



Course Content

Contents

The content of this course has been considerably reduced compared with 2016/17. The following will be covered,

- Time independent perturbation theory to 1st order in the wavefunction and 2nd order in the energy.
Example A - 1D potentials
- Example B: 1D harmonic oscillator. Revision of the H-atom wavefunctions
- Example C: Polarisability of the H-atom, approximations for estimating lower and upper bounds
- Interpretation of C: f sum rule, oscillator strengths. Example D: Van der Waals interaction
- Degenerate Perturbation theory - example A: 2D particle in a square box or similar
- Example B: Quadratic and Linear Stark effect
- Relativistic Corrections to H-atom, spin-orbit interaction and Thomas precession described
- ‘Good’ quantum numbers, angular momentum addition (revised), Clebsch-Gordon coeffs for j
- Other relativistic Corrections to H-atom (mass-velocity, Darwin, Lamb, & Hyperfine) described
- Two electron states, exchange interaction introduced. Example for 1D potentials
- E-levels of the ground and excited states of helium
- Multi-electron atoms, Aufbau principle, Hund’s rules for the ground state, examples
- Rayleigh-Ritz variational method; 1D example and application to helium
- Hamiltonian including magnetic fields, atomic diamagnetism (Larmor)
- Paramagnetic atomic moments, Lande g-factor
- Normal and Anomalous Zeeman splitting, (selection rules given empirically since TDPT not done), Paschen Back effect
- Examples: calculation of magnetic susceptibility of some materials
- Overview of approximations used to describe bonding (Born Oppenheimer, LCAO versus Heitler London) omitting detailed calculation
- Rotations and vibrations of diatomic molecules

Perturbation Theory

1.1 Introduction

There are very few Hamiltonians we can solve exactly in QM. However, often a Hamiltonian can be expressed as an exactly solvable one plus a small correction. To make this concrete we will first consider a particle moving in a 1D potential $V(x) = \frac{m\omega^2}{2}x^2 + \lambda x^\nu$ where λ is small (we'll be considering different powers of $\nu = 1, 3, 4$). Non-harmonicity with $\nu = 3$ is important for the calculation of thermal expansion. The exact Hamiltonian in this case is that for a harmonic oscillator

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}x^2 \quad (1.1)$$

The exact solution for \hat{H}_0 was studied in detail last semester. It is elegantly solved with ladder operators.

The total Hamiltonian can be split into two parts:

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \quad (1.2)$$

where the correction $\hat{H}_1 = \lambda \hat{V}$ with $V = x^\nu$ for our example.

In the following we will develop first and second order perturbation theory (this is the essential material you need to know). After applying this to some examples, we will then give a more formal development of the theory, deriving the same results in a way that can be extended to all orders.

1.2 Derivation of Perturbation Theory

The idea is the following. We consider starting at some distant time in the past $t = -\infty$ with $\hat{H} = \hat{H}_0$ and increase λ slowly from zero to its full values at time $t = 0$. This process is assumed to be adiabatic, which means we don't get any transitions between states and there is a one to one correspondence between the Eigenstates of the perturbed Hamiltonian and the un-perturbed states at all times. Since we can solve H_0 exactly we use the basis of eigenstates of H_0 to describe our wavefunction and start with a particular Eigenstate of interest $|s\rangle$ of H_0 (not necessarily the ground state). Any state can be written as a superposition of the Eigenstates of H_0 . However, since the perturbation is small we expect the final state $|\Psi_s\rangle$ will have most of its weight in $|s\rangle$ but will also contain a small admixture of other states.

$$|\Psi_s\rangle = a_s |s\rangle + \sum_{j \neq s} a_j |j\rangle \quad (1.3)$$

with $|a_s| \approx 1$ and $|a_{j \neq s}| \ll 1$. We have

$$\hat{H}_0 |j\rangle = \epsilon_j |j\rangle \quad (1.4)$$

denoting the eigenenergies of H_0 with ϵ_j . We want to solve

$$(\hat{H}_0 + \hat{H}_1) |\Psi_s\rangle = E_s |\Psi_s\rangle. \quad (1.5)$$

To do this we take the product on the left with $\langle i |$ to get

$$\epsilon_i \langle i | \Psi_s \rangle + \langle i | \hat{H}_1 | \Psi_s \rangle = E_s \langle i | \Psi_s \rangle \quad (1.6)$$

and use the expansion EQN 1.3 ($|\Psi_s\rangle = \sum_j a_j |j\rangle$, not distinguishing $j = s$) noting $\langle i|j\rangle = \delta_{ij}$,

$$\implies \epsilon_i a_i + \sum_j \langle i| \hat{H}_1 |j\rangle a_j = E_s a_i \quad (1.7)$$

$$\sum_j (H_1)_{ij} a_j = (E_s - \epsilon_i) a_i \quad \text{Secular equation} \quad (1.8)$$

which is just a matrix equation. The elements $(H_1)_{ij} \equiv \langle i| \hat{H}_1 |j\rangle$ are *matrix elements* in the basis of the eigenstates of \hat{H}_0 .

(i) We first consider $i = s$,

$$(E_s - \epsilon_s) = \sum_j \frac{(H_1)_{sj} a_j}{a_s} \approx (H_1)_{ss} \quad (1.9)$$

since $|a_s| >> |a_{j \neq s}|$. All the matrix elements are proportional to λ so the final result is also linear in λ . This important result gives an expression for the shift in the energy levels caused by the perturbation \hat{H}_1 . The shift $\Delta E_s = E_s - \epsilon_s$ is

$$\boxed{\Delta E_s = \langle s| \hat{H}_1 |s\rangle} \quad \text{1st order perturbation theory energy shift} \quad (1.10)$$

(ii) We next look at $i \neq s$. Referring back to the secular equation, EQN 1.8

$$a_i = \sum_j \frac{(H_1)_{ij} a_j}{E_s - \epsilon_i} \approx \frac{(H_1)_{is} a_s}{E_s - \epsilon_i} \quad (1.11)$$

The approximate equality follows since $|a_s| >> |a_{j \neq s}|$, so we keep only $j = s$ in the sum. The matrix elements are linear in λ . Writing $E_s = \epsilon_s + \Delta E_s$ we note that since ΔE_s is linear in λ , if we Taylor expand the denominator $\epsilon_s - \epsilon_i + \Delta E_s$ in EQN 1.11 with respect to the small quantity $\Delta E_s / (\epsilon_s - \epsilon_i)$ the first term in the expansion is linear in λ and therefore contributes to order λ^2 to a_i as long as $\epsilon_i \neq \epsilon_s$. Therefore as long as $\epsilon_s \neq \epsilon_i$, E_s can be replaced by ϵ_s if we keep only linear in λ terms in the expression for a_i .

The above analysis also makes clear what is meant by a small perturbation. The energy shift of each level ΔE_s has to be smaller than the spacing between levels $\epsilon_s - \epsilon_i$ (for those levels linked by non-vanishing H_1 matrix elements).

To consider a_s to the same order we note that since

$$|a_s|^2 + \sum_{i \neq s} |a_i|^2 = 1 \quad (1.12)$$

and corrections to the $a_{i \neq s}$ are linear in λ the first correction to $a_s = 1$ is of order λ^2 . Therefore we can put $a_s = 1$ to linear order in λ in EQN 1.11. Thus

$$\boxed{a_{i \neq s} = \frac{(H_1)_{is}}{\epsilon_s - \epsilon_i} \quad \& \quad a_s = 1} \quad \text{1st order perturbation theory for the wavefunction} \quad (1.13)$$

Finally we can substitute this expression for a_i back into EQN 1.9 to obtain a better (good to second order) expression for the energy shift

$$\boxed{\Delta E_s = \langle s| \hat{H}_1 |s\rangle + \sum_{i \neq s} \frac{|\langle i| H_1 |s\rangle|^2}{\epsilon_s - \epsilon_i}} \quad \text{combined 1st and 2nd order energy shift.} \quad (1.14)$$

The above equation is one of the most useful tools in physics! The second order term contains a sum over all intermediate states i except $i = s$. Often the first term is zero so the leading correction to the energy is second order.

The last two boxed equations are well worth memorising.

1.3 Application of perturbation theory

1.3.1 1D potential - a blip in a box

Let's consider adding a particle in a 1D infinite well of size L ; $-L/2 < x < L/2$. The unperturbed energy eigenstates are denoted by a single quantum number $|n\rangle$, $n = 1, 2, 3 \dots$. The wavefunctions are

$$\psi_n \equiv \langle x|n\rangle = \begin{cases} \sqrt{\frac{2}{L}} \cos(\pi n x/L) & n \text{ odd} \\ \sqrt{\frac{2}{L}} \sin(\pi n x/L) & n \text{ even.} \end{cases} \quad (1.15)$$

n odd have even parity (i.e. $\hat{P}|n\rangle = |n\rangle$ where $\hat{P}|x\rangle = |-x\rangle$, while n odd have odd parity ($\hat{P}|n\rangle = -|n\rangle$). The unperturbed energy levels are $\epsilon_n = \frac{1}{2m_q} \left(\frac{\hbar\pi n}{L} \right)^2$ (with m_q the particle's mass).

We can then use perturbation theory to see how these energy levels are shifted when we add a potential $V_0 L \delta(x)$, which is located at the centre of the well. To first order in V_0

$$\Delta E_n = V_0 L \langle n | \delta(x) | n \rangle \quad (1.16)$$

$$= 2V_0 \int_{-L/2}^{L/2} dx \frac{\cos(\pi n x/L)^2 \delta(x)}{\sin(\pi n x/L)^2 \delta(x)} = \begin{cases} 2V_0 & n \text{ odd} \\ 0 & n \text{ even} \end{cases} \quad (1.17)$$

Thus to first order the even-parity states are shifted up in energy. The odd-parity states are unchanged since their wavefunctions are zero at $x=0$. In fact the odd-parity states will be unchanged to any order of perturbation theory; they are Eigenstates of the full Hamiltonian.

1.3.2 An electric field in a box

We now consider the same potential well (i.e. the same \hat{H}_0) but with an applied electric field that adds a gradient to the potential $H_1 = -q\mathcal{E}x$ (charge q , Electric field \mathcal{E}). The first order shifts in energy vanish. This is because the perturbation has odd parity. Consider $\langle n | \hat{x} | n \rangle$. The result of the action of \hat{x} on $|n\rangle$ is to give a state with the opposite parity to the $|n\rangle$. This resultant state is orthogonal to the $|n\rangle$ since the Eigenstates of any Hermitian operator with different Eigenvalues are orthogonal. The vanishing of the first order term can also be seen explicitly from inspection of the integrals:

$$\Delta E_n^{\text{1st order}} = -q\mathcal{E} \langle n | x | n \rangle \quad (1.18)$$

$$= -q\mathcal{E} \int_{-L/2}^{L/2} dx \frac{\cos(\pi n x/L)^2 x}{\sin(\pi n x/L)^2 x} = 0 \quad (1.19)$$

$$(1.20)$$

The vanishing of any linear term could also have been anticipated on physical grounds, since the energy shift cannot depend on the direction of the applied field.

We therefore need to look at the second order terms.

$$\Delta E_n^{\text{2nd order}} = (q\mathcal{E})^2 \sum_m \frac{|\langle m | x | n \rangle|^2}{\epsilon_n - \epsilon_m} = 2m_q \left(\frac{qL\mathcal{E}}{\hbar\pi} \right)^2 \sum_m \frac{|x_{mn}|^2}{n^2 - m^2} \quad (1.21)$$

If n is odd, following our arguments on basis of the parity, we only have to keep even m in the sum and vice versa. We will now just focus on the energy of the ground state $n = 1$ with $m = 2, 4, 6, \dots$. Every term in the sum is negative since $\epsilon_m > \epsilon_n$, as is always the case for the ground state.

$$x_{m1} = \frac{2}{L} \int_{-L/2}^{L/2} dx x \cos(\pi x/L) \sin(m\pi x/L) \quad (1.22)$$

$$= \frac{1}{L} \int_{-L/2}^{L/2} dx x (\sin((m+1)\pi x/L) + \sin((m-1)\pi x/L)) \quad (1.23)$$

$$= \frac{2}{L} \left\{ \left(\frac{L}{\pi(m+1)} \right)^2 \sin((m+1)\pi/2) + \left(\frac{L}{\pi(m-1)} \right)^2 \sin((m-1)\pi/2) \right\} \quad (1.24)$$

where the last line the integral was done by parts. Although the full result can be obtained analytically a very good approximation (less than 1% error) is achieved keeping only the first term $m = 2$ in the sum in EQN 1.21

$$\Delta E_n^{\text{2nd order}} \approx -\frac{512}{243} \frac{m_q L^4 q^2 \mathcal{E}^2}{\hbar^2 \pi^6} \quad (1.25)$$

This expression has some practical consequences. Quantum wells are used in silicon devices. The above calculation shows that the energy of the ground state energy in such a well is decreased by the application of an electric field, which can be used to tune light emitting devices (FIG 1.1).

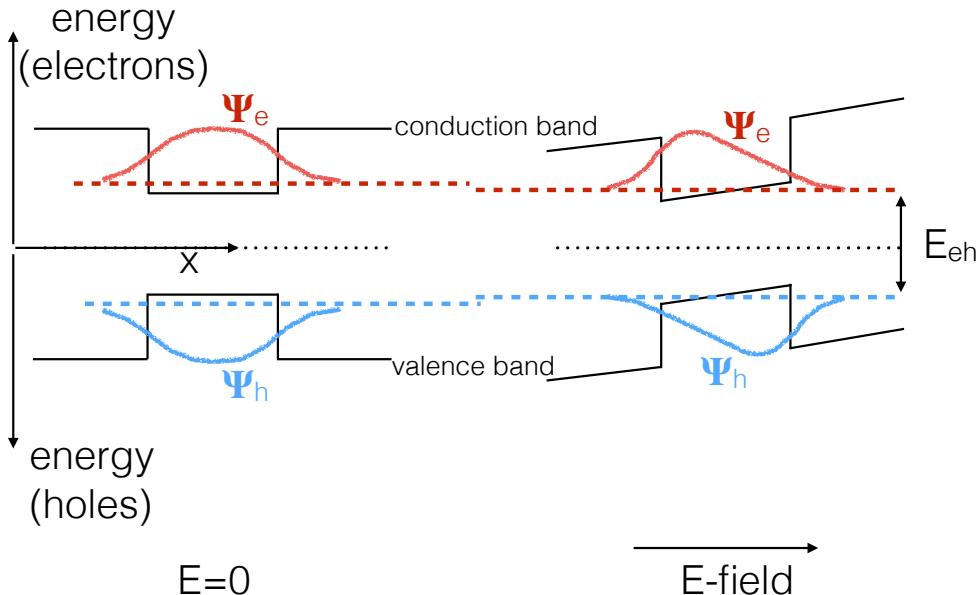


Figure 1.1: The figure shows the band energy levels as a function of position across a quantum well. The quantum well is a narrow region of reduced band gap (owing to a change of composition) in a semiconductor such as Si. The lower band is the valence band and is full of electrons. The upper band is the conduction band and is empty. An excitation is created by promoting an electron from the valence band to the conduction band. The electron has a positive energy measured from the dotted line vertically up and leaves a hole in the valence band that also has a positive energy measured from the dotted line going down. The total energy of the electron-hole pair excitation is E_{eh} . The electron and hole wave functions are confined to the potential wells, and these are also sketched in blue and red (the y-axis shows the wavefunction amplitude, with the origins overlying with the lowest bound state energy level for both electrons and holes). The left half of the image shows the situation in zero electric field and the right half when an electric field is applied. Following the calculation in the notes the energy of the bound state is reduced in the field and so the energy at which light is absorbed and emitted creating and removing eh pairs is also reduced. This is known as the quantum confined Stark effect, useful for changing colour of displays, QLEDs.

1.4 Application of perturbation theory to the Harmonic oscillator

1.4.1 Polarisation in an electric field

Applying an electric field to a harmonic oscillator illustrates how the perturbation calculations can be done with raising and lowering operators. We first briefly review the solution of the unperturbed quantum harmonic oscillator before considering different perturbations.

For the harmonic oscillator EQN 1.1, writing $x = \sqrt{\frac{\hbar}{m\omega}}y$ (y is dimensionless) and measuring energy in units $\hbar\omega$

$$\hat{h}_0 = \frac{\hat{H}_0}{\hbar\omega} = \frac{y^2 - \partial_y^2}{2} \quad (1.26)$$

$$= \underbrace{\frac{(y - \partial_y)}{\sqrt{2}}}_{a^+} \underbrace{\frac{(y + \partial_y)}{\sqrt{2}}}_{a^-} + \frac{1}{2} \quad (1.27)$$

$$(1.28)$$

with a and a^+ lowering and raising operators that are seen to obey $[a^-, a^+] = 1$ (in this section we omit the hats over these operators). The Eigenstates are labelled by an integers $n \geq 0$ with $E_n = (1/2 + n)[\hbar\omega]$. The raising and lowering operators acting on the normalised eigenstates satisfy

$$a^+ |n-1\rangle = \sqrt{n} |n\rangle \quad (1.29)$$

$$a^- |n\rangle = \sqrt{n} |n-1\rangle. \quad (1.30)$$

The perturbation we will consider is $H_1 = \lambda x$ (i.e. $v = 1$). Physically this equates to applying an electric field E with $H_1 = -qEx$ with $\lambda = -qE$ where q is the charge on the particle. The applied field can be arbitrarily small (and also turned on arbitrarily slowly). In our dimensionless units $\hat{h}_1 = H_1/\hbar\omega = \lambda'y$, where $\lambda' = \lambda(\frac{\hbar}{m\omega})^{1/2} \frac{1}{\hbar\omega}$.

$$y = \frac{a^+ + a^-}{\sqrt{2}}. \quad (1.31)$$

It is clear that the first order perturbation term for the energy shifts will be zero since the perturbation changes the eigenstate,

$$y|n\rangle = \frac{1}{\sqrt{2}}(a^- + a^+) |n\rangle \quad (1.32)$$

$$= \frac{1}{\sqrt{2}}(\sqrt{n}|n-1\rangle + \sqrt{n+1}|n+1\rangle). \quad (1.33)$$

$$(1.34)$$

The intermediate states linked to this are $\langle n-1|$ (if $n \geq 1$) and $\langle n+1|$. The squared matrix elements appearing in EQN 1.14 are $n\lambda'^2/2$ and $(n+1)\lambda'^2/2$ respectively. The energy denominators are $+1$ and -1 (in units $\hbar\omega$) respectively. The energy shift is therefore

$$\Delta E_n = \frac{(n - (n+1))}{2} \lambda'^2 = -\frac{\lambda'^2}{2} \quad (1.35)$$

$$\Delta E_n [\text{in Joules}] = -\frac{q^2 E^2}{2m\omega^2}. \quad (1.36)$$

Writing the polarisation energy $-\alpha_{\mathcal{E}} E^2/2$ where $\alpha_{\mathcal{E}}$ is the polarisability we conclude that

$$\alpha_{\mathcal{E}} = \frac{q^2}{m\omega^2}. \quad (1.37)$$

It is independent of the state n . This is the same as the classical result $\alpha_{\mathcal{E}} = q^2/K$ with $K = m\omega^2$ the spring constant.

1.4.2 Anharmonic oscillator

Consider $H_1 = \lambda'y^3$, where $\lambda' = \lambda(\frac{\hbar}{m\omega})^{3/2} \frac{1}{\hbar\omega}$. Then

$$y^3 = \frac{1}{2\sqrt{2}}(a^- + a^+)^3 \quad (1.38)$$

It is clear that the first order perturbation term for the energy shifts will be zero since only terms with equal numbers of a^+ and a^- can connect a state to itself. Let's suppose we are only interested in the change of the ground state energy. Then we only need to keep terms that always have an a^+ to the right of every a^- 's at every point since $a^-|0\rangle = 0$.

$$y^3|0\rangle = \frac{1}{2\sqrt{2}}(a^- + a^+)^3|0\rangle \quad (1.39)$$

$$= \frac{1}{2\sqrt{2}}(a^+ + a^-)((a^+)^2 + a^-a^+)|0\rangle \quad (1.40)$$

$$= \frac{1}{2\sqrt{2}}(a^+ + a^-)((a^+)^2 + 1)|0\rangle \quad (1.41)$$

$$= \frac{1}{2\sqrt{2}}((a^+)^3 + a^-(a^+)^2 + a^+)|0\rangle \quad (1.42)$$

$$= \frac{1}{2\sqrt{2}}((a^+)^3 + 3a^+)|0\rangle \quad (1.43)$$

$$(1.44)$$

This intermediate states linked to this are $\langle 3 |$ and $\langle 1 |$. The squared matrix elements are $3!/8$ and $9/8$. The energy denominators are -3 and -1. The change in energy of the ground state is

$$\Delta E_0 = \left(-\frac{3!}{8}\frac{1}{3} - \frac{9}{8}\frac{1}{1}\right)\lambda'^2 = -\frac{11\lambda'^2}{8} \quad (1.45)$$

$$\Delta E_0[\text{in Joules}] = -\frac{11}{8}\frac{\lambda^2}{\hbar\omega}\left(\frac{\hbar}{m\omega}\right)^3 \quad (1.46)$$

You might notice an important general point. The second order term always causes a *decrease* of energy for the **ground state** since the intermediate states have higher energy than the ground state with $\epsilon_i > \epsilon_0$. i.e. the energy denominator for each term is negative, while the modulus matrix element squared is always positive.

We can also write out the perturbed wavefunction which we denote $|0'\rangle$

$$|0'\rangle = |0\rangle - \frac{3\lambda'}{2\sqrt{2}}|1\rangle - \frac{\lambda'}{2\sqrt{3}}|3\rangle \quad (1.47)$$

The mean position of the oscillator is obtained from $\langle x \rangle = \langle 0'|x|0'\rangle$, which can be written

$$\begin{aligned} \langle x \rangle = \sqrt{\frac{\hbar}{m\omega}}\langle 0'|y|0'\rangle &= \sqrt{\frac{\hbar}{m\omega}}\langle 0| - \frac{3\lambda'}{2\sqrt{2}}\langle 1| - \frac{\lambda'}{2\sqrt{3}}\langle 3|\left(\frac{a+a^+}{\sqrt{2}}\right)|0\rangle - \frac{3\lambda'}{2\sqrt{2}}|1\rangle - \frac{\lambda'}{2\sqrt{3}}|3\rangle \\ &= -\frac{3\lambda'}{2}\sqrt{\frac{\hbar}{m\omega}} \end{aligned} \quad (1.48)$$

The mean position has moved to the left for positive λ and the energy has decreased since it spends more 'time' on the side of the origin with the lower potential. The classical result, in which the particle remains at the local minimum of the potential would be for no shift in position or energy. The quantum result reflects the delocalisation of the particle, aka its zero point motion.

This particular example is pathological, since if we continued the perturbation series to higher orders successive terms would eventually become larger since the particle can escape to $x \rightarrow -\infty$ (for $\lambda > 0$) and lower its potential energy without limit.

1.4.3 Matrix elements in general

It is possible to calculate shifts in matrix elements for any operator \hat{f} with perturbation theory. To first order matrix elements of \hat{f} in the presence of the perturbation become

$$f'_{nm} = \frac{\langle n'|\hat{f}|m'\rangle}{\sqrt{\langle m'|m'\rangle\langle n'|n'\rangle}} = \langle n|\hat{f}|m\rangle + \lambda \sum_{p \neq m} \frac{\langle n|\hat{f}|p\rangle\langle p|\hat{V}|m\rangle}{\epsilon_m - \epsilon_p} + \lambda \sum_{p \neq n} \frac{\langle n|\hat{V}|p\rangle\langle p|\hat{f}|m\rangle}{\epsilon_n - \epsilon_p} + \dots$$

Often we are interested in low energy states n, m where for this subset of states the zeroth order matrix elements $\langle n | \hat{f} | m \rangle = 0$. Higher energy intermediate excitations p nevertheless cause an interaction between the low lying states in first order perturbation theory. We have already calculated a matrix element (for x) for the anharmonic oscillator.

1.5 Formal Derivation of Perturbation Theory

This section contains more advanced non examinable material.

The previous derivation is sufficient for the exam. However it is instructive to look at a more formal derivation, which can be extended to higher orders.

1.5.1 Wavefunctions and energy levels

Denote states with the perturbation switched on with labels $'$. The perturbed states are labelled by the quantum numbers of the unperturbed states from which they evolved. We have

$$(\hat{H}_0 + \lambda \hat{V})|n\rangle' = E_n|n\rangle' \quad (1.50)$$

Normalisation is chosen so that $\langle n | n \rangle = 1$ and $\langle n | n \rangle' = 1$. We note that in general therefore $\langle n' | n' \rangle \neq 1$. We expand the wavefunction in powers of λ with index (r) labelling the coefficient of λ^r .

$$E'_n = \sum_r \lambda^r \epsilon_{n,(r)} \quad (1.51)$$

To keep the notation simple we will drop the label n so the above equation becomes

$$E' = \sum_r \lambda^r \epsilon_{(r)} \quad (1.52)$$

with $\epsilon_{(0)} = \epsilon_n$ the unperturbed energy of state n . Note that (r) in $\epsilon_{(r)}$ has a different meaning from n in ϵ_n in section 1.2 [distinguished by bracketing the subscript]. $|n\rangle' \equiv |\psi\rangle = \sum_r \lambda^r |(r)\rangle$ with $|(0)\rangle \equiv |n\rangle$ the unperturbed state. (r) does not refer to a single state of the unperturbed Hamiltonian but the combination of all the states that increases with the perturbation as λ^r .

The normalisation conditions in our new notation are $\langle (0) | (0) \rangle = 1$ and $\langle (0) | \psi \rangle = 1$. This implies that $\sum_{r \geq 1} \lambda^r \langle (0) | (r) \rangle = 0$. The only way this is possible for all λ is if each coefficient of λ^r in the sum is individually zero i.e. $\langle (0) | (r) \rangle_{r \neq 0} = 0$. Thus $\langle (0) | (r) \rangle = \delta_{r,0}$ or expressed in words $|(r)\rangle_{r \neq 0}$ is orthogonal to $|(0)\rangle$. Substituting our expansion for $|\Psi\rangle$ and E into the Schrodinger equation

$$(\hat{H}_0 + \lambda \hat{V}) \sum_r \lambda^r |(r)\rangle = \sum_{r,s} \lambda^{r+s} \epsilon_{(r)} |(s)\rangle. \quad (1.53)$$

Comparing coefficients of powers of λ^r

$$\hat{H}_0 |(r)\rangle + \hat{V} |(r-1)\rangle = \sum_{m=0}^r \epsilon_{(m)} |(r-m)\rangle \underset{r \geq 2}{=} \epsilon_{(0)} |(r)\rangle + \epsilon_{(1)} |(r-1)\rangle + \sum_{m=2}^r \epsilon_{(m)} |(r-m)\rangle \quad (1.54)$$

$$\Rightarrow (\hat{H}_0 - \epsilon_{(0)}) |(r)\rangle \underset{r \geq 2}{=} (-\hat{V} + \epsilon_{(1)}) |(r-1)\rangle + \sum_{m=2}^r \epsilon_{(m)} |(r-m)\rangle \quad (1.55)$$

$$\text{and} \quad (\hat{H}_0 - \epsilon_{(0)}) |(1)\rangle \underset{r=1}{=} (\epsilon_{(1)} - \hat{V}) |(0)\rangle \quad (1.56)$$

We would like to multiply through by $(\hat{H}_0 - \epsilon_{(0)})^{-1}$. This is only valid if it does not act on the component $|(0)\rangle$ since the latter would give 1/0. However if we first project out this component by acting with $\hat{Q} = 1 - |(0)\rangle \langle (0)|$ i.e. multiply by $(\hat{H}_0 - \epsilon_{(0)})^{-1} \hat{Q}$ the problem is avoided. Since $|(r)\rangle$ for $r \neq 0$ is orthogonal to $|(0)\rangle$ it is unaffected by \hat{Q} . \hat{Q} also commutes with \hat{H}_0 . Thus (with the notation that operators on a numerator act before (i.e. to the right of) those on a denominator)

$$|(r)\rangle = \frac{\hat{Q}}{\epsilon_{(0)} - \hat{H}_0} \left((\hat{V} - \epsilon_{(1)}) |(r-1)\rangle - \sum_{m=2}^{r-1} \epsilon_{(m)} |(r-m)\rangle \right) \quad (1.57)$$

$$= \frac{\hat{Q}}{\epsilon_{(0)} - \hat{H}_0} \left((\hat{V} - \epsilon_{(1)}) |(r-1)\rangle - \epsilon_{(2)} |(r-2)\rangle - \epsilon_{(3)} |(r-3)\rangle - \cdots - \epsilon_{(r-1)} |(1)\rangle \right) \quad (1.58)$$

$$|(1)\rangle = \frac{\hat{Q}}{\epsilon_{(0)} - \hat{H}_0} \hat{V} |(0)\rangle \quad (1.59)$$

This is a recursion relation and can be used to do perturbation theory up to any order. \hat{Q} simply means miss out the state $|n\rangle$ when doing sums over intermediate states. To complete the result we need $\epsilon_{(r)}$. This is obtained by taking the product of our original Schrödinger equation EQN 1.53 with $\langle(0)|$ and again comparing powers of λ^r .

$$\sum_r \lambda^{r+1} \langle(0)|\hat{V}|(r)\rangle = \sum_r \lambda^r \epsilon_{(r)} \quad (1.60)$$

$$\Rightarrow \epsilon_{(r)} = \langle(0)|\hat{V}|(r-1)\rangle \quad (1.61)$$

$$\epsilon_{(1)} = \langle(0)|\hat{V}|(0)\rangle \quad (1.62)$$

After all this we have (slipping in resolutions of the identity in the unperturbed basis $\mathbb{1} = \sum_p |p\rangle\langle p|$ before the \hat{Q} 's and noting $\sum_p |p\rangle\langle p| \hat{Q} = \sum_{p \neq n} |p\rangle\langle p|$)

$$|n\rangle' = |(0)\rangle + \lambda |(1)\rangle + \cdots = |n\rangle + \lambda \sum_{p \neq n} \frac{|p\rangle\langle p|V|n\rangle}{\epsilon_n - \epsilon_p} + \cdots \quad (1.63)$$

$$\epsilon_{n(1)} + \epsilon_{n(2)} = \lambda \langle n|\hat{V}|n\rangle + \lambda^2 \sum_{p \neq n} \left(\frac{\langle n|\hat{V}|p\rangle\langle p|\hat{V}|n\rangle}{\epsilon_n - \epsilon_p} \right) + \cdots \quad (1.64)$$

This is the same as perturbation result derived earlier up to second order for the energy shifts and first order for the change of states. We can however use the recursion formulae to calculate higher orders.

The above formulation of Perturbation theory is the standard Raleigh-Schrödinger one. As an aside, there is another less common form of perturbation theory known as Brillouin-Wigner perturbation theory. It has the full energy shift in the denominators i.e. $1/(E - \hat{H}_0)$ (see a supplementary problem). Brillouin-Wigner and Rayleigh-Schrödinger give identical results to second order.

The Hydrogen Atom

In this chapter non-relativistic wavefunctions for the hydrogen atom are reviewed. Perturbation theory is then applied to estimate the electrical polarisability of an isolated H-atom in its ground state. The Van-der-Waals interaction between two atoms is then discussed.

2.1 Revision

The Hamiltonian for the hydrogen atom is:

$$\hat{H} = \left[\frac{1}{2\mu r^2} \left(\hat{l}^2 - \hbar^2 \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right) \right] + V(r). \quad (2.1)$$

The term in square brackets is the kinetic energy comprising angular momentum and radial motion. \hat{l} is the angular momentum operator. μr^2 can be recognised as the moment of inertia. $\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)$ can be recognised as the radial part of the operator ∇^2 . For a central potential like the Coulomb potential we know that angular momentum is a conserved quantity (constant of the motion).

2.1.1 Angular momentum

A constant of the motion means that the angular momentum operators commutes with the Hamiltonian,

$$[\hat{H}, \hat{l}_z] = [\hat{H}, \hat{l}_x] = [\hat{H}, \hat{l}_y] = 0. \quad (2.2)$$

Thus Eigenstates of the Hamiltonian can be simultaneously eigenstates of \hat{H} and \hat{l} along any particular direction. We also found from the definition $\hat{l} = \hat{r} \times \hat{p}$

$$[\hat{l}_x, \hat{l}_y] = i\hbar \hat{l}_z, \quad [\hat{l}_y, \hat{l}_z] = i\hbar \hat{l}_x, \quad [\hat{l}_z, \hat{l}_x] = i\hbar \hat{l}_y. \quad (2.3)$$

The above commutation relations tell us the same state cannot simultaneously be an eigenstate of any two components of the angular momentum operator eg \hat{l}_x and \hat{l}_y .

Now consider $\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$ we have

$$[\hat{l}^2, \hat{l}_x] = 0, \quad [\hat{l}^2, \hat{l}_y] = 0, \quad [\hat{l}^2, \hat{l}_z] = 0, \quad (2.4)$$

and

$$[\hat{l}^2, \hat{H}] = 0. \quad (2.5)$$

Energy eigenstates can therefore also be chosen to be an eigenstate of both \hat{l}^2 and any one component of \hat{l} , which we choose arbitrarily to be \hat{l}_z .

We then found defining

$$\hat{l}_+ = \hat{l}_x + i\hat{l}_y, \quad \hat{l}_- = \hat{l}_x - i\hat{l}_y, \quad (2.6)$$

that

$$[\hat{l}_z, \hat{l}_+] = \hbar \hat{l}_+, \quad [\hat{l}_z, \hat{l}_-] = -\hbar \hat{l}_-, \quad [\hat{l}_+, \hat{l}_-] = 2\hbar \hat{l}_z. \quad (2.7)$$

From the first of these commutation relations we deduced that if state $|m\rangle$ is an eigenstate of \hat{l}_z with eigenvalue $\hbar m$ then $\hat{l}_+|m\rangle$ is proportional to another eigenstate denoted $|m+1\rangle$ with eigenvalue $\hbar(m+1)$. From the second we deduced $\hat{l}_-|m\rangle$ is proportional to an eigenstate $|m-1\rangle$ with eigenvalue $(m-1)\hbar$. The constant of proportionality has to be checked. Since the state is also an eigenstate of \hat{l}^2 and all $\hat{l}_{x,y,z}^2$ are positive it is clear that there must be maximum and minimum values of m for a given eigenvalue of \hat{l}^2 . This can only be reconciled if the constant of proportionality becomes zero at some point. Suppose this happens for $m = l$, then

$$\hat{l}_+|l\rangle = 0 \quad \text{for maximum } m=l \quad (2.8)$$

$$\hat{l}^2|l\rangle = \hat{l}_z^2 + \frac{1}{2}(\hat{l}_+\hat{l}_- + \hat{l}_-\hat{l}_+)|l\rangle \quad (2.9)$$

$$= \hbar^2 l^2 + \frac{1}{2}(2\hbar\hat{l}_z + 2\hat{l}_-\hat{l}_+)|l\rangle \quad \text{from the 3rd comm. reln in EQN 2.7} \quad (2.10)$$

$$= \hbar^2(l^2 + l)|l\rangle \quad (2.11)$$

$$= l(l+1)\hbar^2|l\rangle. \quad (2.12)$$

Thus the angular momentum states are described by two quantum numbers $|l, m\rangle$. From symmetry the lower cutoff for m must be $m = -l$ so that for a given l we have $-l \leq m \leq l$. Therefore $2l$ must be an integer and m must be an integer or half integer. For a scalar wavefunction the condition that ψ is single valued further constrains m to be an integer, rather than a half integer. The wavefunction for the intrinsic spin of an electron is not a scalar but a two component vector. The two components correspond to $j = 1/2; m_j = \pm 1/2$.

The operators \hat{l}^+ and \hat{l}^- can be used to generate different m eigenvalues with the same l . We can then replace \hat{l}^2 in EQN 2.1 with $l(l+1)$ and for a given l the states have a degeneracy $2l$ which enumerate the different values of m for each l . Solving for the full wavefunction $\Psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi)$ thus reduces to solving a differential equation in variable r ,

$$\left[\frac{\hbar^2}{2\mu r^2} \left(l(l+1) - \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right) \right] R(r) - \frac{e^2}{4\pi\epsilon_0 r} R(r) = ER(r). \quad (2.13)$$

This equation was solved last semester. A different approach to solving it by introducing raising and lowering operators for the three different quantum numbers, n, l, m is given at the end of this chapter. We briefly review the description of the solutions before considering perturbations.

2.2 Summary of Energy Levels

3 integer quantum numbers are needed to describe the scalar solutions for the non-relativistic Hydrogen atom wavefunction (n, l, m) .

$$n = 0, 1, 2, 3 \dots \quad 0 \leq l \leq n \quad -l \leq m \leq +l. \quad (2.14)$$

The energies of the allowed states are

$$E_n = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0} \frac{1}{(n+1)^2} = -\frac{\mu e^2}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{N^2} = -\frac{\text{Ry}}{N^2}. \quad (2.15)$$

The first pre-factor is easy to remember since for a fixed orbit of radius a_0 ; the energy of the lowest orbital is just half the potential energy. An aide memoire for the Bohr radius is that it can be written down from equating the centripetal force to the electrostatic force for a planar orbit of angular momentum \hbar ; i.e. $\mu v^2/a_0 = e^2/4\pi\epsilon_0 a_0^2$ and $\mu v a_0 = \hbar$ give $a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$. The Rydberg (Ry) is 13.6 eV. The levels are summarised in FIG 2.1. Note they are labelled by $N = n + 1$ and $l = 0, 1, 2, 3$ are referred to as s, p, d, f . The degeneracy due to the different allowed values of m is not shown in the figure.

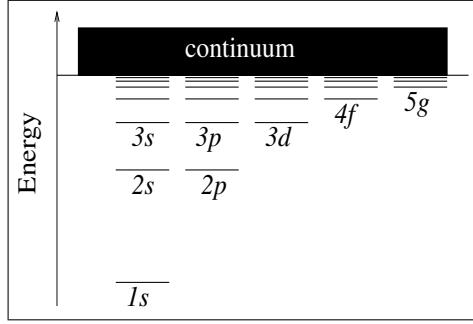


Figure 2.1: The Energy levels in the hydrogen atom.

2.3 Summary of wavefunctions

- Wavefunctions with $l = 0$ are labelled “ s ”, $l = 1$ are called “ p ”, $l = 2$ are called “ d ” and $l = 3$ “ f ”.

2.3.1 The s function - Y_{00}

The normalised wavefunction

$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} \quad (2.16)$$

which is just a constant. The s function is spherically symmetric.

2.3.2 The p functions - $Y_{10}, Y_{1,\pm 1}$

For the normalised $m = 0$ case

$$Y_{10}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta. \quad (2.17)$$

This function is not spherically symmetric. A useful way of representing such functions is on a *polar diagram*; the surface of points which are a distance $|Y_{10}(\theta, \phi)|$ from the origin (FIG 4.4). It comprises two touching spheres. Y_{10} is also called Y_{1z} , or simply p_z . The sphere for which Y_{10} is positive(negative) is often marked with a $+(-)$ (as in FIG 2.3).

$Y_{1,\pm 1}$ are complex. The phase gradient corresponds to a circulating particle current and a net angular momentum (along z for $Y_{1,\pm 1}$). The two states $Y_{1,\pm 1}$ can be combined to form

$$p_x = \frac{1}{\sqrt{2}} (Y_{1,1} + Y_{1,-1}) = \sqrt{\frac{3}{4\pi}} \sin \theta \cos \phi \quad (2.18)$$

$$p_y = -\frac{i}{\sqrt{2}} (Y_{1,1} - Y_{1,-1}) = \sqrt{\frac{3}{4\pi}} \sin \theta \sin \phi \quad (2.19)$$

which are real functions shown in FIG 2.3. These linear combinations are not eigenfunctions of \hat{l}_z . They are however eigenfunctions of \hat{l}^2 and \hat{H} and give a good physical picture of the angular variation of the electron wavefunction for spherical potentials that is useful when we come to think about electron wavefunctions in molecules.

2.3.3 Parity

The parity of the wavefunction is $(-1)^l$. The parity operator \hat{P} changes the sign of $r \rightarrow -r$. Since $\hat{P}^2 = 1$ and \hat{P} commutes with the Hamiltonian the eigenstates can be chosen to have a definite parity, either even (1) or odd (-1). The radial part of the wavefunction is by definition even so the parity is determined by l . Thus “ s ” and “ d ” states have even parity while “ p ” and “ f ” have odd parity.

2.3.4 The radial wavefunction

The solutions of the radial equation are the associated Laguerre functions. A few are shown in table 2.1 and FIG 2.4. Also shown in the figure are the corresponding values of $D(r) = 4\pi r^2 R_{nl}(r)^2$, called the *radial distribution function* or the *radial charge density*. This is the probability of finding an electron in a thin spherical shell of radius r . A number of features are apparent.

- The radial extent of the wavefunction increases with n .
- For a given n , the orbitals are increasingly prevented from approaching the nucleus as l increases in line with our intuition for a ‘centrifugal’ potential
- Only s electrons have non-zero amplitude at the nucleus.
- There are $n - l$ nodes in the radial wavefunction $R_{nl}(r)$.

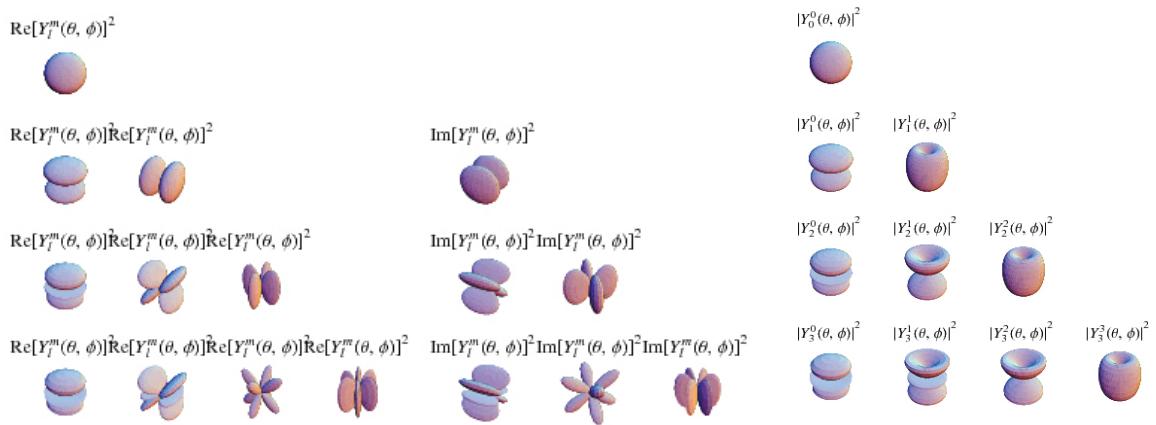


Figure 2.2: Spherical Harmonics. Rows are $l=0,1,2,3$. Columns are for increasing $|m| = 0, 1, 2, \dots$ (note $\pm m$ are not shown separately since $Y_{l,-m} = Y_{lm}^*$). The Real part of the wavefunction is shown in the left panel and the Imaginary part for $l \geq 1$ (it is zero for $l = 0$) in the centre panel. The modulus is shown in the right panel).

2.4 Experiment

Rydberg found that the series of absorption lines identified by Balmer in the optical spectrum of the hydrogen atom satisfied the relation

$$\frac{1}{\lambda} = R \left(\frac{1}{N_2^2} - \frac{1}{N_1^2} \right) \quad (2.20)$$

where $N_2 = 2, N_1 = 3, 4, 5, \dots$ and the constant R , had the value $1.09678 \times 10^7 \text{ m}^{-1}$. It was subsequently discovered that with different values of N_2 Balmer’s formula also described absorption lines in the UV (Lyman series $N_2 = 1$) and IR (Paschen series, $N_2 = 3$). These observations are well described by transitions between the energy levels given by EQN 2.15 as summarised in FIG 2.1. Later, with improved resolution it was found that many of the spectral lines are split; this is something we will return to in the next chapter where we consider relativistic corrections to the energy levels.

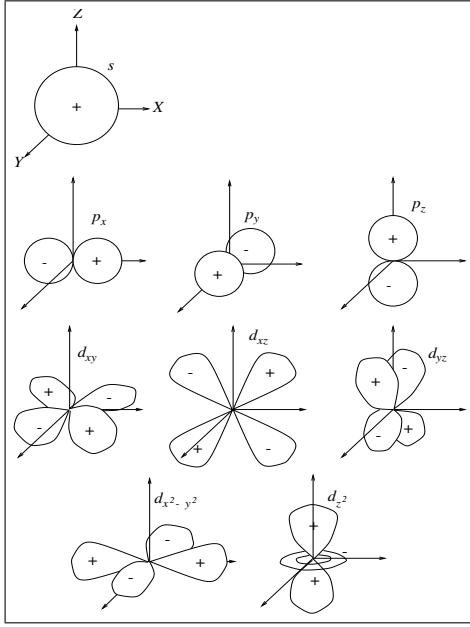


Figure 2.3: Polar diagrams for the s , p and d angular functions.

shell	subshell	n	l	$R_{nl}(r)$	E_n	nodes in R_{nl}	nodes in Y_{lm}	total nodes
K	1s	0	0	$\left[2\left(\frac{Z}{a_0}\right)^{3/2}\right] e^{-\frac{Zr}{a_0}}$	$-\frac{1}{2} \frac{Z^2 e^2}{4\pi\epsilon_0 a_0}$	0	0	0
L	2s	1	0	$\left[2\left(\frac{Z}{2a_0}\right)^{3/2}\right] \left(1 - \frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}}$	$-\frac{1}{4} \frac{1}{2} \frac{Z^2 e^2}{4\pi\epsilon_0 a_0}$	1	0	1
	2p	1	1	$\left[\frac{2}{\sqrt{3}} \left(\frac{Z}{2a_0}\right)^{3/2}\right] \frac{Zr}{2a_0} e^{-\frac{Zr}{2a_0}}$		0	1	1
M	3s	2	0	$\left[2\left(\frac{Z}{3a_0}\right)^{3/2}\right] \left(1 - 2\frac{Zr}{3a_0} + \frac{2}{3} \left(\frac{Zr}{3a_0}\right)^2\right) e^{-\frac{Zr}{3a_0}}$	$-\frac{1}{9} \frac{1}{2} \frac{Z^2 e^2}{4\pi\epsilon_0 a_0}$	2	0	2
	3p	2	1	$\left[\frac{4\sqrt{2}}{3} \left(\frac{Z}{3a_0}\right)^{3/2}\right] \frac{Zr}{3a_0} \left(1 - \frac{1}{2} \frac{Zr}{3a_0}\right) e^{-\frac{Zr}{3a_0}}$		1	1	2
	3d	2	2	$\left[\frac{2\sqrt{2}}{3\sqrt{5}} \left(\frac{Z}{3a_0}\right)^{3/2}\right] \left(\frac{Zr}{3a_0}\right)^2 e^{-\frac{Zr}{3a_0}}$		0	2	2

Table 2.1: Hydrogenic radial functions $R_{nl}(r)$ (the normalizing factors are given in square brackets for $\int_0^\infty dr r^2 |R_{nl}(r)|^2 = 1$).

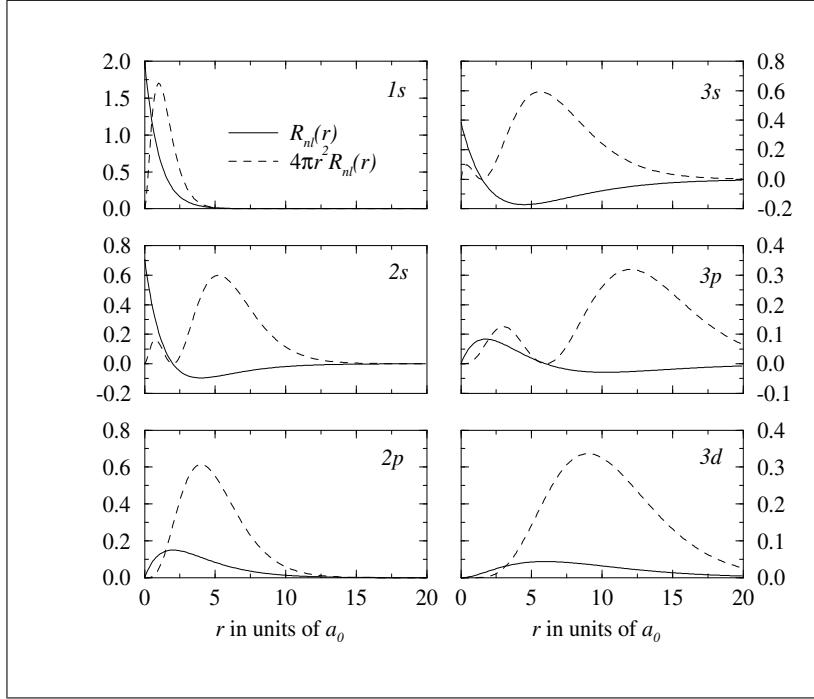


Figure 2.4: The solid lines show the $1s, 2s, 2p, 3s, 3p, 3d$ radial wavefunctions $R_{nl}(r)$ of the hydrogen atom (in units of $a_0^{-3/2}$). The dashed curves are the corresponding radial charge densities given by $4\pi r^2 R_{nl}^2$ (in units of a_0^{-1}).

2.5 Polarisability of the Hydrogen atom an application of perturbation theory

The objective is to calculate the polarisation coefficient α of a hydrogen atom in an electric field \mathcal{E} where the polarisation p is related to \mathcal{E} by $p = \alpha\mathcal{E}$. The change in energy of a hydrogen atom as we increase the electric field from zero to \mathcal{E} calculated with perturbation theory is given by

$$\Delta E_0 = - \int_0^E p.d\mathcal{E} = -\frac{\alpha\mathcal{E}^2}{2} \quad (2.21)$$

where we remain in the ground state (zero entropy). We now justify this expression. The final Hamiltonian with the field applied contains two terms \hat{H}_0 and \hat{H}_1 . \hat{H}_0 corresponds to the internal energy U in thermodynamics and $\hat{H}_1 = -p.\mathcal{E}$ is the interaction energy with the external field. From thermodynamics we know that $\Delta U = \int \mathcal{E}.dp = (1/2)\alpha\mathcal{E}^2$ for changes at constant entropy. Therefore

$$\Delta E_0 = \Delta U - p.\mathcal{E} = (1/2)\alpha\mathcal{E}^2 - \alpha\mathcal{E}^2 = -(1/2)\alpha\mathcal{E}^2 \quad (2.22)$$

ΔE_0 may also be viewed as the change of the thermodynamic analogue of enthalpy $H = U + pV$, that is “ H ” = $U - p.\mathcal{E}$, which includes potential energy due to interaction with the surroundings.

2.5.1 Classical solution

A classical estimate is made by considering the atom to be a metallic sphere of radius a_0 . From classical electromagnetism the induced electric dipole is found by requiring the total potential from a dipole at the centre of the sphere (that may be thought of as an image-charge) and the applied field together give a constant potential on the surface of the sphere. The classical induced dipole moment is then

$$P = 4\pi\epsilon_0 a_0^3 \mathcal{E} \quad (2.23)$$

and

$$\Delta E = -\frac{1}{2}4\pi\epsilon_0 a_0^3 \mathcal{E}^2 \quad (2.24)$$

2.5.2 Quantum treatment

The perturbation is $\hat{V} = e\mathcal{E}z$. The shift in energy due to the perturbation includes the interaction with the field.

The perturbation has odd parity. The shift in energy from first order perturbation theory is proportional to the product of $\langle \psi | V(r) | \psi \rangle \propto \int d^3r z |\psi(r)|^2$. Since the product of any wavefunction with its own complex conjugate always has even parity (whatever the parity of the wavefunction) the integrand is odd and therefore vanishes. We therefore need to look at the second order perturbation theory term. The shift in energy of the ground state is

$$\Delta E = \sum_{\text{excited}} \frac{|\langle (n, l, m)_{\text{etc}} | e\mathcal{E}z | 0, 0, 0 \rangle|^2}{\epsilon_0 - \epsilon_{\text{excited}}} \quad (2.25)$$

The “etc” refers to the fact that as well as bound states we must also include unbound states in the sum. We denote the result ΔE_{bound} if only the bound states $|(n, l, m)\rangle$ are included in the sum. To analyse this contribution note that $zY_{0,0} = r \cos \theta Y_{0,0} = Y_{1,0}/\sqrt{3}$. Thus from the orthogonality of the Y_{lm} we only have a contribution from excited states $(n, 1, 0)$. Thus

$$\Delta E_{\text{bound}} = \frac{1}{3} e^2 \mathcal{E}^2 \sum_{n=1}^{\infty} \frac{|\langle n, 1, 0 | r | 0, 0, 0 \rangle_R|^2}{\epsilon_0 - \epsilon_n} \quad (2.26)$$

$$= \frac{1}{3} e^2 \mathcal{E}^2 \sum_{n=1}^{\infty} \frac{(\int_0^{\infty} R_{n,1}(r) R_{0,0}(r) r^3 dr)^2}{\epsilon_0 - \epsilon_n} \quad (2.27)$$

where the subscript R denotes we are considering only the Radial wavefunctions. The first term of the sum gives

$$\Delta E_{\text{1st term}} \underset{\text{see problems}}{=} -\frac{4!}{18} \frac{4}{3\epsilon_0} \left(\frac{2}{3}\right)^{10} a_0^2 (e^2 \mathcal{E}^2) = -1.48 [4\pi\epsilon_0 a_0^3 \mathcal{E}^2]. \quad (2.28)$$

almost 3 times the classical value. The summed series converges to $-1.83 [4\pi\epsilon_0 a_0^3 \mathcal{E}^2]$. Since inclusion of the unbound states will lower the energy further the above is an upper estimate of ΔE i.e. $\Delta E < \Delta E_{\text{bound}}$.

2.5.3 Sum rules

We can estimate a lower bound for α including the contribution from the unbound states by noting the following

$$\sum_j |V_{j0}|^2 = \sum_j V_{0j}^* V_{j0} = (V^2)_{00} \quad (2.29)$$

$$= \langle 0, 0, 0 | e^2 \mathcal{E}^2 z^2 | 0, 0, 0 \rangle \quad (2.30)$$

$$= e^2 \mathcal{E}^2 a_0^2 \quad (2.31)$$

The sum is over all excited states and $V_{j0} = \langle \text{excited}_j | e\mathcal{E}z | 0, 0, 0 \rangle$. The sum in EQN 2.25 excludes the term $(n, l, m) = (0, 0, 0)$ whereas the sum over j EQN 2.29 includes this term. However, the excluded term EQN 2.25 is zero so this difference is immaterial. $\epsilon_{\text{excited}} - \epsilon_0$ is always positive so it is clearer to remove the minus sign from the denominator in EQN 2.25 and work with $\epsilon_{\text{excited}} - \epsilon_0$. $\epsilon_{\text{excited}} - \epsilon_0 > \epsilon_1 - \epsilon_0$ therefore the sum with denominator replaced by $\epsilon_1 - \epsilon_0 = (3/4) \epsilon_0$ gives an overestimate of the magnitude of ΔE i.e. a lower bound to the value of ΔE ,

$$\Delta E > -e^2 \mathcal{E}^2 \frac{a_0^2}{\epsilon_1 - \epsilon_0} = -\frac{4}{3} e^2 \mathcal{E}^2 \frac{a_0^2}{\epsilon_0} = -\frac{8}{3} [4\pi\epsilon_0 a_0^3 \mathcal{E}^2]. \quad (2.32)$$

2.5.4 Exact answer

Combining the above limits, the exact answer is therefore somewhere between $-2.67 [4\pi\epsilon_0 a_0^3 \mathcal{E}^2] < \Delta E < -1.83 [4\pi\epsilon_0 a_0^3 \mathcal{E}^2]$. A complete calculation including the unbound states gives $\Delta E = -2.25 [4\pi\epsilon_0 a_0^3 \mathcal{E}^2]$. Thus $\alpha = 4.5\alpha_{\text{classical}}$.

2.5.5 f-sum rule

There is another sum rule known as the f-sum rule that we briefly mention here - it is discussed further in the problems. The second order perturbation theory expression for the polarisability we have derived above is

$$\alpha_{\mathcal{E}} = 2e^2 \sum_j \frac{|\langle j|z|0\rangle|^2}{\hbar\omega_{j0}} \quad (2.33)$$

This can be written

$$\alpha_{\mathcal{E}} = \sum_j \frac{e^2/m_e}{\omega_{j0}^2} f_j \quad (2.34)$$

with

$$f_j = |\langle j|z|0\rangle|^2 \frac{2m_e\omega_{j0}}{\hbar}. \quad (2.35)$$

Each term $\frac{e^2/m_e}{\omega_{j0}^2}$ is the same as the polarisability of a harmonic oscillator with resonant frequency ω_{j0} , charge e and mass m_e . The f_j 's are the 'strengths' of the contribution of each 'oscillator' mode to the sum. The f_j 's are therefore called oscillator strengths.

The f-sum rule (see problems for a proof) states

$$\sum_j f_j = 1. \quad (2.36)$$

The polarisability of an atom thus resembles a superposition of the particle attached to a series of different springs with spring constants corresponding to the various frequencies of the excitations from the ground state. The weights of the contributions from each spring 'naturally' add up to 1. The expression for f_j can be re-arranged to

$$f_j = \frac{|z_{j0}|^2}{r_{j0}^2} \quad (2.37)$$

where r_{j0}^2 is the expectation value of the (displacement)² of a 1D harmonic oscillator of frequency ω_{j0} in its ground state and $z_{j0} = \langle j|z|0\rangle$.

2.6 Van der Waals interaction - an application of perturbation theory

2.6.1 Introduction

We consider the case of two hydrogen atoms without spin first and then generalise to discuss Van der Waals bonding more generally.

2.6.2 Van der Waals interaction

The induced dipole-dipole interaction energy can be understood from the following Hamiltonian describing two hydrogen atoms

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1. \quad (2.38)$$

\mathcal{H}_0 describes two isolated atoms with r_1 and r_2 the distances of the electrons to the respective nuclei.

$$\mathcal{H}_0 = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} \quad (2.39)$$

The interaction between the two atoms with R the distance between the nuclei is

$$\mathcal{H}_1 = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{|\vec{R}|} + \frac{1}{|\vec{R} + \vec{r}_2 - \vec{r}_1|} - \frac{1}{|\vec{R} + \vec{r}_2|} - \frac{1}{|\vec{r}_1 - \vec{R}|} \right), \quad (2.40)$$

which can be expanded for $r_1, r_2 \ll R$ and $R \parallel z$ as

$$\mathcal{H}_1 = \frac{e^2}{4\pi\epsilon_0 R^3} (x_1 x_2 + y_1 y_2 - 2z_1 z_2), \quad (2.41)$$

with $\vec{r}_1 = (x_1, y_1, z_1)$ etc. This can be recognised as $-\frac{p_1 \cdot \mathcal{E}_2}{2} - \frac{p_2 \cdot \mathcal{E}_1}{2}$ the energy of each dipole in the electric field of the other (recall the potential from a dipole is $\vec{r} \cdot \vec{p} / (4\pi\epsilon_0 r^3)$) and can also be written

$$\mathcal{H}_1 = \frac{1}{4\pi\epsilon_0 R^3} (p_{1x} p_{2x} + p_{1y} p_{2y} - 2p_{1z} p_{2z}). \quad (2.42)$$

2.6.3 semi-classical value

Semiclassically we might consider the electric field from p_1 to induce a polarisation on the second atom lowering its energy and vice-versa to give

$$\Delta E_{\text{semi-classical}} = -\frac{1}{2} \alpha_2 \mathcal{E}_1(r_2)^2 - \frac{1}{2} \alpha_1 \mathcal{E}_2(r_1)^2 \quad (2.43)$$

$$= 2 \times \frac{1}{2} \alpha_2 \frac{1}{(4\pi\epsilon_0)^2 R^6} (p_{1x}^2 + p_{1y}^2 + 4p_{1z}^2) \quad (2.44)$$

$$= -4.5 \times 6 \frac{e^2 a_0^5}{(4\pi\epsilon_0) R^6} \quad (2.45)$$

where in the last line $p_x^2 = e^2 \langle x^2 \rangle = e^2 a_0^2$ etc. In the line above we simply noted that the terms for p_1 and p_2 are equal and used the expression for the electric field from a dipole $\mathcal{E}_{\parallel} = 2P/4\pi\epsilon_0 R^3$, $\mathcal{E}_{\perp} = -P/4\pi\epsilon_0 R^3$.

2.6.4 QM calculation

We treat the electrons as distinct in what follows so that the wavefunction can be written as a product $|\Psi(r_1, r_2)\rangle \approx |\Psi_n(r_1)\rangle |\Psi_{n'}(r_2)\rangle = |n\rangle |n'\rangle \equiv |n, n'\rangle$ where n and n' label isolated atomic orbitals. This comprises two approximations. (i) the *Heitler-London* approximation, which neglects states where both electrons are associated with the same atom, justified since this costs a lot of energy. (ii) it ignores the requirement that the wavefunction has to be antisymmetric under particle exchange; this is valid if the atoms are sufficiently far apart that the orbitals from each atom have negligible overlap.

First order perturbation theory gives no energy shift (the operator x links states with orbital angular momentum that differ by 1). The gain in energy of the ground state is given by second order perturbation theory (which always lowers the energy).

$$\Delta E = \sum_{n,n'} \frac{|\langle n, n' | \mathcal{H}_1 | 0, 0 \rangle|^2}{2\epsilon_0 - \epsilon_n - \epsilon'_n} \quad (2.46)$$

The sum is over all excited states (n, n') of the two isolated atoms (here n and n' stand for the full set of quantum numbers of the two excited states $n \equiv (n, l, m)$ and $n' \equiv (n', l', m')$) and $(0, 0)$ denotes the ground state. For the case of hydrogen atoms only terms (n, n') with orbital momenta of one will contribute (and with only for one unique combination of m 's for each term $x_1 x_2, y_1 y_2, z_1 z_2$). To get an estimate of the shift in energy we can use the sum rule,

$$\langle 0, 0 | H_1^2 | 0, 0 \rangle = \langle 0, 0 | \frac{e^4}{(4\pi\epsilon_0)^2 R^6} (x_1 x_2 + y_1 y_2 - 2z_1 z_2)^2 | 0, 0 \rangle \quad (2.47)$$

$$= \frac{e^4}{(4\pi\epsilon_0)^2 R^6} \langle 0, 0 | x_1^2 x_2^2 + y_1^2 y_2^2 + 4z_1^2 z_2^2 | 0, 0 \rangle \quad (2.48)$$

$$= \frac{6a_0^4 e^4}{(4\pi\epsilon_0)^2 R^6} \quad (2.49)$$

since the cross terms like $x_1x_2y_1y_2$ vanish for our approximations (since the $1s$ wavefunction is odd under $x \rightarrow -x$). Putting in our lower and upper limits worked out for the polarisability problem gives

$$\frac{6a_0^4 e^4}{(4\pi\epsilon_0)^2 R^6} \frac{1}{2\epsilon_0 - 2\epsilon_1} < \Delta E \quad (2.50)$$

$$-\frac{8a_0^5 e^2}{(4\pi\epsilon_0)R^6} < \Delta E \quad (2.51)$$

The exact value (not derived here) including unbound states is

$$\Delta E = -6.5 \frac{a_0^5 e^2}{(4\pi\epsilon_0)R^6} \quad (2.52)$$

The semi-classical value had a magnitude nearly $4 \times$ too large. The ‘error’ in the semi-classical estimate was assuming that only one of the atoms is excited to give a polarisation and this induced a polarisation in the other. In the rigorous quantum calculation we have just done we saw that the lowest excited state contributing to the interaction had both atoms excited.

2.6.5 Van der Waals Bonding

The key result is that the effective potential $\Delta E(R)$ is proportional to the matrix element squared $\propto R^{-6}$ whatever the nature of the neutral particles. Therefore in general

$$\Delta E = -\frac{A}{R^6} \quad (2.53)$$

with A a material dependent constant.

This induced dipole-dipole attraction will be balanced by a repulsive interaction term at short distances. The origin of the repulsive term comes from the Coulomb potential in combination with the Pauli exclusion principle and is more fully explained in a later section on covalent bonding. To get this term we have to consider that the electrons are no longer distinct particles - incredibly the indistinguishability of electrons keeps matter from imploding.

In words, as two non-degenerate (eg full shell) electron clouds on separate atoms are pushed together the Pauli principle forces the wavefunction to be antisymmetric. The extra wiggles this puts into the wavefunction pushes up the kinetic energy. Since this is coming from an overlap of two wave functions it would be natural to expect it to have an exponential dependence on distance. Adding the induced dipole-dipole part gives an energy dependence on R for the total potential

$$u(r) = -\frac{A}{R^6} + B \exp\left(-\frac{R}{C}\right), \quad (2.54)$$

with A, B, C material dependent constants. This is referred to as the 6-exponential form. The repulsion term is often approximated instead for computational convenience by a power law $1/R^n$ with $n > 6$. Conventionally $n = 12$ is chosen corresponding to the famous Lennard-Jones potential (originally used for the study of gases!).

$$u(R) = -\frac{A}{R^6} + \frac{B}{R^{12}} = 4\epsilon \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right], \quad (2.55)$$

which is expressed in terms of only two material dependent constants (A and B , or ϵ and σ). The symbol ϵ in this section has nothing to do with the symbol for unperturbed energy levels ϵ_i used elsewhere).

Table 2.2 gives some typical values of σ and ϵ for the noble gases. These values were determined by fitting data taken in the gaseous state i.e. low density so there will be some error in them, although they should be of the correct order of magnitude. Notice that ϵ scales with the melting temperature of the solid. The atomic radius (Bohr radius = 0.53 Å) should be compared with the bond length r_0 to assess/confirm the validity of the small r/R ($\approx a/r_0$) approximation used in deriving the Van der Waals attraction.

Some general comments are:

			Ne	Ar	Kr	Xe
a, atomic radius	(Å)	theory	0.38	0.71	0.88	1.03
ϵ	(meV)		3.10	10.40	14.00	20.00
σ	(Å)		2.74	3.40	3.65	3.98
melting point	(K)		24.7	84	116	161
r_0	(Å)	expt.	3.13	3.75	3.99	4.33
$r_0 = 1.09\sigma$	(Å)	theory	2.99	3.71	3.98	4.34
u_0	meV/atom	expt.	-20	-80	-110	-170
$u_0 = -8.6\epsilon$	meV/atom	theory	-27	-89	-120	-172
$B_{T=0}$	GPa	expt.	1.1	2.7	3.5	3.6
$B_{T=0} = 75\epsilon/\sigma^3$	GPa	theory	1.81	3.18	3.46	3.81

Table 2.2: Lennard-Jones parameters for noble gases. The parameters are explained in the text.

- Van der Waals bonds are the weakest type of bonding and therefore only considered between neutral molecules in the absence of stronger bonding. Examples are the bonding between noble gas atoms (except helium, which is a quantum liquid even down to low temperature) and between molecules.
- the interaction is almost isotropic for the Noble gases (since closed shells are isotropic) resulting in close packed structures in the solid state.
- The interaction comprises an induced dipole-dipole attraction which is balanced by a short range Pauli repulsion.

We now apply the Lennard Jones potential to estimate the binding energy and bulk modulus of a molecular crystal.

2.7 Calculation of the wavefunctions for the non-relativistic Hydrogen atom with raising and lowering operators

This section contains more advanced non examinable material.

In this section the wavefunctions for the hydrogen atom are calculated in a different way from last semester. This is closer to the method originally used by Schrödinger. While it is very powerful and may be generalised to other problems, it is almost absent from quantum mechanics textbooks.

2.7.1 Solution of the Radial equation

The objective is to solve EQN 2.13 for the radial wavefunction by introducing appropriate raising and lowering operators. Great care is needed dealing with the radial coordinate in 3D (or any dimension > 1). The inner product between two radial parts of the wave function $\langle R_1 | R_2 \rangle = \int_0^\infty r^2 dr R_1^*(r) R_2(r)$ differs from the 1D expression owing to the weighting r^2 in the integrand. Writing $R(r)r = \phi(r)$ and working with ϕ we revert to our familiar 1D definitions for inner products. There is a natural length scale in the problem, the Bohr radius $a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$. The Schrödinger equation for ϕ (multiplying through by $2\mu r/\hbar^2$) is

$$\frac{l(l+1)}{r^2} \phi - \phi'' - 2\frac{1}{ra_0} \phi = \frac{2\mu E}{\hbar^2} \phi \quad (2.56)$$

If we write the radial coordinate in terms of a_0 by introducing dimensionless coordinate $\rho = r/a_0$, multiply the above equation by a_0^2 and express the energy as $E = -[\frac{1}{2}e^2/(4\pi\epsilon_0 a_0)]\epsilon_{nl}$ where ϵ is dimensionless

(we expect E to be negative (binding) so we chose the sign to make $\epsilon_n > 0$) the radial Schrödinger equation is

$$\hat{H}_l \phi_{nl} \equiv \left[\frac{l(l+1)}{\rho^2} - \frac{2}{\rho} - \frac{\partial^2}{\partial \rho^2} \right] \phi_{nl} = -\epsilon_{nl} \phi_{nl}. \quad (2.57)$$

We can factor the LHS

$$\hat{H}_l = \underbrace{\left(\frac{l}{\rho} - \frac{1}{l} - \frac{\partial}{\partial \rho} \right)}_{\hat{L}_l^+} \underbrace{\left(\frac{l}{\rho} - \frac{1}{l} + \frac{\partial}{\partial \rho} \right)}_{\hat{L}_l^-} - \frac{1}{l^2}. \quad (2.58)$$

The radial Schrödinger equation can be written as

$$\hat{L}_l^+ \hat{L}_l^- \phi_{nl} = \left(\frac{1}{l^2} - \epsilon_{nl} \right) \phi_{nl}. \quad (2.59)$$

L^+ and L^- are Hermitian conjugates. This looks similar to the second quantised form of the harmonic oscillator equation and we will now show that \hat{L}^- gives a solution that lowers by l by 1, but leaves the energy unchanged. Based on our experience with the harmonic oscillator we would like to evaluate the commutator of L^+ and L^- . We can see referring back to EQN 2.57 that

$$\hat{H}_{(l-1)} = \hat{L}_l^- \hat{L}_l^+ - \frac{1}{l^2} \quad (2.60)$$

Thus $[\hat{L}_l^+, \hat{L}_l^-] = \hat{H}_l - \hat{H}_{(l-1)}$ (rather than a constant for the SHO). We now act with \hat{L}_l^- on both sides of EQN 2.59 and use EQN 2.60 to give

$$\left[\hat{H}_{(l-1)} + \frac{1}{l^2} \right] \hat{L}_l^- \phi_{nl} = \left(\frac{1}{l^2} - \epsilon_{nl} \right) \hat{L}_l^- \phi_{nl} \quad (2.61)$$

$$\implies \hat{H}_{(l-1)} (\hat{L}_l^- \phi_{nl}) = -\epsilon_{n,l} (\hat{L}_l^- \phi_{nl}) \quad (2.62)$$

This last equation shows us that $(\hat{L}_l^- \phi_{nl}) \propto \phi_{n,l-1}$ and that the Eigenvalue is unchanged. The different values of l generated by our lowering operator thus have the same energy and we can henceforth drop the subscript l on $\epsilon_{n,l}$. We can also show $\hat{L}_{(l+1)}^+ \phi_{nl} \propto \phi_{n,l+1}$. For a given n the series must terminate when l gets to zero. We could work out the constant of proportionality and find the condition for this to vanish. We can check this for decreasing l but it does not teach us anything further. The sequence of repeated application of \hat{L}_l^+ i.e. $\dots \hat{L}_{l+2}^+ \hat{L}_{l+1}^+ \hat{L}_l^+$ must also terminate since we cannot increase l and the rotational kinetic energy for a given ϵ_n indefinitely while keeping the total energy constant. We assume that the wavefunctions are quadratically integrable (as required by the axioms of QM). Then choosing the constant of proportionality $a_{n,l}$ to enforce normalisation $\hat{L}_{(l+1)}^+ \phi_{nl} = a_{(n,l+1)} \phi_{(n,l+1)}$ (here with respect to ρ) we have

$$a_{(n,l+1)}^2 \int \phi_{n,l+1}^* \phi_{n,l+1} d\rho = a_{(n,l+1)}^2 = \int d\rho (\hat{L}_{(l+1)}^+ \phi_{nl})^* \hat{L}_{(l+1)}^+ \phi_{nl} \quad (2.63)$$

$$= \int d\rho \phi_{nl}^* \hat{L}_{(l+1)}^- \hat{L}_{(l+1)}^+ \phi_{nl} \quad (2.64)$$

$$= \int d\rho \phi_{nl}^* \left(\hat{H}_l + \frac{1}{(l+1)^2} \right) \phi_{nl} \quad (2.65)$$

$$= -\epsilon_n + \frac{1}{(1+l)^2} \quad (2.66)$$

$$\implies a_{(n,l+1)} = \sqrt{\frac{1}{(1+l)^2} - \epsilon_n} \quad (2.67)$$

For the sequence to terminate at a maximum value of $l = n$ then $\epsilon_n = 1/(n+1)^2$.

Thus we have found the values of the allowed energies. It is worth reflecting that we have done this by imposing boundary conditions that the wave-function is square integrable. It does not matter what the exact normalisation choice we make is. To normalise the wavefunction ϕ with respect to integration with respect to r instead of ρ , there is an extra multiplicative factor $1/\sqrt{a_0}$, but the conclusions are unchanged. If we worked with $R(r)$ this would add a complication of including the radial weight function correctly, which we have avoided by working with ϕ .

2.7.2 Generating function for higher n -states of R_{nl}

In the previous section we found the energy levels and how to change l for fixed n . However we are lacking an operator for raising and lowering n . To get this we will factor EQN 2.57 differently. We first replace ϵ_{nl} by $1/(n+1)^2$ and we change our coordinate variable to $\rho = x(n+1)$ (x is a new dimensionless radial coordinate). This serves to move n from the denominators to the numerators in the transformed Schrödinger equation

$$\left(x^2 - 2(n+1)x - x^2 \frac{\partial^2}{\partial x^2}\right) \phi_n = -l(l+1)\phi_n \quad (2.68)$$

The operator on the LHS \hat{h}_n factorizes as

$$\hat{h}_n = \underbrace{\left(x - n - x \frac{\partial}{\partial x}\right)}_{\hat{A}_n^+} \underbrace{\left(x - n + x \frac{\partial}{\partial x} - 1\right)}_{\hat{B}_n^- = \hat{A}_n^- - 2} - n(n+1) \quad (2.69)$$

and

$$\hat{h}_{(n-1)} = \underbrace{\left(x - n + x \frac{\partial}{\partial x} - 1\right)}_{\hat{B}_n^-} \underbrace{\left(x - n - x \frac{\partial}{\partial x}\right)}_{\hat{A}_n^+} - n(n+1) \quad (2.70)$$

The general game plan is hopefully now becoming clear. We have a second order differential equation that depends on some integer quantity (now n , but previously in chapter 2.7.1 this was l). We can always factor a second order equation into a product of two operators that include only first order derivatives. We however do this in such a way that reversing their order generates the solution for a new value of n . The operators are then raising and lowering operators.

Here \hat{A}_n^+ will again be shown to be the raising operator for n . Note in this case the lowering operator \hat{B}_n^- is no longer its Hermitian conjugate. To show that \hat{A}_n^+ is the raising operator we proceed as before applying \hat{A}_n^+ to both sides of EQN 2.70 operating on $\phi_{(n-1,l)}$

$$-l(l+1)(\hat{A}_n^+ \phi_{(n-1,l)}) = \hat{A}_n^+ (\hat{B}_n^- \hat{A}_n^+ - n(n+1)) \phi_{(n-1,l)} \quad (2.71)$$

$$= (\hat{h}_n + n(n+1) - n(n+1))(\hat{A}_n^+ \phi_{(n-1,l)}) \quad (2.72)$$

$$\implies \hat{A}_n^+ \phi_{(n-1,l)} = a_{n,l} \phi_{n,l} \quad (2.73)$$

with $a_{n,l}$ the proportionality constant. We can require the solutions are normalisable which confirms that $n \geq l$.

To summarise this section we have found generating functions that act on R_{nl} to increase l by one or n by one. The precise normalisation constants are most easily found once the required function has been generated; expressions can be derived including normalisation but this is laborious. Without normalisation we have

$$\left(\frac{l}{\rho} - \frac{1}{l} - \frac{\partial}{\partial \rho}\right) \phi_{n,l-1} \propto \phi_{n,l} \quad (2.74)$$

$$\left(x - n - x \frac{\partial}{\partial x}\right) \phi_{(n-1,l)}(x) \propto \phi_{n,l} \quad (2.75)$$

$$(2.76)$$

The use of the last equation requires some care. It requires working with x until the desired (n,l) is reached and then substituting $x = \rho/(n+1)$ at the end.

The ground state is $|n,l,m\rangle = |0,0,0\rangle$. The wavefunction satisfies $\hat{A}_0^- \phi_{0,0} = [x + x(\partial/\partial x) - 1]\phi_{0,0} = 0$.

We can solve this to give

$$\phi_{0,0} = 2xe^{-x} \quad (2.77)$$

$$R_{0,0}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0} \quad (2.78)$$

$$\Psi_{0,0,0} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}. \quad (2.79)$$

We can then generate all R_{nl} with our raising operators. e.g. starting with $\phi_{0,0}$ above we find $\phi_{1,0} \propto (x^2 - x)e^{-x} \implies R_{1,0} = \phi_{1,0}/r \propto (\rho/2 - 1)e^{-\rho/2}$. Again the normalisation is most easily done at the end. The first few Radial eigenfunctions are shown in table 2.1. This is an easy job for a computer to generate.

2.7.3 The generating function for higher l -states of the angular function Y_{lm}

We have already met ladder operators for changing m with fixed l . For completeness, we now derive the raising operator for l operating on the angular part of the wavefunction. The angular coordinates satisfy [with units $\hbar = 1$]

$$\hat{l}^2 Y_{lm} = l(l+1)Y_{lm} \quad (2.80)$$

where $Y_{lm} \equiv Y_{lm}(\theta, \phi)$ is the angular part of the wavefunction (spherical harmonics). Referring back to the definitions of gradient in spherical coordinates (still with $\hbar = 1$).

$$\hat{l}^2 = -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} - \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (2.81)$$

$$= -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{m^2}{\sin^2 \theta} \quad (2.82)$$

Multiplying EQN 2.80 by $\sin^2 \theta$ gives

$$\underbrace{-\left(\sin \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + l(l+1) \sin^2 \theta\right)}_{\hat{h}_l} Y_{lm} = -m^2 Y_{lm} \quad (2.83)$$

which we can factorise as

$$\underbrace{\left(-l \cos \theta - \sin \theta \frac{\partial}{\partial \theta}\right)}_{\hat{L}_l^+} \underbrace{\left(-l \cos \theta + \sin \theta \frac{\partial}{\partial \theta}\right)}_{\hat{L}_l^-} - l^2 Y_{lm} = -m^2 Y_{lm} \quad (2.84)$$

We can then show

$$\hat{L}_l^+ \hat{L}_l^- - l^2 = \hat{h}_l \quad (2.85)$$

$$\hat{L}_l^- \hat{L}_l^+ - l^2 = \hat{h}_{l-1} \quad (2.86)$$

So as usual we have $\hat{h}_l - \hat{h}_{l-1} = [\hat{L}_l^+, \hat{L}_l^-]$ and we can identify \hat{L}_{l+1}^+ as the raising operator for the angular part of the wavefunction $L_{l+1}^+ Y_{l,m} \propto Y_{l+1,m}$.

Similarly L^- is the lowering operator. Further we can see that Y_{00} is a constant since $L_0^- Y_{00} = 0$. Applying L^+ to Y_{00} we get $Y_{10} \propto \cos \theta$ etc. All the angular parts of the wavefunction can thus be generated and the first few are sketched in FIG 4.4.

There is a very useful further result we get from this analysis. We note that

$$\hat{L}_l^+ + \hat{L}_l^- = 2l \cos(\theta) \quad (2.87)$$

$$\hat{L}_l^+ - \hat{L}_l^- = 2l \frac{\partial}{\partial z} = 2l \sin(\theta) \frac{\partial}{\partial \theta} \quad (2.88)$$

The first of these equations shows that $\cos \theta$ can be written as a linear combination of the raising and lowering operators. Thus if we operate on an angular momentum eigenstate $|l, m\rangle$ (ie. a state of definite l) with the z-coordinate operator $z = r \cos \theta$ this will produce states with angular parts $|l+1, m\rangle$ and $|l-1, m\rangle$ i.e. with the total angular momentum quantum number changed by one.

Degenerate Perturbation Theory

3.1 Introduction

Our earlier derivation of perturbation theory made the assumption that the unperturbed state of interest is non-degenerate. The assumption was made when we divided by $\epsilon_s - \epsilon_i$ to get the first order expression for a_s ; if $\exists i (i \neq s)$ such that $\epsilon_i = \epsilon_s$ we commit the cardinal sin of dividing both sides by zero. We use d to denote the set of states degenerate with s .

If there are degenerate states we need to go back to the secular equation, EQN 1.8

$$\sum_j (H_1)_{ij} a_j = (E_s - \epsilon_i) a_i \quad \text{Secular equation} \quad (3.1)$$

If $\epsilon_i \sim E_s$ for $i \in d$ we see that these a_i are not small. The solution is to treat all a_i for $i \in d$ (including a_s) on an equal footing, but to continue to treat $a_i (i \notin d)$ as small. Keeping only first order terms the Secular equation (and dropping the subscript s) then simplifies to

$$\sum_d (H_1)_{id} a_d = (E - \epsilon_d) a_i \quad i \in d \quad (3.2)$$

$$a_i = \sum_d \frac{(H_1)_{id} a_d}{\epsilon_d - \epsilon_i} \quad i \notin d \quad (3.3)$$

The first of these equations is simply a matrix equation. $\Delta E = E - \epsilon_d$ are the eigenvalues of a $d \times d$ sub-matrix of H_1 and the eigenvectors give the corresponding states. To summarise first order degenerate perturbation theory corresponds to exactly diagonalising the Hamiltonian keeping only those states that are degenerate with the state of interest.

The procedure is best illustrated with an example. In the following we write $H_1 \equiv V$.

3.2 An example: two dimensional well

Consider a particle of mass M in a 2D square infinite well. The potential is zero for $-a/2 < x < a/2$ and $-a/2 < y < a/2$ and infinite elsewhere. How are the eigenstates and energy levels changed when a potential $V = \lambda xy$ is applied?

The energy eigenstates for H_0 are

$$\Psi_{n,m}(x,y) \equiv \langle x,y | n,m \rangle = \begin{cases} \left(\frac{2}{a}\right) \cos(\pi n x/a) & \text{n,m odd} \\ \sin(\pi n x/a) & \text{n,m even} \end{cases} \times \begin{cases} \cos(\pi m y/a) & \text{n,m odd} \\ \sin(\pi m y/a) & \text{n,m even} \end{cases} \quad (3.4)$$

with integer $n,m = 1, 2, 3, \dots$. The energy levels are

$$E_{n,m} = \frac{1}{2M} \left(\frac{\pi \hbar}{a} \right)^2 (n^2 + m^2) \quad (3.5)$$

The degeneracies of the first few energy levels are

energy	degeneracy	states (<i>n.m</i>)
$\frac{1}{2M} \left(\frac{\pi\hbar}{a}\right)^2 \times 2$	1	(1,1)
$\frac{1}{2M} \left(\frac{\pi\hbar}{a}\right)^2 \times 5$	2	(1,2), (2,1)
$\frac{1}{2M} \left(\frac{\pi\hbar}{a}\right)^2 \times 8$	1	(2,2)
$\frac{1}{2M} \left(\frac{\pi\hbar}{a}\right)^2 \times 10$	2	(3,1), (1,3)

The shift in ground state energy which is not degenerate is second order in λ since the perturbation is odd in x (and y) i.e. $\langle 1,1 | xy | 1,1 \rangle = 0$. The same is true for the second excited energy level $E = \frac{1}{2M} \left(\frac{\pi\hbar}{a}\right)^2 \times 8$. To calculate the shift in energy of the first excited level degenerate perturbation theory is required. The energy shift is obtained from EQN 3.2

$$\begin{pmatrix} \langle 1,2 | V | 1,2 \rangle & \langle 1,2 | V | 2,1 \rangle \\ \langle 2,1 | V | 1,2 \rangle & \langle 2,1 | V | 2,1 \rangle \end{pmatrix} \begin{pmatrix} a_{(1,2)} \\ a_{(2,1)} \end{pmatrix} = \Delta E \begin{pmatrix} a_{(1,2)} \\ a_{(2,1)} \end{pmatrix} \quad (3.6)$$

The diagonal matrix elements are zero.

$$\begin{aligned} \langle 2,1 | xy | 1,2 \rangle &= \underbrace{\frac{4}{a^2} \int_{-a/2}^{a/2} dx \cos(\pi x/a) x \sin(2\pi x/a) \int_{-a/2}^{a/2} dy \cos(\pi y/a) y \sin(2\pi y/a)}_{\frac{8}{9} \frac{a^2}{\pi^2}} \quad (3.7) \\ &= \frac{256}{81} \frac{a^2}{\pi^4} \end{aligned} \quad (3.8)$$

where the integral was done previously in EQN 1.24. The secular equation is then

$$\begin{pmatrix} 0 & \frac{256}{81} \frac{a^2}{\pi^4} \lambda \\ \frac{256}{81} \frac{a^2}{\pi^4} \lambda & 0 \end{pmatrix} \begin{pmatrix} a_{(1,2)} \\ a_{(2,1)} \end{pmatrix} = \Delta E \begin{pmatrix} a_{(1,2)} \\ a_{(2,1)} \end{pmatrix}. \quad (3.9)$$

The energy shifts are

$$\Delta E_{\pm} = \pm \frac{256}{81} \frac{a^2}{\pi^4} \lambda \quad (3.10)$$

and the eigenvectors are

$$\frac{1}{\sqrt{2}} (|1,2\rangle + |2,1\rangle) \quad \text{for } \Delta E_+ \quad (3.11)$$

$$\frac{1}{\sqrt{2}} (|1,2\rangle - |2,1\rangle) \quad \text{for } \Delta E_- \quad (3.12)$$

$$(3.13)$$

The resulting two states are no longer degenerate and the energy shifts are linear in the perturbation λ .

The potential has a chequer board pattern $\begin{matrix} - & + \\ + & - \end{matrix}$ for positive λ . The wavefunction for E_+ then has an increased density along the direction of the positive potential and a higher energy. The wavefunction for E_- has an increased density along the direction where the potential is negative and $\Delta E_- < 0$.

Corollary

The perturbation removes mirror planes $\hat{\mathcal{M}}_x$, $\hat{\mathcal{M}}_y$ along the x-axis and y-axis but leaves those at 45° , such as $\hat{\mathcal{M}}_{xy}$, along the diagonals of the square well. $\hat{\mathcal{M}}_x$ reverses the sign of x , $\hat{\mathcal{M}}_y$ reverses the sign of y , $\hat{\mathcal{M}}_{xy}$ swaps x and y coordinates. Had we identified this at the outset we could have made a very important observation. Eigenstates of \hat{H}_0 and \hat{H}_1 can always be chosen to be eigenstates of $\hat{\mathcal{M}}_{xy}$ since $[\hat{H}_0, \hat{\mathcal{M}}_{xy}] = 0$ and $[\hat{H}_1, \hat{\mathcal{M}}_{xy}] = 0$. \hat{H}_1 is diagonal in the sub-basis of $\hat{\mathcal{M}}_{xy}$ eigenstates with the same \hat{H}_0 eigenvalue as long as each state in this sub-basis has a different $\hat{\mathcal{M}}_{xy}$ quantum number. We note that the

eigenstates of \hat{M}_{xy} satisfy $\hat{M}_{xy}|\psi_{\pm}\rangle = \pm|\psi_{\pm}\rangle$ since $\hat{M}_{xy}^2 = 1$ so that \hat{M}_{xy} can distinguish at most two states.

In other words we can change our basis from eigenstates of \hat{M}_x and \hat{M}_y such as $|1,2\rangle$ and $|2,1\rangle$ to eigenstates of \hat{M}_{xy} , i.e. $(|1,2\rangle + |2,1\rangle)/\sqrt{2}$ and $(|1,2\rangle - |2,1\rangle)/\sqrt{2}$. Both basis sets span the degenerate eigenstates of \hat{H}_0 , but only the latter basis states are also eigenstates of \hat{H}_1 . The important step was identifying which of the many symmetries of \hat{H}_0 was preserved by \hat{H}_1 and showing that the eigenstates for this symmetry span the basis of degenerate states. In this basis the first order energy shifts are then given by the same result as for non-degenerate perturbation theory $\Delta E_{\pm} = \langle\psi_{\pm}|V|\psi_{\pm}\rangle$.

The matrix calculation may seem the less intellectually taxing method than employing symmetry arguments in the present problem. In more complex problems and in the next chapter when we look at the spin-orbit interaction we will find the symmetry arguments provide a considerable simplification.

3.3 Linear Stark Effect

The Stark effect is the shift in spectral lines owing to an applied electric field. Since polarisation is a second order effect ($\propto \mathcal{E}^2$) we might expect the Stark effect is also second order. It is for some cases (eg Na d-lines). However for hydrogen it is first order. The transition we will consider is $(n=1) \leftrightarrow (n=0)$ (the lowest energy transition) (i.e. the first Lyman line in the spectrum). We wish to estimate how the energy of this absorption line is changed by application of an electric field. To keep things simple we'll ignore fine structure effects on the spectrum which are the subject of later chapters. We have already calculated the energy of the $1s$ level with non-degenerate perturbation theory (it changes only to second order in \mathcal{E}). We now need to calculate the energy of the $2s, 2p_0, 2p_{-1}$ and $2p_1$ levels. Since these have the same energy prior to the application of the electric field degenerate perturbation theory is required. The perturbation is $V = e\mathcal{E}z = e\mathcal{E}r\cos(\theta)$.

The $N=2$ ($n=1$) level wavefunctions are

$$2s_0 : \psi_{1,0,0} = \sqrt{\frac{1}{4\pi}} 2 \left(\frac{1}{2a_0} \right)^{3/2} \left(1 - \frac{r}{2a_0} \right) e^{-r/(2a_0)} \quad (3.14)$$

$$2p_0 : \psi_{1,1,0} = \sqrt{\frac{3}{4\pi}} \cos(\theta) \frac{2}{\sqrt{3}} \left(\frac{1}{2a_0} \right)^{3/2} \left(\frac{r}{2a_0} \right) e^{-r/(2a_0)} \quad (3.15)$$

$$2p_{\pm 1} : \psi_{1,1,\pm 1} = \sqrt{\frac{3}{8\pi}} \sin(\theta) e^{\pm i\phi} \frac{2}{\sqrt{3}} \left(\frac{1}{2a_0} \right)^{3/2} \left(\frac{r}{2a_0} \right) e^{-r/(2a_0)} \quad (3.16)$$

Since the perturbation has odd parity, the diagonal terms in the V matrix (i.e. $\langle 1, l, m | z | 1, l, m \rangle$) are zero. In fact the perturbation only gives non zero elements between $\psi_{1,0,0}$ and $\psi_{1,1,0}$. We can see this by noting that $z = r\cos\theta$ and considering the action of $\cos\theta$ on the angular integrals. The perturbation contains no azimuthal angle ϕ dependence and therefore the resulting expression is zero connecting states with different m . Thus only states with the same m quantum number give non-zero matrix elements. The value of the matrix element $\langle \psi_{1,1,0} | z | \psi_{1,0,0} \rangle = -3a_0$ is found from direct calculation (a_0 is the Bohr radius). The V matrix for the 4 degenerate states is then

$$V = e\mathcal{E} \begin{pmatrix} 0 & -3a_0 & 0 & 0 \\ -3a_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \quad (3.17)$$

which acts on a column vector composed of the amplitudes of $u = (a_{2s}, a_{2p_0}, a_{2p_1}, a_{2p_{-1}})$. The matrix equation is

$$\underline{V} \underline{u} = \Delta E \underline{u} \quad (3.18)$$

The Secular (eigenvalue) equation is

$$|\underline{V} - \Delta E \underline{I}| = 0 \quad (3.19)$$

$$\begin{vmatrix} -\Delta E & -3a_0e\mathcal{E} & 0 & 0 \\ -3a_0e\mathcal{E} & -\Delta E & 0 & 0 \\ 0 & 0 & -\Delta E & 0 \\ 0 & 0 & 0 & -\Delta E \end{vmatrix} = 0. \quad (3.20)$$

The solutions are $\Delta E = 0$ twice and $\Delta E = \pm 3a_0e\mathcal{E}$.

The Eigenvectors for $\Delta E = 0$ are $(0, 0, 1, 0)$ and $(0, 0, 0, 1)$. Generally, states that are not coupled by the perturbation are unaffected by it; $\psi_{2,1,\pm 1}$ in the present example.

The two more interesting solutions are

$$\Delta E = +3a_0e\mathcal{E} : (1/\sqrt{2}, -1/\sqrt{2}, 0, 0) \quad (3.21)$$

$$\Delta E = -3a_0e\mathcal{E} : (1/\sqrt{2}, +1/\sqrt{2}, 0, 0) \quad (3.22)$$

These are sketched in FIG 3.1. The new states are sp hybrids. Unlike the initial states these have a well defined electric dipole but not a well defined angular momentum. Since angular momentum is not conserved in the presence of the applied field this is not a problem. The fact that the final states have a pre-existing electric dipole moment explains why the correction to their energy is linear in \mathcal{E} rather than quadratic.

Since any orthogonal basis of the 4 degenerate states could have been chosen at the outset we could have started with the above choice. We would then have found that the potential gave no coupling between states and we could have used our regular perturbation theory. The problem of dividing by zero would not occur since the matrix element would be zero between different states.

Corollary

In this example the symmetry that is preserved by H_1 is the rotational symmetry about the direction of the applied field (taken along the z-axis). Therefore we needed to consider only eigenstates of \hat{l}_z from each degenerate manifold. There are however two degenerate states with the same quantum number m so we need another symmetry property, also respected by both \hat{H}_0 and \hat{H}_1 to distinguish these. There is no obvious choice here so we had to proceed with the matrix calculation.

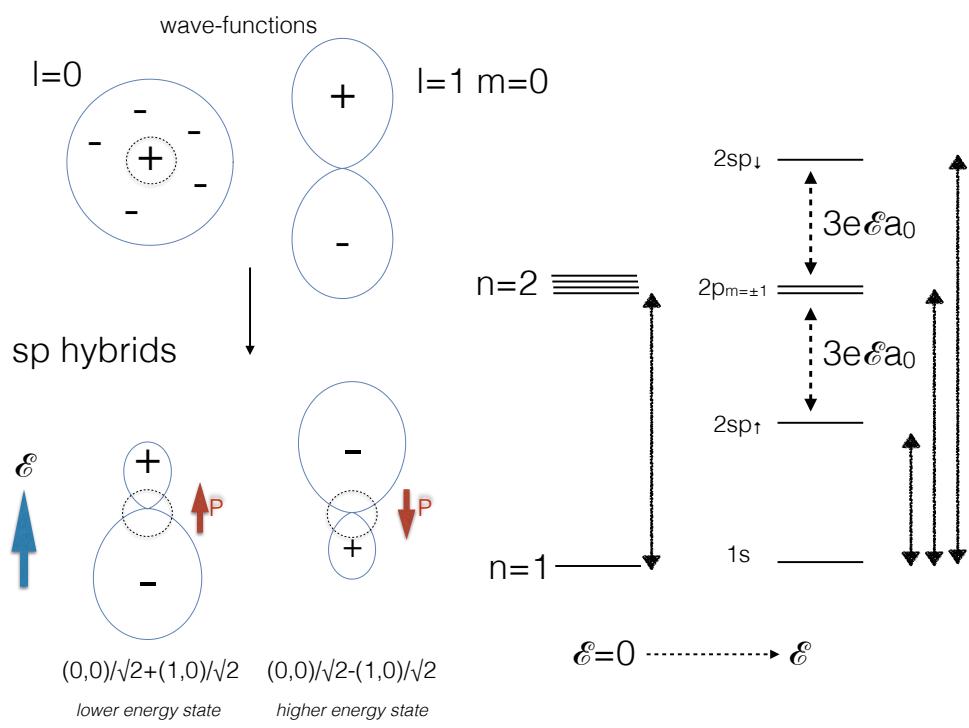


Figure 3.1: The left half of the figure shows the combination of $2s_0$ and $2p_0$ orbitals to form sp-hybrids. The plus and minus denote the phase of the wavefunctions (not charge). The wavefunction is squared to give the charge density. For $2s$ and $2p$ this is centred on the nucleus (no dipole moment), whereas the sp hybrids have a dipole moment. The right of the image shows the levels with and without the electric field. The fuzzy vertical lines are the optic absorption lines. These are split linearly in an electric field for the sp hybrids with respect to the remaining unaffected levels that are unaffected to linear order. The arrows in the symbols sp_\uparrow and sp_\downarrow show the direction of the electric dipole in the hybrid state and do not refer to electron spin.

Relativistic Corrections H-atom fine structure

4.1 Including spin

We know that the electron has a spin $1/2$. This doubles the degeneracy to $2N^2$ for each shell. However if the perturbation does not depend on the electron spin (as in the examples considered up to this point) this will not introduce any further effect. The possibility of $1/2$ integral angular momentum has already been encountered when we considered how angular momentum is quantised.

The electron spin appears naturally along with anti-matter (positrons) when QM is formulated starting with the requirement that it is relativistically invariant. This leads to the Dirac equation which replaces Schrödinger's equation for the wavefunction. The Schrödinger equation can then be derived as the non-relativistic limit of the Dirac equation and the lowest order relativistic corrections found. Here we will work the other way around introducing the relativistic corrections to Schrödinger's equation.

We have seen that the electron orbits have angular momentum and therefore a magnetic moment. We neglected this field energy in our calculation so far. The electron spin is also associated with a magnetic moment $-g\mu_B m_s$ along the quantisation axis with m_s the spin quantum number $\pm(1/2)$ [no units], $g \approx 2$ the g-factor [no units] and $\mu_B = e\hbar/(2m_e)$ the Bohr magneton [units of magnetic moment ($e = 1.6 \cdot 10^{-19} \text{ C}$)]. The gyromagnetic ratio is the ratio of the moment to the angular momentum $\gamma = -ge/(2m_e)$. The exact value of g is very slightly greater than 2 (by about $0.1\% = \alpha/2\pi$ where $\alpha \sim 1/137$ is the fine structure constant) derived in the relativistic formulation of QM / QED. Here we take g as an experimentally determined parameter. The electron moment interacts with the magnetic field generated by the electron motion round an orbit. This interaction introduces a new term in our Hamiltonian which we now derive.

We use the symbol \vec{l} and \vec{s} to refer to angular momentum (orbital and spin) and \hat{s} and \hat{l} as angular momentum quantum number operators such that $\vec{l} = \hbar\hat{l}$ and $\vec{s} = \hbar\hat{s}$. m_s refers to the spin quantum number along the quantisation axis (z-axis), whereas \vec{m}_s refers to the spin magnetic moment.

4.2 The spin-orbit interaction

We can understand the physical origin of part of the *spin-orbit interaction* with classical electromagnetism. As the electron orbits the nucleus, it appears from the electron's point of view that the nucleus is orbiting the electron. The stationary electron therefore experiences a field

$$B' = \frac{\mu_0}{4\pi} \frac{\vec{j} \times \vec{r}}{r^3} = -\frac{Ze\mu_0}{4\pi} \frac{\vec{v} \times \vec{r}}{r^3} \quad (4.1)$$

where the nucleus moves at velocity $-\vec{v}$ relative to the electron and has charge $+Ze$. The Electric field at the electron is $\vec{E} = (\frac{Ze}{4\pi\epsilon_0}) \frac{\vec{r}}{r^3}$ so the above can be written

$$\vec{B}' = -\frac{\vec{p} \times \vec{E}}{\mu c^2} \quad (4.2)$$

with p the momentum of the electron (in the lab frame) and μ the inertial mass of the electron. You might recognise the above as nothing other than the low velocity limit of the relativistic transformation

to an inertial frame instantaneously moving with the electron

$$\vec{B}' = \gamma \left(B + \frac{-\vec{v} \times \vec{E}}{c^2} \right) \quad (4.3)$$

with B (an applied field or field due to other electrons in a multi-electron atom) and E are the values in the lab frame (ie the frame of the nucleus) and $\gamma = 1/\sqrt{1-v^2/c^2} \approx 1$.

$$\vec{E} = \frac{1}{e} \left(\frac{dV}{dr} \right) \frac{\vec{r}}{r} \quad (4.4)$$

where V is the electrostatic potential energy of the electron (as used in the Schrödinger equation). Noting $\vec{l} = \vec{r} \times \vec{p}$, we obtain

$$\vec{B}' = \frac{1}{\mu c^2 e r} \frac{dV}{dr} \vec{l} \quad (4.5)$$

The magnetic interaction energy is $-\vec{m}_s \cdot \vec{B}'$ with $\vec{m}_s = \gamma \vec{s} = -g(\mu_B/\hbar) \vec{s} = -(e/m_e) \vec{s}$ (taking $g = 2$). We don't distinguish between the inertial mass and mass appearing in the Bohr magneton so $m_e \equiv \mu$. Converting to operator notation we obtain

$$\hat{H}_{SO}^{\text{electron frame}} = \frac{1}{\mu^2 c^2} \frac{1}{r} \frac{dV}{dr} \vec{l} \cdot \vec{s} \quad (4.6)$$

This is the change of energy calculated in the rest frame of the electron. It transfers across to the lab frame. However, when we transform back to the lab frame the rotational kinetic energy of the electron is changed generating another contribution (independent of g) cancelling half the magnitude of the above term (calculated with $g = 2$). This is a relativistic effect that can be understood as follows. In the frame of the moving electron one orbit takes a time τ/γ compared with τ in the stationary frame of the nucleus (just the same as in the twins paradox; the travelling twin ages more slowly). The rest and moving frames are not equivalent since the moving electron is accelerating (and experiences a centripetal force) whereas the nucleus does not. This poses an apparent problem since observers in the two frames would then naively measure different values for each others angular velocity. The electron coordinate's angular velocity in the lab frame is $\omega = 2\pi/\tau$ whereas in the electron's frame the nucleus naively appears to be orbiting it with angular velocity $\omega' = 2\pi\gamma/\tau$. This is resolved by noting that the electron's rest frame is in fact rotating at a rate $\omega - \omega' = (1 - \gamma)\omega \approx -\frac{v^2}{2c^2}\omega$ in the lab frame. This rotation is called Thomas precession and can be derived rigorously with special relativity (the expression we have derived is the leading term in powers of v/c of the exact expression for the Thomas precession ω_T).

The Galilean (classical) expression for a change of energy E' in a frame slowly rotating with angular velocity Ω relative to the change of energy in a stationary frame is $E' = E - \vec{\Omega} \cdot \vec{L}$ where L is a change of angular momentum (the same in both frames). We apply this here for $\vec{L} = \vec{s}$ and $\vec{\Omega} = \omega_T$. Then $\vec{\Omega} \cdot \vec{L} = \omega_T \cdot \vec{s} = -\frac{v^2}{2\mu r^2 c^2} \vec{l} \cdot \vec{s}$. We then use the equation for centripetal force $\mu v^2/r = (dV/dr)$ to remove v completing the identification $E' = E + \frac{1}{2\mu^2 r c^2} \frac{dV}{dr} \vec{l} \cdot \vec{s}$. We can use this result to transform the spin rotational kinetic energy in moving frame E' back to the lab frame E . The rotational kinetic energy of the electron around itself is thus changed due to its orbital motion around the nucleus cancelling half the magnetic SO energy. The final result, including both the magnetic energy and correcting for Thomas Precession is

$$\hat{H}_{SO}^{\text{lab frame}} = \frac{1}{2\mu^2 c^2} \frac{1}{r} \frac{dV}{dr} \vec{l} \cdot \vec{s} \quad (4.7)$$

This is the correct formula for the combined magnetic moment and Thomas terms for Hydrogen. The combined term is called the spin-orbit interaction.

Despite all the effort put into justifying the above expression for hydrogen we will work with a generic formula that also covers multiple electron atoms

$$\hat{H}_{SO} = \xi(r) \hat{l} \cdot \hat{s} \quad (4.8)$$

where $\xi(r)$ is simply a function of r (that can include screening due to inner electron shells). The Hamiltonian is now

$$\hat{H} = \hat{H}_0 + \hat{H}_{SO} = \frac{1}{2\mu} \hat{p}^2 + V(r) + \xi(r) \hat{l} \cdot \hat{s}. \quad (4.9)$$

4.2.1 Perturbation theory applied to the SO term

We would like to apply perturbation theory to calculate the shifts in all the energy levels of the hydrogen atom due to $\hat{H}_{SO} = \xi(r) \hat{l} \cdot \hat{s}$. Including spin all the levels of H_0 are arranged in degenerate multiplets, so a priori we will need degenerate perturbation theory. However, luckily the combined angular and electron-spin parts of \hat{H}_{SO} and \hat{H}_0 commute (the radial parts do not). This means we should be able to choose the angular+spin part of the eigenstates of H_0 to also be eigenstates of H_1 . With this basis of states H_1 is diagonal and the results are then equivalent to the non-degenerate case. We now investigate how to construct the correct combinations of states from the degenerate states of H_0 to achieve this.

The wavefunctions of \hat{H}_0 up to now have been written ψ_{n,l,m_l,m_s} . These are eigenfunctions of \hat{H}_0 and also \hat{l}^2 , \hat{l}_z , \hat{s}^2 , and \hat{s}_z . \hat{l}^2 and \hat{s}^2 commute with \hat{H}_{SO} , but \hat{l}_z and \hat{s}_z do not and so the eigenfunctions of \hat{l}_z and \hat{s}_z will not be eigenfunctions of the new Hamiltonian. This is equivalently stated as:

- (i) the eigenvalues of \hat{l}_z and \hat{s}_z are not constants of motion
- (ii) m_l and m_s are not “good” quantum numbers
- (iii) the spin-orbit interaction is not diagonal in the n, l, m_l, m_s basis
- (iv) the spin-orbit interaction mixes different n, l, m_l, m_s states.

We note that groups of degenerate states of \hat{H}_0 have the same n, l, s but different m_l, m_s . The challenge is therefore to find the combinations of m_l and m_s states that diagonalise \hat{H}_{SO} . To do this we need to find “good” quantum numbers, with operators that commute with both \hat{H}_0 and \hat{H}_{SO} .

We can make a good guess. Spin-orbit coupling is just the interaction of the spin magnetic moment of the electron with its own orbital motion around the nucleus, so the total angular momentum and its components should be constants of motion.

4.2.2 The j, m_j quantum numbers

We therefore define new operators $\hat{j} = \hat{l} + \hat{s}$. It is easily checked that \hat{j} commutes with \hat{H}_0 and \hat{H}_{SO} and further $\hat{j}^2, \hat{j}_z, \hat{l}^2$ and \hat{s}^2 all mutually commute (note \hat{s} and \hat{l} act on different spaces and automatically commute with each other). Since \hat{j} is an angular momentum we know how it is quantised. For each quantum number of the total angular momentum j we have

$$\hat{j}^2 |j, m_j\rangle = \hbar^2 j(j+1) |j, m_j\rangle \quad (4.10)$$

$$\text{and} \quad \hat{j}_z |j, m_j\rangle = \hbar m_j |j, m_j\rangle. \quad (4.11)$$

To complete the change from l_z, s_z to j, m_j we need to find which combinations of $|l_z, s_z\rangle$ correspond to each $|j, m_j\rangle$ and more importantly show that our new basis $|j, m_j\rangle$ is complete i.e. contains the same number of states that we had in the old basis $|l_z, s_z\rangle$.

	m_l				
	-2	-1	0	1	2
m_s					
-1	-3	-2	-1	0	1
0	-2	-1	0	1	2
1	-1	0	1	2	3

Table 4.1: All possible values of m_j formed by adding m_l and m_s when $s = 1, l = 2$.

4.2.3 Combining angular momentum

It is clear from combining angular momentum along a single axis that the states $|m_l, m_s\rangle$ are already eigenstates of \hat{j}_z with $m_j = m_l + m_s$. So if we take all the m_l and m_s values in a degenerate set of states of \hat{H}_0 we can get a list of all the m_j values this generates. From this list we can then work out the values of j we require.

To see how this works out, let's do an example. Suppose we combine angular momentum vectors corresponding to the quantum numbers $l = 2$ and $s = 1$. The z component of \vec{l} can be $m_l = -2, -1, 0, 1, 2$ in units of \hbar , while the possible z components of \vec{s} are $m_s = -1, 0, 1$. We can find all the possible z components of $\vec{j} = \vec{l} + \vec{s}$ by forming all possible combinations of m_l and m_s , and these are shown in table 4.1. The largest value of m_j is 3, and so the largest possible j must be 3. An angular momentum vector with quantum number 3 can have $2j+1=7$ possible z projections: $m_j = -3, -2, -1, 0, 1, 2, 3$. If we remove each of these values from the table, the largest of the remaining values is $m_j = 2$. This suggests a \vec{j} vector with $j = 2$ and components $m_j = -2, -1, 0, 1, 2$. Removing these values from the Table leaves only $m_j = -1, 0, 1$ which we associate with a \vec{j} vector with quantum number $j = 1$. So adding an \vec{l} vector with $l = 2$ to an \vec{s} vector with $s = 1$ can give us three different sums corresponding to $j = 3, 2$ or 1 .

In the example we were able to deduce the values of j required from the m_j generated. The above argument can be generalised (and made more formal) to give the angular momentum addition theorem:

The values of permitted quantum numbers j combining two angular momentum states \vec{j}_1 and \vec{j}_2 are $|j_1 - j_2| \leq j \leq |j_1 + j_2|$. (4.12)

Each j value in the range occurs exactly once. The formal proof of the angular momentum addition theorem can be found in books (and is not examinable for this course); an informal proof is given below.

4.2.4 New wavefunctions

We can build up new wavefunctions with the required set of quantum numbers $|l, s, j, m_j\rangle$ from the ψ_{l,s,m_l,m_s} functions. We need to check that these new wavefunctions form a complete basis. For this to be true they must be expressible as linear combinations of the ψ_{l,s,m_l,m_s} :

$$|l, s, j, m_j\rangle = \sum_{m_s, m_l} \underbrace{\langle l, s, m_l, m_s | l, s, j, m_j \rangle}_{C(l, s; m_l, m_s, j, m_j)} |l, s, m_l, m_s\rangle \quad (4.13)$$

where the coefficients C are called *Clebsch-Gordon coefficients*.

If we go back to our energy level diagram in FIG 2.1 on page 12, for a single electron with $s = 1/2$ we recall that the E_n levels are degenerate. We can show that the new basis is complete by counting states. For a given l there are $(2l+1)(2s+1) = 4l+2$ states due to the m_l and m_s degeneracy. In the new basis set, j can take two different values: $l+1/2$ and $l-1/2$, and each of these has an m_j degeneracy of $(2j+1)$ (since for a given j , m_j must satisfy $|m_j| \leq j$). The number of new states is $(2(l+1/2)+1) + (2(l-1/2)+1) = 4l+2$, as before. The spin-orbit interaction will lift some of the degeneracy but the number of states stays the same. The general proof that the the set of j basis is complete is constructed in the tutorial exercises.

We now illustrate how the Clebsch-Gordon coefficients are calculated for the particular example $l = 2, s = 1$. Since (l, s) are repeated in every term in EQN 4.13 we will omit these symbols for the rest of this example writing

$$|j, m_j\rangle = \sum_{m_s, m_l} \langle m_l, m_s | j, m_j \rangle |m_l, m_s\rangle \quad (4.14)$$

There is only one state in each basis with maximum (and minimum) $m_j = m_l + m_s$. These states must therefore be identical in the two basis

$$|j, m_j\rangle = |\pm 2, \pm 1\rangle \quad (4.15)$$

Thus $C(\pm 2, \pm 1, 3, \pm 3) = 1$. To get further coefficients we operate on EQN 4.15 with $\hat{J}^\pm = \hat{L}^\pm + \hat{S}^\pm$. e.g. acting on $|3, 3\rangle$ with the lowering operators \hat{J}^- and recalling $\hat{J}^- |J, m_J\rangle = \sqrt{J(J+1) - m_J(m_J-1)} |J, m_J-1\rangle$ gives

$$\sqrt{12-6} |3, 2\rangle = \sqrt{6-2} |1, 1\rangle + \sqrt{2-0} |2, 0\rangle \quad (4.16)$$

so $C(1, 1, 3, 2) = \sqrt{2/3}$ and $C(2, 0, 3, 2) = \sqrt{1/3}$ and $C(m_l, m_s, 3, 2) = 0$ for all other m_l, m_s . We can continue applying the lowering operator to determine all the coefficients of the form $C(m_l, m_s, 3, m_j)$.

The state $|2, 2\rangle$ is equal to a different linear combination of the states on the RHS of EQN 4.16. Since this state must be orthogonal to $|3, 2\rangle$ it must be

$$|2, 2\rangle = \sqrt{1/3} |1, 1\rangle - \sqrt{2/3} |2, 0\rangle \quad (4.17)$$

There is an ambiguity in the choice of overall sign (or more generally of an overall phase factor $e^{i\theta}$) in each expression that is fixed by convention only. Other states of form $C(m_l, m_s, 2, m_j)$ can be generated with the lowering operator acting on EQN 4.17.

Finally $|1, 1\rangle$ is a linear combination of $|2, -1\rangle, |1, 0\rangle$ and $|0, 1\rangle$ which is uniquely determined since it must be orthogonal to both $|3, 1\rangle$ and $|2, 1\rangle$ which have already been found. The remaining coefficients $C(m_l, m_s, 1, m_j)$ are determined with lowering operator acting on this.

A table listing all the coefficients for L=2 S=1 is given in FIG 4.1. Similar tables exist for all combinations of two spins that are likely to be encountered.

2×1		3		
		$+3$	3	2
$+2$	$+1$	1	$+2$	$+2$
$+2$	0	$1/3 \quad 2/3$	$3 \quad 2 \quad 1$	
$+1$	$+1$	$2/3 \quad -1/3$	$+1 \quad +1 \quad +1$	
			$+2 \quad -1$	$1/15 \quad 1/3 \quad 3/5$
			$+1 \quad 0$	$8/15 \quad 1/6 \quad -3/10$
			$0 \quad +1$	$2/5 \quad -1/2 \quad 1/10$
				$3 \quad 2 \quad 1$
				$0 \quad 0 \quad 0$
			$+1 \quad -1$	$1/5 \quad 1/2 \quad 3/10$
			$0 \quad 0$	$3/5 \quad 0 \quad -2/5$
			$-1 \quad +1$	$1/5 \quad -1/2 \quad 3/10$

Figure 4.1: Clebsch-Gordon coefficients for L=2, S=1. The columns give j, m_j values and the rows m_l, m_s . The Clebsch-Gordon coefficients are the square roots of the entries. The signs of all the m_j, m_l, m_s can be simultaneously reversed to give the entries for negative m_j . From reference <http://pdg.lbl.gov/2002/clebrpp.pdf>.

4.2.5 ‘Proof’ of the angular momentum addition theorem

The use of the lowering operator to generate the Clebsch-Gordon coefficients with reference to table 4.1 makes the origin of the angular momentum addition theorem clearer. Starting from the top left corner of the table we require $j = l + s = 3$ with the top left entry $m_j = -3$. Acting with \hat{J}^+ generates a term composed of states lying on the diagonal running from $m_l, m_s = (-1, -1)$ to $(-2, 0)$. Successive operations give terms on successive diagonals. Since there are two terms with $m_j = -2$ we have one left over on the diagonal $(-1, -1) \rightarrow (-2, 0)$; a state with total angular momentum quantum number $j = l + s - 1$ generates this and further terms. This continues as long as each successive diagonal contains one more state that it not yet assigned a value of j i.e. while each successive diagonal contains one more

element. The number of such diagonals is equal to the shortest side of the rectangle $\min((2l+1), (2s+1))$. Therefore we start with $j = l+s$ and go down in integer steps to $j = l+s - (\min(2l+1, 2s+1) - 1) = |l-s|$.

4.2.6 The spin-orbit operator

We stated above that \hat{H}_{SO} would commute with the operators \hat{j}^2 and \hat{j}_z . This can be shown noting that \hat{l} and \hat{s} commute by writing

$$\hat{j}^2 = (\hat{l} + \hat{s})^2 = \hat{l}^2 + \hat{s}^2 + 2\hat{l}\cdot\hat{s}, \quad \hat{j}_z = \hat{l}_z + \hat{s}_z. \quad (4.18)$$

We can now write \hat{H}_{SO} in a more helpful form:

$$\hat{H}_{SO} = \xi(r)\hat{l}\cdot\hat{s} = \frac{\xi(r)}{2} (\hat{j}^2 - \hat{l}^2 - \hat{s}^2). \quad (4.19)$$

4.2.7 The energy shifts

It follows immediately that the spin-orbit energy shift is

$$\begin{aligned} \Delta E_{n,l,j}^{SO} &= \frac{1}{2} \langle n, l, s, j, m_j | \xi(r) [\hat{j}^2 - \hat{l}^2 - \hat{s}^2] | n, l, s, j, m_j \rangle \\ &= \frac{\hbar^2}{2} \langle \xi(r) \rangle [j(j+1) - l(l+1) - s(s+1)]. \end{aligned} \quad (4.20)$$

The spin-orbit interaction has lifted the degeneracy of the E_n levels. First each shell is now split according to the value of l . Next each (n, l) subshell (with the exception of the $l = 0$ subshell) splits into two levels, one for each possible value of j . For the s subshell only one j is possible. When spin-orbit splitting is apparent, it is conventional to add the value of j as a subscript to the standard (N, l) designation, e.g. the $2p$ subshell splits into the $2p_{1/2}$ and $2p_{3/2}$ levels. The splitting for hydrogen is shown in FIG 4.2.

For a general level (N, l) ($l \neq 0$) the split states are $l_{l+1/2}$ and $l_{l-1/2}$. For $j = l + 1/2$ we have $[j(j+1) - l(l+1) - s(s+1)] = l$ and for $j = l - 1/2$, $[j(j+1) - l(l+1) - s(s+1)] = -(l+1)$.

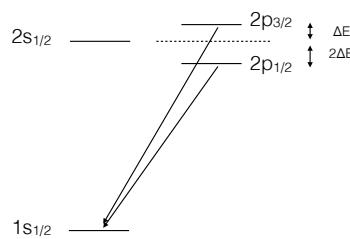


Figure 4.2: Relativistic splitting of the Lyman L_α line of hydrogen due to the spin-orbit interaction only. The splitting including all contributions is shown in FIG 4.5. The allowed optical transitions are shown with arrows. A similar splitting applies to the sodium D-line (3s-3p transition) that gives the characteristic orange emission of sodium street lamps (we will see later than the 3s and 3p states are significantly split in multi-electron atoms). The doublet can be resolved with a diffraction grating.

4.2.8 The coupling constant and trends

The $\hat{l} \cdot \hat{s}$ operator only affects the angular part of our $|n, l, m_l, m_s\rangle$ functions, and so the new $|n, l, j, m_j\rangle$ have the same radial dependence $R_{nl}(r)$ as for the non relativistic case. $\langle \xi(r) \rangle$ is called the *spin-orbit coupling constant* and is usually written as simply ξ . It is determined by a purely radial integral and for hydrogen-like atoms

The magnitude of the splitting between $2p_{1/2}$ and $2p_{3/2}$ is

$$\frac{\hbar^2}{2\mu^2 c^2} \frac{1}{r} \frac{dV}{dr} \sim \frac{\hbar^2}{2\mu^2 c^2} \frac{e^2}{4\pi\epsilon_0 a_0^3} = \alpha^2 \frac{e^2}{8\pi a_0} = \alpha^2 \epsilon_0 \quad (4.21)$$

with a_0 the Bohr radius and ϵ_0 the (non-relativistic) hydrogen ground state energy. (In writing the above we used $\epsilon_0 = 1/(8\pi\epsilon_0 a_0)$ and $a_0 = 4\pi\epsilon_0\hbar^2/\mu e^2$). $\alpha = e^2/(4\pi\epsilon_0\hbar c) \sim 1/137$ is the dimensionless fine structure constant. Thus the magnitude of the spin-orbit shift is of the order α^2 times the spacing between the N levels.

For hydrogen-like orbitals with higher Z, N, l it can be shown that

$$\xi_{nl} = \langle R_{nl} | -\frac{1}{\mu^2 c^2 r} \frac{dV}{dr} | R_{nl} \rangle \propto \frac{Z^4}{n^3 l(l+1/2)(l+1)}. \quad (4.22)$$

It follows that spin-orbit effects increase dramatically with Z , decrease with n , and decrease with l .

4.3 Vector model of angular momentum

A useful pictorial expression of how angular momenta are combined can be constructed from classical mechanics. Of course, not everything from classical mechanics can be carried across. We will briefly review the classical description of a spinning top in a gravitational field and a spinning charged disc in a magnetic field. Only the aspects of this description that provide insight into the quantum mechanical description of a spin are developed.

4.3.1 The classical spinning top

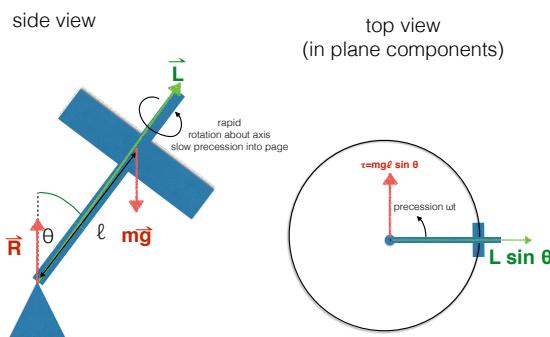


Figure 4.3: A gyroscope consisting of a heavy disc that spins around its axle, balanced on a pencil point. The forces are shown in red. There is a gravitational force $m\vec{g}$ acting through the centre of mass vertically and an equal and opposite reaction force from the point of the pencil, \vec{R} . This results in a couple of magnitude $mgl \sin \theta$ acting into the page which causes the gyroscope to precess. A top view of the precession is shown in the image on the right with the projected values for the components of various quantities shown in this plane.

Consider the simplest motion of a gyroscope (spinning top) shown in FIG 4.3 in which the axis of the gyroscope precesses around the vertical direction at a constant rate and inclination. The angular momentum is inclined at angle θ to the vertical. Since the potential energy is constant the kinetic energy and the *magnitude* of the angular momentum are also constant. The equation of motion is

$$\dot{\vec{L}} = \vec{\tau} = \vec{F} \times \vec{r} = m\vec{g} \times \ell \frac{\vec{L}}{|L|}. \quad (4.23)$$

The angular momentum has to lie in the plane perpendicular to the torque because no work is done (since the potential energy is constant). \vec{L} is almost aligned with the axle, but not quite owing to the precession. For this geometry we have

$$\dot{\vec{L}} = \vec{\omega} \times \vec{L} \quad (4.24)$$

with the magnitude of ω equal to the rate of precession and directed vertically. The proof of this formula can be seen in two ways; (i) we have in polar coordinates in the frame of the top $\vec{L} = |L|\vec{e}_r(t)$ so that $\dot{\vec{L}} = |L|\dot{\phi}\frac{\partial}{\partial\phi}\vec{e}_r$. Using $\frac{\partial\vec{e}_r}{\partial\phi} = \sin\theta\vec{e}_\phi$ gives $\dot{\vec{L}} = |L|\dot{\phi}\sin\theta\vec{e}_\phi = \vec{\omega} \times \vec{L}$. (ii) alternatively from examining the components in the horizontal plane in FIG 4.3 $\dot{L} = |L|\omega\sin\theta\vec{e}_\phi = \vec{\omega} \times \vec{L}$.

Combining EQN 4.23 and EQN 4.24 we have

$$\vec{\tau} = \vec{\omega} \times \vec{L} \quad (4.25)$$

For the gyroscope $\tau = mg\ell\sin\theta = |\omega||L|\sin\theta$, so the magnitude of ω is $mg\ell/|L|$ which is independent of θ . We can also write the potential energy of the gyroscope

$$E = \cos\theta m\ell|g| = -\frac{m\ell}{|L|}\vec{g} \cdot \vec{L} = \vec{\omega} \cdot \vec{L} \quad (4.26)$$

In the above example we considered the torque due to gravity. We can apply the same analysis to a charged spinning top in a magnetic field (neglecting gravity). The spinning top would have a magnetic moment $\vec{M} = -\gamma\vec{L}$. Here γ is a constant reflecting the charge distribution on the top (negative charge would correspond to a positive γ) known as the gyromagnetic ratio. From electromagnetism such a moment would experience a couple in a magnetic field $\tau = \vec{M} \times \vec{B}$ equivalent to EQN 4.25 and have an energy $E = -\vec{M} \cdot \vec{B}$ corresponding to EQN 4.26. We can identify $\gamma B \equiv \omega$. Classically the moment's direction would precess around the direction of the field with angular velocity ω .

Classically the moving charges and currents would radiate and the motion would be damped. The motion of the gyroscope can also be more complex than discussed above with oscillations of θ known as nutation. The vector model for the quantum description of angular momentum however requires only the simple behaviour we have described. The two equations that summarise this section are

$E = \vec{\omega} \cdot \vec{L}$	Energy expression for angular momentum \vec{L}	(4.27a)
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$\dot{\vec{L}} = \vec{\omega} \times \vec{L}$	Corresponding equation of motion	(4.27b)
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4.3.2 Quantum mechanics

In quantum mechanics in place of the classical equation of motion $\dot{\vec{L}} = \vec{\tau}$ the angular momentum operators obey Heisenberg's equation

$$i\hbar \frac{d\hat{L}}{dt} = [\hat{L}, \hat{H}] \quad (4.28)$$

For a Hamiltonian $\hat{H} = -\vec{B} \cdot \hat{\vec{M}} = \gamma \vec{B} \cdot \hat{\vec{L}}$ which represents a quantum mechanical spin in an applied magnetic field \vec{B} let's look at one cartesian component

$$i\hbar \frac{d\hat{L}_x}{dt} = \gamma [\hat{L}_x, B_x \hat{L}_x + B_y \hat{L}_y + B_z \hat{L}_z] \quad (4.29)$$

$$= \gamma (B_y [\hat{L}_x, \hat{L}_y] + B_z [\hat{L}_x, \hat{L}_z]) \quad (4.30)$$

$$= i\hbar \gamma (B_y \hat{L}_z - B_z \hat{L}_y) \quad (4.31)$$

$$\implies \frac{d\hat{L}_x}{dt} = \gamma (B \times \hat{L})_x \quad (4.32)$$

The same equation can be derived for each component so that

$$\frac{d\hat{\vec{L}}}{dt} = \vec{\omega} \times \hat{\vec{L}} \quad (4.33)$$

with $\vec{\omega} = \gamma B$ identical with the classical equation of motion. The same argument applies to any angular momentum operator $\hat{\vec{J}}$ in place of $\hat{\vec{L}}$. Thus the dynamics of angular momentum operators is described by the same equations as apply to classical angular momentum vectors.

For angular momentum with quantum number j we know that the magnitude of the angular momentum $\hbar \sqrt{j(j+1)}$ is larger than the maximum value along any one direction, namely $\hbar j$. This can be represented by the vector model FIG 4.4a. We can think of the QM angular momentum as a ‘precessing’ gyroscope precessing around whatever direction we have chosen as the quantisation axis. Only certain θ are allowed corresponding to different m_j values. This image is alright as long as we accept the precession angle ϕ cannot be determined (the uncertainty principle for non-commuting operators tells us we cannot simultaneously know the x or y components and the z -component of \vec{j} at the same time).

We now examine how the vector description can be extended to visualise combinations of angular momentum.

4.3.3 Combinations of angular momentum

We can combine two angular momenta shown in FIG 4.4b in the absence of a field. An interaction term in the Hamiltonian of the form $\xi \vec{j}_1 \cdot \vec{j}_2$ is equivalent to a couple acting between \vec{j}_1 and \vec{j}_2 that will cause them to precess around each other. The common axis about which both spins precess is $\vec{j} = \vec{j}_1 + \vec{j}_2$.

The vector model helps us see this. The equations for each spin individually are

$$\dot{\vec{j}}_1 = \xi \vec{j}_2 \times \vec{j}_1 \quad (4.34)$$

$$\dot{\vec{j}}_2 = \xi \vec{j}_1 \times \vec{j}_2 = -\xi \vec{j}_2 \times \vec{j}_1 \quad (4.35)$$

$$\implies \dot{\vec{j}} \equiv \dot{\vec{j}}_1 + \dot{\vec{j}}_2 = 0 \quad (4.36)$$

showing that the total angular momentum $\vec{J} = \vec{j}_1 + \vec{j}_2$ is conserved. The first two equations above are difficult to interpret individually since both axes are moving. They can however be rewritten noting $\vec{j}_1 \times \vec{j}_1 = \vec{j}_2 \times \vec{j}_2 = 0$,

$$\dot{\vec{j}}_1 = \xi \vec{J} \times \vec{j}_1 \quad (4.37)$$

$$\dot{\vec{j}}_2 = \xi \vec{J} \times \vec{j}_2 \quad (4.38)$$

from which it is clear that both \vec{j}_1 and \vec{j}_2 precess at the same rate $\xi |\vec{J}|$ around the fixed vector \vec{J} . This is shown in FIG 4.4(b).

We cannot choose this common axis to be the quantisation axis for the components m_J , since just as for a single angular momentum the total angular momentum \vec{J} cannot be fully aligned. i.e. \vec{J} itself precesses around any axes we choose as shown in FIG 4.4(c).

In the vector model time averages correspond to taking expectation values in quantum mechanics. Thus quantities such as j_{1z} in the above example which oscillate in time in the vector model are not constants of the motion quantum mechanically. Therefore m_1 is no longer a good quantum number.

The rate of precession is a measure of the significance of a perturbation (the coefficient of the energy term in the Hamiltonian). If the ξ is large in the above example compared with an applied field it is then valid to consider first the rapid precession around fixed J and then the slow precession of J about B .

It should be stressed that the vector model is an imperfect way of visualising what is going on, rather than offering a deep understanding of quantum mechanics.

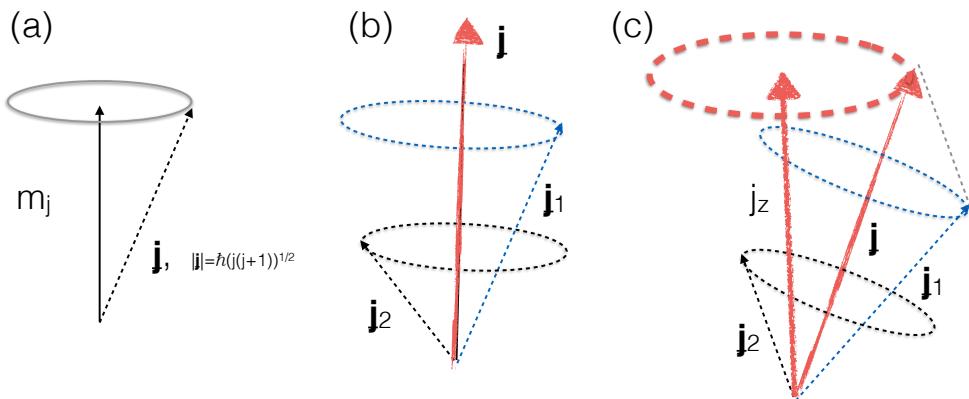


Figure 4.4: (a) The Vector model for an isolated angular momentum. The spin precesses around the vertical direction in an applied field. However it does not have a definite azimuthal angle. (b) Combining two angular momentum to give j . The individual angular momentum vectors precess around \vec{j} . (c) \vec{j} itself is inclined to the quantization axis and precesses in a field. It is now clear that j_{1z} and j_{2z} no longer have definite values.

4.4 Other relativistic corrections

There are two further relativistic correction terms to consider.

1. The mass-velocity term

The kinetic energy is given relativistically by $E = \sqrt{p^2 c^2 + \mu^2 c^4} - \mu c^2$ which gives a correction to the Schrödinger equation

$$\Delta \hat{H}_{\text{kin}} = -\frac{p^4}{8\mu^3 c^2} \quad (4.39)$$

It is shown in the problems that this leads to a correction to the energy levels

$$\Delta E_{\text{kin}} = -E_N \frac{(Z\alpha)^2}{N^2} \left[\frac{3}{4} - \frac{N}{l+1/2} \right] \quad (4.40)$$

It breaks the degeneracy between different l .

2. The Darwin term

This is related to the singularity of the Coulomb potential at the origin and has no classical analogue. The following is an account of its origin.

Based on the energy-time uncertainty principle a positron-electron pair requiring energy $2\mu c^2$ can be created for a short time $T \sim \hbar/2\mu c^2$. In this time a positron and electron can separate and recombine. For a periodic oscillation with relative velocity $c \cos(\pi t/T)$ they reach a maximum separation $\delta r \sim cT/\pi \sim \hbar/\mu c \sim 4 \times 10^{-11}$ cm.

The electron coordinate fluctuates for wavepackets smaller than this length scale (in detail this arises from an interference between positive and negative energy solutions of the relativistic Dirac equation; the resulting motion is termed ‘Zitterbewegung’ or trembling). The potential energy should then be averaged over this length scale $\delta r \sim \hbar/\mu c$.

If the potential is Taylor expanded

$$V(r + \delta \vec{r}) = V(r) + \delta \vec{r} \cdot \nabla V + \frac{1}{2} \sum_{ij} \delta r_i \delta r_j \frac{\partial^2 V}{\partial r_i \partial r_j} \quad (4.41)$$

Averaging over time

$$\langle V(r) \rangle = V(r) + \frac{1}{2} \sum_i \langle \delta r_i^2 \rangle \frac{\partial^2 V}{\partial r_i^2} \quad (4.42)$$

$$= V(r) + \frac{1}{6} \left(\frac{\hbar}{\mu c} \right)^2 \nabla^2 V \quad (4.43)$$

Finally, $\nabla^2(1/r) = 4\pi\delta(r)$ so we see this only gives a contribution at the origin where the potential diverges. The exact result differs only by replacing the numerical factor 1/6 by 1/8 and is

$$\Delta \hat{H}_{\text{Darwin}} = \frac{\pi \hbar^2}{2\mu^2 c^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \delta(0) \quad (4.44)$$

Levels with $l \neq 0$ have no amplitude at the origin and are unaffected. The shift in energy can be rewritten

$$\Delta E_{\text{Darwin}} = -E_n \frac{(Z\alpha)^2}{N} \delta_{l,0} \quad (4.45)$$

where α is referred to as the *fine structure constant* and is given by $e^2/(4\pi\epsilon_0\hbar c)$.

4.4.1 Summary of relativistic corrections for the H-atom

In hydrogen the mass-velocity and Darwin corrections are comparable to the spin-orbit correction in magnitude. All 3 combine to give the total relativistic correction:

$$\Delta E_{nj}^{\text{rel}} = E_n \left(\frac{Z\alpha}{N} \right)^2 \left(\frac{N}{j+1/2} - \frac{3}{4} \right) \quad (4.46)$$

The Dirac theory lifts some but not all of the degeneracy of the E_n from the Schrödinger treatment. The bottom line for hydrogen is that the energy levels are determined by n and j , as shown in FIG 4.5.

As Z increases, the spin-orbit interaction becomes by far the dominant relativistic effect.

4.5 Hyperfine Interactions

This is the name given to further corrections to the energy levels found in QED and due to the nuclear spin.

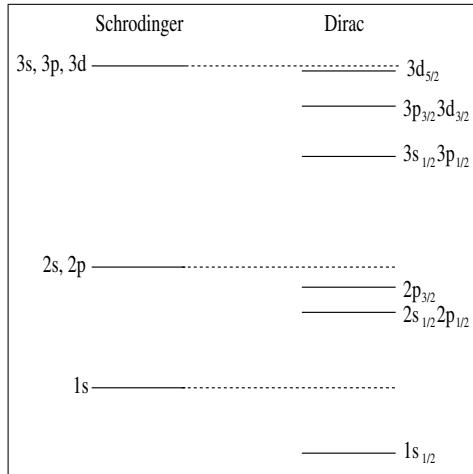


Figure 4.5: Comparison of the Schrödinger and Dirac energy levels of the hydrogen atom.

4.5.1 Lamb shift

So far we have found relativistic shifts of order $\alpha^2 \epsilon_0 \sim 10^{-4}$ Ry. The actual numbers are even smaller $\sim 2.10^{-5}$ eV. The two states $l = j \pm 1/2$ (e.g. $2s_{1/2}$ and $2p_{1/2}$) are still degenerate. This final degeneracy is lifted in quantum electrodynamics (QED). QED considers fluctuations of the electromagnetic field (zero-point motion). This is stronger nearer the nucleus where the potential is most attractive and acts to counteract the attractive Coulomb potential slightly. The s-level feels this more strongly than the p-level since it has more weight closer to the nucleus and thus the state $2s_{1/2}$ will have a slightly *higher* energy than $2p_{1/2}$. The difference is only 4.10^{-6} eV. It is smaller than the broadening due to the Doppler shift from the random motion of atoms in a gas at room temperature and it was not observed experimentally until 1947 by Lamb and Rutherford. Its detection was instrumental in motivating the development of the theory of QED by Feynman and others.

4.5.2 Nuclear moments

There is an interaction between the moment of the nucleus and that of the electrons. As its name suggests it produces shifts smaller than the fine structure interactions, since the moment of the nucleus is smaller than that of the electron by the ratio m_e/m_p . It is important for NMR and the physics of gases of cold (neutral) atoms.

4.6 Link with Group Theory

This section is non-examinable and puts the subject in a wider context of theory you may cover in later courses.

In later courses if you study Group theory, you will see that the angular momentum addition theorem corresponds to combining irreducible representation of the rotation group SO3. In this context it is written

$$\hat{j}_1 \otimes \hat{j}_2 = \sum_{\oplus, |j_1 - j_2|}^{|j_1 + j_2|} j \quad (4.47)$$

In words it tells us how the product space of two irreducible vector spaces can be decomposed into irreducible representations of the rotation group. As shown in one of the problems $\hat{j}_1 \otimes \hat{j}_2 \otimes \hat{j}_3$ is associative i.e. $(\hat{j}_1 \otimes \hat{j}_2) \otimes \hat{j}_3 = \hat{j}_1 \otimes (\hat{j}_2 \otimes \hat{j}_3)$ so it does not matter in which order the j 's are combined.

The example we worked through in the text corresponds to

$$(1) \otimes (2) = (1) \oplus (2) \oplus (3). \quad (4.48)$$

We also saw a similar decomposition when we examined the Stark effect. We acted on an orbital angular momentum state l with the electric field, an operator $\propto z$ and found that the resulting state only coupled with states $l \pm 1$. This is an example of the application of the more general Wigner-Eckart theorem (one of the most important theorems in quantum mechanics).

This theorem is used to compare matrix elements of products of cartesian coordinates (eg. $V(\vec{r}) = z$ or $V(\vec{r}) = 2z^2 - x^2 - y^2$) taken between different angular momentum states. The first step is to express the operator in the matrix element as sums of products of radial parts \times spherical harmonics and consider each of these terms separately. The examples we have chosen correspond to single spherical harmonics $r\cos(\theta) = r\sqrt{4\pi/3} Y_{10}$ and $r^2(3\cos\theta^2 - 1) = r^2 4\sqrt{\pi/5} Y_{20}$. The spherical harmonic is then treated like an angular momentum state l, m . It is combined with the ket $|n, L, M\rangle$ in the matrix element to give total angular momentum states in the same way we combined angular momenta. The product of this with the bra $\langle n', L' M'|$ completes the expression. The matrix element is then

$$\langle n'L', M' | g(r) Y_{lm} | n, L, M \rangle = \underbrace{\langle L, l; L', M' | L, l; m, M \rangle}_{\text{Clebsch-Gordon coeff}} \langle n', L' | g(r) | n, L \rangle \quad (4.49)$$

The second matrix element on the right does not depend on M or M' and involves only the radial part of the wavefunctions. The theorem is useful since it allows us to compare the ratios of matrix elements between different pairs of angular momentum states without ever having to calculate messy radial integrals. To get absolute matrix elements the radial integral only has to be calculated once. It can also be used with total angular momentum states in place of the single particle orbital angular momentum states we have discussed.

Multi-electron atoms

5.1 Introduction

In this chapter we look at higher Z atoms. As well as multiplying the potential by Z this introduces several new effects

- (1) The Coulomb interaction between the electrons

$$H_1 = \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \quad (5.1)$$

where \vec{r}_i refers to the coordinates of the i 'th electron. This combines the coordinates of different electrons and means we cannot use separation of variables to write the state as a product i.e. $\psi(r_1, r_2) \neq \psi_1(r_1)\psi_2(r_2)$.

(2) We now have to ensure the wavefunction is anti-symmetric under particle exchange, since electrons are fermions.

- (3) There will be more complex interactions between the orbital motions and spins.

We will first consider (1) and (2) and work in the absence of spin-orbit terms and then come back to include spin-orbit coupling (3).

5.2 Identical particles

5.2.1 Spin Statistics Theorem (Pauli, 1940)

When we are dealing with several distinguishable particles we identify the particles by the order parameters are listed in ‘ket’s or ‘bra’s. $|r_1\rangle|r_2\rangle$ and $\langle r_1|\langle r_2|$ mean particle one has coordinate r_1 and particle two has coordinate r_2 . $|r_2\rangle|r_1\rangle$ and $\langle r_2|\langle r_1|$ mean particle one has coordinate r_2 and particle two has coordinate r_1 .

The particle exchange or permutation operator \hat{P}_{21} swaps the particle states attributed to particle one and two so that $\hat{P}_{21}|r_1\rangle|r_2\rangle = |r_2\rangle|r_1\rangle$ and $\hat{P}_{21}|r_2\rangle|r_1\rangle = |r_1\rangle|r_2\rangle$. Acting twice clearly leaves any state unchanged $\hat{P}_{21}\hat{P}_{21}|r_1\rangle|r_2\rangle = |r_1\rangle|r_2\rangle$ so $\hat{P}_{21}^2 = 1$.

If the particles are indistinguishable then swapping the labels leaves the Hamiltonian (and any physical operator) unchanged so $[\hat{P}_{21}, \hat{H}] = 0$. The energy eigenstates for two identical particles can therefore always be *chosen* to be eigenstates of \hat{P}_{21} . Since $\hat{P}_{21}^2 = 1$ its eigenvalues are $\alpha = \pm 1$. The wavefunction is called anti-symmetric if the particle exchange eigenvalue is -1 and symmetric if it is 1 . Particles whose wavefunctions reverse sign under particle exchange ($\alpha = -1$) are fermions and those whose wavefunction is unchanged ($\alpha = 1$) under particle exchange are bosons.

The above ideas can be extended to a collection of more than two identical particles. Any permutation can be built up as a sequence of particle swaps. We can then show that for a collection of identical particles if the state obtained swapping all pairs of states are eigenstates of the exchange operator and one pair has a particular eigenvalue, all other single exchange operations have the same eigenvalue. To see this consider the case where swapping the first two particles in a set of three corresponds to an eigenvalue α (either $\alpha = 1$ or -1) i.e. $\hat{P}_{213}|r_1, r_2, r_3\rangle = \alpha|r_1, r_2, r_3\rangle$. Since $\hat{P}_{132} = \hat{P}_{213}\hat{P}_{321}\hat{P}_{213}$ (see

FIG 5.1) and $\alpha^2 = 1$ we have $\hat{P}_{132} = \hat{P}_{321}$. In fact any cyclic permutation of an odd number of indices gives an equivalent operator. Therefore if \hat{P}_{213} has eigenvalue α so does \hat{P}_{132} . Thus if two particles in a collection of identical particles are demonstrated to be fermions or bosons, then all the particles in the collection have the same exchange symmetry.

The spin statistics theorem, which we do not prove here states that integer spin particles are always bosons and half-integer spin particles are always fermions. In relativistic quantum field theory it has been shown that spin 1/2 particles cannot be bosons and integer spin particles cannot be fermions, but this does not explain why we have to have a definite exchange symmetry in the first place (recall we can *choose* energy eigenstates states to have a definite symmetry since $[\hat{P}_{12}, \hat{H}] = 0$, but we could also choose superpositions of symmetric and anti-symmetric states with no definite exchange symmetry for degenerate states. Feynman points out in his lectures that since there is no simple explanation of the ‘spin statistics theorem’ we cannot say we understand it.

All observed particles in 3D to date are either fermions or bosons. Examples of fermions are electrons, protons and neutrons. Examples of bosons are composite particles such as atoms where the spins combine to give entities with integer spin e.g. ${}^4\text{He}$ atoms. Photons and phonons (lattice vibrations) are also Bosons.¹

The next task is to write down explicit expressions for the eigenfunctions when we have two or more identical particles.

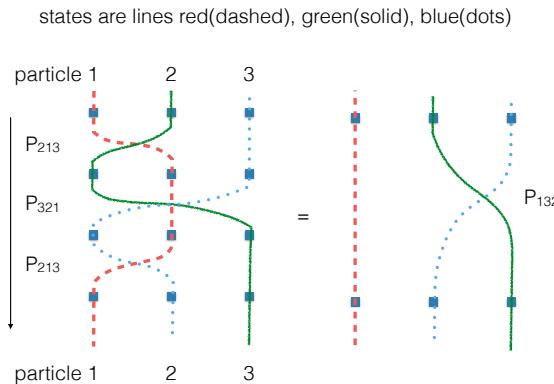


Figure 5.1: Permutation of particle states. The vertical lines of dots represent particular particles. \hat{P}_{132} means leave particle 1 in the same state, but swap the states of particles 2 and 3. At the end of the operations shown particle 1 is in the red (dashed line) state, particle 2 is in the blue (dots) state and particle 3 is in the green state (solid). This is the same as produced in the right hand figure.

5.3 Symmetric and anti-symmetric wavefunctions

Even when we cannot use separation of variables, products of the single electron wavefunctions $\phi_i(r)$ still form a complete basis.

We’ll consider just two fermions or two bosons and then generalise the result to N-particles. For two particles in specific states there are two degenerate product states $|\phi_1\rangle|\phi_2\rangle$ and $|\phi_2\rangle|\phi_1\rangle$, neither of which has a defined symmetry under particle exchange. Linear combinations can be chosen that are symmetric

¹In 2D it may be possible to have ‘anyons’ that are neither bosons or fermions. Supersymmetry theories also consider composite fermion-boson excitations, but this is beyond the scope of this course.

or atnisymmetric under particle exchange

$$|\phi_1, \phi_2\rangle_+ = (|\phi_1\rangle |\phi_2\rangle + |\phi_2\rangle |\phi_1\rangle)/\sqrt{2} \quad \text{symmetric} \quad (5.2)$$

$$|\phi_1, \phi_2\rangle_- = (|\phi_1\rangle |\phi_2\rangle - |\phi_2\rangle |\phi_1\rangle)/\sqrt{2} \quad \text{antisymmetric} \quad (5.3)$$

For fermions we only retain the antisymmetric combination and for bosons only the symmetric combination. Wavefunctions can be written acting with $\langle r_1 | \langle r_2 |$

$$\Psi_{\pm}(r_1, r_2) = \langle r_1 | \langle r_2 | (|\phi_1\rangle |\phi_2\rangle \pm |\phi_2\rangle |\phi_1\rangle)/\sqrt{2} \quad (5.4)$$

$$= (\phi_1(r_1)\phi_2(r_2) \pm \phi_2(r_1)\phi_1(r_2))/\sqrt{2} \quad (5.5)$$

with the subscript + denoting symmetric and - antisymmetric wavefunctions in EQN 5.2 -EQN 5.4; in general we can drop this subscript since we know whether we are talking about fermions or bosons.

A general 2-electron wavefunction can be constructed as a superposition of such products, spanning all combinations of the single particle states:

$$|\Psi\rangle_{\pm} = \sum_{i>j} c_{ij} \frac{1}{\sqrt{2!}} (|\phi_i\rangle |\phi_j\rangle \pm |\phi_j\rangle |\phi_i\rangle) \quad \text{only for bosons} \quad (5.6)$$

$$\equiv \sum_{i \geq j} c_{ij} |\phi_i, \phi_j\rangle \quad (5.7)$$

The c_{ij} are coefficients and in the second line $c_{ii} = 0$ for fermions; this is the Pauli exclusion principle. The sum is restricted to $i \geq j$ to avoid double counting. From now on when there are several particles listed in the same ket as in EQN 5.7, it is automatically implied that the wavefunction is symmetric (for bosons) or antisymmetric (for fermions). If this is not intended then round brackets are used e.g. $|r_1, r_2\rangle \equiv |r_1\rangle |r_2\rangle$. The order of the states in $|\phi_i, \phi_j\rangle$ does not matter for bosons ($|\phi_i, \phi_j\rangle \equiv |\phi_j, \phi_i\rangle$) but determines an overall sign for fermions ($|\phi_i, \phi_j\rangle = -|\phi_j, \phi_i\rangle$).

If there is no interaction between the particles then the eigenstates of the Hamiltonian are built up from combinations of two single particle states with energy $\epsilon_i + \epsilon_j$. This may already require more than one non zero c_{ij} in EQN 5.7. We can use perturbation theory as usual.

5.3.1 An example. Two particles in a harmonic potential

(a) What are the 3 lowest eigenstates for two non-interacting identical spinless particles in a 1D potential $Kx^2/2$?

Since the particles have zero spin we are dealing with bosons. The single particle energy states for a harmonic potential are denoted $|n\rangle$ with energy $E_n = (1/2 + n)\hbar\omega$ with $m\omega^2 = K^2$. The 3 lowest energy single particle wavefunctions are list in table 5.1.

Table 5.1: Harmonic oscillator wavefunctions with $a_0^2 = \hbar/m\omega$.

ψ_0	$\frac{1}{(\pi a_0^2)^{1/4}} e^{-x^2/2a_0^2}$
ψ_1	$\frac{1}{(\pi a_0^2)^{1/4}} \sqrt{2} \frac{x}{a_0} e^{-x^2/2a_0^2}$
ψ_2	$\frac{1}{(\pi a_0^2)^{1/4}} \frac{1}{\sqrt{2}} \left(2\frac{x^2}{a_0^2} - 1\right) e^{-x^2/2a_0^2}$

The ground state has both bosons in the same state $|0, 0\rangle = |0\rangle |0\rangle$ and energy $\hbar\omega$.

The first excited state has one particle in the $n = 1$ level $|1, 0\rangle = (|1\rangle |0\rangle + |0\rangle |1\rangle)/\sqrt{2}$, energy $2\hbar\omega$.

The second excited level is degenerate, since both $|2, 0\rangle = (|2\rangle |0\rangle + |0\rangle |2\rangle)/\sqrt{2}$ and $|1, 1\rangle = |1\rangle |1\rangle$ have energy $E = 3\hbar\omega$.

(b) Suppose there is now a weak interaction potential between the particles $V = \lambda \delta(x_1 - x_2)$. How are the energies of these states modified?

The ground state energy is shifted by

$$\Delta E_0 = \langle 0 | \langle 0 | \lambda \delta(x_1 - x_2) | 0 \rangle | 0 \rangle \quad (5.8)$$

$$= \lambda \int dx_1 \int dx_2 |\psi_0(x_1)|^2 |\psi_0(x_2)|^2 \delta(x_1 - x_2) \quad (5.9)$$

$$= \lambda \int dx_1 |\psi_0(x_1)|^4 \quad (5.10)$$

$$= \lambda \int dx_1 \frac{1}{\pi a_0^2} e^{-2x_1^2/a_0^2} = \frac{\lambda}{\sqrt{2\pi} a_0} \quad (5.11)$$

where in the last line we used the single particle ground state wavefunction from table 5.1

The first excited state energy is shifted by

$$\Delta E_1 = \frac{1}{2} (\langle 0 | \langle 1 | + \langle 1 | \langle 0 |) \lambda \delta(x_1 - x_2) (\langle 0 | 1 \rangle + \langle 1 | 0 \rangle) \quad (5.12)$$

$$= 2\lambda \int dx_1 \psi_0^2(x_1) \psi_1^2(x_1) \quad (5.13)$$

$$= 4\lambda \int dx_1 \frac{1}{\pi a_0^2} \frac{x_1^2}{a_0^2} e^{-2x_1^2/a_0^2} \quad (5.14)$$

$$= \frac{\lambda}{\sqrt{2\pi} a_0} \quad (5.15)$$

To estimate the shifts for the second excited state we would need to use degenerate perturbation theory.

5.3.2 Spin

For fermions (or spinful bosons) we have to consider spin. The electron spin can be included by replacing \mathbf{r} with $x = \{\vec{r}, s\}$ where s is the two component spinor. Conventionally we work with linear combinations of the following two spin states:

$$\alpha \equiv \uparrow \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \beta \equiv \downarrow \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (5.16)$$

We can consider the spin to be part of description of the particle state. However it is sometimes useful to consider the spin as a more independent entity. If $[\hat{H}, \hat{S}] = 0$ we can choose an energy eigenstate to be an eigenstate of the total spin and factor the wavefunction

$$\Psi(x_1, x_2) = \sum_i \psi_i(\mathbf{r}_1, \mathbf{r}_2) \chi_i(s_1, s_2). \quad (5.17)$$

where $\chi_i(s_1, s_2)$ are eigenstates of $\hat{S}^2 = (\hat{s}_1 + \hat{s}_2)^2$ and $\hat{S}_z = \hat{s}_{1z} + \hat{s}_{2z}$ with the same eigenvalues. For two electrons the spin eigenstates are unique (see below) so there is only one term in the sum for each set of quantum numbers S, M_S . These states also have a definite symmetry under exchange of the spin coordinate alone.

Two spins have 4 possible states. The spins s_1 and s_2 can be combined (exactly as we combined l and s) to give a total spin $S = 0$ or 1 . The $S = 1$ state comprises $M_S = -1, 0, 1$ whereas the $S = 0$ state only has $M_S = 0$. The states with fixed S have definite symmetries under particle exchange as is seen by writing out the wave functions explicitly.

S	$M_S \equiv S_z$	$\chi(s_1, s_2)$	symmetry
0	0	$\frac{1}{\sqrt{2}}(\alpha\rangle \beta\rangle - \beta\rangle \alpha\rangle)$	odd
1	-1	$ \beta\rangle \beta\rangle$	even
1	0	$\frac{1}{\sqrt{2}}(\alpha\rangle \beta\rangle + \beta\rangle \alpha\rangle)$	even
1	1	$ \alpha\rangle \alpha\rangle$	even

The coefficients in the 3rd column of the table are nothing other than the Clebsch-Gordon coefficients. The eigenstate with total spin $S = 0$ is seen to be odd (antisymmetric) and the $S = 1$ states are even (symmetric) under particle exchange. Overall the wavefunction (spin and space parts combined) must be antisymmetric so the corresponding spatial parts of the wavefunction must be even for $S = 0$ and odd for $S = 1$. The three $S=1$ states are referred to collectively as the spin triplet states and the $S = 0$ state as the spin singlet state.

If we look back at EQN 5.5 we see that a single anti-symmetric state (determinant) is not necessarily a spin eigenstate.

$$(r_1, s_1; r_2, s_2 | \phi_1, \phi_2) = \frac{1}{\sqrt{2}} (\phi_1(r_1)\chi_1(s_1)\phi_2(r_2)\chi_2(s_2) - \phi_2(r_1)\chi_2(s_1)\phi_1(r_2)\chi_1(s_2)) \quad (5.18)$$

$$= \frac{1}{2\sqrt{2}} \underbrace{(\phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2))}_{\sqrt{2}\phi_a} \underbrace{(\chi_1(s_1)\chi_2(s_2) + \chi_2(s_1)\chi_1(s_2))}_{\sqrt{2}\chi_s} \quad (5.19)$$

$$+ \frac{1}{2\sqrt{2}} \underbrace{(\phi_1(r_1)\phi_2(r_2) + \phi_2(r_1)\phi_1(r_2))}_{\sqrt{2}\phi_s} \underbrace{(\chi_1(s_1)\chi_2(s_2) - \chi_2(s_1)\chi_1(s_2))}_{\sqrt{2}\chi_a} \quad (5.20)$$

$$= \frac{1}{\sqrt{2}} (\phi_a(r_1, r_2)\chi_s(s_1, s_2) + \phi_s(r_1, r_2)\chi_a(s_1, s_2)) \quad (5.21)$$

which is combination of two spin states if $s_1 \neq s_2$ (if $s_1 = s_2$ then $\chi_a(s_1, s_2) = 0$). Conversely the eigenstates $(S, M_S) = (1, 0)$ and $(0, 0)$ have two non zero coefficients in EQN 5.7.

If we consider 3 electrons the spin part and space parts of the wavefunction are no longer necessarily separately symmetric and antisymmetric under particle exchange (the total wavefunction is however always antisymmetric). We could combine 3 electrons to obtain $S = 3/2$ (once) and $S = 1/2$ (twice). The total number of spin states is $4 + 2 + 2 = 2^3$. The special case where $M_s = S$ is spin symmetric (since it contains the combination with all the spins parallel) and therefore has an antisymmetric space part. The two $S = 1/2$ states however individually have mixed symmetry (ie are neither even or odd under particle exchange). They have to be combined with mixed symmetry spatial states to give overall anti-symmetric wavefunctions. We will limit our consideration to just two electrons in the next section and return to consider larger numbers of electrons later.

To summarise this section: for 2 electrons the basis (S, M_S) imposes spatial wave-functions with a definite exchange symmetry. This simple decomposition does not work for more than 2 electrons.

5.4 Helium

The starting point is the Hamiltonian with no electron-electron interactions

$$H_0 = \frac{Ze^2}{4\pi\epsilon_0 r_1} + \frac{Ze^2}{4\pi\epsilon_0 r_2} \quad (5.22)$$

This is separable and the single electron states are simply those of the hydrogen atom but with $Z = 2$ (the energies are the sum of two hydrogen levels multiplied by $Z^2 = 4$; the orbit radius is divided by Z so the Coulomb energy goes as $Z/r \propto Z^2$). The two electron wavefunction has to be antisymmetric. Putting two electrons in the lowest $N = 1$ state requires them to have opposite spin. The energy of the ground state is -8 Ry. The next excited state has one electron in the $N = 2$ shell. $S = 0$ and $S = 1$ combinations are possible for this. These states can have $L = 0$ ($1s^1 + 2s^1$) or 1 ($1s^1 + 2p^1$). To label atomic configurations in general we use Russell-Saunders notation.

5.4.1 Russell-Saunders notation

A level is described by 3 angular momentum quantum numbers and represented by a symbol

$$^{2s+1}L_J \quad (5.23)$$

where $2s + 1$ is the spin degeneracy. L the total orbital angular momentum and J the total angular momentum.

For example the ground state of He is 1S_0 . The excited states with one electron promoted to $N = 2$ can have $S = 0$ or 1 and $L = 0$ or 1 . The allowed states are given in the following table

S	L	J	$^{2s+1}L_J$	$r_1 \leftrightarrow r_2$
0	0	0	1S_0	even
0	1	1	1P_1	even
1	0	1	3S_1	odd
1	1	0	3P_0	odd
1	1	1	3P_1	odd
1	1	2	3P_2	odd

The elements in the table are obtained by liberal use of the angular momentum addition theorem. The even or odd designation is determined from S and indicates whether a symmetric combination (even) or anti-symmetric (odd) combination of the constituent single-electron spatial wavefunctions applies.

The promoted electron has 8 possible states ($2 \times s$ and $6 \times p$) that are each combined with 2 possible spin directions for the electron left in the $N = 1$ shell giving 16 states in total (no state is excluded by Pauli-exclusion). The total number of states may also be obtained by noting there are $(2J + 1)$ states of J_z for each entry in the table; $\sum(2J + 1) = 1 + 3 + 3 + 1 + 3 + 5 = 16$. Ignoring the electron-electron interaction these will all have energy $-4/1^2 - 4/2^2 = -5$ Ry.

As we turn on the perturbations we retain the above labelling. The Eigenstates could in principle become linear combinations of these states due to mixing by the perturbation.

5.4.2 Electron-Electron Coulomb Energy

The inter-electron Coulomb interaction H_1 (EQN 5.1) is symmetric under particle exchange and does not involve spin. Therefore $L, L_z \equiv M_L, S, S_z \equiv M_s$ are good quantum numbers. The set L, S, J, M_J are equally good. l_1, l_2, s_1, s_2 are clearly not good since the individual particles are indistinguishable.

We can use perturbation theory to calculate corrections to the energy levels. Different values of these quantum numbers could have different energies. However, the Hamiltonian is symmetric under rotation of the electron and spin coordinates separately (in so far that we neglect spin-orbit). The energy cannot depend on the direction chosen for our quantisation axes therefore for a given L and S the energies must remain degenerate for different M_L and M_S . Thus at this stage we only need label the states 1S (degeneracy 1), 1L (degeneracy 3), 3S (degeneracy 3) and 3L (degeneracy 9); J is redundant.

We can explain the degeneracy described above formally starting from $[\hat{H}, \hat{S}_x] = [\hat{H}, \hat{S}_y] = [\hat{H}, \hat{S}_z] = 0$. For eigenstates $|M_S\rangle$ of \hat{H} with eigenvalue E , $\hat{S}_x|M_S\rangle$ and $\hat{S}_y|M_S\rangle$ must generate other eigenstates with the same E . In particular the raising and lowering operators must generate new (orthogonal) eigenstates or 0. $\hat{S}_x \pm i\hat{S}_y|M_S\rangle \propto |M_S \pm 1\rangle$. Thus the fact that \hat{H} commutes with $\hat{S}_{x,y,z}$ implies that states with the same S and different M_S are degenerate. Since $[\hat{H}, \hat{L}_x] = [\hat{H}, \hat{L}_y] = [\hat{H}, \hat{L}_z] = 0$, states with different M_L within an L multiplet are also degenerate. Thus the energy levels only depend on $L = 0, 1$ and $S = 0, 1$.

Ground State Energy

The ground state 1S_0 is non degenerate. The first order correction to the ground state energy is

$$\Delta E = \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z^3}{\pi a_0^3} \right)^2 \int \int d^3 r_1 d^3 r_2 \frac{1}{r_{12}} e^{-2Z(r_1+r_2)/a_0} \quad (5.24)$$

$$= \frac{5}{4} Z \text{ Ry} = 2.5 \text{ Ry} \quad (5.25)$$

The integral is done analytically in one of the tutorial problems (also see Bransden and Joachain, *Intro to QM*, p465). The net result is the first order estimate of the ground state energy is -5.5 Ry = - 74.8 eV compared with the ‘exact’ answer -78.957 eV.

Lowest Excited States

We will work in the basis (L, S, M_L, M_s) . As already explained the Hamiltonian is diagonal in this basis. We are free to choose a particular value of M_L (eigenstate of \hat{L}_z) to calculate the energy shift, which is independent of M_L . The first order perturbation expressions are, denoting the singlet state ($S = 0$) with “+” and the triplets ($S = 1$) with “−”:

$$\Delta E(L=0)_{\pm} = \frac{1}{2}(\langle 1s | \langle 2s | \pm \langle 2s | \langle 1s |) \frac{1}{4\pi\epsilon_0 r_{12}}(|1s\rangle |2s\rangle \pm |2s\rangle |1s\rangle) \quad (5.26)$$

$$\Rightarrow \Delta E(L=0)_{\pm} = \underbrace{\int \int d^3 r_1 d^3 r_2 \frac{|\psi_{1s}(r_1)|^2 |\psi_{2s}(r_2)|^2}{4\pi\epsilon_0 |r_1 - r_2|}}_{\mathcal{J}_0} \pm \underbrace{\int \int d^3 r_1 d^3 r_2 \frac{\psi_{1s}(r_1)^* \psi_{2s}(r_1) \psi_{2s}(r_2)^* \psi_{1s}(r_2)}{4\pi\epsilon_0 |r_1 - r_2|}}_{\mathcal{K}_0} \quad (5.27)$$

and

$$\Delta E(L=1)_{\pm} = \frac{1}{2}(\langle 1s | \langle 2p | \pm \langle 2p | \langle 1s |) \frac{1}{4\pi\epsilon_0 r_{12}}(|1s\rangle |2p\rangle \pm |2p\rangle |1s\rangle) \quad (5.28)$$

$$\Rightarrow \Delta E(L=1)_{\pm} = \underbrace{\int \int d^3 r_1 d^3 r_2 \frac{|\psi_{1s}(r_1)|^2 |\psi_{2p}(r_2)|^2}{4\pi\epsilon_0 |r_1 - r_2|}}_{\mathcal{J}_1} \pm \underbrace{\int \int d^3 r_1 d^3 r_2 \frac{\psi_{1s}(r_1)^* \psi_{2p}(r_1) \psi_{2p}(r_2)^* \psi_{1s}(r_2)}{4\pi\epsilon_0 |r_1 - r_2|}}_{\mathcal{K}_1} \quad (5.29)$$

(5.30)

The *direct* terms \mathcal{J}_0 and \mathcal{J}_1 are the same as obtained for distinguishable particles. The *exchange* terms \mathcal{K}_0 and \mathcal{K}_1 come from working with identical particles. The \pm show that although the Hamiltonian does not depend explicitly on spin the energy levels do depend on the total spin, owing to the spin’s role in determining the overall particle exchange symmetry. The exchange terms have no classical analogue. The energy levels are summarised in FIG 5.2. Choosing wavefunctions with $M_L = 0$ in the above expressions means the wavefunctions are real and helps clarify that both \mathcal{J} ’s and \mathcal{K} ’s are positive. The triplet terms therefore have lower energies than the singlets for each L ; the spatially antisymmetric wavefunctions hold the electrons further apart and thus reduce their mutual repulsion energy. The $1s$ -level has less overlap with the $2s$ level than with the $2p$ levels and therefore the $L = 0$ state has lower energy than $L = 1$.

We have found that the $S = 1$ states have a different energy from the $S = 0$ states for the same L even though the Hamiltonian does not depend on the spin. This resulted from the spin-statistics theorem that selected different spatial dependences dependent on the choice of S .

For the special case of just two electron in the same nl i.e. an $(nl)^2$ configuration it turns out that only $L + S = \text{even}$ satisfies the anti-symmetry requirement, since $L = \text{even}$ is symmetric and $L = \text{odd}$ is antisymmetric under exchange (not proven here).

5.5 Many electrons

To consider higher atomic number atoms we need to write an anti-symmetric wavefunction for N electrons.

$$\Psi = \sum_{\substack{i j k \dots \\ \text{N indices}}} c_{ijk\dots} |\phi_i, \phi_j, \phi_k \dots\rangle \quad (5.31)$$

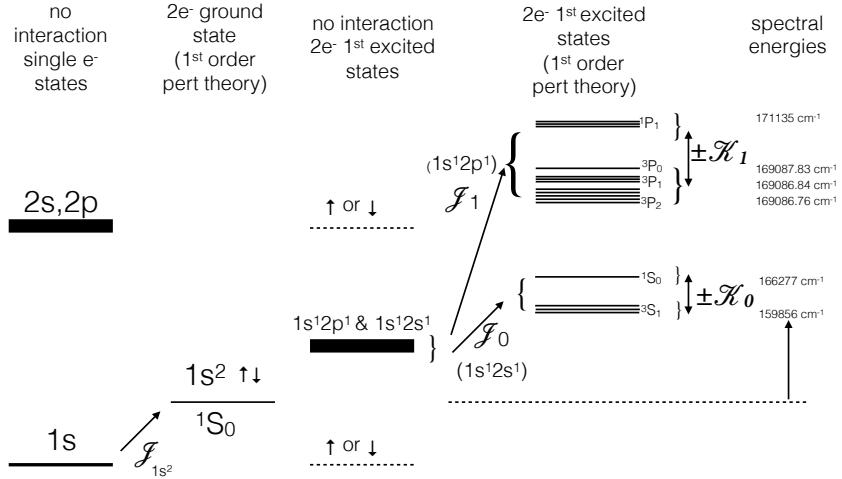


Figure 5.2: The ground state and lowest excited energy levels of the neutral helium atom (energies per electron). The wavenumber ($1/\lambda$) of the excitations from the ground state are shown. $\Delta E = \hbar c(1/\lambda)$. Degenerate levels are shown close together or as thick lines. Dashed lines serve only as guide lines linking different columns.

where the states on the right are totally symmetric or anti-symmetric

$$|\phi_i, \phi_j, \phi_k \dots\rangle = \frac{1}{\sqrt{N!}} \sum_{P_{ijk\dots}} \zeta^P |\phi_{Pi}\rangle |\phi_{Pj}\rangle |\phi_{Pk}\rangle \dots \quad (5.32)$$

The sum in this last expression is not over $i, j, k \dots$ but permutations P of their order. ζ is -1 for fermions and 1 for bosons. The power P is the number of swaps of indices required to get each specific permutation. An initial ordering of wavefunctions needs to be defined by convention (e.g. according to increasing quantum numbers of the one particle states). There are $N!$ (N is the number of electrons) terms to sum over on the right hand side. The pre-factor $1/\sqrt{N!}$ is for normalisation, so that $\langle \Psi | \Psi \rangle = 1$ (each of the $N!$ terms only gives a non-zero term when paired with one term in the conjugate wavefunction ²).

Acting on the left with (r_1, r_2, \dots, r_N) gives the wavefunctions

$$\Psi_{ijk\dots N}(r_1 \dots r_N) = \frac{1}{\sqrt{N!}} \sum_P \zeta^P \phi_{Pi}(r_1) \phi_{Pj}(r_2) \dots \quad (5.33)$$

$$= \frac{1}{\sqrt{N!}} \text{Det} \begin{bmatrix} \phi_1(\underline{r}_1) & \phi_2(\underline{r}_1) & \phi_3(\underline{r}_1) & \dots \\ \phi_1(\underline{r}_2) & \phi_2(\underline{r}_2) & \phi_3(\underline{r}_2) & \dots \\ \phi_1(\underline{r}_3) & \phi_2(\underline{r}_3) & \phi_3(\underline{r}_3) & \dots \\ \dots & & & \dots \end{bmatrix} \quad (5.34)$$

The order of the terms in the product on the right of this expression can be rearranged since these are just functions and commute. Choosing this order to be the standard order of the 1 particle wavefunctions and enumerating these to be $i = 1, j = 2, \dots, N$ the expression can be rewritten with the permutation now applying to the order of the coordinates

$$\Psi(r_1 \dots r_N) = \frac{1}{\sqrt{N!}} \sum_P \zeta^P \phi_1(r_{P1}) \phi_2(r_{P2}) \dots \phi_N(r_{PN}) \quad (5.35)$$

²For bosons a similar expression to EQN 5.32 can be used with $\zeta = 1$ and with an extra normalisation factor $\prod_i \frac{1}{\sqrt{n_i!}}$ where n_i is the number of times each ϕ_i is repeated

This can be written as a Slater determinant.

$$\Psi_{\text{Slater}} = \frac{1}{\sqrt{N!}} \sum_{ijklm\dots} \epsilon_{ijklm\dots} \phi_1(\underline{r}_i) \phi_2(\underline{r}_j) \phi_3(\underline{r}_k) \phi_4(\underline{r}_l) \dots \quad (5.36)$$

$$= \frac{1}{\sqrt{N!}} \text{Det} \begin{bmatrix} \phi_1(\underline{r}_1) & \phi_1(\underline{r}_2) & \phi_1(\underline{r}_3) & \dots \\ \phi_2(\underline{r}_1) & \phi_2(\underline{r}_2) & \phi_2(\underline{r}_3) & \dots \\ \phi_3(\underline{r}_1) & \phi_3(\underline{r}_2) & \phi_3(\underline{r}_3) & \dots \\ \dots & & & \end{bmatrix} \quad (5.37)$$

where $\epsilon_{ijklm\dots}$ is the Levi cevita symbol. In some texts the Slater product is called a determinantal function and is denoted by the list of the wavefunctions in the order they appear along the diagonal.

5.6 Many electron atoms

We have seen that the wavefunction can be expressed as a sum of Slater determinants for fermions.

The total spin can be built up by combining individual spins to give the total spin quantum number S . Likewise we can combine the orbital wavefunctions to give an orbital state with total orbital angular momentum L which is also a good quantum number.

Before we look at a particular example we comment on the order levels are filled with respect to the individual n 's and l 's. This will determine the sets of $\phi_1 \dots \phi_N$ we want to consider for a particular atom or ion.



Figure 5.3: Aufbau Principle: orbits are filled in the sense of the arrows moving from right to left

5.7 The Aufbau Principle

This states that orbitals are filled in order of increasing $n + l$ FIG 5.3 (Aufbau is the German word for building up). Within each set of states having the same $n + l$ they are filled in order of increasing n . There are exceptions, for example copper has electronic configuration $1s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ instead of $1s^2 2p^6 3s^2 3p^6 4s^2 3d^9$ owing to the stability of completing a sub-shell.

The explanation is that the energies of the many electron states are not labelled by n alone as found for hydrogen, but by both n and l . This is the result found for a general central potential (rather than $V \propto 1/r$). The screening of nuclear charge by the inner electrons can be taken into account in a mean field way known as the Hartree and Hartree Fock approximations mentioned briefly at the end of the chapter. The order of filling of levels can then be calculated numerically. The principle is an empirical summary of the ordering of the elements in the periodic table also reflected in these calculations. In most cases the principle correctly identifies which combination of (n, l) known as a ‘sub-shell’ (reserving ‘shell’ to refer to n alone) we should start with to discuss the lowest energy states for a given atom or ion.

Finally we note that filled (n, l) will have zero angular momentum and zero spin and therefore not contribute to the *splitting* of energy levels of unfilled ‘sub-shells’. They of course do contribute to the total energy shift, but this is often a less interesting quantity.

5.7.1 Ground state of nitrogen

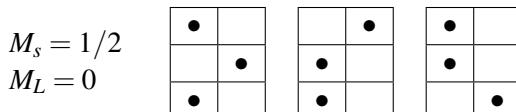
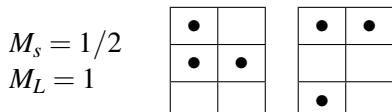
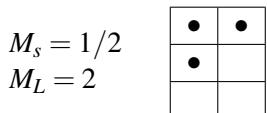
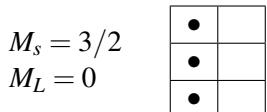
We will look at nitrogen to illustrate how an incompletely filled (n, l) state given from the Aufbau principle is split by electron-electron interactions and then spin-orbit coupling.

The idea is the following. We consider the filled ‘sub-shells’ to be already included in \hat{H}_0 and this simply modifies the radial potential. We then consider the remaining electrons in the unfilled ‘sub-shell’. Ignoring electron-electron interactions the states in the sub-shell are degenerate. We could construct products of one electron states from these. The key idea is that the Pauli principle rules out products in which a single state is doubly occupied. This restricts the values of L and S that are allowed, as we will see for nitrogen. This is the only way that such product states are eliminated. Each of the remaining simple products must therefore overlap with at least one of the anti-symmetric products that describe the eigenstates. L, S, J and M_J form a complete basis for describing the eigenstates (as we will show for nitrogen).

Nitrogen has atomic number 7 and electronic configuration $(1s^2)(2s^2)2p^3$. We are interested only in the $2p$ orbitals which are half occupied. We can represent the occupation of the individual levels within this manifold by putting the 3 electrons on the following grid:

		m_s	
		$1/2$	$-1/2$
m_l	1		
	0		
	-1		

The Pauli principle means there can be only one electron per cell. Possible states are



plus those with negative M_L and negative M_S making $2 + 4 + 8 + 6 = 20$ (since $C_3^6 = 20$ we have them all).

We can count the number of combinations possible for each M_L and M_s (table 5.2).

- There are far fewer states than when the exclusion principle does not operate (the exclusion principle does not operate when electrons are in different n -shells as for the excited state of He considered earlier).

- The states in table 5.2 form rectangles which can be identified with different Russel-Sanders multiplets:

If we start at an outside edge, $M_s = 1/2, M_L = 2$. This state can be assigned to $S = 1/2, L = 2, J = 5/2$ (recalling $m_j = m_l + m_s$) giving in spectroscopic notation ${}^2D_{5/2}$ (6 states). Lowering operators will move us down and to the right in the table (producing linear combinations of the states along the diagonal

	M_s			
	$3/2$	$1/2$	$-1/2$	$-3/2$
2	0	1	1	0
1	0	2	2	0
M_L	0	1	3	1
	-1	0	2	0
	-2	0	1	0

Table 5.2: number of independent states for each M_L and M_S for nitrogen $2p^3$

(elements $(M_L, M_S) = (2, -1/2) \& (1, 1/2)$). From $L = 2$ and $S = 1/2$ we also get ${}^2D_{3/2}$ (4 states). This completes the rectangle spanning $M_L = -2, 1, 0, 1, 2$ and $M_S = -1/2, 1/2$ (10 states in total). The other edge not covered by the above has $M_L = 0$ and $M_S = 3/2$ which corresponds to a RS state ${}^4S_{3/2}$ (4 states) covering the rectangle $M_L = 0, M_S = -3/2, -1/2, 1/2, 3/2$. The final rectangle left over starts with a state at $M_L = 1 M_S = 1/2$ corresponding to ${}^2P_{3/2}$ (4 states) and ${}^2P_{1/2}$ (2 states).

In summary we have catalogued the states as ${}^2D_{5/2}$, ${}^2D_{3/2}$, ${}^4S_{3/2}$, ${}^2P_{3/2}$, ${}^2P_{1/2}$, but we don't know how they are split or which one of these is the ground state. We have also shown that our catalogue is complete and contains all the product states permitted by the exclusion principle.

5.7.2 Relation to determinantal functions / Slater determinants

The above construction can be used to calculate Clebsch-Gordon coefficients relating the states $|L, S, J, J_z\rangle$ to the single electron states.

e.g. a particularly simple state in this case is the one with maximum S and J_z which is a symmetric in the spin part and therefore anti-symmetric in its space part.

$$(r_1, r_2, r_3 | {}^4S_{3/2}, J_z = 3/2\rangle \propto \left| \begin{array}{lll} \phi_{m_l=-1,\uparrow}(r_1), & \phi_{m_l=0,\uparrow}(r_1), & \phi_{m_l=1,\uparrow}(r_1) \\ \phi_{m_l=-1,\uparrow}(r_2), & \phi_{m_l=0,\uparrow}(r_2), & \phi_{m_l=1,\uparrow}(r_2) \\ \phi_{m_l=-1,\uparrow}(r_3), & \phi_{m_l=0,\uparrow}(r_3), & \phi_{m_l=1,\uparrow}(r_3) \end{array} \right| \quad (5.38)$$

For atomic states for several electrons in a ‘term’ our eigenstates can be expressed as a sum of Slater determinants of single electron wavefunctions in the m_l and m_s basis. $m_s = 1/2$ is denoted + and $m_s = -1/2$ is denoted -. A short hand for the determinantal function is then a sequence of \vec{m}_l^+ and \vec{m}_l^- states $\{\vec{m}_1^+, \vec{m}_1^-, \vec{m}_2^+, \vec{m}_2^-, \dots\}$. For example consider two electrons in a p^2 state with no spin-orbit splitting. There is no 1P state since we require $S + L = \text{even}$ for 2 electrons. Allowed determinantal functions with $L = 2, S = 0$ and $M_L = 1$ are $\{\vec{1}, \vec{0}\}$ and $\{\vec{1}, \vec{0}\}$. The actual state turns out to be an equal superposition of these two determinantal functions. Since $S = 0$ there is no spin-orbit splitting for this state which is ${}^1D_2; M_J = 1$.

We now wish to comment on the relative energies of the different levels.

5.8 Hund’s Rules for isolated atoms

The effects on the energy may be ranked in decreasing order of importance:

- (1) $1/r$ Coulomb potential. The energy levels depend only on n .
- (2) Central Field Approximation. The energy now includes screening of the nuclear charge by the inner shells of electrons. The effective potential is now given by Hartree or Hartree-Fock approximations and is no longer $1/r$. The outer single electron level energies now depend on n and l .
- (3) Non-central energies (electron-electron interactions). (i) The exchange energy favours putting electrons in antisymmetric spatial states which can best be achieved with parallel spins. States with different S now have different energies. (ii) The electrons are further apart if they are all orbiting in the same

direction. Thus states with larger L have lower energy. States with the same S and different L now have different energies. The collection of all the $(2L+1)(2S+1)$ states for a given (L, S) is called a ‘term’.

(4) Spin-orbit. Starting with definite L, S the levels are now split according to J .

$$\hat{H}_{SO} = \sum_i \xi \hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i \quad (5.39)$$

$$\approx \sum_i \xi \frac{(\hat{\mathbf{l}}_i \cdot \vec{L})(\hat{\mathbf{s}}_i \cdot \vec{S})}{LS} \mathbf{L} \cdot \mathbf{S} \quad (5.40)$$

$$= \xi(L, S) \hat{L} \cdot \hat{S} \quad (5.41)$$

In writing the above the hierarchy of the energy terms is important. The individual \vec{l} 's precess around the direction of \vec{L} (and the \vec{s} 's around \vec{S}) much more rapidly than \vec{L} and \vec{S} precess around \vec{J} . They have therefore been projected onto these average directions before considering the perturbation.

It turns out that the sign of $\xi(L, S)$ is positive if a sub-shell is less than half full and negative otherwise. $\hat{L} \cdot \hat{S}$ can be linked to \hat{J} via the *vector* identity

$$J^2 = L^2 + S^2 + 2\vec{L} \cdot \vec{S} \quad (5.42)$$

For fixed L and S states with different J therefore have energies proportional to $J(J+1)$. The separation between two successive levels J and $J-1$ is proportional to J . The states within a ‘term’ are now split into levels with different J . Each ‘level’ is described by a ‘term symbol’ $^{2S+1}L_J$. We will see later that each ‘level’ can be split into individual ‘states’ with different M_J by applying a magnetic field.

(5) Hyperfine interactions. Lamb shifts and coupling with nuclear spins. These are small and we don't consider them further in this chapter.

Hund's rules summarise how to choose the ground state from all the possible states, such as those enumerated for N in chapter 5.7.1.

5.8.1 Statement of Hund's rules

1. Maximise S
2. Maximise L
3. If the shell is less than half fill minimise J . If more than half full maximize J .

Hund's rules only apply to the ground state and do not give reliable predictions for ordering excited states.

Applying Hund's rules to Nitrogen we predict its ground state to be $^4S_{3/2}$.

As a second example consider Dy^{3+} important for magnetism. It has electron configuration (full shells) $(4f^9)$. Filling the f -shell with 9 electrons corresponds to the following Hund's rule configuration

		m_s
		1/2 -1/2

3		• •
2		• •
1		•
m_l		-----
0		•
-1		•
-2		•
-3		•

which is $^6H_{15/2}$. The high value of J explains why Dy has a large magnetic moment.

5.8.2 $j-j$ coupling

For cases where the spin-orbit coupling is stronger than the exchange interaction. l and s are coupled to give j 's before coupling the l 's to form L and the s 's to form S . This coupling scheme is called $j-j$ coupling as opposed to LS -coupling (Russell Saunders coupling). $j-j$ coupling applies to very heavy atoms (remember ξ increases like Z^4) and inner shells (generally for $Z^* > 35$ where Z^* is the screened charge), and for the structure of the nucleus. The change from Russell Saunders coupling to jj-coupling with increasing Z for the group 4 elements is shown in FIG 5.4.

The behaviour seen in figure FIG 5.4 can be understood from Hund's rules. The ground state for light group 4 atoms which have p^2 configuration has $L = 1, S = 1$ and $J = 0 \implies {}^3P_0$. Excited spin triplet states are 3P_1 and 3P_2 (including J_z degeneracy this makes 9 states in total). These initially split from each other linearly with the SO interaction in proportion to the value of J . This exhausts all the triplet states (since there are only 3C_2 possible fully polarised states). The next highest levels are spin singlets 1S_0 and 1D_2 (6 states). The total number of states is thus 15 (6C_2). The same number of states is found on the RHS of FIG 5.4 noting the Pauli principle prevents us putting two electrons in the same $|j, j_z\rangle$ state. e.g. for the lowest state we have two electrons in $j = 1/2$ and therefore must have one in each of $j_z = \pm 1/2$ which is a unique state and has $J = 0$.

In practice the coupling for heavy elements is intermediate between Russell Saunders and jj. This is seen from the deviation of the splitting of levels from the Russell Saunders prediction.

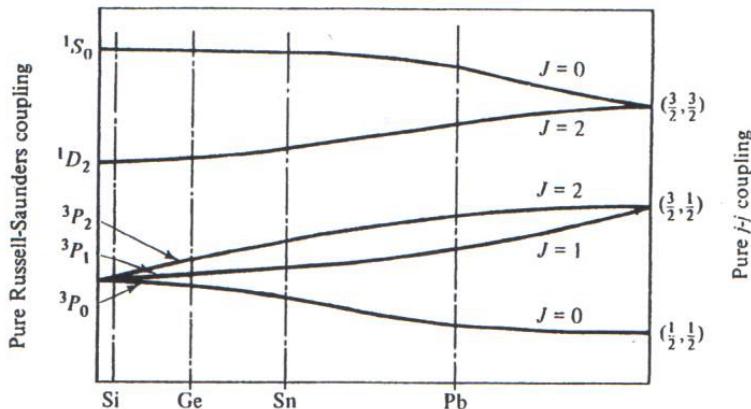


Figure 5.4: The lowest energy levels of the group 4 elements

5.8.3 solids

In solids the presence of nearby neighbouring atoms mean the potential is no longer rotationally symmetric but has a symmetry reflecting that of the crystal lattice. This correction to the potential is known as the crystalline electric field (CEF). For incomplete f-electron shells (rare earth metals; row 4f and 5f of the periodic table), this has a smaller effect than the spin-orbit interaction. The states may therefore be labelled according to the Russell Saunders scheme. The perturbation does however split the energies of the M_J levels. The splitting depends on the local point group symmetry at the atomic site (we shall not investigate this further here). For incomplete d-orbitals (transition metals; 3d and 4d rows of the periodic table) the orbitals extend further relative to the inter-ion separation and the CEF is a larger perturbation than the spin-orbit term. In fact it results in the orbits directing themselves along preferred inter-ion directions (see LCAO later when we discuss covalent bonding). Such directed orbits carry no angular momentum, so generally the orbital angular momentum is quenched in transition metal solids.

5.9 RayleighRitz Variational Method

This is an alternative method to perturbation theory for estimating shifts in energy levels. It is also a useful point of departure for understanding the Hartree and Hartree-Fock methods.

5.9.1 The method

A general wavefunction can be written in terms of a series of increasing energy eigenfunctions of the full Hamiltonian

$$|\Psi\rangle = \sum_n c_n |n\rangle \quad \text{with } E_1 \leq E_2 \leq E_3 \leq \dots \quad (5.43)$$

The expectation value of the energy is

$$\frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2} \geq E_1 \frac{\sum_n |c_n|^2}{\sum_n |c_n|^2} = E_1 \quad (5.44)$$

$$\Rightarrow \langle E \rangle \geq E_1 \quad (5.45)$$

Thus if we take a guess at the form of Ψ called a trial wavefunction Ψ_v (for example based on a modification of a solution for a similar Hamiltonian) that depends on parameters $\alpha_1, \alpha_2, \dots, \alpha_n$, we may vary $\Psi_v(\alpha_1, \alpha_2, \dots, \alpha_n)$ with respect to $\alpha_1, \alpha_2, \dots, \alpha_n$ to minimize $E(\alpha_1, \alpha_2, \dots, \alpha_n) = \langle \Psi_v | \hat{H} | \Psi_v \rangle / \langle \Psi_v | \Psi_v \rangle$ by solving

$$\frac{\partial E(\alpha_1, \alpha_2, \dots, \alpha_n)}{\partial \alpha_i} = 0 \quad i = 1 \dots n. \quad (5.46)$$

The minimum value of $E(\alpha_1, \alpha_2, \dots, \alpha_n)$ is the best estimate upper bound for the actual energy of the true ground state for a wavefunction of this form. Although the wavefunction is optimised to give the best estimate of the energy it may not be a good estimate for calculating other quantities.

A convenient simplification is achieved if we constrain the trial wavefunction to be normalised; this avoids the need for the denominator in EQN 5.44. A slightly different way of coping with the normalisation condition that can be generalised to include other constraints is to include Lagrange underdetermined multipliers. Consider minimising

$$E_\lambda(\alpha_1, \dots, \alpha_n) = \langle \Psi | H | \Psi \rangle - \lambda (\langle \Psi | \Psi \rangle - 1) \quad (5.47)$$

with respect to $\alpha_1, \dots, \alpha_n, \lambda$. The last condition enforces the normalisation. The constrained minimisation is achieved by solving the $n+1$ equations $\partial E / \partial \alpha_i = 0; \partial E / \partial \lambda = 0$. λ is referred to as the undetermined multiplier (it is so named since it is often eliminated from these simultaneous equations and never explicitly determined). In physics the optimum value of the multiplier often however has a physical significance - for the current example $\lambda = E$. This result may be seen by taking the unconstrained extremum of $\langle \psi | \hat{H} | \psi \rangle / \langle \psi | \psi \rangle$ which satisfies $\partial / \partial \alpha (\langle \psi | \hat{H} | \psi \rangle / \langle \psi | \psi \rangle) = 0$ and comparing with the same derivative of EQN 5.47.

5.9.2 Ground state energy of Helium by Rayleigh Ritz method

Our knowledge of hydrogen suggests a trial wavefunction $\Psi_v(r_1, r_2) = \frac{Z^*^3}{\pi a_0^3} e^{-Z^*(r_1+r_2)/a_0}$ which is just the product of two normalised single hydrogen states but with a single parameter to be determined, an effective charge Z^* , to capture the effect of screening.

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2\mu}(\nabla_1^2 + \nabla_2^2)}_{H_T} + \underbrace{\frac{Ze^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right)}_{H_V} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{H_{ee}} \quad (5.48)$$

The kinetic energy term $\langle \Psi_v(r_1, r_2) | \hat{H}_T | \Psi_v(r_1, r_2) \rangle$ gives a contribution to the energy

$$E_T = -2 \frac{\hbar^2}{2\mu} \left(\frac{Z^{*3}}{\pi a_0^3} \right) \int d^3r e^{-Z^*r/a_0} \nabla^2 e^{-Z^*r/a_0} \quad (5.49)$$

$$\stackrel{\text{parts}}{=} 2 \frac{\hbar^2}{2\mu} \left(\frac{Z^{*3}}{\pi a_0^3} \right) \int d^3r (\nabla e^{-Z^*r/a_0}) (\nabla e^{-Z^*r/a_0}) \quad (5.50)$$

$$= \frac{\hbar^2 Z^{*2}}{\mu a_0^2} \quad (5.51)$$

$$= 2(Z^*)^2 \text{ Ry} \quad (5.52)$$

The potential energy term gives a contribution

$$E_V = -2 \frac{Ze^2}{4\pi\epsilon_0} \left(\frac{Z^{*3}}{\pi a_0^3} \right) \int d^3r \frac{1}{r} e^{-2Z^*r/a_0} \quad (5.53)$$

$$= -2 \frac{Ze^2}{4\pi\epsilon_0 a_0} Z^* \quad (5.54)$$

$$= -4ZZ^* \text{ Ry} \quad (5.55)$$

Finally (see EQN 5.25)

$$E_{ee} = \langle \Psi_v | \frac{e^2}{4\pi\epsilon_0 r_{12}} | \Psi_v \rangle \quad (5.56)$$

$$= \frac{5}{4} Z^* \text{ Ry} \quad (5.57)$$

Thus in units of 1 Ry,

$$E(Z^*) = 2(Z^*)^2 - 4ZZ^* + \frac{5}{4} Z^* \quad (5.58)$$

Minimising with respect to Z^* gives $Z^* \equiv Z_{\text{eff}} = Z - 5/16$ and $E(Z_{\text{eff}}) = -2Z_{\text{eff}}^2 = -5.695 \text{ Ry} = -77.46 \text{ eV}$ which is significantly better (almost 3 eV lower) than the first order perturbation theory result obtained earlier.

5.9.3 Excited states

The method may be extended to calculate the lowest excited states. We do this by choosing the trial wavefunction to be orthogonal to the ground state. Although the true ground state is not known, this may still be done if symmetry can be used to distinguish different states. For example for the modified Harmonic oscillator Hamiltonian with potential $x^2 + g x^4$ we know that the ground state has even parity and the first excited state has odd parity. Thus if we constrain our trial to have odd parity we can estimate the energy of the first excited state.

5.10 The Hartree-Fock method

The variational principle allows us to get the ground state energy of a system, but the result is only as good as the trial wavefunctions we use.

We can account for antisymmetry by writing Ψ as a *Slater determinant* of one-electron wavefunctions. To be explicit this is

$$\Psi_{\text{Slater}} = \frac{1}{\sqrt{N!}} \sum_{ijklm\dots} \epsilon_{ijklm\dots} \phi_1(\underline{r}_i) \phi_2(\underline{r}_j) \phi_3(\underline{r}_k) \phi_4(\underline{r}_l) \dots \quad (5.59)$$

$$= \frac{1}{\sqrt{N!}} \text{Det} \begin{bmatrix} \phi_1(\underline{r}_1) & \phi_1(\underline{r}_2) & \phi_1(\underline{r}_3) & \dots \\ \phi_2(\underline{r}_1) & \phi_2(\underline{r}_2) & \phi_2(\underline{r}_3) & \dots \\ \phi_3(\underline{r}_1) & \phi_3(\underline{r}_2) & \phi_3(\underline{r}_3) & \dots \\ \dots & & & \end{bmatrix} \quad (5.60)$$

where the subscripts on the single particle wavefunctions $\phi_1, \phi_2, \phi_3, \dots$ label the occupied states.

The true wavefunction is a weighted sum of such terms with different choices of single particle states belonging to a particular basis (say the eigenstates of a simplified Hamiltonian). The Hartree-Fock method takes a different approach. It takes a *single* Slater determinant as the trial wavefunction and varies the single particle state wavefunctions arbitrarily (subject to continuity and differentiability) to give the lowest estimate of the energy. This generates N variational equations that determine these wavefunctions (constrained to be normalised). The mathematics requires functional derivatives - the result is however quite intuitive:

$$\begin{aligned} & \left[-\frac{\hbar^2}{2\mu} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right] \varphi_{\lambda_i}(x_i) + \underbrace{\left[\sum_j \int dx_j \frac{e^2}{4\pi\epsilon_0 r_{ij}} |\varphi_{\lambda_j}(x_j)|^2 \right]}_{\text{Hartee: } \mathcal{J}(x)} \varphi_{\lambda_i}(x_i) \\ & - \underbrace{\sum_j \int dx_j \frac{e^2}{4\pi\epsilon_0 r_{ij}} \varphi_{\lambda_j}^*(x_j) \varphi_{\lambda_j}(x_i) \varphi_{\lambda_i}(x_j)}_{\text{Fock: } \int dx' \mathcal{K}(x-x')} = \epsilon_{\lambda_i} \varphi_{\lambda_i}(x_i). \end{aligned} \quad (5.61)$$

These are known as the *Hartree-Fock* equations and there is one of them for each electron in the atom. The ϵ_{λ_i} are Lagrange multipliers introduced to ensure the wavefunctions for each 1-particle state is normalised (and mutually orthogonal). The Hartree term without the Fock term is obtained for a trial wavefunction taken to be a simple product of wavefunctions without antisymmetrisation. The Fock or exchange term looks similar to the Hartree term but has the opposite sign and some of the labels switched. The idea is that if we know the wavefunctions the Hartree and Fock terms can then be viewed as potentials acting on the wavefunction φ_{λ_i} . The Fock term is non-local in that it depends on the wavefunction $\varphi_{\lambda_i}(x_j)$ integrated over all points in space x_j rather than just at x_i . The equations need to be solved self consistently. An estimate of the wavefunctions is used to calculate the potentials and then the 1-particle ‘Schrödinger’ equations are solved with these potentials to get new estimates for the wavefunctions and the process repeated until the solution converges (FIG 5.5). The energy is not $\sum \epsilon_{\lambda_i}$, rather the energy is given by evaluating $\langle \Psi_{\text{Slater}} | H | \Psi_{\text{Slater}} \rangle$; the sum $\sum \epsilon_{\lambda_i}$ doubly counts the interaction energies. To see this note:

$$E_{HF} = \sum_i \langle \lambda_i | \hat{h}_i + \frac{1}{2} (\hat{\mathcal{J}} - \hat{\mathcal{K}}) | \lambda_i \rangle \quad (5.62)$$

whereas the individual 1-particle Schrödinger equation was

$$\epsilon_{HF,i} \phi_i = [\hat{h}_i + \hat{\mathcal{J}} - \hat{\mathcal{K}}] \phi_i. \quad (5.63)$$

The Hartree and Fock potentials can be averaged over angle to simplify the calculation by working with central potentials, although with modern computers this simplification is not needed. Historically, calculations keeping only the Hartree term were done by hand until modern computers allowed the more computationally intense HF method to be applied.

5.10.1 Beyond the Hartree-Fock approximation

The HF calculation considers each single electron state to experience the interaction with the other electrons averaged over their positions. It is referred to as a *mean field theory*. In actual fact the positions of the other electrons will be correlated with the position of the electron under consideration (the electrons repel) and the electrons will be further apart and the energy lower than given by HF. The Slater determinant includes the statistical correlation from the requirement that the electron wavefunction must be antisymmetric, but no additional correlation arising from the interaction. To capture this additional correlation we must consider a superposition of Slater determinants. This gives further corrections to the energy referred to as the *correlation energy*. The correlation energy (difference between the true energy and HF value) is around 1% of the true energy.

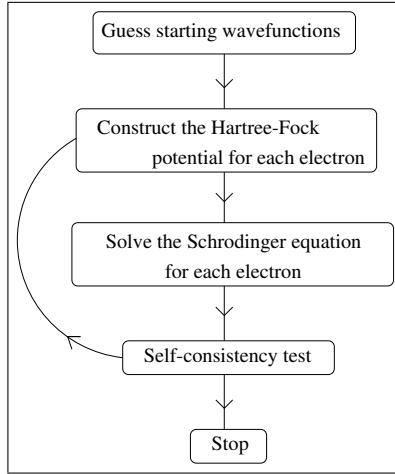


Figure 5.5: The main steps in a Hartree-Fock self-consistent field calculation.

5.11 Selection Rules

Transitions take place between states if there is an overlap of their wavefunctions. Perturbations such as the electric field can cause this overlap. The perturbation also has to oscillate in time for energy to be exchanged (absorbed or emitted). A full description requires time dependent perturbation theory, which is left for another course. In the following we explore whether an electric field, treated as a perturbation, can give the required overlap between different states. If the matrix element for the perturbation between two states is zero this means that there is no transition between these states (and no absorption or emission of electromagnetic radiation); the transition is forbidden. Conversely, we find the selection rules for allowed transitions to occur.

The electromagnetic field interacts primarily with matter via the induced polarisation; known as E1 processes with a Matrix element between initial and final atomic states proportional to $e\mathcal{E}_z \sum_i \langle \psi_F | z_i | \psi_I \rangle$ (the I and F indicate initial and final wavefunctions of the system) for radiation with its electric field $\vec{\mathcal{E}}$ polarised along the z -direction. The perturbation acts on each individual electron and therefore we need to sum over all the electrons (i) in the atom. The initial state is an eigenstate of the unperturbed Hamiltonian. The final state also has to be an eigenstate of the unperturbed Hamiltonian with good L, S, J, J_z quantum numbers and (n, l) subshell configuration.

When studying the polarisability we have already seen³ from which it is seen that that the matrix element for z is only non-zero between states with l that differ by one. The perturbation is diagonal in \hat{s} . z has no effect on the azimuthal ϕ coordinate of the wavefunction so the m 's and therefore M is unchanged. Changing one of the l 's by ± 1 changes L by $0, \pm 1$ (but not $0 \rightarrow 0$) according to the angular momentum addition theorem. To summarise for an electromagnetic field polarised along the z -axis we have selection rules

$$\mathcal{E}_z \left\{ \begin{array}{l} \Delta M_L = 0 \\ \Delta L = 0, \pm 1 (\text{not } 0 \rightarrow 0) [\text{hydrogen } \Delta l = \pm 1 \text{ only}] \\ \Delta S = 0 \\ \Delta M_J = 0 \\ \Delta J = 0, \pm 1 (\text{not } 0 \rightarrow 0). \end{array} \right. \quad (5.64)$$

The changes of l , L and S cannot depend on our choice of quantisation axis (which is arbitrary). So

³The unperturbed wavefunctions have a definite parity and we saw that z will only give matrix elements between states that differ in parity. Since parity is $(-1)^l$ l must change by an odd number. Since z can be written as $r \cos(\theta) \propto r Y_{10}$ we also saw that multiplying an atomic state ket by z was equivalent to combining an angular momentum ($L = 1, m_L = 0$) with the orbital part of the ket. The resulting states can have orbital angular momentum that differ by $0, \pm 1$ from the ket. Putting both rules together we have $\Delta l = \pm 1$. Another way this selection rule can be deduced is by rewriting $z = r \cos(\theta)$ using $\cos(\theta) = \frac{1}{2l} (\hat{L}_l^+ + \hat{L}_l^-)$ (EQN 2.87)

the rules for ΔL and ΔS and ΔJ are true whatever the polarisation of the electric field. The rules for ΔM_L and ΔM_J however depend explicitly on our choice that the direction of the quantisation axis was parallel to the electric field.

To address the case for other polarisations we need to consider \mathcal{E}_x and \mathcal{E}_y while maintaining our choice of quantisation axis along \hat{z} . To illustrate this we will consider the matrix element proportional to $\langle \psi_F | x | \psi_I \rangle$ for \mathcal{E}_x and consider a single electron state with no relativistic corrections,

$$\langle \psi_F | x | \psi_I \rangle = \langle n', l', m'_l, m'_s |_F r \sin(\theta) \cos(\phi) | n, l, m_l, m_s \rangle_I \quad (5.65)$$

$$= \langle n', l', m'_l, m'_s |_F r \sin(\theta) \frac{e^{i\phi} + e^{-i\phi}}{2} | n, l, m_l, m_s \rangle_I \quad (5.66)$$

Since the azimuthal dependence of an eigenstate is $e^{im_l\phi}$ this gives $m'_l = m_l \pm 1$. For circularly polarised light incident along the quantisation axis we will get either $+1$ or -1 depending on the helicity.

Often the em radiation is not polarised. For a light beam this would correspond to two directions of $\vec{\mathcal{E}}$ perpendicular to the propagation direction. For radiation in a cavity it will include all polarisation directions.

For linearly polarised light with $\vec{\mathcal{E}}$ inclined to the quantisation axis or unpolarised light we then have

$$\text{unpolarised light } \left\{ \begin{array}{ll} \Delta M_L = 0, \pm 1 & [\text{spin-orbit neglected}] \\ \Delta L = 0, \pm 1 (\text{not } 0 \rightarrow 0) & [\text{spin-orbit neglected, for H } \Delta l = \pm 1 \text{ only}] \\ \Delta S = 0 & [\text{spin-orbit neglected}] \\ \Delta M_J = 0, \pm 1 & \\ \Delta J = 0, \pm 1 (\text{not } 0 \rightarrow 0). & \end{array} \right. \quad (5.67)$$

The above selection rules are for dipole transitions. This is valid for a constant electric field. In radiation the electric field however changes with position over the length scale of the wavelength. This change of electric field with position yields further (much smaller) terms in the perturbation. The first of these extra terms represents a quadrupole instead of a dipole. The absorption/emission is called E2. E2 and higher terms can still give some intensity when the transitions are not allowed for E1, (e.g. $\Delta L = 2$ is possible for E2 but the matrix element squared will be $\alpha^2 \sim 10^{-4}$ times the magnitude of E1 so the intensities will be exceedingly weak.)

We have also neglected the spin-orbit interaction in the above analysis. This couples l 's and s 's. L and S no longer remain good quantum numbers as the strength of the spin-orbit coupling is increased (we have seen we cross over to $j-j$ coupling for strong spin-orbit coupling). Thus for heavy atoms such as mercury selection rules for these quantum numbers may also be broken. The selection rules for ΔM_J and ΔJ are however absolute.

Dipole transitions in which M_J doesn't change are referred to as π transitions. They are associated with an oscillating dipole along the quantisation direction and a corresponding dipole radiation pattern with radiation polarised parallel to the dipole. Dipolar transitions in which $M_J = \pm 1$ are referred to as σ transitions. Along the direction of the quantisation axis they are associated with circularly polarised light but in the plane perpendicular to the quantisation axis they are associated with light polarised linearly in this plane. The total radiation field is the sum from two dipoles at 90 deg to each other in the plane and is much more isotropic.

Magnetism

Introduction

Magnetism is a purely quantum phenomena. Classically electrical currents would always decay meaning classically there can be no magnetism in equilibrium even in an externally applied magnetic field. There is even a theorem known as the Bohr-van Leeuwen theorem to prove this (not covered here). In this chapter we cover the different contributions to the magnetic moments induced in an atom in the presence of an applied magnetic field.

6.1 The Hamiltonian in magnetic and electric fields

Electromagnetism is included in the Lagrangian treatment of classical physics and this is carried over to the Hamiltonian formulation and hence to quantum mechanics. The result is that the non-relativistic Hamiltonian for a free particle of charge $-e$ is

$$\hat{H} = \frac{(\hat{p} + e\vec{A})^2}{2m} - e\phi \quad (6.1)$$

where \vec{A} is the magnetic vector potential and ϕ the electrostatic scalar potential. There is also an interaction between the spin moment and magnetic field which we will consider later. The important points are:

- the commutation relation $[\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ij}$ is unchanged
- in coordinate representation \hat{p} is still defined as $\hat{p} = -i\hbar\vec{\nabla}$
- \vec{A} and ϕ are in general functions of \vec{r} and also of t
- The velocity is now given by $m\hat{v} = \hat{p} + e\vec{A}$ so the first term still looks like the familiar expression for kinetic energy
- The expression does not include the interaction between particles only with external fields

We can establish the expression for the velocity as follows. We know from $\hat{H}|\Psi\rangle = i\hbar\frac{d|\Psi\rangle}{dt}$ that the rate of change of the expectation value of any operator \hat{A} is given by

$$\frac{d\langle\hat{A}\rangle}{dt} = \frac{1}{i\hbar} \langle [\hat{A}, \hat{H}] \rangle \quad (6.2)$$

If we apply this to \hat{r}

$$\frac{d\langle\hat{r}\rangle}{dt} = \frac{1}{i\hbar} \langle [\hat{r}, \hat{H}] \rangle = \frac{1}{2i\hbar m} \langle [\hat{r}, (\hat{p} + e\vec{A})^2] \rangle = \frac{1}{2i\hbar m} \langle [\hat{r}, \hat{p}^2 + e\vec{A}\cdot\hat{p} + e\hat{p}\cdot\vec{A}] \rangle \quad (6.3)$$

$$(6.4)$$

The commutators are evaluated with the use of $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$ (proof by expansion) to yield

$$\frac{d\langle\hat{r}\rangle}{dt} = \frac{1}{m} \langle (\hat{p} + e\vec{A}) \rangle \quad (6.5)$$

Relation of the Hamiltonian to the classical equation of motion

The algebra in this paragraph is included for completeness but may be skipped

We can verify we get the correct classical equation of motion from \hat{H} by looking at the expectation for the acceleration:

$$\frac{d^2 \langle \hat{r} \rangle}{dt^2} = \frac{1}{i\hbar m} \langle [\hat{p} + e\vec{A}, \hat{H}] \rangle = -\frac{1}{m} \langle (\nabla \hat{H}) \rangle + \frac{1}{i\hbar m} \langle [e\vec{A}, \hat{H}] \rangle \quad (6.6)$$

The contraction symbol above $\nabla \hat{H}$ implies that the derivative only acts on \hat{H} and not the ket. We resort to summation convention to make sense of the above expression and set $e = 1$ since it can easily be re-instanted by association with each A and ϕ at the end of the calculation:

$$\begin{aligned} m \frac{d^2 \langle \hat{r}_i \rangle}{dt^2} &= \left\langle -\frac{(\partial_i A_j A_j) - i\hbar(\partial_i A_j) \partial_j - i\hbar \partial_j(\partial_i A_j)}{2m} + \partial_i \phi + \frac{2A_j(\partial_j A_i) - i\hbar(\partial_j A_i) \partial_j - i\hbar \partial_j(\partial_j A_i)}{2m} \right\rangle \\ &= \left\langle \frac{i\hbar(\partial_i A_j - \partial_j A_i) \partial_j + i\hbar \partial_j(\partial_i A_j - \partial_j A_i) - 2(\partial_i A_j - \partial_j A_i) A_j}{2m} - \partial_i \phi \right\rangle \end{aligned} \quad (6.7)$$

Operators in (\cdot) only operate on terms in the (\cdot) . At this point it is easiest to choose a single component, say $i = x$. We can identify the magnetic field from $B = \nabla \times \vec{A}$

$$m \frac{d^2 \langle \hat{r}_x \rangle}{dt^2} = \left\langle \frac{i\hbar(B_z \partial_y - B_y \partial_z + \partial_y B_z - \partial_z B_y) - 2B_z A_y + 2B_y A_z}{2m} - \partial_x \phi \right\rangle \quad (6.8)$$

$$= \left\langle \langle (-[B_z, (-i\hbar \partial_y + A_y)]_+ + [B_y, (-i\hbar \partial_z + A_z)]_+) \rangle - \langle \partial_x \phi \rangle \right\rangle \quad (6.9)$$

$$= -e \frac{\langle \vec{v} \times \vec{B} - \vec{B} \times \vec{v} \rangle_x}{2} - e \langle \nabla_x \phi \rangle \quad (6.10)$$

where $[A, B]_+$ signifies an anti-commutator $[A, B]_+ = AB + BA$. We have thus obtained an expression that resembles the classical expression for the force on an electric charge $F = -e(\vec{v} \times \vec{B} - e\vec{E})$. Since operators don't commute the expression maintains a quantum mechanical flavour, products of operators in classical expressions are replaced by symmetrized products of operators in QM.

You might worry how we got away with $\hat{l} = \hat{r} \times \hat{p}$ in place of $\hat{l} = \frac{1}{2}(\hat{r} \times \hat{p} - \hat{p} \times \hat{r})$; the cross product involves products of different cartesian components of \hat{x} with \hat{p} which commute.

6.2 An electron in a constant magnetic field

A constant magnetic field can be described by $\vec{A} = \frac{1}{2}\vec{B} \times \vec{r}$ (with \vec{B} constant) as is readily checked:

$$\nabla \times \vec{A} = \frac{1}{2} \nabla \times (\vec{B} \times \vec{r}) = \frac{(\nabla \cdot \vec{r})\vec{B} - (\vec{B} \cdot \nabla)\vec{r}}{2} = \frac{3\vec{B} - \vec{B}}{2} = \vec{B}. \quad (6.11)$$

This choice of \vec{A} of course represents a gauge choice ($\nabla \cdot \vec{A} = 0$). The same choice is easily visualised in cylindrical coordinates. From Ampère's theorem the integral around a circular loop of radius r in the plane perpendicular to the field gives $\oint \vec{A} \cdot d\vec{l} = \int B d^2 r \implies 2\pi r A_\phi = B\pi r^2 \implies \vec{A} = \hat{e}_\phi B r / 2$ where we have made a symmetric choice for A_ϕ (no dependence on ϕ).

Expanding the kinetic energy term in the Hamiltonian,

$$\hat{H}_{\text{ke}} = \frac{1}{2m} \left(\hat{p}^2 + e(\vec{A} \cdot \hat{p} + \hat{p} \cdot \vec{A}) + e^2 A^2 \right) \quad (6.12)$$

and substituting for \vec{A}

$$2m\hat{H}_{\text{ke}} = \hat{p}^2 + \frac{e((\vec{B} \times \hat{r}) \cdot \hat{p} + \hat{p} \cdot (\vec{B} \times \hat{r}))}{2} + \frac{e^2}{4}(\vec{B} \times \hat{r}) \cdot (\vec{B} \times \hat{r}) \quad (6.13)$$

$$= \hat{p}^2 + e\vec{B} \cdot (\hat{r} \times \hat{p}) + \underbrace{\frac{e^2}{4} ((\vec{B} \times \hat{r}) \times \vec{B}) \cdot \hat{r}}_{B^2 \hat{r}^2 - (\vec{B} \cdot \hat{r})^2} \quad \text{uniform B} \quad (6.14)$$

$$= \hat{p}^2 + e\vec{B} \cdot \hat{l} + \frac{e^2}{4} B^2 \hat{r}_\perp^2 \quad (6.15)$$

\hat{l} is the angular momentum operator. r_\perp is the distance from the origin in the plane perpendicular to \vec{B} . e.g. for $B \parallel z$ we have $\hat{r}_\perp^2 = \hat{x}^2 + \hat{y}^2$. For small applied fields we can treat the second two terms in EQN 6.15 as a perturbation. Specialising to $B \parallel z$

$$\boxed{\hat{H}_1 = \frac{e}{2m} \vec{B} \cdot \hat{l} + \frac{e^2}{8m} B^2 (\hat{x}^2 + \hat{y}^2)} \quad (6.16)$$

Putting the field along the z-direction the first term corresponds to the interaction energy between the field and a permanent moment $\mathcal{M}_l = \frac{(-e)}{2m} \hat{l}_z$. The ratio of the moment to the angular momentum, known as the gyromagnetic ratio is identified as $\gamma = \frac{(-e)}{2m}$. We can also write the field energy for this term $m_l \mu_B B$ where $\mu_B = e\hbar/2m$ is the Bohr magneton and m_l is the orbital quantum number. If the atom has $\hat{m}_l \neq 0$ this will contribute to an energy shift in first-order perturbation theory proportional to B .

As for the earlier discussion of the electric field the Hamiltonian includes the energy of interaction with the surroundings (not just the internal energy). The change in energy with field is therefore given by $dE = - \int \mathcal{M} dB$. In this expression $\mathcal{M} = \mathcal{M}_l + \delta\mathcal{M}$ includes pre-formed moments such as \mathcal{M}_l but also contributions to the moment that are induced by the field $\delta\mathcal{M} = \alpha_B B$ where α_B is the differential atomic magnetic polarisability. Integrating

$$\Delta E = -\mathcal{M}_l \cdot B - \frac{\alpha_B B^2}{2}. \quad (6.17)$$

The first order perturbation treatment of the second term in EQN 6.16 which is already quadratic in B therefore contributes to α_B (Larmor diamagnetic contribution) along with the second order perturbation correction from the first term (called Van-Vleck paramagnetism). We consider these terms first and then look at the more important first order term when local moments are present.

6.2.1 Larmor diamagnetism

If there are no local moment which as we will see corresponds to $L = 0$ and $S = 0$ (e.g. for filled shells) there are two contributions to the magnetic polarisability α_B . The first is sometimes called the Larmor diamagnetic response and comes from the A^2 (also B^2) term in our Hamiltonian.

$$\alpha_L = -\frac{e^2}{4m} \langle x^2 + y^2 \rangle \quad (6.18)$$

Considering the shells to be spherically symmetric

$$\alpha_L = -\frac{e^2}{6m} \langle r^2 \rangle \quad (6.19)$$

The contribution to the susceptibility is summed over all electrons. Consider just Z electrons per atom with n the atomic density. The magnitude of α_L is

$$\chi_L = n \frac{d\mathcal{M}}{dH} = n\mu_0 \frac{d\mathcal{M}}{dB} = -\frac{n\mu_0 e^2}{6m} \sum_{e^-} \langle r^2 \rangle \quad (6.20)$$

The outer electrons will contribute the most. Since we are interested in estimating the order of magnitude only we will only consider these electrons and set $\langle r^2 \rangle \approx a^2$ where a is an effective radius of the atom. For a solid the density is $n \sim (\frac{4}{3}\pi a^3)^{-1}$. This is an overestimate of the density. Taking there to be of the order 2 outer electrons,

$$\chi_L \sim -\frac{1}{4\pi a} \frac{\mu_0 e^2}{m} = -\frac{a_0}{a} \alpha^2 \sim -(10^{-6} - 10^{-5}) \quad (6.21)$$

where α is the fine structure constant and a_0 the Bohr radius and we also used $c^2 = \sqrt{\mu_0 \epsilon_0}$ in obtaining the final expression.

The second contribution (known as the Van-Vleck contribution) will be considered after we have looked at permanent moments, but turns out to be smaller.

6.3 Permanent moments

If the ions/atoms have permanent moments these moments give the dominant magnetic response.

6.3.1 Contribution from electron spin

The electron spin also has a moment. Its has a gyromagnetic ratio that is g times that of the orbital moment. $g = 2 + \alpha/2\pi \approx 2.00$. The value of g , called the g-factor, comes from the relativistic theory. We will treat $g = 2$ as an experimentally determined constant. Therefore $\mathcal{M}_s = -g\mu_B m_s = -\gamma_e \hbar m_s$ with $\gamma_e = 2e/2m$ (m_s is the quantum number of the z-component of the spin. The electron has charge $-e$).

6.3.2 The total moment

We consider the magnetic field to be a small perturbation compared with the direct and exchange Coulomb interactions that determined good quantum numbers L and S . For small fields we also consider the interaction with the magnetic field to be smaller than the spin orbit interaction $\xi \hat{L} \cdot \hat{S}$, so we start with states of $|(n,l), L, S, J, M_J\rangle$ as eigenstates of our atom before considering the effect of the magnetic field. In getting to $|(n,l), L, S, J, m_j\rangle$ we found that replacing the m_l and m_s with J and m_j diagonalised the combined angular and spin part of the full Hamiltonian *exactly* (the radial states are however mixed in higher than first order of perturbation theory). This happy situation (due to $[\hat{L} \cdot \hat{S}, \hat{H}_0] = 0$) exceeded that required for degenerate perturbation theory. All that is required is for the perturbation to be diagonalised amongst the subset of degenerate states.

We now start with $|(n,l), L, S, J, M_J\rangle$ and treat the field terms as an additional perturbation. According to degenerate perturbation theory we only need consider a subset of different M_J values with $((n,l), L, S, J)$ all fixed. We will work to first order in B . We have

$$\hat{H}_1 = \frac{\mu_B}{\hbar} B(g\hat{S}_z + \hat{L}_z) = \frac{\mu_B}{\hbar} B(\hat{J}_z + \hat{S}_z) \quad (6.22)$$

We need to re-express this in terms of \hat{J}_z and possibly \hat{J}_{\pm} getting rid of \hat{S}_z . \hat{H}_1 does not change L or S nor does it change the radial part of the wavefunction. For degenerate perturbation theory we are only concerned with the action of \hat{H}_1 on the reduced basis with a fixed J . We are therefore free to multiply \hat{S} on the right by $\hat{J}^2/(J(J+1))$. We then use an operator relation that is subsequently proven that $\hat{S} \hat{J}^2 = (\hat{S} \cdot \hat{J}) \hat{J}$ in this restricted basis to re-express the perturbation as

$$\hat{H}_1 = \frac{\mu_B}{\hbar} B(\hat{J}_z + \frac{(\hat{S} \cdot \hat{J})}{J(J+1)} \hat{J}_z) \quad (6.23)$$

An expression for $(\hat{S} \cdot \hat{J})$ is easily derived

$$\hat{S} \cdot \hat{J} = \frac{1}{2} (\hat{J}^2 + \hat{S}^2 - (\hat{J} - \hat{S})^2) \quad (6.24)$$

$$\implies \hat{S} \cdot \hat{J} |L, S, J, m_j\rangle = \frac{1}{2} (J(J+1) + S(S+1) - L(L+1)) \quad (6.25)$$

Bringing everything together

$$\hat{H}_1 = \frac{\mu_B}{\hbar} \left(\frac{3}{2} + \frac{1}{2} \frac{S(S+1) - L(L+1)}{J(J+1)} \right) B \hat{J}_z \quad (6.26)$$

The starting states M_J therefore already diagonalise the perturbation. The atom/ion as a whole behaves as though it has a single magnetic moment parallel to the total angular momentum but having a modified g-factor known as the Landé Factor.

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

Landé Factor

(6.27)

the expression reduces to $g_L = 1$ for a pure orbital moment and $g_L = 2$ for a pure spin moment as expected. The splitting of the levels in a weak field is therefore given simply by

$$\Delta E = g_L(J, L, S) \mu_B B M_J$$

(6.28)

This splitting of spectral lines in a magnetic field is known as the Zeeman effect.

6.3.3 Zeeman effect: An example, the Sodium d-line

This is a well known example that you may have the good fortune to see in the lab class or if you find yourself in possession of a diffraction grating as you walk by a sodium street lamp. It is called the d-line simply because Fraunhofer labelled the main absorption lines in the visible solar spectrum with letters in alphabetical order of their frequencies (inverse wavelength). It is the excitation from the 3s level in sodium vapour to the 3p level. The term symbols are $^2S_{1/2}$ for the ground state and $^2P_{1/2}$ and $^2P_{3/2}$ for the excited states. The $^2P_{1/2}$ and $^2P_{3/2}$ levels have different energies owing to spin-orbit splitting, so the Na-d line is a doublet. In a magnetic field the lines split further. The Landé g-factors calculated from EQN 6.27 are $g_L = 2$ for the ground state, $g_L = 2/3$ for $^2P_{1/2}$ and $g_L = 4/3$ for $^2P_{3/2}$. This gives the splitting shown schematically in FIG 6.1. The classification of the transitions according to the selection rules for σ and π are also shown along with the radiation and polarisation patterns as a function of angle from the \mathbf{B} -axis.

6.3.4 Proof that $\hat{S}\hat{J}^2 = (\hat{S}\cdot\hat{J})\hat{J}$ in the basis of fixed J

The algebra in this paragraph is included for completeness but may be skipped

To prove this equality, the first thing that comes to mind is to look at the commutation relations involving \hat{S} and \hat{J} . The term that \hat{S} does not commute with is $L \cdot S$ so we start by looking at the commutation of this with \hat{S}_i (using summation convention)

$$[\hat{S}_i, \hat{L} \cdot \hat{S}] = \hat{L}_j [\hat{S}_i, \hat{S}_j] = i\hbar \hat{L}_j \epsilon_{ijk} \hat{S}_k = i\hbar (\hat{L} \times \hat{S})_i \quad (6.29)$$

$$\implies i\hbar \hat{L} \times \hat{S} = [\hat{S}, \hat{L} \cdot \hat{S}] \quad \text{any basis} \quad (6.30)$$

$$\implies i\hbar \hat{L} \times \hat{S} = 0 \quad \text{fixed L,J,S basis} \quad (6.31)$$

In deriving the last line we noted $\hat{L} \cdot \hat{S}$ is just a number when we limit matrix elements to the reduced basis of fixed (J, L, S) recalling $2\hat{L} \cdot \hat{S} = J(J+1) - L(L+1) - S(S+1)$. The order of \hat{L} and \hat{S} can be changed in the cross product (not forgetting a minus sign) since \hat{L} and \hat{S} commute. We can also replace \hat{L} with $\hat{J} - \hat{S}$ but need to note that $\hat{S} \times \hat{S} = i\hbar \hat{S}$ (as can be checked from the angular momentum commutation relations). So equivalently we can write $0 = \hat{S} \times \hat{L} = \hat{S} \times \hat{J} - i\hbar \hat{S} \implies \hat{S} \times \hat{J} = i\hbar \hat{S}$. Taking the cross product of this last equation with \hat{J}

$$(\hat{S} \times \hat{J}) \times \hat{J} = i\hbar \hat{S} \times \hat{J} \quad (6.32)$$

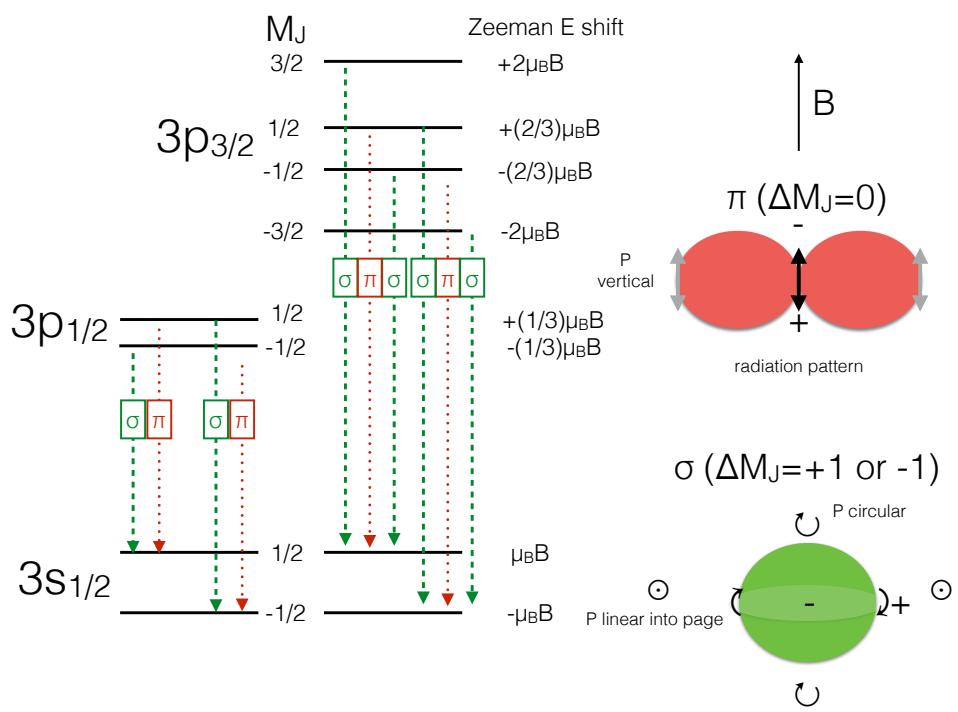


Figure 6.1: Sodium d line: This is the spectral line responsible for the orange colour of sodium lamps. In fact it is split into two closely space lines. The outer electron of Na is excited from a $3s$ to a $3p$ level. The $3p$ level has LS states $^2P_{1/2}$ and $^2P_{3/2}$ which are separated owing to the spin-orbit interaction. These levels are Zeeman split by a small magnetic field as shown on the left side of the figure. The selection rule $\Delta J = 0, \pm 1$ allows transitions back to the ground state. The rule $\Delta M_J = 0, \pm 1$ restricts the allowed transitions slightly and can be used to separate the processes into π ($\Delta M_J = 0$) and σ ($\Delta M_J = \pm 1$), which absorb and reradiate light with the different polarisations as a function of direction with the angular dependences shown on the right of the figure.

The left hand side can be evaluated with summation convention,

$$[(\hat{S} \times \hat{J}) \times \hat{J}]_i = \epsilon_{ijk} \epsilon_{ilm} \hat{S}_l \hat{J}_m \hat{J}_k \quad (6.33)$$

$$= (\delta_{kl} \delta_{im} - \delta_{km} \delta_{il}) \hat{S}_l \hat{J}_m \hat{J}_k \quad (6.34)$$

$$= \hat{S}_k \hat{J}_i \hat{J}_k - \hat{S}_i \hat{J}_k \hat{J}_k \quad (6.35)$$

$$= \hat{S}_k \hat{J}_k \hat{J}_i + i\hbar \epsilon_{ikm} \hat{S}_k \hat{J}_m - \hat{S}_i \hat{J}^2 \quad (6.36)$$

$$\implies (\hat{S} \times \hat{J}) \times \hat{J} = (\hat{S} \cdot \hat{J}) \hat{J} + i\hbar \hat{S} \times \hat{J} - \hat{S} \hat{J}^2 \quad (6.37)$$

Combining EQN 6.32 and EQN 6.37 gives the required result

$$(\hat{S} \cdot \hat{J}) \hat{J} - \hat{S} \hat{J}^2 = 0 \quad (6.38)$$

6.4 Strong field splitting

In a strong field the perturbation due to \mathbf{B} exceeds that due to the spin orbit interaction. This requires a field of at least several Tesla (25 Tesla for sodium). The calculation then begins with definite M_L and M_S states. The possible states are shown in FIG 6.2. Splitting in this high field regime is called the Paschen-Back effect.

If $S = 0$ the strong field splitting is identical with the low field one. Since transitions between states with $S = 0$ were studied first this was historically called the *normal* Zeeman effect. Subsequently atoms with $S \neq 0$ were studied and the different low field result in that case was called the *anomalous* Zeeman effect.

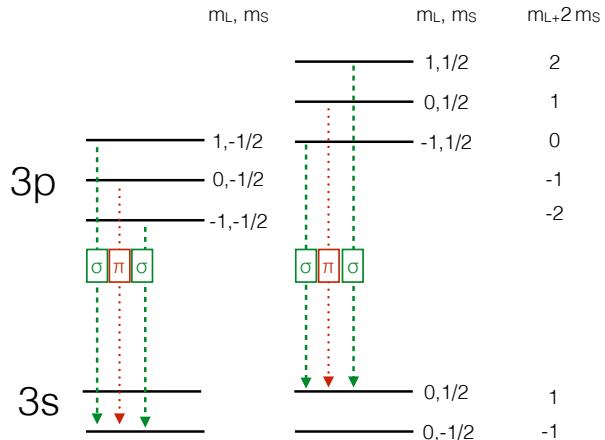


Figure 6.2: The splitting of the sodium d-line in high magnetic field ignoring the spin-orbit interaction, showing the allowed transitions (note $\Delta M_S = 0$). The degenerate levels $(M_L, M_S) = (1, -1/2)$ and $(-1, 1/2)$ are degenerate and it has to be considered if they could be mixed and split by the spin orbit interaction; since they differ by 2 in M_L the spin-orbit interaction however does not connect them to lowest order. The energies of all the levels will evolve with increasing SO (or decreasing B) to the low field states given in FIG 6.1.

6.4.1 Van Vleck term

This is of interest when there is no permanent moment. We then have to look at the second order field induced moment. Then from second order perturbation theory

$$\Delta E_{VV} = -\frac{\alpha_{VV}B^2}{2} = \frac{\mu_B^2}{\hbar^2} B^2 \sum_j \frac{|\langle j | \hat{L}_z + 2\hat{S}_z | 0 \rangle|^2}{E_0 - E_j} \quad (6.39)$$

The sum is over all excited states. Since the second order contributions to the ground state energy are always negative the contribution to α is positive (paramagnetic).

$$\chi_{VV} = -n\mu_0 \frac{2\mu_B^2}{\hbar^2} \sum_j \frac{|\langle j | \hat{L}_z + 2\hat{S}_z | 0 \rangle|^2}{E_{1s^2} - E_j} > 0 \quad (6.40)$$

with the n the atomic density. Including the the diamagnetic contribution we found earlier the susceptibility for atoms with no permanent moment is

$$\chi = (\underbrace{\chi_{VV}}_{>0} + \underbrace{\chi_L}_{<0}) \quad (6.41)$$

In more complex atoms contributions from all the filled shells have to be added together. The diamagnetic term is easy to calculate since this only depends the shell under consideration. The Van-Vleck term is usually smaller but depends on the occupancies of all the shells, since this determines what excited states are allowed.

If a permanent moment is present the above contributions still exist. However at low temperature these are dominated by the contribution from the pre-formed moments. At zero temperature the susceptibility from pre-formed moments is infinite (since the ΔE is linear in B rather than quadratic). At finite temperature we would obtain Curie's law (see Statistical Mechanics course) where

$$\chi = \chi_{VV} + \chi_L + n \frac{\mu_0 (g_L \mu_B)^2 J(J+1)}{3k_B T} \quad (6.42)$$

The factor of μ_0 appears when the susceptibility is defined as $d\mathcal{M}/dH$ which is dimensionless (preferred choice). If it is defined as $d\mathcal{M}/dB$ then there is no μ_0 in the above equation. The last term in EQN 6.42 if present dominates and then $\chi_{VV} + \chi_L$ are often neglected. The Van-Vleck term is constant at low temperature but can have a Curie like dependence at higher temperature $k_B T > (E_j - E_0)$.

Molecules

7.1 Introduction

So far except for a short excursion on Van der Waals solids we have focussed on single atoms. We now extend our discussion to covalent bonding in simple molecules.

7.2 Covalent bonds

7.2.1 Introduction

The distinguishing property of covalent bonding is the enhanced electron density between adjacent atoms. Elements that are on the right side of the periodic table with electron-depleted outer shells (\equiv nearly-full shells) can share electrons with a similar atom, creating a bond between them. The covalent or molecular bond holds gaseous, diatomic molecules (e.g. O_2 , H_2) together. *Molecular orbital theory* describes the extension of the concept to more complex molecules and solids when there are multiple bonds (for example carbon and silicon).

The calculation of the cohesive energy of a covalently-bonded solid is a complicated many-body quantum mechanical problem. In order to understand how this binding arises we will consider the simplest covalent bond; that binding two protons in an H_2^+ ion. We then consider the bond in an H_2 molecule, which now includes two electrons and introduces the important concept of exchange energy. In passing, this also serves to justify the short range repulsion we encountered in the Lennard Jones potential. The chapter is rounded off with a brief qualitative discussion of molecular orbitals.

7.2.2 H_2^+

We make several assumptions to reduce the problem to its simplest form. First, assume that the nuclei (protons for the case of H_2^+) labelled A and B are a fixed distance apart and do not move (**Born-Oppenheimer approximation**). This assumption was already used in our consideration of the Van der Waals solid. The wavefunctions then only give the amplitude for electrons and not the nuclei; the nuclei co-ordinates are treated as classical variables. The Schrödinger equation is

$$\hat{\mathcal{H}}\Psi(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r}) + \left(-\frac{e^2}{4\pi\epsilon_0 r_A}\frac{1}{r_A} - \frac{e^2}{4\pi\epsilon_0 r_B}\frac{1}{r_B} + \frac{e^2}{4\pi\epsilon_0 R}\frac{1}{R}\right)\Psi(\vec{r}). \quad (7.1)$$

R is the separation of the H^+ nuclei. $r_A = r$ is the distance of the electron from the first nucleus (w.l.g. at the origin) labelled A and $r_B = |\vec{r} - \vec{R}|$ the distance to the second nucleus labelled B. The one electron wave-functions obtained by solving EQN 7.1 are called molecular orbitals. $|\Psi(r)|^2$ is proportional to the electron density. We will not solve EQN 7.1 explicitly but rather manipulate it to get an insight into the structure of the energy levels. The second assumption we make is another common one: we assume that the wave-function can be written as the linear combination of the atomic orbitals (LCAO).

$$\Psi = (c_A\psi_A + c_B\psi_B) \quad (7.2)$$

For H_2^+ , $c_A = \pm c_B \equiv N_{\pm}$ from symmetry: since the Hamiltonian is symmetric Ψ has to have a definite parity. $|\Psi|^2$ is therefore always symmetric. ψ_A and ψ_B are ground state orbitals centred on A and B

respectively and for hydrogen s-states can be taken as real. N_{\pm} is the normalisation constant (different for the two cases). Thus we have two solutions

$$\Psi_{\pm} = N_{\pm}(\psi_A \pm \psi_B) \quad (7.3)$$

with

$$1 = \int |\Psi_{\pm}|^2 d^3r = |N_{\pm}|^2 \int d^3r (|\psi_A|^2 + |\psi_B|^2 \pm (\psi_A^* \psi_B + \psi_A \psi_B^*)) = |N_{\pm}|^2 2(1 \pm \rho_{AB}) \quad (7.4)$$

$$\Rightarrow |N_{\pm}|^2 = \frac{1}{2(1 \pm \beta)} \quad (7.5)$$

$$\text{with } \beta = \int d^3r \rho_{AB} \quad \text{and} \quad \rho_{AB} = \psi_A \psi_B \quad \text{taking } \psi_A, \psi_B \text{ to be Real} \quad (7.6)$$

$$\text{i.e. } \beta = \int d^3r \psi_A(\vec{r}) \psi_B(\vec{r} - \vec{R}). \quad (7.7)$$

The objective is to calculate the bonding energy. To do this note,

$$\mathcal{H}|\Psi_{\pm}\rangle = \left\{ \left(E_0 + \frac{e^2}{4\pi\epsilon_0 R} \right) |\Psi_{\pm}\rangle - N_{\pm} \frac{e^2}{4\pi\epsilon_0} \left(\pm \frac{|\psi_B\rangle}{r_A} + \frac{|\psi_A\rangle}{r_B} \right) \right\}. \quad (7.8)$$

E_0 is the energy for an electron in an isolated atom. The expectation value of the energy (first order perturbation theory) is then

$$\langle \Psi_{\pm} | \hat{\mathcal{H}} | \Psi_{\pm} \rangle = \left(E_0 + \frac{e^2}{4\pi\epsilon_0 R} \right) - |N_{\pm}|^2 (V_1 \pm V_2) = \left(E_0 + \frac{e^2}{4\pi\epsilon_0 R} \right) - \frac{(V_1 \pm V_2)}{(1 \pm \beta)} \quad (7.9)$$

with

$$V_1 = \frac{e^2}{4\pi\epsilon_0} \int d^3r \frac{\Psi_B^2}{r_A} = \frac{e^2}{4\pi\epsilon_0} \int d^3r \frac{\Psi_A^2}{r_B} = \frac{e^2}{4\pi\epsilon_0} \int d^3r \frac{\rho_{AA}}{r_B} \quad (\text{with } \rho_{AA} = \psi_A \psi_A), \quad (7.10)$$

$$V_2 = \frac{e^2}{4\pi\epsilon_0} \int d^3r \frac{\Psi_B \Psi_A}{r_A} = \frac{e^2}{4\pi\epsilon_0} \int d^3r \frac{\Psi_B \Psi_A}{r_B} = \frac{e^2}{4\pi\epsilon_0} \int d^3r \frac{\rho_{AB}}{r_B}. \quad (7.11)$$

We now explore what can be deduced from EQN 7.9. For little overlap $\beta \ll 1$. V_1 is always positive and gives the interaction between an unperturbed electron cloud on one nucleus with the second nucleus. It will approximately cancel the term $e^2/4\pi\epsilon_0 R$ that describes the repulsion between the positive nuclei. The V_2 term is always positive and gives the interaction from the extra charge density coming from the superposition of the orbitals. It is the decisive term in determining the energy shift with respect to E_0 . As a result Ψ_+ will have a lower energy and Ψ_- a higher energy than the energy E_0 . The above analysis is for intermediate distances with weak overlap (and for first order perturbation theory). At shorter distances a single electron can no longer cancel the Coulomb repulsion between the nuclei and the energy for both Ψ_{\pm} rise substantially at smaller R .

Physically at intermediate distances, locating extra electron density in the region between the two nuclei as shown in FIG 7.1 lowers the potential energy. The Ψ_+ state is called the bonding orbital and is usually denoted σ_g . g stands for *gerade* which translates from german as ‘even’, referring to the symmetry of the atomic wave-functions (that make up the linear combination). The orbital Ψ_- is called the anti-bonding orbital and it has an energy that is greater than for non-interacting atoms. It is often denoted σ_u where u stands for *ungerade* meaning ‘odd’. Notice that the probability of finding the electron between the protons for the anti-bonding orbital is near zero. At larger distances the electron will choose one proton to reside near (in Schrödinger’s cat fashion) and the idea of a molecule is no longer useful.

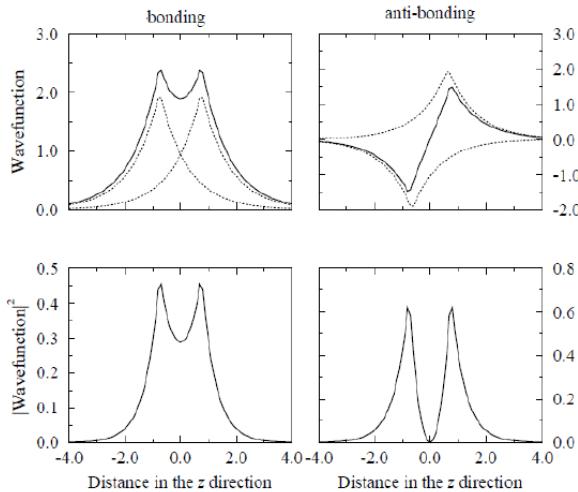


Figure 7.1: Bonding and anti-bonding wavefunctions for the hydrogen ion

7.2.3 Hydrogen molecule

When we have two (or more) electrons forming the bond the antisymmetry of the wavefunction under particle exchange must be respected.

$$\Psi(r_1, s_1, r_2, s_2) = -\Psi(r_2, s_2, r_1, s_1). \quad (7.12)$$

The subscripts label the electrons, r is the position and s the spin state. If spin-orbit coupling can be neglected (an approximation with better validity for lighter elements) the wavefunction can be factored as a product of a spin part $\chi(s_1, s_2)$ and a spatial part $\Psi(r_1, r_2)$. For a bond between two identical atoms symmetry imposes that $\Psi(r_1, r_2)$ is either symmetric or anti-symmetric. Anisymmetry under particle exchange then imposes that an antisymmetric spatial wavefunction is associated with a spin symmetric $\chi(s_1, s_2) = \{\uparrow_1 \uparrow_2\}, \{\downarrow_1 \downarrow_2\}, \{\uparrow_1 \downarrow_2 + \downarrow_1 \uparrow_2\}/\sqrt{2}$, which in the absence of any magnetic terms in the Hamiltonian is triply degenerate (spin-triplet). A symmetric spatial wavefunction is associated with an antisymmetric $\chi(s_1, s_2) = \{\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2\}/\sqrt{2}$ which is non-degenerate (spin-singlet). A suitable wavefunction is therefore

$$\Psi(r_1, r_2)_{s,t} = N_{s,t} [\psi_A(1)\psi_B(2) \pm \psi_B(1)\psi_A(2)] \chi_{s,t}(s_1, s_2). \quad (7.13)$$

The $\{s, t\}$ refer to the triplet/singlet nature of the spin part. The lower case $\psi_{A,B}$ refer to single-electron atomic orbitals centred on A and B (s goes with the $+$ sign and t goes with the $-$ sign).

We have made some important approximations in writing the wavefunction in the above form. Firstly, we have neglected mixing with excited states of the single atom basis functions. Secondly, we have neglected the possibility that both electrons in the singlet can be located on the same atom i.e. terms $\psi_A(1)\psi_A(2)$ and $\psi_B(1)\psi_B(2)$. This second approximation is called the **Heitler-London approximation**. It fixes the number of electrons on each atom to be one and implies that such bonds will be electrically insulating (electrons would need to hop between atoms to conduct electricity). This turns out to be a good approximation if the atoms are not too close together. In another extreme we could consider a wavefunction in which double occupancy is as likely as single occupancy (i.e. include terms $\psi_A(1)\psi_A(2)$ and $\psi_B(1)\psi_B(2)$ with equal weight to $\psi_A(1)\psi_B(2)$; this limit corresponds to itinerant electrons and is a better approximation at small R). We will meet this when discussing metallic bonding in the introduction to condensed matter course, but for now we stick with the Heitler London approximation, EQN 7.13.

7.2.4 Solution for \mathbf{H}_2

$\chi_{s,t}(s_1, s_2)$ is dropped from the notation in the following but we keep the subscripts s, t for the spatial part to remind us of the spin degeneracy. The normalisation condition for a single spin state

$$\int d^3r_1 d^3r_2 \Psi_{s,t}^*(r_1, r_2) \Psi_{s,t}(r_1, r_2) = 1 \quad (7.14)$$

gives,

$$N_{s,t}^2 = \frac{1}{2} \frac{1}{1 \pm \beta^2} \quad (7.15)$$

with + sign for s and - sign for t . $\beta = \int d^3r \rho_{AB} = \int d^3r \psi_A \psi_B$ is the atomic wavefunction overlap integral. The Schrödinger equation is the same as EQN 2.1- EQN 2.40. It differs from EQN 7.1 by the addition of the interaction potential between the electrons. As before we consider \mathcal{H}_0 to represent non-interacting atoms. The interaction, described by \mathcal{H}_1 , is now written in a slightly more compact notation as

$$\mathcal{H}_1 = \frac{e^2}{4\pi\epsilon_0 R} \left(\frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} \right). \quad (7.16)$$

r_{A1} is the distance of electron ‘1’ from nucleus A etc and r_{12} is the distance between the two electrons. Previously, to get the energy shift owing to the induced dipole-dipole interaction, we considered the atoms to be far apart with the electrons approximated as distinguishable in that limit. We are now interested in the atoms being in closer proximity and have to take account of their indistinguishability. First order perturbation theory gives

$$\Delta E_{s,t} = \frac{Q \pm J}{1 \pm \beta^2}. \quad (7.17)$$

Q is the direct interaction between the unperturbed atoms. J is the *exchange integral* coming from the cross-terms due to the symmetrisation of the wavefunction under particle exchange. Explicitly,

$$\begin{aligned} Q &= \frac{e^2}{4\pi\epsilon_0 R} + \int d^3r_1 d^3r_2 \rho_{AA}(r_1) \frac{e^2}{4\pi\epsilon_0 r_{12}} \rho_{BB}(r_2) \\ &\quad - 2 \int d^3r_1 d^3r_2 \rho_{AA}(r_1) \frac{e^2}{4\pi\epsilon_0 r_{A2}} \rho_{BB}(r_2) \end{aligned} \quad (7.18)$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \int d^3r_1 d^3r_2 \rho_{AA}(r_1) \frac{e^2}{4\pi\epsilon_0 r_{12}} \rho_{BB}(r_2) - 2V_1, \quad (7.19)$$

$$\begin{aligned} J &= \frac{e^2}{4\pi\epsilon_0 R} \int d^3r_1 d^3r_2 \rho_{AB}(r_1) \rho_{AB}(r_2) + \int d^3r_1 d^3r_2 \rho_{AB}(r_1) \frac{e^2}{4\pi\epsilon_0 r_{12}} \rho_{AB}(r_2) \\ &\quad - 2 \int d^3r_1 d^3r_2 \rho_{AB}(r_2) \frac{e^2}{4\pi\epsilon_0 r_{A2}} \rho_{AB}(r_1) \end{aligned} \quad (7.20)$$

$$= \frac{e^2}{4\pi\epsilon_0 R} \beta^2 + \int d^3r_1 d^3r_2 \rho_{AB}(r_1) \frac{e^2}{4\pi\epsilon_0 r_{12}} \rho_{AB}(r_2) - 2\beta V_2. \quad (7.21)$$

$\rho_{AB}(r_1)$, V_1 , V_2 are defined as per EQN 7.6, EQN 7.7, EQN 7.10 & EQN 7.11. Q describes the repulsion between the two nuclei (first term), the repulsion between the two unperturbed electron orbits (second term) and attraction between electrons on A to nucleus B and vice-versa (third term). Q is positive (repulsive) but falls off rapidly with R . For large R second order perturbation theory gives a term that falls off more slowly with R that is attractive; Van der Waals bonding (chapter 2.6.1). In what follows we focus on small separations.

J is only significant when the orbitals overlap and represents the exchange contributions. At intermediate distances $|J| > |Q|$ and J is negative. The reason is that the overlap of the atomic wavefunctions between the charges lowers the potential energy of interaction with both nuclei more than it is raised by the direct electron-electron interaction. The energy for the singlet is thus lowered relative to the unbound case, whereas the energy for the triplet is raised. In the above model the strong increase in the potential at short distance is due to the electron-electron interaction term in J at short distances.

FIG 7.2 shows the calculated energy for bonding as a function of R in hydrogen based on the Heitler London model. At large R the first order shifts become vanishingly small and there is no difference between E_+ and E_- since the electrons can be treated as distinguishable in this limit. At the minimum of E_- , Heitler and London in 1927 calculated the bondlength to be 0.80 Å (the Bohr radius is 0.54 Å) and the bonding energy 3.14 eV, This compares to experimental values of 0.74 Å and the bonding energy 4.72 eV (HB of chemistry and physics ed. 85). By 1933 James and Coolidge had already improved on the approximations used to get agreement with experiment to better than 0.1%!

The charge distribution is shown in FIG 7.3. It follows a similar pattern to that seen for H_2^+ although not quite as dramatic. The charge density is no longer zero between the atoms for the anti-bonding state.

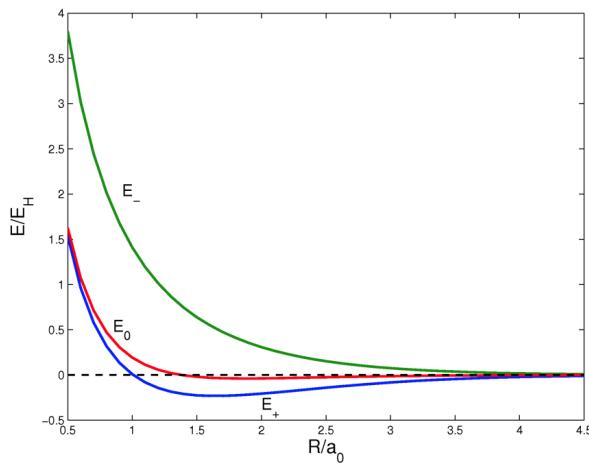


Figure 7.2: Bond energy versus nuclei separation R for H_2 . E_+ is a singlet, E_- is a triplet and E_0 is an unsymmetrised wavefunction. a_0 is the Bohr radius 52.9 pm and E_H the binding energy of the hydrogen atom 13.6 eV. (http://en.citizendium.org/wiki/Chemical_bond)

7.2.5 The chemistry of covalent bonds

Based on the similarity in electron density for H_2^+ and H_2 , an oversimplified picture of bonding can be constructed considering the single electron orbits and the Pauli exclusion principle. In this the two atomic levels combine to form a bonding (symmetric) and anti-bonding orbit (antisymmetric) as for H_2^+ . Each orbit can hold two electrons, a maximum of one of each spin, according to the Pauli exclusion principle. In hydrogen there are two electrons therefore the lowest energy state is to put these in the bonding orbital with opposite spin. A third and 4th electron would need to go into the anti-bonding orbital. Clearly this model needs to be taken with a big pinch of salt since it ignores completely the interaction between the electrons, but is nevertheless a useful picture for understanding the chemistry of covalent bonds.

Helium atoms have electronic configuration $1s^2$. He_2 molecules do not form because this would require as many electrons in the anti-bonding as in bonding states so there is no cohesive energy. What about Li_2 ($1s^2 2s^1$)₂? This is unstable for a different reason: the ionization energy of the $2s^1$ electron in Li is very low (5eV) (compared to 13.6eV for the $1s^1$ electron in H) and it is more favourable for Li to lose its $2s^1$ electron (and form a metallic bond), than to form a bonding molecular orbital with another Li. Generally, only elements with nearly full orbitals (e.g. phosphorous, arsenic, carbon) form molecular bonds.

Covalet bonds (other than those formed uniquely from s-orbitals) are very directional since the electrons spend most of their time between the atoms in the bond. Hence the structures formed by covalent bonding are often low density. The bond is exceptionally strong – carbon in its diamond structure has four covalent bonds per atom and is the hardest material known.

It is complicated to extrapolate our simple model of the covalent bond in H_2^+ and H_2 to estimate the cohesive energy of more complex solids and we will just briefly discuss some of the trends expected. An

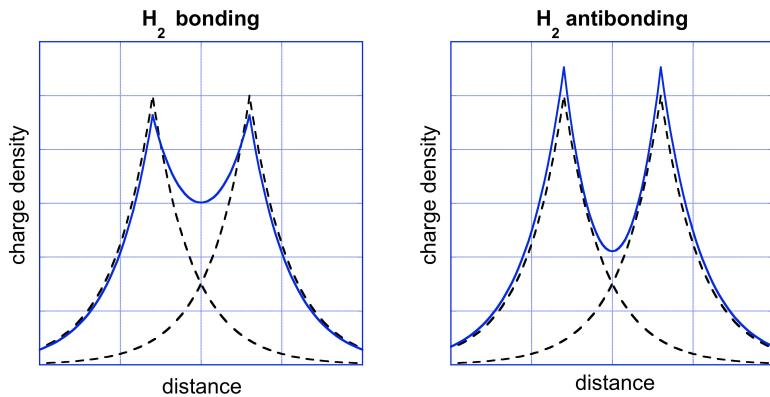


Figure 7.3: Schematic of electron density for H_2 . Dashed lines show this for the isolated atoms ($\rho_{AA}(1)$ and $\rho_{BB}(2)$) solid lines show $N_+^2(\rho_{AA}(1) + \rho_{BB}(1) + \beta\rho_{AB})$ for bonding and $N_-^2(\rho_{AA}(1) + \rho_{BB}(1) - \beta\rho_{AB})$ for antibonding orbitals. We are plotting a one particle property, the density, which does not depend on whether the 2-particle wavefunction is symmetric or anti-symmetric for combinations of orthogonal 1-particle states; here however our basis states (the atomic orbitals on each atom) are not orthogonal but overlap $\beta \neq 0$. It is the symmetrisation of the wavefunction under particle exchange that leads to an excess charge between the nuclei that lowers the potential energy. For H_2^+ it was the symmetrisation of the wavefunction in the LCAO method that led to the accumulation.

idea of the magnitude of the cohesive energy can be inferred from melting points. Structures with more bonds per atom (4 in group IV and 3 in group V), have higher melting points. Comparing elements in group II (metallic) and group VI (covalent) in the same line of the periodic table; the melting point of the metal is noticeably higher. For example calcium melts at 1115 K whereas sulphur melts at 389 K. This is because sulphur forms only two bonds per atom leading to chains or rings rather than 3D networks of covalent bonds.

The covalent Group IV elements merit additional discussion. As free atoms their valence electronic configuration is s^2p^2 . Since the s subshell is filled, one might think that only the p^2 electrons are available for bonding. In fact it is highly beneficial to promote the atomic electron arrangement to the sp^3 configuration (which costs a small amount of energy) so that four bonds can then be formed (which releases a lot of energy). Solids of group IV elements thus have tetrahedral bond arrangements. The sp^3 orbitals are called hybridised orbitals and are made from a linear combination of the atomic orbitals (FIG 7.4).

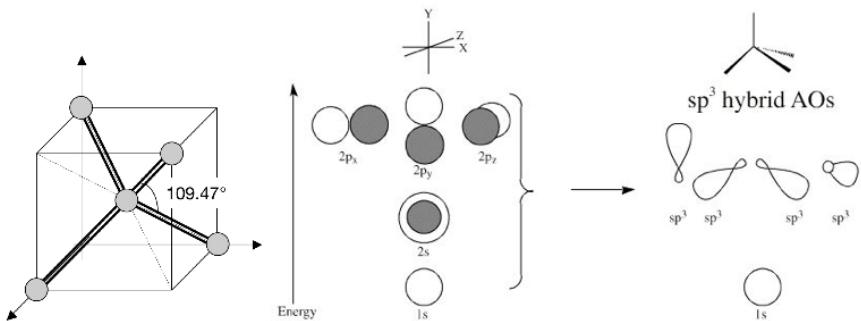


Figure 7.4: hybridised sp^3 orbitals in group IV form strong covalent and highly directional bonds

In elemental covalent crystals, symmetry suggests that the charge resides exactly in between the ion cores. This is no longer the case in materials such as GaAs (zincblende structure), where different atoms

bind. For GaAs the shared electrons reside nearer to the group V element, As, than to the group III element, Ga. Thus the bond has also some ionic character.

Rotations Vibrations and Phonons

8.1 Introduction

Having established the formation of molecules in Born-Oppenheimer approximation we are now equipped to treat the slower degrees of freedom with which the molecules can rotate and vibrate with quantum mechanics.

8.1.1 Rotations

The molecules can be considered as rigid rotors with angular momentum \hat{J} that is quantised in the same way as for the angular momentum as a single electron in an atom. We will limit consideration to a diatomic molecule. The motion of the relative coordinate in the centre of mass frame defines an angular momentum analogous to that of the electron orbiting the nucleus.

The Hamiltonian is

$$\hat{H} = \frac{1}{2} \frac{\hat{J}^2}{I} \quad (8.1)$$

Where the inertia $I = \mu a^2$ where a is the equilibrium separation of the atoms and $\mu = m_1 m_2 / (m_1 + m_2)$ is the reduced mass of the two atoms.

The solution for the energy are $E_J = \frac{\hbar^2}{2I} J(J+1)$ with degeneracy $2J+1$. If the molecule is polar (e.g. HCl) the dipole can interact directly with an electromagnetic field giving characteristic absorption and emission lines. For pure rotation transitions:

- The dipole selection rule requires $\Delta J = \pm 1$ (true as long as the total orbital moment of the electronic orbitals is zero)
- Adjacent energy levels are separated by $\frac{\hbar^2}{2I} ((J+1)(J+2) - J(J+1)) = \frac{\hbar^2}{I} (J+1)$ for $J = 0, 1, 2, \dots$. The absorption/emission spectrum therefore comprises lines at these energies.
- Transition energies correspond to microwave frequencies. Room temperature corresponds to infrared energies, so many excited levels are typically populated at room temperature.
- Homonuclear diatomic molecules (such as H₂) have no dipole moment and pure rotation transitions for these are not coupled to the EM field.

8.1.2 Vibrations

The effective energy as a function of separation can be expanded as a Taylor series relative to the equilibrium distance.

$$V(r) = V(a) + \underbrace{V'(a)}_0 (r-a) + \frac{1}{2!} V''(a) (r-a)^2 + \dots \quad (8.2)$$

Adding the kinetic energy of the motion of the atoms gives

$$\hat{H} = \frac{1}{2\mu} P^2 + \frac{1}{2!} V''(a) (R)^2 \quad (8.3)$$

where $R = r - a$ and $P = -i\hbar\nabla_R$. This is nothing but the equation for a Harmonic oscillator and gives a series of vibration energy levels $E_n = \hbar\omega_0(n + 1/2)$ with $\omega_0 = \sqrt{V''(a)/\mu}$.

We have already studied the polarisation of the harmonic oscillator. If the molecule is polar this will interact with an EM field and give absorption/emission at the characteristic frequency ω_0 . For pure vibration transitions:

- The dipole selection rule requires $\Delta n = \pm 1$. In the harmonic approximation this only gives a single spectral line.
- Typical energies are in the infrared.
- Non-harmonic corrections will give very weak absorption/emission at $2\omega_0$, $3\omega_0$ etc.
- Homonuclear diatomic molecules (such as H_2) produce no dipole moment when the atoms are displaced and will therefore give no absorption/emission in the dipole approximation.
- Moreover, since single photons have an angular momentum and since a vibration transition in a non-homonuclear molecule such as HCl cannot by itself absorb or source angular momentum a pure vibrational transition cannot occur even for polar diatomic molecules.

8.1.3 Vibrons; coupling of vibrations and rotations

The electronic, rotation and vibration modes are not independent. First we suppose there is no electronic transition. The transitions predicted treating the rotation and vibration modes as independent are shown in FIG 8.1(b), which might apply to a molecule such as HCl . States in which $\Delta J = +1$ are denoted R and $\Delta J = -1$ denoted P . The modes are however coupled for two reasons

1. The centripetal term: the increased centripetal acceleration required at higher J means bonds in these states are slightly stretched and the rotation levels are no longer equally spaced but become closer at higher J . This leads to a decreasing separation of lines at higher energy.
2. Rotation-vibration coupling: larger n vibration states experience greater anharmonicity. The atomic separation also increases with n and this leads to an increase in the moment of inertia and reduces the step between rotation levels in the higher n state. This causes the lines to split.

For homonuclear diatomic molecules the vibrations have a null dipolar matrix element between pure vibration states, pure rotation states or even combinations of both (owing to both atoms having identical charges). We can however probe these states by using photons of higher optical energies that can induce electronic transitions between different electronic states.

8.1.4 Coupling of Vibrons and Electronic Transitions

We briefly review the quantum mechanics of a transition involving all three degrees of freedom. We take the most common case where the excited electronic state has its minimum at a slightly longer bond length FIG 8.2. Electronic excitation usually corresponds to excitation of an electron from a bonding to an anti bonding level which tends to favour a slightly longer bond. The transition rate for absorption is determined by the matrix element of the dipole operator:

$$\underline{M} = \langle \psi' | \hat{D} | \psi'' \rangle \quad (8.4)$$

where \hat{D} is the dipole operator. Born-Oppenheimer separability allows us to factor out the molecular wavefunction into an electronic, vibrational and a rotational function. We can omit the latter (since rotational motion is purely kinetic) and separates completely from the rest (in the rigid rotor approximation at least). We consider the electronic and vibrational parts together.

$$\underline{M} = \langle \psi'_e \psi'_v | \hat{D} | \psi''_e \psi''_v \rangle. \quad (8.5)$$

Writing the dipole moment as a sum of electronic and nuclear components:

$$\underline{M} = \langle \psi'_e \psi'_v | \hat{D}_e | \psi''_e \psi''_v \rangle + \langle \psi'_e \psi'_v | \hat{D}_N | \psi''_e \psi''_v \rangle \quad (8.6)$$

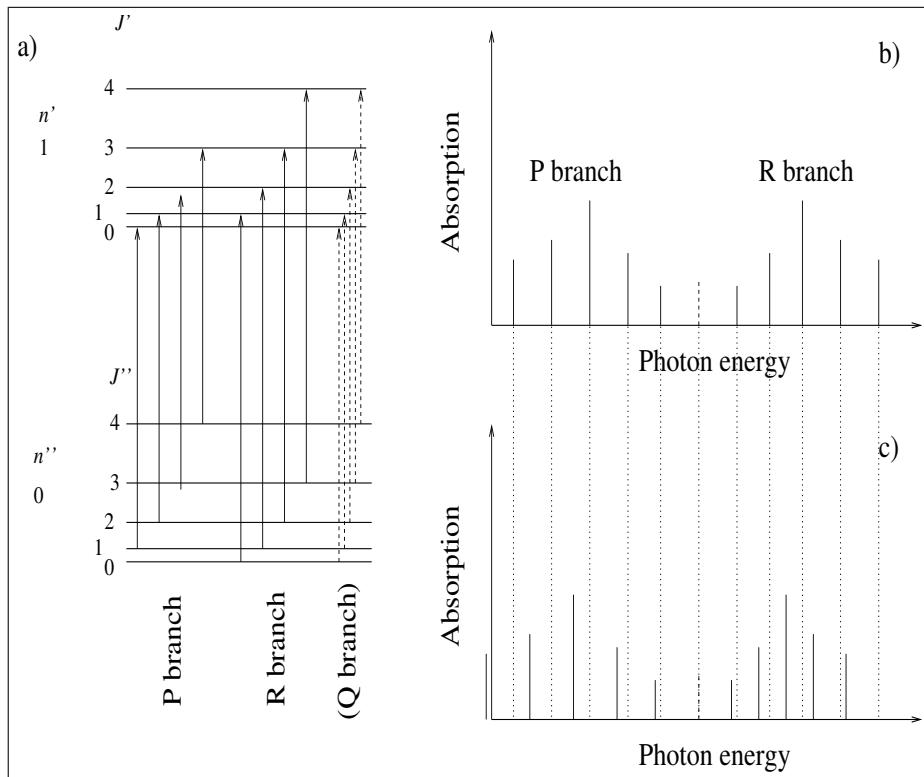


Figure 8.1: Schematic representation of the origin of vibration-rotation absorption spectra in a diatomic molecule. a) shows the relevant energy levels while b) shows the vibration-rotation spectrum in the rigid-rotator harmonic-oscillator approximation. The effect of vibration-rotation coupling is included in the spectrum shown in c). Notice the characteristic variation intensity of rotational spectra.

we can see that if the nuclear positions do not change then the second term is zero since the electronic wavefunctions are orthogonal. Finally we get

$$\underline{M} = \langle \psi'_e | \hat{D}_e | \psi''_e \rangle \langle \psi'_v | \psi''_v \rangle. \quad (8.7)$$

For the case shown in FIG 8.2 the interpretation of this equation becomes clear. The electronic transition leaves the molecule in a vibrational state which has a large overlap with the initial vibrational state, even if this is an excited vibrational state. This is known as the Franck-Condon principle.

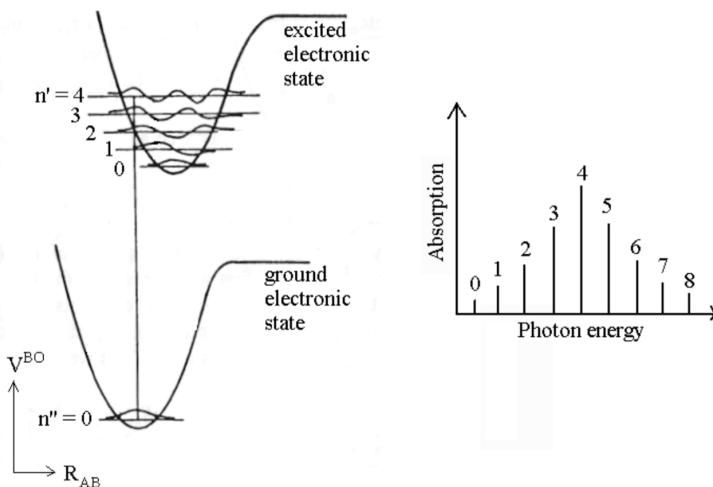


Figure 8.2: Schematic representation of a transition between the ground electronic state and an excited electronic state of a diatomic molecule. The most intense transition occurs for the final vibrational state which has the largest overlap with the initial vibrational wavefunction. Notice that transitions are not observed for $n' > 8$ since this amount of vibrational energy causes the molecule to dissociate (i.e. we snap the electronic “spring” which holds the atoms together).

Another way of looking at the Franck-Condon principle is that the electronic interaction is extremely fast (the timescale is a manifestation of the uncertainty principle for a large energy change). The lower energy processes such as the vibron transitions occur on longer timescales. The system thus finds itself with relative atomic velocities and atomic separations of the electronic state from which it was excited rather than those at the potential minimum of the excited electronic state. Decomposing this into rotational and vibrational states for the new electronic contribution gives the strongest components in those states whose velocity and coordinates overlap with the original state.

8.2 Phonons

In a solid we no longer have the rotation modes (in most cases anyway). The vibration spectrum is however more involved and leads to propagating modes known as phonons. These are analogous to photons but on a discrete lattice. By studying phonons we will begin to see how we can quantise the electromagnetic field. They are also interesting in their own right, determining how materials conduct heat and expand with temperature. They also interact with electrons, giving such interesting phenomena as superconductivity.

Many of the properties of vibrating crystals can be understood without detailed knowledge of the interactions between the atoms. In fact we will explore the main concepts using a simple model of atoms connected together to nearest neighbours by springs. It is tempting to associate these springs with chemical bonds, but such a physical interpretation is not always appropriate. Nor is it necessary since more complicated theories which account for longer range interactions lead to substantially similar results.

The notion of vibrations in crystals seems like a very promising avenue. When we displace an atom then we would expect the disturbance to spread through the crystal like a wave. In other words, we have a mechanism for thermal conduction.

Before we start, one more observation is appropriate: condensed matter conducts sound waves. These waves have wavelengths which are enormous compared to the size of atoms and they are usually treated using macroscopic elastic theory (Hooke’s law etc.). This shows that the displacement u induced by

longitudinal sound waves satisfies an equation of the form

$$\frac{C}{\rho} \frac{\partial^2 u}{\partial x^2} = \frac{\partial^2 u}{\partial t^2} \quad (8.8)$$

where x is distance in the direction of the wave, C is the modulus of elasticity (something like Young's modulus) and ρ is the density of the crystal, and so the speed of sound is $\sqrt{C/\rho}$. This is typically of order of a few thousand ms⁻¹.

We might also note here that for plane waves $\exp(ikx - i\omega t)$ the wave velocity (sometimes called the *phase velocity*) is ω/k . For sound waves this is independent of wavelength. Whatever λ (or k), the wave velocity is the same. This is rather like the behaviour of light in vacuum.

8.3 The many-body problem, coupled oscillators and “normal modes”

The simplified view of a solid as an array of balls connected by springs is not so simple mathematically; to understand its vibrations we need to describe the simultaneous movements of all its particles. They are interacting and so this is a many-body problem. A good strategy in many-body physics is to try to re-arrange the coupled equations of motion for the N interacting particles to give a set of independent equations. This “canonical transformation” gives us equations of motion for N combinations of coordinates which we can solve one at a time. In the language of many-body physics these entities are called “elementary excitations”. If they resemble particles in their propagation they are called *quasiparticles*, while more generally they are called *collective modes*.

In reality, the best one can usually do is to find entities that are *weakly* interacting. This at least allows approximate methods such as perturbation theory to be used. But you may already be aware that our ball and spring model is a special case; it assumes that all the forces acting between atoms are *harmonic*, i.e. the forces are proportional to the atomic displacements. Mathematically, this means that we truncate the Taylor expansion for the potential energy of the crystal after the second order derivatives. The potential energy of two atoms at separation r becomes

$$V(r) \approx V(a) + (r-a) \left(\frac{dV}{dr} \right)_{r=a} + \frac{(r-a)^2}{2} \left(\frac{d^2V}{dr^2} \right)_{r=a} \quad (8.9)$$

where a is the interatomic separation in the ground state. It is easy to see that the linear term disappears since $-(dV/dr)_{r=a}$ is the force on the atoms in the ground state which must be zero. (The potential is always flat at the bottom on an energy well.) So we readily obtain

$$F = -\frac{dV}{dr} = -(r-a) \left(\frac{d^2V}{dr^2} \right)_{r=a} \quad (8.10)$$

which is the well known equation for “simple harmonic motion”. The second derivative of the interatomic potential energy near the bottom of the well gives us the “spring constant”.

We have shown that, provided the displacement from a is small, Taylor's theorem always allows us to approximate interatomic forces by harmonic springs. This is reassuring, but the best part of it is that when we couple together lots of balls using harmonic springs it is *always* possible to rearrange the *coupled* equations of motion of the balls to give a set of *uncoupled* equations. These describe the *normal modes* of the system of coupled oscillators. It is enough to appreciate that:

- (i) in the harmonic approximation the equations of motion can always be decoupled so as to describe independent modes, and
- (ii) since the normal modes don't interact, the excitation energy of a system of coupled oscillators is just the sum of the energies of the normal modes.

8.3.1 Monatomic solids

Linear monatomic chain

Consider atoms having equilibrium positions ra with r an integer and a the lattice constant (FIG 8.3) and displacements u_r from these positions. If a linear elastic restoring force with elastic constant μ (Hook's

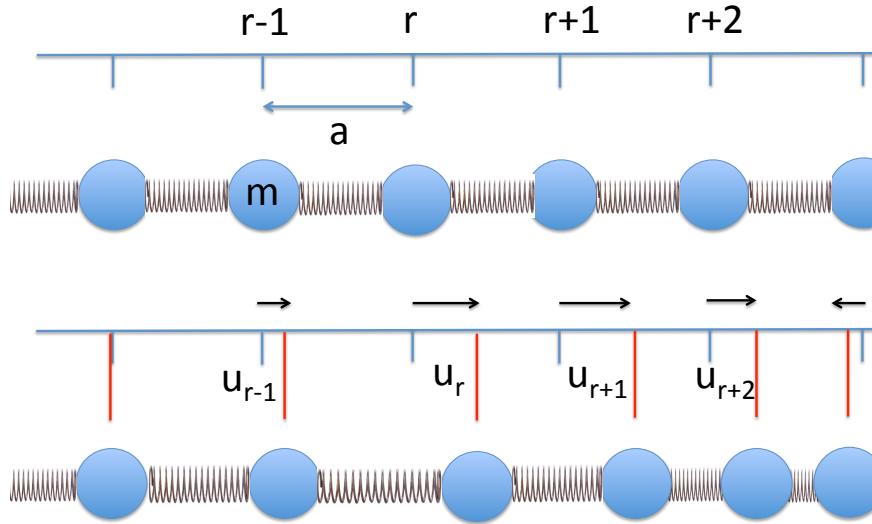


Figure 8.3: Linear chain: Top panel shows equilibrium positions and lower panel shows displaced positions.

law) is assumed, the force on the atom at position r is

$$F_r = \mu(u_{r+1} - u_r) - \mu(u_r - u_{r-1}) = \mu(u_{r+1} + u_{r-1} - 2u_r). \quad (8.11)$$

Newton's second law equates this to an acceleration,

$$F_r = m\ddot{u}_r. \quad (8.12)$$

Thus

$$m\ddot{u}_r = \mu(u_{r+1} + u_{r-1} - 2u_r). \quad (8.13)$$

Solutions to this linear differential equation may be sought of the form $u = Ae^{i(kra - \omega t)}$. The displacements must be real so it is implied we take either the Real or Imaginary part of this function (that both Real and Imaginary parts are separately solutions is true generally true for a *linear* differential equation, but not for non-linear equations). Substituting our trial solution in EQN 8.13

$$-m\omega^2 = \mu(e^{ika} + e^{-ika} - 2) = 2\mu(\cos(ka) - 1) = -4\mu\sin^2(ka/2) \quad (8.14)$$

$$\Rightarrow \omega = \pm 2\sqrt{\frac{\mu}{m}}\sin(ka/2) \quad (8.15)$$

$$\equiv \pm \omega_0 \sin(ka/2) \quad \text{with } \omega_0 = 2\sqrt{\frac{\mu}{m}}. \quad (8.16)$$

The solutions thus corresponds to travelling waves. For small k these have a linear dispersion

$$\omega = v_s k \quad \text{for small } k \quad (8.17)$$

$$\text{with } v_s \equiv a\sqrt{\frac{\mu}{m}} = \sqrt{B/\rho}, \quad (8.18)$$

with density $\rho = m/a$ and bulk modulus $B = a\delta F/\delta a = a\mu$. Thus for long wavelengths the solution is the same as the classical result for the speed of sound in an isotropic elastic medium (also valid for an

ideal gas). This is no accident, since in the long wavelength limit the atomic structure of the crystal is averaged on the scale of a wavelength so only the density, which is a bulk property, matters. The group velocity $d\omega/dk$ is the same as ω/k .

For shorter wavelengths we need to distinguish the group velocity from the ‘phase velocity’ ω/k . A wave packet, which represent an actual disturbance will move at the group velocity.

Boundary conditions

The ends of the chain satisfy a boundary condition. The ends could be free or fixed or the two ends of the chain could be connected to form a loop. For fixed ends and equilibrium positions labelled from $r = 0$ to $r = N$ the condition at $r = 0$ restricts solutions to stationary waves of form $u = \sin(kra)e^{-i\omega t}$ (Re and Im parts give the same solution but shifted in time). The condition $u_N = 0$ at $r = N$ requires $kNa = n\pi \Rightarrow k = n\pi/L$ with L the chain length and n an integer $0 < n < N$ ($n \geq N$ duplicates the same solutions as do negative values of n). The density of solutions for interval $d|k|$, per unit length of chain is denoted $g(k)$ and is given by $g(k).d|k| = \frac{1}{\pi}d|k|$ for $0 < k \leq \frac{\pi}{a}$ (the modulus sign may seem superfluous here since we have restricted $k > 0$, but it is useful when comparing the density of states for fixed boundaries with those with a periodic boundary condition that we consider next)

A periodic boundary (i.e. with the ends of the chain joined to form a loop) is a more standard choice of boundary condition. For this $u_0 = u_N$, which requires $kNa = 2\pi n \Rightarrow k = 2\pi n/L$ with integer n . Again, $n \rightarrow n + N$ repeats solutions. It is conventional to choose $-\pi/a \leq k \leq \pi/a$. The solutions are travelling waves moving to the left or right (independent of the choice of the range of n). For $-\pi/a \leq k \leq \pi/a$ the density of solutions for unit change of $|k|$ is $g(k) = 1/\pi$, the same as for the fixed boundary condition.

$$g(k).d|k| = \frac{1}{\pi}.d|k| \quad 0 < |k| \leq \frac{\pi}{a} \quad (8.19)$$

$$= 0 \quad |k| > \frac{\pi}{a} \quad (8.20)$$

$k = \pm\pi/a$ corresponds to

- neighbouring atoms oscillating exactly out of phase
- zero group velocity -i.e. a standing wave.
- an infinite density of states per interval of energy (see below).

The density of states with respect to the energy is given by equating numbers of states $g(\omega)d\omega = g(k)d|k|$. Rearranging,

$$g(\omega) = g(k) \frac{d|k|}{d\omega} = \frac{2}{\pi a} \frac{1}{\sqrt{\omega_0^2 - \omega^2}}, \quad (8.21)$$

which is infinite at the zone edge ($\omega = \omega_0$), but integrable.

Quantum mechanical solution

A quantum mechanical solution of the lattice problem gives the same dispersion equation for the excitations, which we will henceforth call phonons, as the classical analysis. The QM treatment starts from diagonalising the Hamiltonian

$$\hat{H} = \sum_r \frac{p_r^2}{2m} + \frac{\mu}{2}(u_r - u_{r+1})^2. \quad (8.22)$$

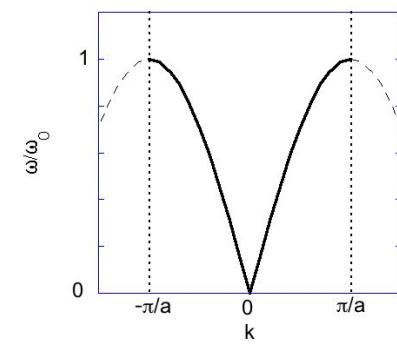


Figure 8.4: phonon dispersion for a linear chain. All solutions are contained in the first Brillouin zone π/a (see text). $\omega_0 = 2\sqrt{\mu/m}$

The full formal derivation is given later in the chapter. The additional information that the QM treatment provides is that phonons are Bosons. The number of Bosons in a given k state is (see Stat Mech course)

$$n(k) = \frac{1}{\exp\left(\frac{\hbar\omega_k}{k_B T}\right) - 1}, \quad (8.23)$$

with ω_k the solution of EQN 8.16 for ω at a given k . From the QM solution there is also zero point motion, so that the energy of the ground state for each mode k is not 0 but $\frac{1}{2}\hbar\omega_k$. The energy in each mode is therefore

$$\epsilon_k = \left(\frac{1}{2} + n(k)\right)\hbar\omega_k. \quad (8.24)$$

8.4 More formal derivation of phonons for a 1D elastic lattice

This section contains more advanced material that is not examinable

The derivation in section chapter 8.3.1 was based on classical physics - although we then quantised the excitations at the end by referring to the harmonic oscillator. In this section it is shown how the problem can be solved applying quantum mechanics from the start.

We start with a simpler problem, that of a single harmonic oscillator.

8.4.1 Revision of the Quantum Harmonic Oscillator

The Hamiltonian for a harmonic oscillator is

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + \frac{m\omega_0^2}{2}\hat{x}^2 \quad (8.25)$$

where ω_0 is a constant defined for later convenience in terms of the spring constant μ by $\mu = m\omega_0^2$. The expression is conveniently factored (as one might try to do to solve any second order differential equation) as

$$\hat{H} = \hbar\omega_0 \left(\sqrt{\frac{m\omega_0}{2\hbar}}\hat{x} - i\sqrt{\frac{1}{2m\hbar\omega_0}}\hat{p} \right) \left(\sqrt{\frac{m\omega_0}{2\hbar}}\hat{x} + i\sqrt{\frac{1}{2m\hbar\omega_0}}\hat{p} \right) - i\frac{\omega_0}{2}[\hat{x}, \hat{p}] \quad (8.26)$$

The square brackets denote a commutator ($[\hat{x}, \hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x}$ noting operators act on everything to their right). Thus defining

$$\hat{\mathbf{a}} = \left(\sqrt{\frac{m\omega_0}{2\hbar}}\hat{x} + i\sqrt{\frac{1}{2m\hbar\omega_0}}\hat{p} \right) \quad (8.27)$$

$$\Rightarrow \hat{\mathbf{a}}^\dagger = \left(\sqrt{\frac{m\omega_0}{2\hbar}}\hat{x} - i\sqrt{\frac{1}{2m\hbar\omega_0}}\hat{p} \right) \quad (8.28)$$

and noting

- $\hat{x}^\dagger = \hat{x}$, $\hat{p}^\dagger = \hat{p}$ which must be true since they are observables!
- and $[\hat{x}, \hat{p}] = i\hbar$.

We have

$$\hat{H} = \hbar\omega_0 \left(\frac{1}{2} + \hat{\mathbf{a}}^\dagger \hat{\mathbf{a}} \right) \quad (8.29)$$

and

$$[\hat{\mathbf{a}}, \hat{\mathbf{a}}^\dagger] = 1. \quad (8.30)$$

Thus

- if $|\Psi\rangle$ is an Eigenstate with energy E then $\hat{\mathbf{a}}|\Psi\rangle$ is an eigenstate with energy $E - \hbar\omega_0$. Since there is a lowest energy ground state (that we label $|0\rangle$) and all the terms in the Hamiltonian are positive definite, consistency is only possible if $\hat{\mathbf{a}}|0\rangle = 0$. The states must have discrete energies spaced by $\hbar\omega_0$.
- $\hat{\mathbf{a}}^\dagger$ increases the energy by $\hbar\omega_0$
- The ground state energy is $\hbar\omega_0/2$; this represents zero point motion (the quantum world never sleeps!).
- Excited states can be labelled by $n \geq 0$ with energy $\hbar\omega_0(1/2 + n)$. Call the normalised states $|\Psi_n\rangle$.
- $\mathbf{a}^\dagger|\Psi_n\rangle = \sqrt{n+1}|\Psi_{n+1}\rangle \quad \Rightarrow \quad |\Psi_n\rangle = \frac{(\mathbf{a}^\dagger)^n}{\sqrt{n!}}|0\rangle$
- $\mathbf{a}|\Psi_n\rangle = \sqrt{n}|\Psi_{n-1}\rangle$
- The creation and destruction operators (\mathbf{a}^\dagger and \mathbf{a}) can be viewed in two ways: (i) As ladder operators moving a marker up and down runs of a ladder (ii) As creating and destroying additional boson particles of energy $\hbar\omega_0$. The lowest rung of the ladder or empty ground state has energy $(1/2)\hbar\omega_0$.

8.4.2 Quantum 1 D atomic chain

The above method can be extended to arrays of atoms. Rewriting the Hamiltonian given earlier (r is just an integer dummy index and the hats now emphasize we are dealing with operators)

$$\hat{H} = \sum_r \frac{\hat{p}_r^2}{2m} + \frac{\mu}{2}(\hat{u}_r - \hat{u}_{r+1})^2. \quad (8.31)$$

The commutation relations are $[u_r, p_{r'}] = i\hbar\delta_{rr'}$ and $[u_r, u_{r'}] = 0$, $[p_r, p_{r'}] = 0$. This almost looks like the harmonic oscillator Hamiltonian, except the quadratic terms on the right couple together different coordinates. We untangled a similar term for the classical case by working with Fourier components. We suspect the same approach will work here. We can also impose periodic boundary conditions from the start. Writing the displacements in terms of Fourier components and the same for the momenta defines new operators

$$\hat{u}_r = \frac{1}{\sqrt{N}} \sum_k e^{i\vec{k} \cdot \vec{a} r} \hat{U}_k \quad \text{with } k = 2n \frac{\pi}{L} \text{ and } -\frac{\pi}{a} < k \leq \frac{\pi}{a} \quad (8.32)$$

$$\hat{p}_r = \frac{1}{\sqrt{N}} \sum_k e^{i\vec{k} \cdot \vec{a} r} \hat{\Pi}_k \quad \text{with } k = 2n \frac{\pi}{L} \text{ and } -\frac{\pi}{a} < k \leq \frac{\pi}{a} \quad (8.33)$$

With inverse relations

$$\hat{U}_k = \frac{1}{\sqrt{N}} \sum_r e^{-i\vec{k} \cdot \vec{a} r} \hat{u}_r \quad (8.34)$$

$$\hat{\Pi}_k = \frac{1}{\sqrt{N}} \sum_r e^{-i\vec{k} \cdot \vec{a} r} \hat{p}_r \quad (8.35)$$

With this choice the commutation relations are conserved i.e.

$$[U_k, \Pi_{k'}] = i\hbar\delta_{k,-k'}, \quad (8.36)$$

which can be checked by direct calculation. The $1/\sqrt{N}$ normalisations of the Fourier series were chosen to avoid factors of N appearing in the transformed commutation relations. A transformation (as above)

that preserves commutation relations is called a **canonical transformation**. In terms of the transformed variables the quadratic terms in EQN 8.31 are indeed untangled:

$$\hat{H} = \sum_k \frac{\hat{\Pi}_k^\dagger \hat{\Pi}_k}{2m} + \mu(1 - \cos(ka)) \hat{U}_k^\dagger \hat{U}_k \quad (8.37)$$

In arriving at the above we have used $\hat{U}_k = \hat{U}_{-k}^\dagger$ which is required for Hermitian \hat{u}_r (\hat{u}_r itself has to be Hermitian to ensure that it has Real eigenvalues: a must for a directly measurable quantity such as u_r). A similar result is used for $\hat{\Pi}_k$.

The problem has reduced to an uncoupled set of simple harmonic oscillators (with the slight twist that our $\hat{\Pi}_k$'s and \hat{U}_k 's are no longer Hermitian operators). The solution follows the same procedure as applied for the single simple harmonic oscillator. Raising and lowering operators are defined for each k as for the harmonic oscillator. They obey commutation relations:

$$[a_k, a_{k'}^+] = \delta_{k,k'} \quad (8.38)$$

$$[a_k, a_{k'}] = 0 \quad (8.39)$$

$$[a_k^+, a_{k'}^+] = 0 \quad (8.40)$$

These are the commutation relation for bosons - thus we have proved that the Eigenstates are indeed bosons. The Hamiltonian is

$$\hat{H} = \sum_{k_i} \left(\frac{1}{2} + a_{k_i}^+ a_{k_i} \right) \omega_{k_i} \quad \text{with} \quad \omega_{k_i} = 2\hbar \sqrt{\frac{\mu}{m}} \sin\left(\frac{k_i a}{2}\right) \quad (8.41)$$

The Eigenenergies are

$$E_{k_1, k_2, \dots, k_N} = \sum_{k_i} \left(\frac{1}{2} + n(k_i) \right) 2\hbar \sqrt{\frac{\mu}{m}} \sin\left(\frac{k_i a}{2}\right) \quad (8.42)$$

where the sum is over the modes k_i allowed by the boundary condition and $n(k_i)$ are integers.

Generalisation to 3D

In 3-dimensions there are two additional independent directions the atoms can move perpendicular to the chain. This gives two transverse modes in addition to the longitudinal mode we have already considered. For a 3D lattice, the quantisation arising from the periodic boundary condition now gives modes spaced by $2\pi/L_x, 2\pi/L_y, 2\pi/L_z$ along x, y, z . The density of states for each mode in k-space per unit volume is then

$$g_{L,T}(k) d^3k = \frac{1}{(2\pi)^3} dk_x dk_y dk_z \quad (8.43)$$

We are often interested in intervals of energy rather than d^3k , since the boson occupation factor EQN 8.23 is more simply expressed in terms of energy ω_k . For free-electrons the dispersion relation is spherically symmetric ($\epsilon = \hbar^2 k^2 / 2m$) and we can easily convert between $d|k|$ and $d\epsilon$. For phonons the dispersion relation is not spherically symmetric; in fact for fixed $|k|$, $\epsilon(\vec{k})$ has the point group symmetry of the lattice. For example, a simple cubic lattice (with lattice constant a) has dispersion for longitudinal waves (generalising EQN 8.14 to 3 dimensions)

$$\omega_{\vec{k}} = 2\sqrt{\frac{\mu}{m}} \sqrt{\left(\sin^2(k_x a/2) + \sin^2(k_y a/2) + \sin^2(k_z a/2) \right)}. \quad (8.44)$$

In the limit $k \rightarrow 0$ this reduces to a spherically symmetric result, but not for larger values of k . Conversion of the density of states from an integral over d^3k to one over $d\omega$ then has to be handled carefully.

$$g^\omega = \int d^3k g^{\vec{k}} \delta(\omega - \omega_{\vec{k}}) = \int_{\omega(\vec{k})=\omega} d^2k_\omega \frac{g^{\vec{k}}}{|\vec{\nabla}_k \omega_{\vec{k}}|} = \int_{\omega(k)=\omega} \frac{1}{(2\pi)^3} \frac{dS_k}{|\vec{\nabla}_k \omega_{\vec{k}}|} \quad (8.45)$$

The δ function confines us to a constant energy surface. The integral over d^3k is factored into the component of k perpendicular to the surface (k_\perp) and an integral $d^2k_\omega \equiv dS_k$ over the surface itself. The integral over the perpendicular component knocks out the delta function (using the identity $\delta(f(x)) = \sum_{x_0} \delta(x - x_0)/|f'(x)|_{x=x_0}$ with x_0 the roots of $f(x) = 0$). $\vec{V}_k \omega_k$ is the group velocity for a phonon at \vec{k} and is always perpendicular to the constant energy surface passing through \vec{k} (this follows from the definition of \vec{V}). If we measure the speed of sound (eg excite a long bar at one end at a particular frequency and time how long it takes before we pick up the disturbance at the other end of the bar) it is the group velocity we measure.

For **each** acoustic mode in the limit $k \rightarrow 0$ spherical symmetry can be used and the result for small ω reduces to

$$g_{(\omega \rightarrow 0)} = \frac{1}{2\pi^2} \frac{\omega^2}{v_s^3}. \quad (8.46)$$

8.4.3 Example of phonons: Cu

An example of phonons in real material is shown in FIG 8.5. The phonon dispersions throughout k-space can be measured with neutron scattering and now also with inelastic X-ray scattering. The different symbols X (along the a-axis), L (along the $(1,1,1)$ direction), K (along the $(1,1,0)$ direction) represent different crystallographic directions. The most important point is labelled Γ which is the origin $q = 0$. The dispersion pattern repeats if one continues along any direction since the crystal structure is periodic. The dispersion is also symmetric about the origin.

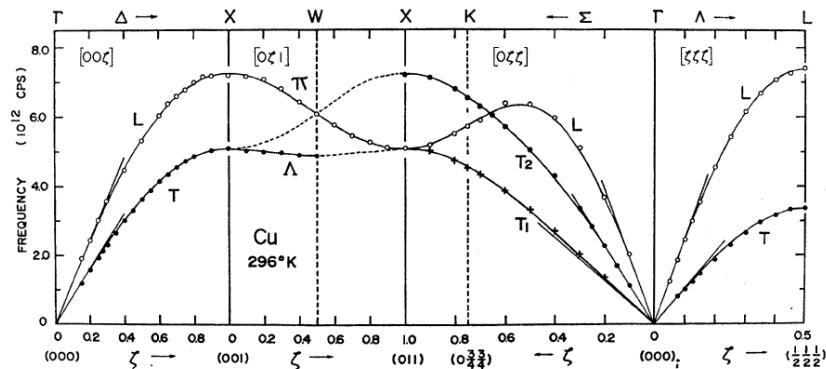


Figure 8.5: Phonon spectra in Cu measured with neutron scattering (Svensson, Brockhouse and Rowe, Physical Review **155** 619 (1967)). Cu is FCC and dashed vertical lines are BZ boundaries of the primitive unit cell.

Some comments on the phonon dispersion for Cu are:

- Modes have zero component of group velocity across at the zone edges.
- Two transverse modes are degenerate along $[0,0,1]$ owing to the 4-fold symmetry axis of the structure.
- Two transverse modes are degenerate along $[1,1,1]$ owing to the 3-fold symmetry axis.
- Close to the zone centre transverse modes have lower energy than longitudinal modes, since transverse modes do not give charge separation and therefore have weaker restoring forces.
- There is only one atom/primitive cell, so no optic (higher energy) modes.

How we can understand the heat capacity of solids, thermal conduction and thermal expansion in terms of phonons will be developed in the introduction to condensed matter physics course next year.

Revision

The exams is structured as follows:

Section A: 6 questions; answer all of these. The last three cover this semester's material and it is intended that each question can be completed in 5 mins.

Sections B and C: you have to do 3 questions with at least one from section B and one from section C. Section B covers semester 1 and sections C covers semester 2. There will be three questions to choose from in section C. It is intended that each of these questions should take around 30 mins to complete.

I have tabulated the key items covered in the second semester of the course classifying them into the following categories:

- Learn: Equations and facts you should learn (eg the meaning of term symbols and Hund's rules) and be able to apply to solve problems.
- Derive: Derivations you should be able to perform under exam conditions. Where these are marked 'guided' some guidance would be given in a question (e.g. the question might break down the derivation down into constituent steps).
- Apply: Material you should be able to apply to solve problems, but where key equations would be given in the exam.
- Background material (material you should have read once). Material you should be aware of but won't be asked detailed questions on (eg. you should be aware that there are higher order terms in perturbation theory - you will not be asked to calculate such terms)
- Advanced material: this is more advanced material such as on Berry phase. It is labelled as such in the notes and can be skipped if your primary focus is passing the exam. This material is a useful primer for those planning to do more advanced courses in the future.

Chap.	Item	Learn	Derive	Apply	Bckd
1	TIPT (1st order in Ψ , 1st & 2nd order in E)	EQN 1.10 EQN 1.13 EQN 1.14	✓	✓	
1	Solve variations of Harmonic oscillator problems			✓	
1	Higher order Pert ⁿ theory				✓
tut	Brillouin-Wigner Pert ⁿ theory				Adv.
2	Non-relativistic hydrogen atom (wavefunctions)	1s,2s,2p unnormalised eg. EQN 3.16		✓	
2	Non-relativistic hydrogen atom (energy levels)	$E_N = \frac{1}{8\pi\epsilon_0 a_0 N^2}$		✓	
2	Raising operators for generating higher n,l wavefunctions				✓
2	Polarisability of harmonic oscillator		✓		
2	Polarisability of hydrogen atom (upper & lower limit)		guided		
2	f-sum rule				✓
2	Van der Waals interaction		guided	✓	
3	Degenerate Pert ⁿ theory	EQN 3.2 EQN 3.3	✓	✓	
3	Linear Stark Effect		guided		
4	Relativistic Corrections to H-atom	One sentence descriptions. Final result FIG 4.5		✓	
4	Clebsch-Gordon Coeffs				✓
5	Good quantum numbers with spin-orbit	$\frac{2}{\hbar^2} \hat{L} \cdot \hat{S} = J(J+1) - L(L+1) - S(S+1)$ etc..		✓	
5	Angular Mom. Addition Th.	✓		✓	
5	Spin statistics theorem	✓		✓	
5	2-electrons: helium	triplet and singlet spin wavefunctions			
5	Direct and Exchange interactions		✓		
5	Ground & Lowest excited states of He		✓		
5	Russell-Saunders notation	Term symbols			
5	Aufbau principle	✓			
5	Multiple electron atoms	Hund's rules		✓	
5	Variational Method	Rayleigh Ritz (without Lagrange multipliers)	✓	✓	
5	Hartree and Hartree Fock				✓

Chap.	Item	Learn	Derive	Apply	Bckd
5	Selection Rules	$\Delta M_L = 0, \pm 1$ $\Delta l = \pm 1$	✓	✓	
5	Selection Rules (no SO)	$\Delta L = 0, \pm 1$ $\Delta S = 0$		✓	
5	Selection Rules (with SO)	$\Delta J = 0, \pm 1$ (not $0 \rightarrow 0$)		✓	
5	σ and π transitions	✓		✓	
6	Magnetic Hamiltonian	$\frac{\mu_B}{\hbar} \vec{B} \cdot \hat{L} + \frac{e^2 B^2 r_\perp^2}{8m}$	✓		
6	Zeeman splitting Landè g-factor $g_L = \left(\frac{3}{2} + \frac{1}{2} \frac{S(S+1) - L(L+1)}{J(J+1)} \right)$		guided	✓	
6	Vector model, $\hat{S}\hat{J}^2 = (\hat{S}.\hat{J})\hat{J}$				✓
6	Paschen-Back (strong field Zeeman)			✓	
6	Larmor Diamagnetism, EQN 6.19		✓	✓	
7	Molecules	Born-Oppenheimer			
7	LCAO H ₂			✓	✓
7	Heitler-London H ₂			✓	✓
7	Rotation transitions	✓	outline	✓	
7	Rotation selection rules	$\Delta l = \pm 1$ homonuclear =absent	outline	✓	
7	Molecular vibrations	Selection rule $\Delta n = \pm 1$ Revision of H.O.	✓	✓	
7	Combined rot & vib transitions			✓	
7	Frank Condon principle combined vib+rot+electronic				✓
7	phonons: linear chain phonon dispersion				✓

As well as application of the above techniques to atoms and molecules you should also look at applications to harmonic oscillators, free particles in 1D potentials as covered in the tutorial problems.