Muantum Qemanichs

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These notes were made for my own use during the second semester of my Juniour Honours Quantum Mechanics course.

Contents

1 Stuff the Professor expects me to know from Sem 1

1.1 Dirac notation

"In quantum mechanics a physical state—for example, a silver atom with a definite spin orientation—is represented by a state vector in a complex vector space." This vector is called a ket, and is denoted by $|\alpha\rangle$. The ket contains complete information about the physical state.

$$|\alpha\rangle + |\beta\rangle = |\gamma\rangle$$

$$c * |\alpha\rangle = |\alpha\rangle * c$$

where c is a complex number, if $c = 0$ the result is called a null ket.

An observable can be represented by an operator, generally, an operator acts on a ket from the left:

$$A * (|\alpha\rangle) = A|\alpha\rangle$$

To every ket there exists a bra. Bra space is a vector space 'dual to' ket space. The bras are essentially a mirror image of the kets. $|\alpha\rangle \longleftrightarrow \langle\alpha|$

The inner product: $\langle\beta|\alpha\rangle$

Fundamental postulate 1: $\langle\beta|\alpha\rangle = \langle\alpha|\beta\rangle^*$

Fundamental postulate 2: $\langle\alpha|\alpha\rangle \geq 0$ where the equality sign only holds if $|\alpha\rangle$ is a null ket, i.e equal to 0.

Orthogonality: $\langle m|n\rangle = \delta_{m,n}$

Closure: $\sum_n |n\rangle\langle n| = 1$

Normalized ket: $|\tilde{\alpha}\rangle = (\frac{1}{\sqrt{\langle\alpha|\alpha\rangle}})|\alpha\rangle$, $\langle\tilde{\alpha}|\tilde{\alpha}\rangle = 1$

1.2 Operators

Act from the left on a ket: $X * (|\alpha\rangle) = X|\alpha\rangle$

X and Y are equal if $X|\alpha\rangle = Y|\alpha\rangle$

X is a null operator if $X|\alpha\rangle = 0$

Operators can be added: $X + Y = Y + X$; $X + (Y + Z) = (X + Y) + Z$

Operators are generally linear

Act from the right on a bra: $(\langle\alpha|) * X = \langle\alpha|X$

X^+ is the Hermitian adjoint, or adjoint, of X. An operator is Hermitian if $X = X^+$

Multiplication:

$$XY \neq YX$$

$$X(YZ) = (XY)Z = XYZ$$

$$X(Y|\alpha\rangle) = (XY)|\alpha\rangle = XY|\alpha\rangle$$

$$(XY)^+ = Y^+X^+$$

$$XY|\alpha\rangle = X(Y|\alpha\rangle) \longleftrightarrow (\langle\alpha|Y^+)X^+ = \langle\alpha|Y^+X^+$$

The outer product: $|\beta\rangle\langle\alpha| \rightarrow$ this is regarded as an operator

Useful operators from Sem 1:
Position: $\hat{\mathbf{r}} = \mathbf{r}$;   Momentum: $\hat{\mathbf{p}} = -i\hbar\nabla$

$$\hat{X} = \sqrt{\frac{m\omega}{\hbar}}X \text{ and } \hat{P} = \frac{1}{\sqrt{m\hbar\omega}}P$$

For an operator t hat does not depend on time:

$$\frac{\partial}{\partial t}\langle A\rangle = \frac{i}{\hbar}\langle[H,A]\rangle$$

The associative axiom of multiplication:

$$(|\beta\rangle\langle\alpha|) * |\gamma\rangle = |\beta\rangle * (\langle\alpha|\gamma\rangle)$$

Here, $\langle\alpha|\gamma\rangle$ is just a number, therefore the outer product can be seen as just another operator since if it is acted on a ket the result is just another ket.
If $X = |\beta\rangle\langle\alpha|$ then $X^+ = |\alpha\rangle\langle\beta|$

$$\langle\beta|X|\alpha\rangle = \langle\beta| * (X|\alpha\rangle) = \{(\langle\alpha|X^+) * |\beta\rangle)\}^* = \langle\alpha|X^+|\beta\rangle^*$$

Hence, $\langle\beta|X|\alpha\rangle = \langle\alpha|X|\beta\rangle^*$

Don't forget!! $\psi(x) \equiv \langle x|\psi\rangle$

1.3   Commutators

Commutator: $[A,B] \equiv AB - BA$
Anti-commutator: $\{A,B\} \equiv AB + BA$

If an observable commutes with the Hamiltonian, then it is by definition a conserved quantity. Worth noting, ***the definition of an observable*** is that it is Hermitian, $A = A^+$ (meaning it also has real eigenvalues) and its eigenvectors also form a basis, meaning $I = \sum_i |u_i\rangle\langle u_i|$ where I is the identity matrix.

$$[AB,C] = A[B,C] + [A,C]B$$

Useful commutator relations:
$[X,P] = i\hbar$
$[X,X] = [P,P] = 0$
$[a,a^+] = 1$
$[L^2,H] = 0 \longrightarrow$ total angular momentum is conserved
$[N,a] = -a$
$[N,a^+] = a^+$
$[a,a^+] = 1$
$[J_z,J_-] = -J_-\hbar$

1.4   Ladder operators

$a^+|n\rangle = \sqrt{n+1}|n+1\rangle \Rightarrow$ Raises the eigenvalue by one (increases from one excited state to the next)
$a|n\rangle = \sqrt{n}|n-1\rangle \Rightarrow$ Lowers the eigenvalue by one, when acted on the ground state always equals 0.
In bra form: $\langle n|a = \sqrt{n+1}\langle n+1|$ **and** $\langle n|a^+ = \sqrt{n}\langle n-1|$

$$a = \frac{1}{\sqrt{2}}(\hat{X} + i\hat{P}) \text{ and } a^+ = \frac{1}{\sqrt{2}}(\hat{X} - i\hat{P})$$

$$\hat{X} = \sqrt{\frac{\hbar}{2m\omega}}(a^+ + a) \text{ and } \hat{P} = i\sqrt{\frac{\hbar m\omega}{2}}(a^+ - a)$$

1.5 Angular momentum

$$J^2 = J_x^2 + J_y^2 + J_z^2$$

$$[J_x, J_y] = i\hbar J_z, \ [J_y, J_z] = i\hbar J_x, \ [J_z, J_x] = i\hbar J_y, \ [J^2, J_{x,y,z}] = 0$$

$$4 \text{ observables} \rightarrow J^2, J_x, J_y, J_z$$

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

$$J_z|j,m\rangle = m\hbar|j,m\rangle$$

$$J_+ = J_x + iJ_y, \ J_- = J_x - iJ_y, \ J_- = J_+^+$$

$$[J^2, J_\pm] = 0$$

$$J_- J_+ = J^2 - J_z^2 - \hbar J_z$$

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

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

$$-j \leq m \leq j$$

1.6 Other useful stuff from sem 1 I should remember

Expectation value: $\langle X \rangle_\psi = \int_{-\infty}^{\infty} x|\psi(x)|^2 dx = \int_{-\infty}^{\infty} \psi(x)^* x\psi(x)dx = \langle \psi|X|\psi\rangle$

The Harmonic Oscillator:

$E = \hbar\omega(n + \frac{1}{2})$ The Hamiltonian / energy levels of a harmonic oscillator

$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2$ The exact Hamiltonian for a harmonic oscillator

The Infinite square well:

$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2} \longrightarrow$ Energy levels of the infinite square well of length a.

$$\psi_n \equiv \langle x|n\rangle = \begin{cases} \sqrt{\frac{2}{L}}cos(\pi nx/L) & \text{when n is odd} \\ \sqrt{\frac{2}{L}}sin(\pi nx/L) & \text{when n is even} \end{cases} \tag{1}$$

The wavefunction for the infinite square well size L where $-L/2 < x < L/2$ Be careful as the functions will flip if the centre of the well isn't about x=0, i.e. the well is size a where $0 < x < a$, since the location of the peak of the wave changes.

The states of the infinite square well are mutually orthogonal, hence $\int \psi_m(x)^* \psi_n(x)dx = \delta_{m,n}$

$c_n = \int \psi_n(x)^* f(x)dx$

$\langle H \rangle = \sum |c_n|^2 E_n$

The finite square well:

General solution: $\psi(x) = Aexp(-kx) + Bexp(kx)$

$E = \frac{k^2\hbar^2}{2m}$ where $k = \frac{\sqrt{2mE}}{\hbar}$
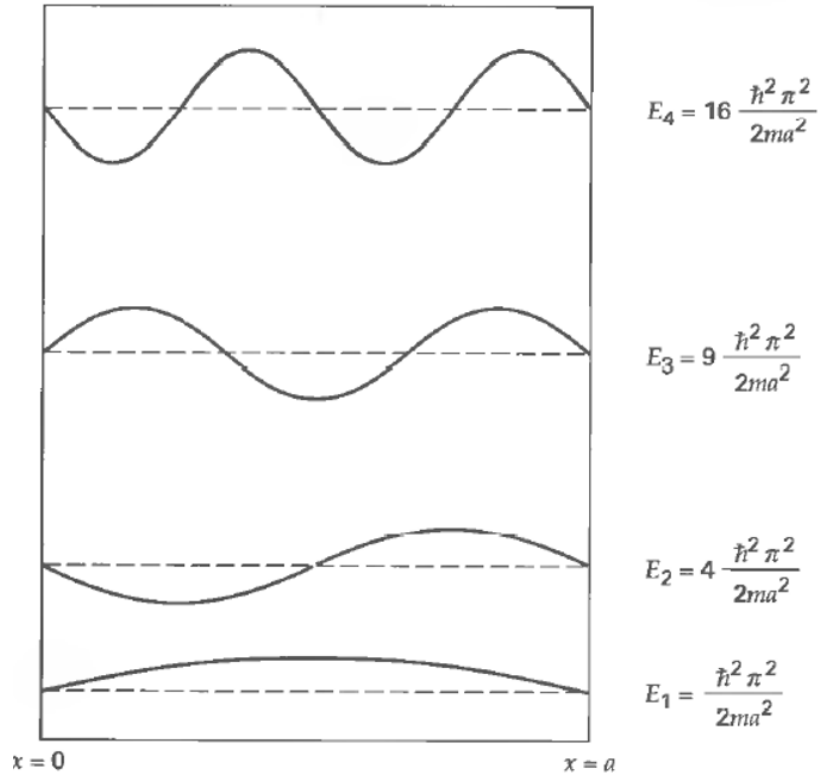
Figure 1: Eigensolutions for a particle in a box (Gasiorowicz)

First four harmonic oscillator normalized wavefunctions

$$\Psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-y^2/2}$$

$$\Psi_1 = \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{2}\, y\, e^{-y^2/2}$$

$$\Psi_2 = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{2}} (2y^2 - 1) e^{-y^2/2}$$

$$\Psi_3 = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{3}} (2y^3 - 3y) e^{-y^2/2}$$

$$\alpha = \frac{m\omega}{\hbar} \qquad y = \sqrt{\alpha}\, x$$

Figure 2: Wavefunctions for the Harmonic Oscillator

2 Time-independent non-degenerate perturbation theory

$\Delta E_s = \langle s|\hat{H}_1|s\rangle \rightarrow$ Equation for the first order perturbation theory energy shift (the Professor's notation). My preferred notation:

$$\Delta E_n = \langle \psi_n^0|H^1|\psi_n^0\rangle \tag{2}$$

In words, the first order correction to the energy is the expectation value of the perturbation value in the unperturbed state. Key - remember the expectation value equation from semester 1 in integral form and plug into that. Deriving this could come up on the exam, Griffith's has a great derivation and the MIT lectures provide an especially nice one, it has been derived to death, there are no shortages of derivations for this online.

$a_{is} = \frac{(H_1)_{is}}{\epsilon_s - \epsilon_i} a_s = 1 \rightarrow$ The first order correction to the wavefunction from the Professor's notes, not sure how to use it in this form, it doesn't make sense to me.
My preferred notation that I can use:

$$\psi_n^1 = \sum_{nm} \frac{\langle \psi_m^0|H^1|\psi_n^0\rangle}{\left(E_n^0 - E_m^0\right)} \psi_m^0 \tag{3}$$

The second order energy correction equation, taken from Griffiths:

$$E_n^2 = \sum_{mn} \frac{|\langle \psi_m^0|H^1|\psi_n^0\rangle|^2}{E_n^0 - E_m^0} \tag{4}$$

The combined 1st and 2nd order energy shift equation as the Professor presents it:

$$\Delta E_s = \langle s|\hat{H}_1|s\rangle + \sum_{is} \frac{|\langle i|H_1|s\rangle|^2}{\epsilon_s - \epsilon_i} \tag{5}$$

In this equation s represents the unperturbed ground state. A commonly asked question is *"why does the second energy shift lower the energy of the ground state?"* This is because the denominator will always be negative if i is a state higher than the unperturbed ground state, since the unperturbed ground state is of course by definition the lowest energy state. This is a bit confusing, since it's easy to mix up the unperturbed ground state, labelled by s, and the perturbed ground state which is an approximation of what the ground state energy actually is, which is of course what these energy corrections are attempting to approximate.

3 Hydrogen atom

shell	subshell	n	l	$R_{nl}(r)$	E_n	nodes in R_{nl}	nodes in Y_{lm}	total nodes
K	1s	0	0	$\left[2\left(\frac{Z}{a_0}\right)^{3/2}\right]e^{-\frac{Zr}{a_0}}$	$-\frac{1}{2}\frac{Z^2e^2}{4\pi\epsilon_0 a_0}$	0	0	0
L	2s	1	0	$\left[2\left(\frac{Z}{2a_0}\right)^{3/2}\right]\left(1-\frac{Zr}{2a_0}\right)e^{-\frac{Zr}{2a_0}}$	$-\frac{1}{4}\frac{1}{2}\frac{Z^2e^2}{4\pi\epsilon_0 a_0}$	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	$\left[2\left(\frac{Z}{3a_0}\right)^{3/2}\right]\left(1-2\frac{Zr}{3a_0}+\frac{2}{3}\left(\frac{Zr}{3a_0}\right)^2\right)e^{-\frac{Zr}{3a_0}}$	$-\frac{1}{9}\frac{1}{2}\frac{Z^2e^2}{4\pi\epsilon_0 a_0}$	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 3: Wavefunctions for the Hydrogen atom

The allowed energies for the Hydrogen atom:

$$E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2} \tag{6}$$

The ground state:

$$E_1 = -\left[\frac{m_e}{2\hbar^2}\left(e^2 4\pi\epsilon_0\right)\right] = -13.6eV \tag{7}$$

The ground state wavefunction:

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}}e^{-r/a} \tag{8}$$

Useful to know, the integral of a Gaussian:

$$\int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}} \tag{9}$$

4 Degenerate perturbation theory

If the unperturbed states are degenerate - if two or more distinct states share the same energy - then ordinary perturbation theory fails. This is due to the fact that you would be dividing by 0 when using the energy shift equation.

The first step is to use this matrix eigenvalue equation:

$$\sum_{d' \in D} (H_1)_{dd'} a_{d'} = (\Delta E) a_d \tag{10}$$

This looks confusing, but wrote out it is simply:

$$\begin{pmatrix} H_{11} & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} & \dots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} & \dots & \dots & H_{nn} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_n \end{pmatrix} = \Delta E \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_n \end{pmatrix} \tag{11}$$

Which is just a regular matrix eigenvalue equation. To put it into words, the energy shifts, ΔE, are the eigenvalues of a sub-matrix of the perturbation H_1, and the eigenvectors give their corresponding states. When going through this process, the diagonal will all go to zero and all the off-diagonals will be the perturbations.

The process is difficult to explain, best described with an example. Problem sheet 3, question 3b:

A 2D harmonic oscillator is given a perturbation $H_1 = \lambda xy$ From semester 1, it is known that:

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a_x^+ + a_x) \text{ and } y = \sqrt{\frac{\hbar}{2m\omega}}(a_y^+ + a_y) \tag{12}$$

These equations are then plugged into the following matrix:

$$\begin{pmatrix} \langle 0,1|H_1|0,1 \rangle & \langle 0,1|H_1|1,0 \rangle \\ \langle 1,0|H_1|0,1 \rangle & \langle 1,0|H_1|0,1 \rangle \end{pmatrix} \tag{13}$$

Which, after some gross maths, gives the following Matrix:

$$\begin{pmatrix} 0 & \frac{\lambda\hbar}{2m\omega} \\ \frac{\lambda\hbar}{2m\omega} & 0 \end{pmatrix} \tag{14}$$

Hence, the energy shifts are:

$$\Delta E_\pm = \pm \frac{\lambda\hbar}{2m\omega} \tag{15}$$

The total shift in energy is simply the addition of these two, then the splitting in energies is the difference in the two.

5 The Relativistic corrections

In physics, the fine structure of the hydrogen atom describes the splitting of spectral lines atoms due to two mechanisms - a relativistic correction and spin-orbit coupling / spin-orbit interaction.The fine structure is a tiny perturbation to the Bohr energies found before in Semester 1, shown below:

$$E_n = -\left[\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2} \tag{16}$$

The Bohr Hamiltonian:

$$H_{Bohr} = \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \tag{17}$$

This is simply the electron kinetic energy plus Coulombic potential energy.

5.1 The relativistic correction

The first term, the kinetic energy term, comes about from substiting the operator $\hat{p}$ into the equation for kinetic energy $T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$, this is however the classical kinetic energy.

The relativistic formulas for kinetic energy and momentum:

$$T = \frac{mc^2}{\sqrt{1 - (v/c)^2}} - mc^2 \text{ and } p = \frac{mv}{\sqrt{1 - (v/c)^2}} \tag{18}$$

Expressing T in terms of p, then performing a taylor expansion, leads to the lowest-order relativistic correction to the Hamiltonian being given as:

$$H_r^1 = -\frac{p^4}{8m^3c^2} \tag{19}$$

This can be used to find the first order energy correction, which comes out as: (full derivation Griffiths pg 297-298)

$$E_r^1 = -\frac{(E_n)^2}{2mc^2} \left[\frac{4n}{l + 1/2} - 3 \right] \tag{20}$$

5.2 Spin-orbit coupling / the spin-orbit interaction

Imagine an electron in orbit around a nucleus. From the electrons point of view, the proton is circling around it. The orbiting positive charge sets up a magnetic $\underline{B}$ field in the electron's frame. This exerts a torque on the spinning electron, aligning its magnetic moment $\underline{\mu}$ along the direction of the field. The Hamiltonian is: $\boldsymbol{H = -\mu \cdot B}$

The Hamiltonian for the spin-orbit interaction is derived fully in Griffiths pg 299-303. This Hamiltonian is found to be:

$$H_{so} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2c^2r^3} \underline{s} \cdot \underline{l} \tag{21}$$

This looks different to what the Professor gives in his notes, but I believe all you generally need to remember is that $H_{so} \propto \underline{s} \cdot \underline{l}$ in the exam. Could be wrong, obviously. This commutes with L^2, S^2 and the total angular momentum J. ($J \equiv L + S$) and hence these quantities are conserved. In other words, the eignstates of L_z and S_z are not good states, but the eigenstates of, L^2, S^2, J^2 and J_z are. The H_{SO} perturbation can then be used to find the energy correction to the spin-orbit term, which is then added with the relativistic correction to get the complete fine structure formula:

$$E_{fs}^1 = \frac{(E_n)^2}{2mc^2} \left(3 - \frac{4n}{j + 1/2} \right) \tag{22}$$

Combining this with the Bohr formula, the grand result for the energy levels of hydrogen, including fine structure is found to be:

$$E_{nj} = -\frac{13.6eV}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - 3/4\right)\right] \qquad (23)$$

5.3 Hyperfine interactions

There are more corrections mentioned in the Professor's notes, which come from quantum electrodynamics (QED) and the nuclear spin.

The Lamb Shift - This relates to the degeneracy in the $2s_{1/2}$ and $2p_{1/2}$ levels states, this is lifted by QED. QED considers fluctuations of the electromagnetic field. This is strongest near the nucleus where the potential is most attractive, acting to counteract the Coulomb potential. The s-level feels it more than the p-level since it is heavier and closer to the nucleus, thus the s-state has a slightly higher energy than the p-state. It can also be thought of as a correction to Coulomb's law at short distances.

Nuclear moments - There is an interaction between the moment of the nucleus and the electrons. It produces shifts smaller than the fine structure interactions, and is important for NMR and the physics of gases of cold (neutral) atoms.

5.4 Section A style question

Section A style question

1. (a) Explain why the Stark effect (the shift in energy levels induced by an applied electric field) depends quadratically in the electric field for the 1s levels for the non-relativistic hydrogen atom. **[2]**

(b) By explaining how N=2 levels may be combined, to from a dipole moment or otherwise explain why the N=2 shell is split linearly by an electric field (linear Stark effect). **[3]**

Figure 4: Problem sheet 5

1. (a) The Stark effect is the shift in spectral lines owing to an applied electric field. The perturbation is $V = e\xi Z$. Since the question is looking at 1s, the spin can be ignored since it doesn't interact with the electronic field.

$$\Delta E = \langle 1s|e\xi x|1s\rangle + \sum_{n,l} \frac{|\langle n,l|e\xi x|1s\rangle|^2}{\epsilon_{1s} - \epsilon_{nl}} \qquad (24)$$

The first term cancels since the perturbation has odd parity, and $\psi_{1s}^*\psi_{1s}$ is even, since it's unique it has definite parity. This leaves just the second term, which is quadratic for ξ^2.

(b) 2s, 2p are degenerate, so can be mixed to from a dipole, eg $2s + 2p_z$.
$\Delta E \approx \epsilon \longrightarrow$ The energy shift depends on the first order of the electric field.

Explanation for why the electric field doesn't interact with the 1s state, meaning spin can be ignored:

$$|1\,0\,0\rangle = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \text{ (Eq. 4.80)}, \quad E_s^1 = \langle 1\,0\,0|H'|1\,0\,0\rangle = eE_{\text{ext}}\frac{1}{\pi a^3}\int e^{-2r/a}(r\cos\theta)r^2\sin\theta\,dr\,d\theta\,d\phi.$$

But the θ integral is zero: $\int_0^\pi \cos\theta\sin\theta\,d\theta = \left.\frac{\sin^2\theta}{2}\right|_0^\pi = 0.$ So $\quad E_s^1 = 0.$ QED

Figure 5: Making the perturbation $V = e\xi Z$ on the n = 1 state of Hydrogen, taken from Griffiths ISM 3rd Ed

6 Multi-electron atoms

New things in this chapter:

$$H_1 = \sum_{i>j}\frac{e^2}{4\pi\epsilon_0|\underline{r}_i - \underline{r}_j|} \quad \text{The Coloumb interaction between electrons} \tag{25}$$

We now have to ensure the wave function is anti-symmetric under particle exchange, since electrons are fermions. There is also more complex interactions between orbital motions and spins.

6.1 Pauli Exclusion Principle / Spin-statistics theorem

Integer spins (Bosons) cannot form totally anti-symmetric states - they must be in totally symmetric states.
Half-integer spins (fermions) cannot form totally symmetric states - they must be in totally anti-symmetric states.

All particles with integer spins are bosons.
All particles with half-integer spins are fermions.

$$|\phi_1, \phi_2\rangle_+ = (|\phi_1\rangle|\phi_2\rangle + |\phi_2\rangle|\phi_1\rangle)/\sqrt{2} \longrightarrow \text{Symmetric}$$
$$|\phi_1, \phi_2\rangle_- = (|\phi_1\rangle|\phi_2\rangle - |\phi_2\rangle|\phi_1\rangle)/\sqrt{2} \longrightarrow \text{Anti-symmetric}$$

6.1.1 Permutation exchange operator

$$\hat{P}_{12}|r_1\rangle|r_2\rangle = |r_2\rangle|r_1\rangle$$
$$\hat{P}_{12} \equiv \hat{P}_{21} \; ; \; \hat{P}_{12}^2 = 1$$

$$\text{Eigenvalues} = \pm 1 \longrightarrow \begin{cases} \text{negative is anti-symmetric} \\ \text{positive is symmetric} \end{cases}$$

Under $\hat{P}_{12}$, particle 1 having k' becomes particle 1 having k". Particle 2 having k" becomes particle 2 having k'. In other words, it has the effect of interchanging 1 and 2.

6.2 Spin

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

In the absence of spin-orbit interactions, we can choose an energy eigenstate to be an eigenstate of the total spin and the factor wavefunction.

$$\Psi(x_1, x_2) = \sum_i \psi(\underline{r}_1, \underline{r}_2)\chi_i(S, M_s)$$

Where χ_i are the eigenstates of $\hat{s}^2$ and $\hat{s}_z$, with the same S^2 eigenvalue and the same S_z eigenvalue. The spins S_1 and S_2 can be combined to give a total spin of 0 or 1.
$S = 1$ comprises $M_s = -1, 0, 1$
$S = 0$ only has $M_s = 0$

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

Figure 6: Spin table from the Professor's notes

6.3 The Helium atom

The Hamiltonian for the Helium atom with no electron-electron interactions:

$$H_0 = \frac{Ze^2}{4\pi\epsilon_0 r_1} + \frac{Ze^2}{4\pi\epsilon_0 r_2} \tag{26}$$

This is separable and the single electron states are simply those of the hydrogen atom but with $Z = 2$. The two electron wavefunction has to be anti-symmetric. Putting two electrons in the lowest N=1 state requires them to have opposite spin. The energy of the ground state is -8Ry. 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 $L = 1(1s^1 + 2p^1)$

7 Russell Saunders Notation

$$^{2s+1}L_J \tag{27}$$

This symbol represents a level, where s is spin, (2s + 1) is the spin degeneracy, L is the total orbital angular momentum and J is the total angular momentum.

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

Figure 7: The allowed states for the ground state of Helium $^1S_0$
- taken from the Professor's notes.

Symbol	Description	Range of values
n	Principal quantum number	1, 2, 3...
l	Azimuthal/orbital quantum number	$0 \leq l \leq n-1$
m_l	Magnetic quantum number	$-l \leq m_l \leq l$
m_s	Spin quantum number	$\pm 1/2$

Good quantum numbers - A good quantum number is associated with an operator that commutes with the Hamiltonian. In other words, it is an eigenvalue of an operator that commutes with the Hamiltonian. Systems that can be labelled by good quantum numbers are eigenstates of the Hamiltonian. For example, in Hydrogen, l is a good quantum number since the orbital angular momentum L commutes with the Hamiltonian.

7.1 Spin-spin coupling

S - the resultant spin quantum number for a system of electrons. S arises from adding the individual m_s

7.2 Orbit-orbit coupling

L - the total orbital angular momentum quantum number defines the energy state for a system of electrons.

L	Orbital
0	S
1	P
2	D
3	F
4	G
5	H

7.3 Spin-orbit coupling

Coupling occurs between the resultant spin and orbital momenta of an electron which gives rise to J, the total angular momentum quantum number.

$$J = L + S \ \text{ or } \ J = |L - S|$$

7.4 Hund's rules

Hund's rules are used to find the term symbol that corresponds to the ground-state of a multi-electron atom.

(1) Maximise S

(2) Maximise L

(3) If subshell $\begin{cases} < 1/2 \text{ full, minimise J} \\ > 1/2 \text{ full, maximise J} \end{cases}$
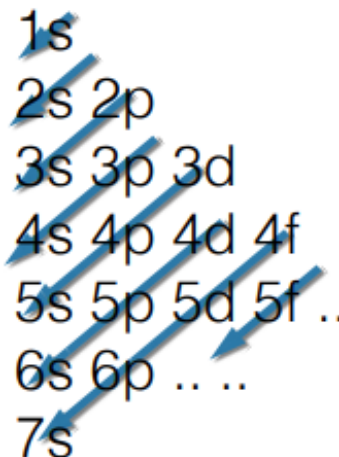
7.5 Aufbau principle

Figure 8: Electrons fill shells in this order.

7.6 Hartree and Fock energy

Only the background is examinable in this section.

The Hartree energy is approximately the electric potential energy of the Hydrogen atom in its ground state. The Hartree-Fock method is a method of approximation for the determination of the wave function and energy of a quantum many body system in a stationary state.

Different effects on the energy of electrons in the same shell ranked by most to least important:
(1) The $1/r$ Coulomb potential from the nucleus, depends only on n.
(2) Central field approximation. The energy here includes the combined electric fields of the nucleus and all the electrons in the system and takes them to all be the same for all electrons within the atom. The effective potential is given by Hartree and Hartree-Fock approximations, and is therefore no longer $1/r$. The outer single electron level energies now depend on n and also l.
(3) Non-central energies (electron-electron interactions). *"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."* The exchange energy is essentially the energy difference between having two spins aligned versus anti aligned, which arises because of the Pauli exclusion principle. What the Professor is saying here is that this energy prefers to put electrons in states with opposite alignments. *"(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 a 'term' having definite L and S the levels are now split according to J. Not sure what the Professor is rambling on about in this paragraph, but I'm assuming it's going to be the same as the spin-orbit interaction explained earlier.
(5) Hyperfine interactions, such as the lamb shift, they are very small and not really considered. They were explained earlier in the relativist corrections.

8 Rayleigh Ritz / Variational Method

This is alternate method for estimating shifts in energy levels. A general wavefunction can be written as a series of increasing energy eigenfunctions of the full Hamiltonian.

$$|\psi\rangle = \sum_n c_n |n\rangle \text{ with } E_1 \le E_2 \le E_3 \le ...$$

The expectation value of the energy is:

$$\frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2} \ge \frac{\sum_n |c_n|^2}{\sum_n |c_n|^2} = E_1$$

$$\Rightarrow \langle E \rangle \ge E_1$$

The minimum value of E is the best estimate upper bound for the actual energy of the true groudn state for a wavefunction of this form.

Alternate form of the Variational principle (Griffiths):

$$E_{gs} \le \langle \psi | H | psi \rangle \equiv \langle H \rangle$$

$\Rightarrow$ The expectation value of H, in the state ψ, is certain to overestimate the ground state energy.

There is some waffle on lagrange undertermined multipliers but it is not examinable and makes little sense.

8.1 Useful maths / gamma functions

$$\int_0^\infty x^z e^{-x} = Z! = \Gamma(Z+1) \rightarrow \text{ The gamma function}$$

$$\text{With } x = y^2 \Rightarrow \int_0^\infty \frac{2y}{y} e^{-y^2} dy = \int_{-\infty}^\infty dy e^{-y^2} = \sqrt{\pi}$$

$$\Gamma(1/2) = (-1/2)! = \sqrt{\pi}$$
$$\Gamma(3/2) = (1/2)! = (1/2)(1/2)! = \sqrt{pi}/2$$
$$\Gamma(5/2) = (3/2)! = (3/2)(1/2)(-1/2)! = (3/4)\sqrt{\pi}$$

9 Selection rules

Transitions take place between states if there is an overlap of their wavefunctions. Perturbations such as the electric field can cause this. If the matrix element for the perturbation between two state is 0, there is no transition between states and the transition is forbidden.

<u>Selection rules can be summarised as:</u>

$$\Delta l = \pm 1$$

$$\Delta L = 0, \pm 1 \quad (\underline{\text{not}} \ 0 \rightarrow 0)$$

$$\Delta S = 0$$

$$\Delta J = 0, \pm 1 \quad (\underline{\text{not}} \ 0 \rightarrow 0)$$

Basically, if the quantum numbers don't follow these rules, the transition is forbidden.

9.1 Examples:

$^3P_2 \implies {}^3D_2$ Take this transition, here L goes $1 \to 2$, so it's change in L is allowed. It's S component is left unchanged, going from $1 \to 1$, which is allowed. It's J component is left unchanged, going from $2 \to 2$, which is also allowed. Hence, this transition is allowed.

$^3S_1 \implies {}^3D_1$ This transitions L component goes from $0 \to 2$, since $L = 0$ for S and $L = 2$ for D, this transition is forbidden since a $\Delta L = 2$ is not allowed.

10 Magnetism

This section of the course is very boring and the Professor's notes are especially difficult to understand. Not sure how much could actually come up in the exam, the notes for this chapter seem rather excessive compared to how much of it is used in Problem sheet 9.

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

$$\hat{H} = \frac{(\hat{h} + e\underline{A})^2}{2m} - e\phi$$

Where $\underline{A}$ is the magnetic vector potential and ϕ the electrostatic scalar potential.

The important points are:

- The commutation relation $[\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ih}$ is unchanged.

- In coordinate representation, $\hat{p}$ is still defined as $\hat{p} = -i\hbar\underline{\nabla}$

- $\underline{A}$ and ϕ are in general functions of r and t.

- The velocity is given by $m\hat{v} = \hat{p} + e\underline{A}$ 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.

Expression for the velocity of the magnetic Hamiltonian:

$$\frac{d\langle\hat{r}\rangle}{dt} = \frac{1}{m}\langle(\hat{p} + e\underline{A})\rangle \tag{28}$$

Full derivation in the Professor's notes pg 79

10.1 An electron in a constant magnetic field

A constant magnetic field can be described as $\underline{A} = (1/R)\underline{B}x\underline{r}$ (with $\underline{B}$ constant).

After the Professor does some maths, the Hamiltonian for the perturbation of an electron in a constant magnetic field is produced as:

$$\hat{H}_1 = \frac{e}{2m}\underline{B} \cdot \underline{l} + \frac{e^2}{8m}B^2(\hat{x}^2 + \hat{y}^2) \tag{29}$$

This is specialised to when B is parallel to z.

10.2 Lamor diamagnetism

If there are no local moments, which 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 called the Larmor diamagnetic response and comse from the A^2/B^2 term in our Hamiltonian.

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

The magnitude of α_L is χ_l and is equal to:

$$\chi_L = \frac{-n\mu_0 e^2}{6m} \sum_{e^-} \langle r^2 \rangle$$

The outer electrons contribute the most so these are the only ones considered. Taking there to be order 2 outer electrons gives a value of $\chi_l \approx -(10^{-6} - 10^{-5}$

10.3 Permanent moments

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

The electron spin also has a moment, it has a gyromagnetic ratio that is g times that of the orbital ratio. $g = 2 + \alpha/2\pi \approx 2.00$. The value of g, called the g-factor, comes from the relativistic theory.

10.3.1 The total moment

We have

$$\hat{H}_1 = \frac{\mu_B}{\hbar} B(g\hat{S}_z + \hat{L}_z = \frac{\mu_B}{\hbar} B(\hat{J}_z + \hat{S}_z) \tag{30}$$

We need to re-express it in terms of $\hat{J}_z$ and $\hat{J}_\pm$ getting rid of $\hat{S}_z$. The full thing of this is in the Professor's notes page 82. Eventually, this spits out the Lande factor. The atom/ion as a whole behaves as thought it has a single magnetic moment parallel to the total angular momentum, but having a modified g-factor, which is known as the Lande factor:

$$g_L = \left(\frac{3}{2} + \frac{1}{2} \frac{S(S+1) - L(L+!)}{(J(J+1)} \right) \tag{31}$$

This reduces to $g_L = 1$ for a pure orbital moment, and $g_L = 2$ for a pure spin moment.
The splitting of levels in a week field is given by

$$\Delta E = g_L(J, L, S)\mu_B B M_J \tag{32}$$

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

10.4 Strong field splitting

In a strong field the perturbation due to B exceeds that due to the spin orbit interaction. This requires a field of at least several Tesla. The calculation begins with definite M_L and M_S states. 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.

$$S = 0 \Rightarrow \text{ Normal Zeeman effect}$$

$$S \neq 0 \Rightarrow \text{ Anomalous Zeeman effect}$$

10.4.1 Van Vleck term

This is of interest when there is no permanent moment. We have to look at the second order induced moment. From second order perturbation theory:

$$\Delta E_{VV} = -\frac{\alpha_W B^2}{2} = \frac{\mu_B^2}{\hbar^2} B^2 \sum_j \frac{|\langle j|\hat{L}_z + 2\hat{S}_z|0\rangle|^2}{\epsilon_0 - \epsilon_j} \tag{33}$$

The sum is over all excited states. Since the second order contributions to the ground state energy are negative, the contribution to α is negative. Where x is chi.

$$\chi_{vv} = -n\mu_0 2\frac{\mu_B^2}{\hbar^2} \sum_j \frac{|\langle j|\hat{L}_z + 2\hat{S}_z|0\rangle|^2}{\epsilon_0 - \epsilon_j} > 0 \tag{34}$$

Including the diamagnetic contribution we found the earlier susceptibility for atoms with no permanent moment is

$$\chi = \chi_{vv} + \chi_L$$

Where $\chi_{vv} > 0$ and $\chi_L < 0$

For completely filled shells or sub-shells, S and L are both 0.

$$\text{Curie's law: } \chi = \chi_{vv} + \chi_L + n\frac{\mu_0(g_L\mu_B)^2 J(J+1)}{3k_B T} \tag{35}$$

11 Parity

"what the heck is parity " - me

Parity is basically the quantum mechanics equivalent of an even or odd function and refers to the symmetry of a wavefunction representing a particle. Take a Cos function for example, $Cos(x) = Cos(-x)$ since it's an even function, but with a Sin function $Sin(x) \neq Sin(-x)$ and instead $Sin(-x) = -Sin(x)$. Parity is similar, for example to test if a wavefunction $\psi(x, y, z)$ has odd or even parity, change all the variable to be negative, if you get back $\psi(x, y, z)$ then it has even parity, if you get back $-\psi(x, y, z)$ then it has odd parity.

For a state / energy level, the parity can be tested simply with $(-1)^L$ where L is the total orbital angular momentum. For example, the state $2s_{1/2}$ has $L = 0$, so $(-1)^0 = 1$ meaning it has even parity. The state $2p_{1/2}$ however has $L = 1$ so $(-1)^1 = -1$ meaning this has odd parity. Worth noting, in a linear electric field splitting requires a set of states to contain both even and odd parity states, otherwise the states will not split.

If a matrix element has odd parity (-1) then the function will vanish, since when you integrate it over all space it will go to 0. Here's this displayed in an example from 2020 C2 a:

Here, a perturbation $H_1 = e\epsilon\hat{z}$ is applied to a hydrogen atom. This perturbation will have odd parity, since $-z \neq z$. Plugging this into the first order energy shift equation looks like this:

$$\Delta E = \langle \psi_{1s} | ez | \psi_{1s} \rangle$$

The perturbation in the middle has a parity of (-1), but the two ground state wavefunctions on either side have even parity [**worth remembering, the ground state of Hydrogen has even parity, due to it being "completely rotationally symmetric about the origin"**] so the total parity of the energy shift will be $1 \cdot (-1) \cdot 1 = -1$ meaning this whole matrix has odd parity, so will vanish, much like how integrating a sin function over all of space vanishes.

12 Chapters 7 and 8

Lectures and hence my notes finish at the end of chapter 6, the table at the end of the Professor's notes state that chapters 7 and 8 are examinable, but during lectures it was stated that Chapter 6 is the end of examinable material.