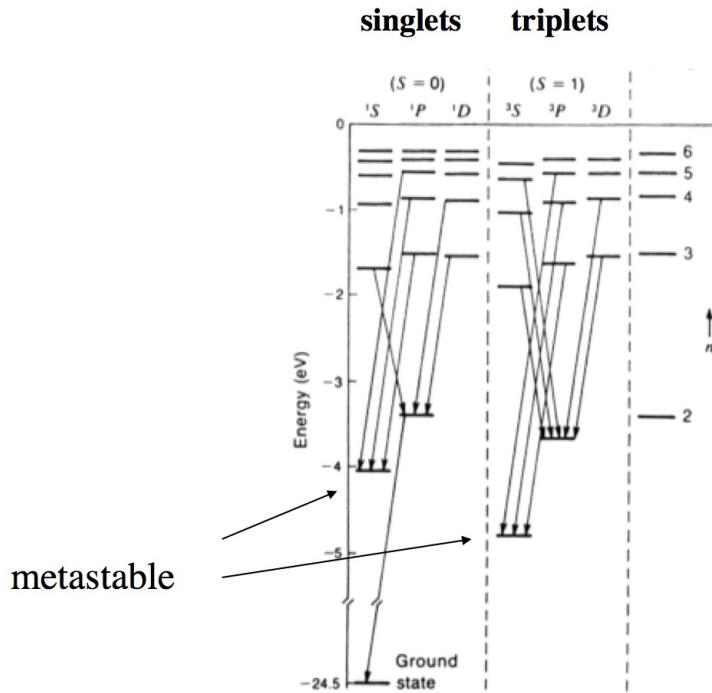

Figure 20: Energy levels and allowed transitions for helium. Singlet and triplet states are shown separately. Note that the lowest singlet and triplet states are metastable. Based on Figure 13-5, *An Introduction to Quantum Mechanics*, A.P. French & E.F. Taylor (Thomas Nelson 1979).

12   Zeeman and Paschen-Back effect

The Zeeman effect is the splitting of atomic energy levels by an externally applied magnetic field. As a result spectral lines are split into several lines whose spacing increases with increasing magnitude of the field. We will discuss the effect in detail for two limiting circumstances: when the applied field is small relative to the internal magnetic field of the atom ($\sim 1T$), and when it is much greater than the internal magnetic field. The intermediate case, where the external and internal fields are comparable, is much more complicated and will not be considered.

The quantitative treatment of the Zeeman effect is an example of time-independent perturbation theory. Suppose the unperturbed atom (i.e. $\mathbf{B} = 0$) has a Hamiltonian operator $\hat{H}_0$, with eigenstates $\left|n^{(0)}\right\rangle$ and corresponding eigenvalues $E_n^{(0)}$, where the zero superscript signifies the unperturbed atom. Suppose the atom experiences a small perturbation (due to the applied magnetic field, i.e. $\mathbf{B} \neq 0$), represented by the new Hamiltonian $\hat{H}^0 + \hat{H}'$. This different Hamiltonian will, in general, have different eigenstates and eigenvalues.

The essence of perturbation theory is the assumption that the perturbation is sufficiently small that we can use the unperturbed eigenstates to estimate the small changes in the eigenvalues. Typically the eigenvalues are shifted by small amounts, often in such a way that any degeneracy in the unperturbed system is reduced. The simplest situation is when the eigenfunctions of $\hat{H}^0$ are also eigenfunctions for $\hat{H}'$. In this case, which, as we will see is true for the Zeeman effect, the energy shift is given by the expectation value of the perturbation Hamiltonian $\hat{H}'$ according to the unperturbed eigenstates. The first-order correction to the unperturbed energy $E_n^{(0)}$ is therefore given by[31]

$$E_n^{(1)} = \left\langle n^{(0)} | \hat{H}' | n^{(0)} \right\rangle \tag{12.1}$$

We will consider three situations:

1. The Zeeman effect for a state without spin, i.e. a singlet state, for which $\mathbf{S} = 0$. This is know as the normal Zeeman effect as it can be explained classically.

2. The Zeeman effect for a state with spin in a weak magnetic field. Although this is called the anomalous Zeeman effect it is in fact the general case of the effect of a weak external magnetic field where in general $\mathbf{S} \neq 0$. The normal Zeeman effect is a special case where $\mathbf{S} = 0$.

3. The Zeeman effect for a state with spin in a strong magnetic field. This is called the Paschen-Bach effect.

12.1   Zeeman effect without spin

The perturbation to the Hamiltonian is the energy of the magnetic moment due to orbital angular momentum in the external magnetic field. The additional energy is given by

$$E = -\boldsymbol{\mu}_L \cdot \mathbf{B} = \frac{\mu_B B}{\hbar} L_z \tag{12.2}$$

---

[31]In the terminology of perturbation theory this is called the zeroth approximation to the solution of the perturbed problem. We will consider the first order correction only, but perturbation theory allows for higher order corrections.

where we have used

$$\boldsymbol{\mu}_L = -\frac{\mu_B}{\hbar}\mathbf{L} \tag{12.3}$$

The perturbation Hamiltonian is therefore

$$\hat{H}' = \frac{\mu_B B}{\hbar}\hat{L}_z \tag{12.4}$$

As the unperturbed eigenstates are $|lm_l\rangle$, the energy shifts are given by

$$E^{(1)} = \left\langle lm_l\Big|\frac{\mu_B B}{\hbar}\hat{L}_z\Big|lm_l\right\rangle = \mu_B B m_l \langle lm_l|lm_l\rangle \tag{12.5}$$

where we have used the fact that $\hat{L}_z |lm_l\rangle = m_l\hbar |lm_l\rangle$. Noting that $\langle lm_l|lm_l\rangle = 1$, the energy shifts are

$$E^{(1)} = \mu_B B m_l \tag{12.6}$$

Thus the external magnetic field removes the degeneracy with respect to the magnetic quantum number m_l. Figure 21 shows the effect on a level corresponding to $l = 1$, resulting in separate energies for $m_l = 1, 0, -1$.
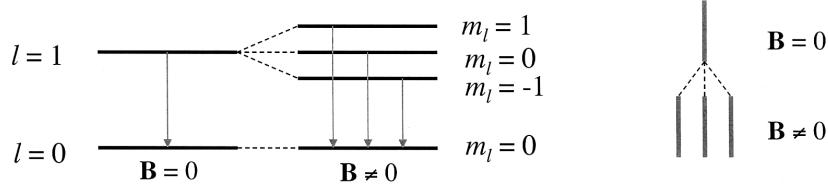

Figure 21: The effect of a weak external magnetic field on singlet states with $l = 1$ and $l = 0$. The splitting of the allowed transition between the levels is also shown on the right.

In the absence of an external magnetic field, the transition between levels E_2 and E_1 produces radiation at frequency $\nu_0 = (E_2 - E_1)/h$. In the presence of an external field, the energy difference becomes

$$(E_2 - E_1) \to (E_2 - E_1) + \mu_B B \Delta m_l \tag{12.7}$$

The selection rules are $\Delta m_l = 0, \pm 1$, resulting in the spectral line splitting into three: two lines equally space about an undeviated line (see Figure 21):

$$\nu_0 \to \nu_0 - \frac{\mu_B B}{h}, \quad \nu_0 \quad \nu_0 + \frac{\mu_B B}{h} \tag{12.8}$$

12.2 Zeeman effect with spin

In this case the magnetic moment is given by[32]

---

[32]For simplicity we use $g_e = 2$ instead of the more precise value $g_e = 2.00232\ldots$

$$\boldsymbol{\mu} = \boldsymbol{\mu}_S + \boldsymbol{\mu}_L = -2\mu_B \frac{\mathbf{S}}{\hbar} - \mu_B \frac{\mathbf{L}}{\hbar} \tag{12.9}$$

and the perturbation Hamiltonian is given by

$$\hat{H}' = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z B = \frac{\mu_B B}{\hbar}(2\hat{S}_z + \hat{L}_z) \tag{12.10}$$

Lecture 18 12.3; Read: M: 12.3.1

12.2.1   Weak magnetic field - anomalous Zeeman effect

The unperturbed eigenstates are $|ljm_j\rangle$, which are degenerate with respect to m_j. The fact that, due to $g_e \approx 2$, $\boldsymbol{\mu}$ is not parallel to $\mathbf{J} = \mathbf{S} + \mathbf{L}$ is a complication. However the assumption of a weak magnetic field allows the following simplification.

If the external field is weak compared to the internal magnetic field of the atom, $\boldsymbol{\mu}$ precesses around $\mathbf{J}$ much faster than it does about $\mathbf{B}$. Thus the component of $\boldsymbol{\mu}$ in the direction of $\mathbf{B}$ is to a good approximation equal to its component parallel to $\mathbf{J}$ multiplied by the cosine of the angle between $\mathbf{J}$ and $\mathbf{B}$ - see Figure 22. Hence the additional energy due to the external field is
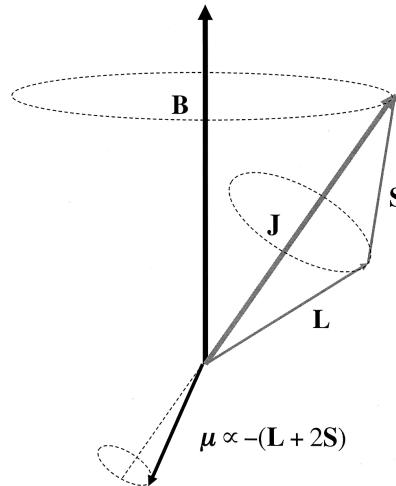

Figure 22: Precession about an external magnetic field of total angular momentum $\mathbf{J}$ and total magnetic moment $\boldsymbol{\mu}$ for the case of a weak magnetic field.

$$E = -\mu_z B \tag{12.11}$$

where

$$\mu_z = \frac{\boldsymbol{\mu} \cdot \mathbf{J}}{J} \times \frac{\mathbf{J} \cdot \mathbf{B}}{JB} \tag{12.12}$$

$$= -\frac{\mu_B}{\hbar} \frac{(\mathbf{L} + 2\mathbf{S}) \cdot (\mathbf{L} + \mathbf{S})}{J} \frac{J_z B}{JB} \tag{12.13}$$

$$= -\frac{\mu_B}{\hbar} \frac{(L^2 + 2S^2 + 3\mathbf{L} \cdot \mathbf{S})}{J^2} J_z \tag{12.14}$$

With a little algebraic manipulation we get (using $J^2 = L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S}$)

$$E = \frac{\mu_B B}{\hbar} \frac{(3J^2 + S^2 - L^2)}{2J^2} J_z \tag{12.15}$$

$$= \frac{g_L \mu_B}{\hbar} B J_z \tag{12.16}$$

where

$$g_L = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \tag{12.17}$$

is called the *Landé g factor*.

The perturbation Hamiltonian is therefore

$$\hat{H}' = \frac{g_L \mu_B B}{\hbar} \hat{J}_z \tag{12.18}$$

and following the same procedure used for the normal Zeeman effect, the first order correction to the energy level is

$$E^{(1)} = \left\langle ljm_j | g_L \mu_B B \hat{J}_z | ljm_j \right\rangle = g_L \mu_B B m_j \tag{12.19}$$

When a magnetic field is present energy levels that were degenerate with respect to m_j split into $2m_j + 1$ different levels. In addition to the selection rules already discussed there is now a selection rule for m_j:

$$\Delta m_j = 0, \pm 1 \tag{12.20}$$

The discussion above obviously applies to the hydrogen atom but it is also applicable to any atom where the energy levels are determined by LS-coupling i.e. the energy levels of a multielectron atom that are characterised by quantum numbers S, L, J, M_J[33].

Example

Consider the Zeeman effect for the $3^2P_{1/2}$ excited states of sodium and the $3^2S_{1/2}$ ground state. The g_L values are $\frac{2}{3}$ and 2 respectively. In the presence of a weak magnetic field, the energy levels will split according to:

---

[33]The convention is to use upper case for angular momenta quantum numbers of multielectron atoms where the angular momenta are the result of summation over two or more electrons. Lower case is used where only one electron is involved - hydrogen and alkali atoms

$$E_2 \quad \rightarrow \quad E_2 + \frac{2}{3}\mu_B B m_j \tag{12.21}$$

$$E_1 \quad \rightarrow \quad E_1 + 2\mu_B B m_j \tag{12.22}$$

where in both cases $M_J = \pm 1/2$. Thus the split energy levels are:

$$E_2 \quad \pm \quad \mu_B B/3 \tag{12.23}$$

$$E_1 \quad \pm \quad \mu_B B \tag{12.24}$$

Applying the selection rules, there will be four transitions, from each of the two excited states to each of the two ground states, and because the g_L values are different there will be four different lines, given by

$$\nu_0 \pm \frac{2}{3}\frac{\mu_B B}{h} \tag{12.25}$$

$$\nu_0 \pm \frac{4}{3}\frac{\mu_B B}{h} \tag{12.26}$$

Thus we see in Figure 23 that the Zeeman components consist of four lines in two groups of two, symmetrically spaced on either side of the unperturbed line, ν_0, but note that there is no line at ν_0.
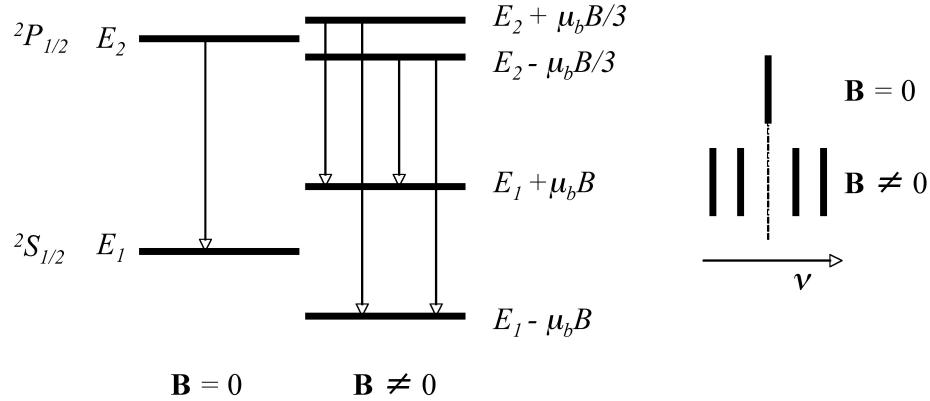

Figure 23: The Zeeman splitting of the $^2S_{1/2}$ and $^2P_{1/2}$ levels of an alkali atom. Also shown are the four allowed transitions,

12.3 Strong magnetic field - Paschen-Bach effect

If the external magnetic field is stronger than the internal magnetic field of the atom $\boldsymbol{\mu}_S$ and $\boldsymbol{\mu}_L$ precess about $\mathbf{B}$ much more rapidly than they do about $\mathbf{J}$. Thus their interactions with the external field are much greater than the effect of the spin-orbit interaction, which can be ignored as a first approximation. We take, therefore, the unperturbed eigenstates to be the uncoupled states $|lsm_lm_s\rangle$. The perturbation Hamiltonian is given by,

$$\hat{H}' = -\boldsymbol{\mu} \cdot \mathbf{B} \quad = \quad \frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B} \tag{12.27}$$

$$= \quad \frac{\mu_B B}{\hbar}(\hat{L}_z + 2\hat{S}_z) \tag{12.28}$$

In the presence of a strong magnetic field, the first order correction to the unperturbed energy level is

$$E^{(1)} = \left\langle lsm_lm_s \left| \frac{\mu_B B}{\hbar}(\hat{L}_z + 2\hat{S}_z) \right| lsm_lm_s \right\rangle = \mu_B B(m_l + 2m_s) \tag{12.29}$$

The selection rules are $\Delta m_s = 0, \Delta m_l = 0, \pm 1$. This leads to spectral lines being split into three components as in the normal Zeeman effect:

$$\nu = \nu_0 - \frac{\mu_B B}{h}, \quad \nu_0, \quad \nu_0 + \frac{\mu_B B}{h} \tag{12.30}$$

12.4 Arbitrary magnetic field

For the first excited state of the optical electron of an alkali atom (np), Figure 24 shows how the energy level spitting varies as the magnetic field increases from zero to large values. The energy level structure varies from that of the anomalous Zeeman effect at low fields to that of the Paschen-Bach effect at high fields. The intermediate region where the external field is of comparable magnitude to the internal field cannot be treated simply.

12.5 Summary

If an external magnetic field causes a spectral line to split into three lines, two of which are equally spaced about an undeviated line, it is either a case of the normal Zeeman effect (weak field, transitions between singlet states) or the Paschen-Bach effect (strong field). In either case (we do not need to know which), the line spacing $\Delta\nu$ is related to the magnetic field by

$$|\Delta\nu| = \frac{\mu_B B}{h} \tag{12.31}$$

In such circumstances, the line spacing can be used to measure the magnitude of the magnetic field.[34] If the line is split into an even number of components, displaced symmetrically about the position of the undeviated line (and there is no line in that undeviated position), it is a case of the anomalous Zeeman effect, and the relation between the spacing between lines and the magnetic field is proportional to $\mu_B B/h$, where the constant of proportionality is of the order of unity but dependent upon the quantum numbers of the energy levels involved.

---

[34]This is how magnetic fields on the surface of the Sun in the vicinity of sunspots have been measured - it is a strong field case. Information about the direction of the magnetic field is also available as the polarisation of the Zeeman lines is determined by the relative direction between the line of observation and the direction of the field.
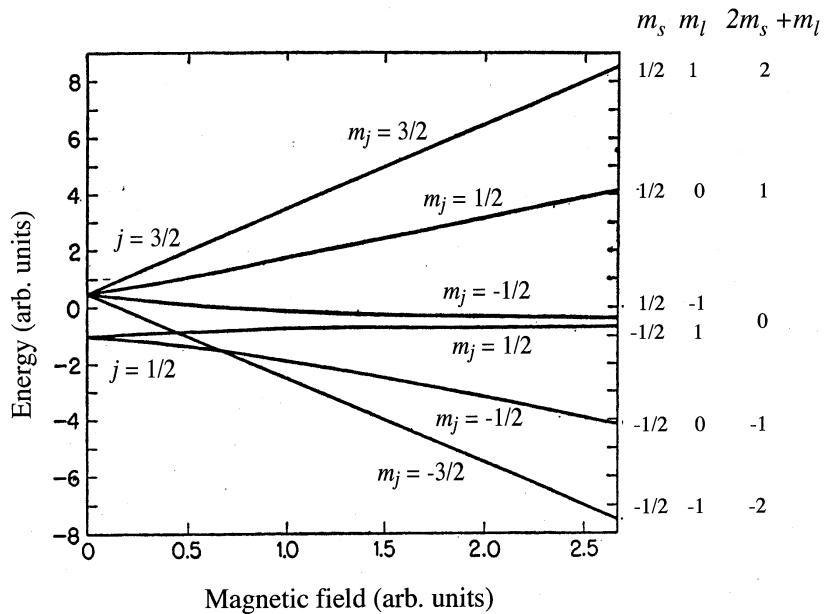
Figure 24: The energy levels of the *np* first excited state of the optical electron of an alkali atom as a function of magnetic field. The two levels have spectroscopic notations $^2P_{3/2}$ and $^2P_{1/2}$. (based on Figure 93, *Introduction to Modern Physics*, F.K. Richtmeyer, E.H. Kennard and T. Lauritsen (McGraw-Hill, New York, 1955)

13   Time-dependent Perturbation Theory

We have already argued that as the energy eigenstate contains all the information we can know about a stationary state of an atom, the transition probability for a transition between two states must depend upon the wave functions of those states. We will now seek this relationship, focussing on absorption and stimulated emission. Once we have the Einstein coefficients for these processes, the spontaneous emission transition probability can be obtained using the the Einstein relations.

The rigorous treatment is an example of time-dependent perturbation theory: the perturbing Hamiltonian is a function of time, $\hat{H}'(t)$.[35] In Sec. 6 we discussed how we can obtain an approximate solution to the energy eigenvalue equation of an Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}'$, if we know the solution to $\hat{H}_0$ and can consider $\hat{H}'$ a small perturbation. We however assumed that the Hamiltonian does not depend on time. In the following we will consider perturbations which depend on time, like the absorption or emission of a photon.

13.1   Interaction Picture

As we are dealing with a time-dependent Hamiltonian, we have to return to the Schrödinger equation (1.1) in its original form. So far we always considered the Hamiltonian to be time-independent, while the quantum states evolved with time. This is commonly denoted as *Schrödinger picture*. If we however consider the states

$$|\psi\rangle_H \equiv e^{i\hat{H}(t-t_0)/\hbar} |\psi(t)\rangle \tag{13.1}$$

we find that

$$i\hbar\frac{\partial}{\partial t} |\psi\rangle_H = i\hbar\frac{\partial}{\partial t}e^{i\hat{H}(t-t_0)/\hbar} |\psi(t)\rangle = e^{i\hat{H}(t-t_0)/\hbar} \left(-\hat{H} |\psi(t)\rangle + i\hbar\frac{\partial}{\partial t} |\psi(t)\rangle \right) = 0 \tag{13.2}$$

This is commonly denoted as *Heisenberg picture*. In this picture, all operators

$$\hat{A}_H(t) = e^{i\hat{H}(t-t_0)/\hbar} \hat{A} e^{-i\hat{H}(t-t_0)/\hbar} \ , \tag{13.3}$$

e.g. momentum operator, will be time-dependent and satisfy

$$\frac{d}{dt}\hat{A}_H(t) = \frac{i}{\hbar}[\hat{H}_H(t), \hat{A}_H(t)] + \frac{\partial}{\partial t}\hat{A}_H(t) \ . \tag{13.4}$$

We will now consider the *interaction picture*, in which both the Hamiltonian and the quantum state will depend on time. It is useful for cases, where we can split the Hamiltonian $\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$ in a time-independent part $\hat{H}_0$ and a time-dependent one $\hat{H}'$. It is defined by

$$|\psi(t)\rangle_I = e^{i\hat{H}_0(t-t_0)/\hbar} |\psi(t)\rangle \qquad\qquad \hat{A}_I(t) = e^{i\hat{H}_0(t-t_0)/\hbar} \hat{A} e^{-i\hat{H}_0(t-t_0)/\hbar} \ . \tag{13.5}$$

[35]See McIntyre, §14, p445.

13.2   Transition probabilities

We rewrite the Schrödinger equation for the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}'(t)$ in the interaction picture

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle_I = i\hbar \frac{\partial}{\partial t} e^{i\hat{H}_0(t-t_0)/\hbar} |\psi(t)\rangle \tag{13.6}$$

$$= -\hat{H}_0 |\psi(t)\rangle_I + e^{i\hat{H}_0(t-t_0)/\hbar} i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle \tag{13.7}$$

$$= -\hat{H}_0 |\psi(t)\rangle_I + e^{i\hat{H}_0(t-t_0)/\hbar} \left(\hat{H}_0 + \hat{H}'(t) \right) |\psi(t)\rangle \tag{13.8}$$

$$= -\hat{H}_0 |\psi(t)\rangle_I + e^{i\hat{H}_0(t-t_0)/\hbar} \left(\hat{H}_0 + \hat{H}'(t) \right) e^{-i\hat{H}_0(t-t_0)/\hbar} |\psi(t)\rangle_I \tag{13.9}$$

$$= e^{i\hat{H}_0(t-t_0)/\hbar} \hat{H}'(t) e^{-i\hat{H}_0(t-t_0)/\hbar} |\psi(t)\rangle_I \tag{13.10}$$

$$= \hat{H}'_I(t) |\psi(t)\rangle_I \ . \tag{13.11}$$

We can now formally integrate the equation and obtain

$$|\psi(t)\rangle_I = |\psi(t_0)\rangle_I + \frac{1}{i\hbar} \int_{t_0}^{t} \hat{H}'_I(t') |\psi(t')\rangle_I \, dt' \ . \tag{13.12}$$

This integral equation can be iteratively solved by plugging the solution back in on the right-hand side of the equation, i.e.

$$|\psi(t)\rangle_I = |\psi(t_0)\rangle_I + \frac{1}{i\hbar} \int_{t_0}^{t} \hat{H}'_I(t') |\psi(t_0)\rangle_I \, dt' + \left(\frac{1}{i\hbar} \right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \hat{H}'_I(t') \hat{H}'_I(t'') |\psi(t_0)\rangle_I + \dots \ . \tag{13.13}$$

We will only consider the leading order transitions. If we have the set of solutions $|n\rangle$ to the Hamiltonian $\hat{H}_0$, we can calculate the amplitude to find our particle in state $|n\rangle$ at time t if we start in state $|m\rangle$ at time t_0. The states in the interaction picture are given by

$$|n, t\rangle_I = e^{iH_0(t-t_0)/\hbar} |n\rangle \ . \tag{13.14}$$

Inserting the states in Eq. 13.13, we obtain

$$\langle n, t | \psi(t) \rangle = \langle n, t | m, t_0 \rangle_I + \frac{1}{i\hbar} \int_{t_0}^{t} \left\langle n, t | \hat{H}'_I(t') | m, t_0 \right\rangle_I \, dt' \tag{13.15}$$

$$= e^{i(E_m t_0 - E_n t)/\hbar} \left(\delta_{nm} + \frac{1}{i\hbar} \int_{t_0}^{t} e^{i(E_n - E_m)t'/\hbar} \left\langle n | \hat{H}'(t') | m \right\rangle \, dt' \right) \ . \tag{13.16}$$

Hence the probability for a transition from the state $|m\rangle$ to the state $|n\rangle$ is given by

$$P_{mn}(t) = \left| \frac{1}{i\hbar} \int_{t_0}^{t} e^{i(E_n - E_m)t'/\hbar} \left\langle n | \hat{H}'(t') | m \right\rangle \right|^2 \ . \tag{13.17}$$

13.3   Fermis Golden Rule

What is the mechanism for the interaction of an electromagnetic wave with an atom? The electric field of the wave will in general induce an electric dipole $\mathbf{d} = -e\mathbf{r}$ in the atom. There will be energy associated with the dipole in the electric field given by

$$-\mathbf{d} \cdot \mathbf{E} \tag{13.18}$$

where the electric field due to the electromagnetic wave can be represented as[36]

$$\mathbf{E}(t) = 2\mathcal{E}_0 \hat{\epsilon} \cos \omega t \tag{13.19}$$

where $\hat{\epsilon}$ is a unit vector specifying the polarisation of the radiation. The perturbing Hamiltonian is, therefore

$$\hat{H}' = 2e\mathcal{E}_0 \hat{\epsilon} \cdot \mathbf{r} \cos \omega t \tag{13.20}$$

More generally for Hamiltonians of the form

$$\hat{H}'(t) = 2V(\mathbf{r}) \cos \omega t , \tag{13.21}$$

the transfer rate $R \equiv \frac{d}{dt}P$ from an initial level i to a final level f with an energy difference $\hbar\omega_{fi} = |E_f - E_i|$ is encapsulated in the following equation, called *Fermi's Golden Rule*,

$$R_{i \to f} = \frac{2\pi}{\hbar^2}|V_{if}|^2 \delta(\omega_{fi} - \omega) , \tag{13.22}$$

which we obtain by inserting $\hat{H}'$ in Eq.(13.17).

For the problem under consideration, $V(\mathbf{r}) = e\mathcal{E}_0 \hat{\epsilon} \cdot \mathbf{r}$ so that

$$V_{fi} \propto \langle f|\mathbf{r}|i \rangle \tag{13.23}$$

Leaving aside the various multiplying constants we can see that the transfer rate is proportional to $|\langle f|\mathbf{r}|i \rangle|^2$ and also to $\mathcal{E}_0^2$. The latter is proportional to the radiation density $\rho(\nu_{fi})$ allowing us to conclude that the former is proportional to the Einstein coefficient B_{if} ($\equiv B_{fi}$). Including now the various constants, we quote the final result in terms of the upper state $|2\rangle$ and a lower state $|1\rangle$:

$$B_{21} \equiv B_{12} = \frac{\pi e^2}{3\epsilon_0 \hbar^2}|\langle 2|\mathbf{r}|1 \rangle|^2 \tag{13.24}$$

and using the Einstein relations we obtain an expression for the spontaneous emission transition probability for $|2\rangle$ to $|1\rangle$,

$$A_{21} = \frac{e^2 \omega_{21}^3}{3\pi \epsilon_0 \hbar c^3}|\langle 2|\mathbf{r}|1 \rangle|^2 \tag{13.25}$$

We see that when radiation of frequency ω_{21} is incident upon an atom, the probabilities of absorption ($\propto B_{12}$) and stimulated emission ($\propto B_{21}$) are equal. The actual rates will depend upon the population densities of the lower and upper states respectively. If the density of the lower $|1\rangle$ exceeds that of the upper $|2\rangle$, absorption will dominate. If, however, the density of the upper $|2\rangle$ exceeds that of the lower $|1\rangle$, there is a population inversion and stimulated emission dominates; the medium will be able to amplify radiation at frequency ω_{21}. With the addition of an optical cavity and an output coupling mechanism (e.g. a partially transmitting mirror at one end), we have a laser.

---

[36]The factor of 2 may not seem necessary. It is introduced in order to remain consistent with the way McIntyre represents the electromagnetic field. It has no effect, of course, on the results for the Einstein coefficients . See the discussion on p454 of McIntyre.

13.4 Selection rules

We are now in a position to understand the origin of selection rules. They are the conditions that ensure the transition between $|2\rangle$ and $|1\rangle$ is allowed, which will require

$$\langle 2|\mathbf{r}|1\rangle \neq 0 \qquad (13.26)$$

These conditions are usually specified in terms of the difference in quantum numbers between states $|2\rangle$ and $|1\rangle$. For example for the states $|nlm_l\rangle$ of hydrogen, if the selection rules $\Delta l = \pm 1$ and $\Delta m_l = 0, \pm 1$ are satisfied for a transition, the transition will be allowed.

On the other hand a transition will be forbidden if

$$\langle 2|\mathbf{r}|1\rangle = 0 \qquad (13.27)$$

This does not necessarily mean that there is no interaction with electromagnetic radiation or spontaneous emission. Rather it means that there is no dipole interaction: radiation incident on the atom will not induce an electric dipole moment. It may however induce a quadrupole moment, resulting in a much weaker interaction between the atom and the radiation. In this case the Einstein coefficients will not be zero, but many orders of magnitude smaller than for an allowed transition.

A Bohr's model of the atom (revision)

Bohr put forward the first quantum model of the atom in 1913. It explained some features of atomic spectra, and although it has been superseded by modern quantum mechanics, it is instructive to review its successes and deficiencies. Bohr assumed Rutherford's model of the atom in which the atom consisted of a very small positively charged nucleus at the centre with the electrons occupying the full volume of the atom. To this he added the following postulates.

A.1 Bohr's postulates

1. an electron moves in a circular orbit about the nucleus according to classical mechanics

2. only those orbits for which the orbital angular momentum of the electron is an integral multiple of $\hbar$ are possible ($\hbar = h/2\pi$)

3. an electron in such an allowed orbit does not radiate electromagnetic radiation - its energy remains constant

4. electromagnetic energy is emitted (or absorbed) when an electron changes from one allowed orbit to another

The equation of motion for an hydrogen-like atom ($Z = 1 \rightarrow$ H, $Z = 2 \rightarrow$ He$^+$, etc) in which a single electron orbits a nucleus of charge $+Ze$ is

$$\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r^2} = \frac{mv^2}{r} \tag{A.1}$$

The quantisation of orbital angular momentum gives

$$L = mvr = n\hbar \tag{A.2}$$

where $n = 1, 2, 3, \ldots$ is an integer. Solving these two equations simultaneously we get expressions for the two unknowns, the velocity and the radius of the orbiting electron:

$$v = \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{n\hbar} \rightarrow \frac{v}{c} = Z\alpha n \tag{A.3}$$

where $\alpha = e^2/(4\pi\epsilon_0\hbar c) = 7.30 \times 10^{-3} \approx 1/137$ is called the *fine structure constant*[37], and.

$$r = 4\pi\epsilon_0\frac{n^2\hbar^2}{mZe^2} = \frac{n^2}{Z}a_0 \tag{A.4}$$

where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 5.29 \times 10^{-11}\text{m} \tag{A.5}$$

is called the *Bohr radius*. It is the radius of the orbit of the ground state ($n = 1$) of hydrogen ($Z = 1$).

The energy of an orbiting electron is the sum of its kinetic and potential energies.

---

[37]We will encounter the fine structure constant at various times during this course. Note that it is a dimensionless ratio of fundamental constants, and its value is an indicator of the extent to which the motion of the electron in the hydrogen atom is relativistic.

$$E = K + V = \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{2r} - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{2r} \tag{A.6}$$

Substituting for r from eqn A.4,

$$E = -\frac{m}{2n^2\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 = \frac{-Z^2}{n^2}Ryd \tag{A.7}$$

where

$$Ryd = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \tag{A.8}$$

Ryd has the units of energy and its value is 13.6 eV.
For hydrogen $(Z = 1)$,

$$
\begin{aligned}
v/c &= \alpha/n & \text{(A.9)}\\
r &= n^2 a_0 & \text{(A.10)}\\
E &= -Ryd/n^2 & \text{(A.11)}
\end{aligned}
$$

Figure 25 shows low energy levels for hydrogen and transitions to the ground state.
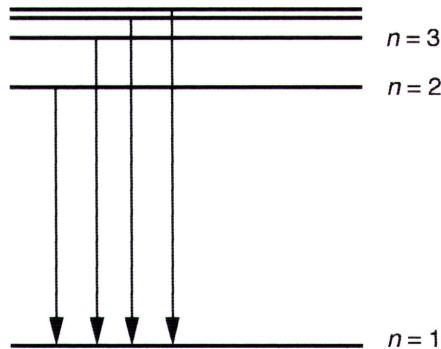

Figure 25: Energy level diagram for hydrogen showing the first four transitions of the Lyman series of spectral lines - transitions from higher levels to level $n = 1$: L_α (122 nm), L_β (102 nm), L_γ (97 nm).

A.2 Emission and absorption spectra

If the hydrogen atom $(Z = 1)$ undergoes a transition from state n_i to state n_f where $n_i > n_f$, the frequency of the emitted radiation is given by $\nu = (E_i - E_f)/h$. The wavenumber κ and wavelength λ are given by

$$\kappa \equiv \frac{1}{\lambda} = R_\infty\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{A.12}$$

73

where

$$R_\infty = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{me^4}{4\pi\hbar^3 c} = \frac{Ryd}{hc} \tag{A.13}$$

A.3 Finite nuclear mass

The equations above assume that the nucleus is infinitely massive. When the mass of the nucleus is taken into account m is replaced by the reduced mass of the atom, μ, where

$$\mu = \frac{mM}{m+M} \tag{A.14}$$

where M is the mass of the hydrogen nucleus. The constant in Equation A.12 becomes

$$R_H = \frac{M}{m+M} R_\infty \tag{A.15}$$

and is called the Rydberg constant.

$$\begin{aligned} R_\infty &= 1.09737 \times 10^7 \text{m}^{-1} \\ R_H &= 1.09681 \times 10^7 \text{m}^{-1} \end{aligned} \tag{A.16}$$

A.4 The hydrogen spectrum

The wavelengths of emission spectral lines of the hydrogen Balmer series ($n_f = 2$) are given by

$$\frac{1}{\lambda} = R_H \left(\frac{1}{4} - \frac{1}{n_i^2}\right) \tag{A.17}$$

where $n_i = 3, 4, 5, \ldots$. The resulting spectral lines are in the visible and near ultraviolet, and are known respectively as H_α (656 nm), H_β (486 nm), H_γ (434 nm), ... Several transitions of the Lyman series ($n_f = 1$) are shown in Figure 25, corresponding to L_α (122 nm), L_β (102 nm), L_γ (97 nm).

B The Dirac equation

The (time dependent) Schrödinger equation can be written as

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{B.1}$$

where

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \tag{B.2}$$

Paul Dirac's aim was to find a relativistic version of this that was also specific to a spin-$\frac{1}{2}$ particle. This required finding an expression for H that made the equation Lorentz invariant. We also know that spin operators are matrices and their eigenfunctions are vectors. So it should be no surprise that the equation Dirac arrived at is not simply a scalar equation. His equation is

$$(E/c + \alpha \cdot p + \alpha_4 m_0 c)\psi = 0 \tag{B.3}$$

where α_i is a 4×4 matrix, p is the momentum 4-vector and $\psi = (\psi_1, \psi_2, \psi_3, \psi_4)$ is a four component wave function. The α_i are given by

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \tag{B.4}$$

where $i = x, y, z$ and σ_i are the Pauli matrices, and

$$\alpha_4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{B.5}$$

This is Dirac's equation for a free electron with spin $\frac{1}{2}$. When Dirac modified this equation for an electron in a magnetic field, $E \rightarrow E - e\phi$ and $p \rightarrow p - e/cA$ he found that the solution included an energy term that corresponded to the energy of a magnetic moment in the magnetic field ($B = \nabla \times A$) associated with a particle of spin $\frac{1}{2}$, provided $g = 2$.

Dirac's equation also predicted a particle with the mass of an electron and charge $+e$, now called a positron (the anti-particle of an electron) and first detected experimentally by Carl Anderson in 1932 (for which he received the Nobel Prize for Physics in 1936).

C   Selection rules

Selection rules are a consequence of the fact that angular momentum (in addition to energy) must be conserved during absorption or emission of a photon. Photons have spin angular momentum ($\mathbf{s}$, quantum number 1), so when a photon is absorbed or emitted by an atom the angular momentum of the atom ($\mathbf{L}$, quantum number l) will change. Ignoring electron spin,

$$\mathbf{L} \rightarrow \mathbf{L}' = \mathbf{L} + \mathbf{s} \tag{C.1}$$

The final angular momentum quantum number is $l' = l + 1$, l, or $l - 1$. From this we would conclude that when a photon is absorbed or emitted the change in l is $\Delta l = 0, \pm 1$. For an electric dipole transition the transition probability for the case $\Delta l = 0$ is, however, identically zero. We can understand this in terms of the parity of the upper and lower states. The dipole transition probability involves the integral

$$\langle 2|\mathbf{r}|1\rangle \tag{C.2}$$

As $\mathbf{r}$ has odd parity, the integral will be zero if the upper and lower states have the same parity. As the parity of a state is determined by $(-1)^l$, $\Delta l = 0$ corresponds to a forbidden transition. So we conclude that for electric dipole radiation the selection rule for orbital angular momentum quantum number is

$$\Delta l = \pm 1 \tag{C.3}$$

It should be noted that the concept of a forbidden transition applies to *dipole* transitions. Emission and absorption of photons can still occur due to higher multipole interactions (with much smaller

transition probabilities). Examples of such transitions are associated with upper and lower states of the same parity and involve emission and absorption of two photons.

D Einstein relations

Consider a two-level atomic system that is in thermal equilibrium with radiation, in which case the transition rate $2 \rightarrow 1$ (spontaneous emission plus stimulated emission) must equal the transition rate $1 \rightarrow 2$ (absorption):

$$n_2(A_{21} + B_{21}\rho(\nu)) = n_1 B_{12}\rho(\nu) \tag{D.1}$$

Because of thermal equilibrium the densities n_1 and n_2 are related by the Boltzmann distribution

$$\frac{n_2}{n_1} = \exp(-h\nu/kT) \tag{D.2}$$

and the radiation density is given by the Planck's law (for radiation of a black body)

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1} = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{h\nu/kT}-1} \tag{D.3}$$

From Equation D.1, and substituting from Equation D.2,

$$\rho(\nu) = \frac{(A_{21}/B_{21})(n_2/n_1)}{B_{12}/B_{21} - n_2/n_1} = \frac{A_{21}/B_{21}}{B_{12}/B_{21}e^{h\nu/kT}-1} \tag{D.4}$$

Requiring that this corresponds to the black body formula leads to the Einstein relations

$$\frac{B_{12}}{B_{21}} = 1 \tag{D.5}$$

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3} \tag{D.6}$$

E Spherical Coordinates
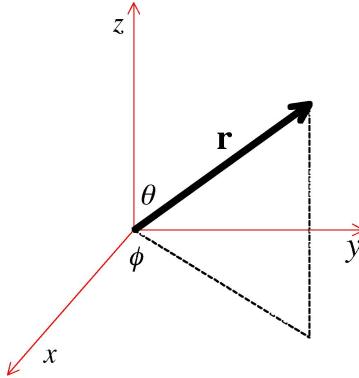
Figure 26: The spherical polar coordinate system.

76

The appendix is a short summary of spherical coordinates which are most suitable for any problem which is spherically symmetric. The coordinates are defined according to Fig. 26 as follows

$$
\begin{aligned}
x &= r \sin\theta \cos\phi \\
y &= r \sin\theta \sin\phi \\
z &= r \cos\theta \ .
\end{aligned}
\tag{E.1}
$$

The spherical volume element can be obtained by a change of variables from (x, y, z) to (r, θ, ϕ)

$$
dxdydz = \left| \frac{\partial(x, y, z)}{\partial(r, \theta, \phi)} \right| dr d\theta d\phi = r^2 \sin\theta dr d\theta d\phi
\tag{E.2}
$$

and the Laplace operator

$$
\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \phi^2} \ .
\tag{E.3}
$$

Revised on January 4, 2016