ADVANCED QUANTUM PHYSICS

Michaelmas 2008 **D A Ritchie**

OUTLINE SOLUTIONS TO EXAMPLES

Many of these solutions were written by Prof D R Ward, though any inaccuracies are the responsibility of the current Lecturer. Please report any errors you spot to dar11@cam.ac.uk.

1 Eigenvectors, eigenvalues and time development

(a) We are told that: $\hat{H}|\psi_1\rangle = E_1|\psi_1\rangle$ and $\hat{H}|\psi_2\rangle = E_2|\psi_2\rangle$ where $E_1 \neq E_2$

So: $$\langle\psi_1|\hat{H}|\psi_2\rangle = \int \psi_1^* \hat{H}\psi_2 dx = \int \psi_1^* E_2 \psi_2 dx = E_2\langle\psi_1|\psi_2\rangle$$

Since $\hat{H}$ is Hermitian we can write:

$\langle\psi_1|\hat{H}|\psi_2\rangle = \int \psi_2\left(\hat{H}\psi_1\right)^* dx = \int \psi_2\left(E_1\psi_1\right)^* dx = E_1^*\langle\psi_1|\psi_2\rangle = E_1\langle\psi_1|\psi_2\rangle$ since E_1, E_2 are real.

So: $$(E_1 - E_2)\langle\psi_1|\psi_2\rangle = 0$$

and if $E_1 \neq E_2$ then $\langle\psi_1|\psi_2\rangle = 0$ i.e. $|\psi_1\rangle$ and $|\psi_2\rangle$ are orthogonal.

(b) If $\hat{A}|\psi_1\rangle = |\psi_2\rangle$ and $\hat{A}|\psi_2\rangle = |\psi_1\rangle$ then adding them: $\hat{A}\left(|\psi_1\rangle + |\psi_2\rangle\right) = |\psi_2\rangle + |\psi_1\rangle$
and subtracting: $\hat{A}\left(|\psi_1\rangle - |\psi_2\rangle\right) = |\psi_2\rangle - |\psi_1\rangle = -\left(|\psi_1\rangle - |\psi_2\rangle\right)$.
Hence we have an eigenvector of $a = +1$ corresponding to a normalised eigenvector $\frac{1}{\sqrt{2}}\left(|\psi_1\rangle + |\psi_2\rangle\right)$ and an eigenvalue $a = -1$ corresponding to eigenvector $\frac{1}{\sqrt{2}}\left(|\psi_1\rangle - |\psi_2\rangle\right)$.

(c) The time dependent Schrodinger equation is $\hat{H}\psi = E\psi = i\hbar\frac{\partial\psi}{\partial t}$ hence $\psi(t) = \psi(t=0)\,\mathrm{e}^{-iEt/\hbar}$. Since $|\psi_1\rangle$ and $|\psi_2\rangle$ are eigenstates of the Hamiltonian $\hat{H}$ then we can write: $|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left[|\psi_1\rangle\exp(-iE_1t/\hbar) - |\psi_2\rangle\exp(-iE_2t/\hbar)\right]$.

$$P = \left|\langle\psi(t=0)|\psi(t)\rangle\right|^2 = \left|\tfrac{1}{2}\left[\langle\psi_1| - \langle\psi_2|\right]\left[|\psi_1\rangle\exp(-iE_1t/\hbar) - |\psi_2\rangle\exp(-iE_2t/\hbar)\right]\right|^2$$
$$= \tfrac{1}{4}\left|\left[\langle\psi_1|\psi_1\rangle\exp(-iE_1t/\hbar) + \langle\psi_2|\psi_2\rangle\exp(-iE_2t/\hbar) - 0 - 0\right]\right|^2$$
$$= \tfrac{1}{4}\left[\exp(iE_1t/\hbar) + \exp(iE_2t/\hbar)\right]\left[\exp(-iE_1t/\hbar) + \exp(-iE_2t/\hbar)\right]$$
$$= \tfrac{1}{4}\left[2 + \exp\left(i(E_1 - E_2)t/\hbar\right) + \exp\left(i(E_2 - E_1)t/\hbar\right)\right] = \tfrac{1}{4}\left[2 + 2\cos\left((E_1 - E_2)t/\hbar\right)\right]$$
$$= \tfrac{1}{2}\left[1 + \cos\left((E_1 - E_2)t/\hbar\right)\right] = \cos^2\left((E_1 - E_2)t/2\hbar\right)$$
(since $\langle\psi_1|\psi_2\rangle = 0$ and $\langle\psi_1|\psi_1\rangle = \langle\psi_2|\psi_2\rangle = 1$)

2 Harmonic Oscillator :Ladder operators

(a) From definition of $\hat{a}^{\dagger}, \hat{a}$ **:**

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a}+\hat{a}^{\dagger}\right) \qquad \hat{p} = i\sqrt{\frac{m\hbar\omega}{2}}\left(\hat{a}^{\dagger}-\hat{a}\right)$$

$$\langle n|\hat{x}|n\rangle = \langle n|\sqrt{\tfrac{\hbar}{2m\omega}}\left(\hat{a}+\hat{a}^{\dagger}\right)|n\rangle = \sqrt{\tfrac{\hbar}{2m\omega}}\langle n|\sqrt{n}|n-1\rangle + \sqrt{\tfrac{\hbar}{2m\omega}}\langle n|\sqrt{n+1}|n+1\rangle = 0$$

$$\langle n|\hat{p}|n\rangle = i\sqrt{\frac{m\hbar\omega}{2}}\langle n|\left(\hat{a}^{\dagger}-\hat{a}\right)|n\rangle = i\sqrt{\frac{m\hbar\omega}{2}}\langle n|\sqrt{n+1}|n+1\rangle - i\sqrt{\frac{m\hbar\omega}{2}}\langle n|\sqrt{n}|n-1\rangle = 0$$

since $\langle n|n-1\rangle = \langle n|n+1\rangle = 0$.

(b) The expectation value of potential energy $V(x)$

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a}+\hat{a}^{\dagger}\right) \Rightarrow \hat{x}^2 = \frac{\hbar}{2m\omega}\left(\hat{a}^2+\hat{a}^{\dagger 2}+\hat{a}\hat{a}^{\dagger}+\hat{a}^{\dagger}\hat{a}\right)$$

$$\langle n|\hat{x}^2|n\rangle = \frac{\hbar}{2m\omega}\langle n|\hat{a}^2+\hat{a}^{\dagger 2}+\hat{a}\hat{a}^{\dagger}+\hat{a}^{\dagger}\hat{a}|n\rangle$$

$$= \frac{\hbar}{2m\omega}\left[\langle n|\sqrt{n}\sqrt{n-1}|n-2\rangle + \langle n|\sqrt{n+1}\sqrt{n+2}|n+2\rangle + \langle n|n+1|n\rangle + \langle n|n|n\rangle\right] = \frac{\hbar}{2m\omega}[2n+1]$$

$$\Rightarrow \langle n|V(x)|n\rangle = \frac{m\omega^2}{2}.\frac{\hbar}{2m\omega}[2n+1] = \frac{1}{2}\left[n+\tfrac{1}{2}\right]\hbar\omega$$

The expectation value of kinetic energy is given by: $K = \dfrac{\hat{p}^2}{2m}$

$$\hat{p} = i\sqrt{\frac{m\hbar\omega}{2}}\left(\hat{a}^{\dagger}-\hat{a}\right) \Rightarrow \qquad \hat{p}^2 = -\frac{m\hbar\omega}{2}\left(\hat{a}^2+\hat{a}^{\dagger 2}-\hat{a}\hat{a}^{\dagger}-\hat{a}^{\dagger}\hat{a}\right)$$

$$\langle n|\hat{p}^2|n\rangle = -\frac{m\hbar\omega}{2}\langle n|\hat{a}^2+\hat{a}^{\dagger 2}-\hat{a}\hat{a}^{\dagger}-\hat{a}^{\dagger}\hat{a}|n\rangle$$

$$= -\frac{m\hbar\omega}{2}\left[\langle n|\sqrt{n}\sqrt{n-1}|n-2\rangle + \langle n|\sqrt{n+1}\sqrt{n+2}|n+2\rangle - \langle n|n+1|n\rangle - \langle n|n|n\rangle\right] = \frac{m\hbar\omega}{2}[2n+1]$$

$$\Rightarrow \langle n|K|n\rangle = \frac{1}{2m}\frac{m\hbar\omega}{2}[2n+1] = \frac{1}{2}\left[n+\tfrac{1}{2}\right]\hbar\omega$$

(c)

$$\Delta x^2 = \langle x^2\rangle - \langle x\rangle^2 = \frac{\hbar}{2m\omega}[2n+1] - 0 = \frac{\hbar}{2m\omega}[2n+1]$$

$$\Delta p^2 = \langle p^2\rangle - \langle p\rangle^2 = \frac{m\hbar\omega}{2}[2n+1] - 0 = \frac{m\hbar\omega}{2}[2n+1]$$

$$\Delta x^2\Delta p^2 = \frac{\hbar}{2m\omega}[2n+1]\frac{m\hbar\omega}{2}[2n+1] = \frac{\hbar^2}{4}[2n+1]^2$$

$$\Rightarrow \Delta x\Delta p = \hbar\left[n+\tfrac{1}{2}\right]$$

3 Spin

The spin operator in the (θ,ϕ) direction, $\hat{S}_{\theta\phi}$, can be found by forming the dot product of the spin operator $\hat{S}$ with a unit vector in the (θ,ϕ) direction, $(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$:

$$\hat{S}_{\theta\phi} = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\sin\theta\cos\phi + \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\sin\theta\sin\phi + \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\cos\theta = \frac{\hbar}{2}\begin{pmatrix} \cos\theta & \sin\theta e^{-i\phi} \\ \sin\theta e^{i\phi} & -\cos\theta \end{pmatrix}$$

We need the eigenvalues of the matrix, i.e.

$$\frac{\hbar}{2}\begin{pmatrix} \cos\theta & \sin\theta e^{-i\phi} \\ \sin\theta e^{i\phi} & -\cos\theta \end{pmatrix}\begin{pmatrix} u \\ v \end{pmatrix} = \lambda \begin{pmatrix} u \\ v \end{pmatrix}$$

Multiplying out,

$$(\cos\theta - \lambda)u + \sin\theta e^{-i\phi} v = 0$$
$$\sin\theta e^{i\phi} u - (\cos\theta + \lambda)v = 0$$

and by eliminating u and v we find $\lambda^2 = 1$ and hence the eigenvalues of $\hat{S}_{\theta\phi}$ are $\pm\frac{1}{2}\hbar$, as expected. Substituting the values $\lambda = \pm 1$ back into the equations relating u and v, we can infer the ratios:

$$\frac{u}{v} = \frac{\cos\frac{1}{2}\theta}{\sin\frac{1}{2}\theta} e^{-i\phi} \quad or \quad -\frac{\sin\frac{1}{2}\theta}{\cos\frac{1}{2}\theta} e^{-i\phi}$$

and so, in matrix notation, the eigenstates are

$$\begin{pmatrix} \cos\frac{1}{2}\theta \\ \sin\frac{1}{2}\theta\, e^{i\phi} \end{pmatrix} \quad and \quad \begin{pmatrix} \sin\frac{1}{2}\theta \\ -\cos\frac{1}{2}\theta\, e^{i\phi} \end{pmatrix}$$

for eigenvalues $+\frac{1}{2}\hbar$; $-\frac{1}{2}\hbar$ respectively. The spin states in the x-direction are obtained by setting $\theta = \frac{1}{2}\pi$ $\phi = 0$, and the spin states in the y-direction are obtained by setting $\theta = \frac{1}{2}\pi$ $\phi = \frac{1}{2}\pi$ in these general formulæ.

4 Addition of angular momentum

a) To construct the states explicitly, we start by writing the $L = 3$ $M = 3$ state, since there is only one way of forming $M = 3$:

$$|3,3\rangle = |1,1;2,2\rangle$$

We then operate with the lowering operator $\hat{L}_-$, which is simply the sum of the lowering operators for the two separate particles. Recalling that:

$$\hat{L}_- |\ell, m\rangle = \sqrt{\ell(\ell+1) - m(m-1)}\hbar |\ell, m-1\rangle$$

we obtain

$$\sqrt{6}\hbar|3,2\rangle = \sqrt{2}\hbar|1,0;2,2\rangle + \sqrt{4}\hbar|1,1;2,1\rangle$$

where the first term on the right hand side comes from lowering the $\ell = 1$ state and the second from lowering the $\ell = 2$ state. Hence

$$|3,2\rangle = \sqrt{\tfrac{1}{3}}\hbar|1,0;2,2\rangle + \sqrt{\tfrac{2}{3}}\hbar|1,1;2,1\rangle$$

The state $|2,2\rangle$ must be the orthogonal linear combination, i.e.

$$|2,2\rangle = \sqrt{\tfrac{2}{3}}\hbar|1,0;2,2\rangle - \sqrt{\tfrac{1}{3}}\hbar|1,1;2,1\rangle$$

Further states could be computed in the same way if required.

b) The four states are:

$$\begin{aligned}
\phi_1 &= \chi_+(1)\chi_+(2) \\
\phi_2 &= \chi_-(1)\chi_-(2) \\
\phi_3 &= [\chi_+(1)\chi_-(2) + \chi_-(1)\chi_+(2)]/\sqrt{2} \\
\phi_4 &= [\chi_+(1)\chi_-(2) - \chi_-(1)\chi_+(2)]/\sqrt{2}
\end{aligned}$$

where ϕ_1, ϕ_2 and ϕ_3 are symmetric under particle interchange and ϕ_4 is antisymmetric. ϕ_3 may be obtained from ϕ_1 by using a lowering operator which is the sum of the lowering operators for each particle. ϕ_4 is orthogonal to ϕ_3.

ϕ_1, ϕ_2, ϕ_3 all have $S = 1$, while ϕ_4 has $S = 0$.

The state ψ is clearly an eigenstate of $\hat{S}_z$ with eigenvalue 0, and must thus be a linear combination of ϕ_3 and ϕ_4. The $S = 1$ component is thus the ϕ_3 term in the wavefunction with amplitude

$$c_3 = \langle \phi_3 \,|\, \psi \rangle = \left\langle \sqrt{\tfrac{2}{3}}\chi_+(1)\chi_-(2) + \sqrt{\tfrac{1}{3}}\chi_-(1)\chi_+(2) \,\middle|\, \sqrt{\tfrac{1}{2}}\chi_+(1)\chi_-(2) + \sqrt{\tfrac{1}{2}}\chi_-(1)\chi_+(2) \right\rangle$$
$$= \sqrt{\tfrac{1}{3}} + \sqrt{\tfrac{1}{6}}$$

The probability of $S = 1$ is thus

$$|c_3|^2 = \frac{3 + 2\sqrt{2}}{6} = 0.971$$

5 Matrix Methods

The basis states chosen are the eigenstates of $\hat{L}_z$, and therefore the matrix representation of $\hat{L}_z$ is diagonal, with the eigenvalues appearing on the diagonal:

$$\hat{L}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

We know how the ladder operators $\hat{L}_\pm$ affect these states, namely

$$\hat{L}_\pm \left| \ell, m \right\rangle = \hbar \sqrt{\ell(\ell+1) - m(m\pm 1)} \left| \ell, m\pm 1 \right\rangle$$

from which we can trivially write these operators in matrix form:

$$\hat{L}_+ = \hbar \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix} \quad ; \quad \hat{L}_- = \hbar \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix}$$

and from these we can infer

$$\hat{L}_x = \tfrac{1}{2}(\hat{L}_+ + \hat{L}_-) = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad ; \quad \hat{L}_y = \frac{1}{2i}(\hat{L}_+ - \hat{L}_-) = i\frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$$

The operator $\hat{H} = \hat{L}_x^2/2I_x + \hat{L}_y^2/2I_y + \hat{L}_z^2/2I_z$ can then be written in matrix form using these results yielding

$$\frac{\hbar^2}{4} \begin{pmatrix} \frac{1}{I_x} + \frac{1}{I_y} + \frac{2}{I_z} & 0 & \frac{1}{I_x} - \frac{1}{I_y} \\ 0 & \frac{2}{I_x} + \frac{2}{I_y} & 0 \\ \frac{1}{I_x} - \frac{1}{I_y} & 0 & \frac{1}{I_x} + \frac{1}{I_y} + \frac{2}{I_z} \end{pmatrix}$$

As usual the eigenvalues can be found by subtracting E from the diagonal of this matrix, and setting the determinant to zero, yielding

$$\left(\frac{\hbar^2}{4I_x} + \frac{\hbar^2}{4I_y} + \frac{\hbar^2}{2I_z} - E \right)^2 \left(\frac{\hbar^2}{2I_x} + \frac{\hbar^2}{2I_y} - E \right) = \left(\frac{\hbar^2}{4I_x} - \frac{\hbar^2}{4I_y} \right)^2 \left(\frac{\hbar^2}{2I_x} + \frac{\hbar^2}{2I_y} - E \right)$$

from which we readily obtain the energy eigenvalues and eigenstates:

$$\frac{\hbar^2}{2}\left(\frac{1}{I_x}+\frac{1}{I_y}\right) \quad \frac{\hbar^2}{2}\left(\frac{1}{I_x}+\frac{1}{I_z}\right) \quad \frac{\hbar^2}{2}\left(\frac{1}{I_y}+\frac{1}{I_z}\right)$$

$$\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \qquad \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \qquad \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

6 Identical particles

A single particle in the potential well has (unnormalised) wavefunction and energy:

$$\psi_n(x) = \sin(n\pi x/L) \quad ; \quad E = \frac{\hbar^2\pi^2}{2mL^2} \equiv \varepsilon$$

The wavefunction for a system of two identical particles must be either symmetric or antisymmetric, i.e.

$$\sin(n_1\pi x_1/L)\sin(n_2\pi x_2/L) \pm \sin(n_2\pi x_1/L)\sin(n_1\pi x_2/L)$$

with energy $(n_1^2 + n_2^2)\varepsilon$. If $E = 5\varepsilon$, we must have $n_1 = 1$, $n_2 = 2$ (or vice versa).

(a) Spin-zero particles are bosons and must have a symmetric wavefunction, i.e.

$$\begin{aligned}&\sin(\pi x_1/L)\sin(2\pi x_2/L) + \sin(2\pi x_1/L)\sin(\pi x_2/L)\\&= 2\sin(\pi x_1/L)\sin(\pi x_2/L)\left[\cos(\pi x_1/L) + \cos(\pi x_2/L)\right]\end{aligned}$$

Clearly, this has zeroes when $x_1 = 0, L$, when $x_2 = 0, L$ and when $x_1 + x_2 = L$.

(b) Spin-$\frac{1}{2}$ particles are fermions and must have an antisymmetric wavefunction. In the singlet case, the spin wavefunction is antisymmetric, and hence the spatial wavefunction is symmetric, just as in **(a)**.

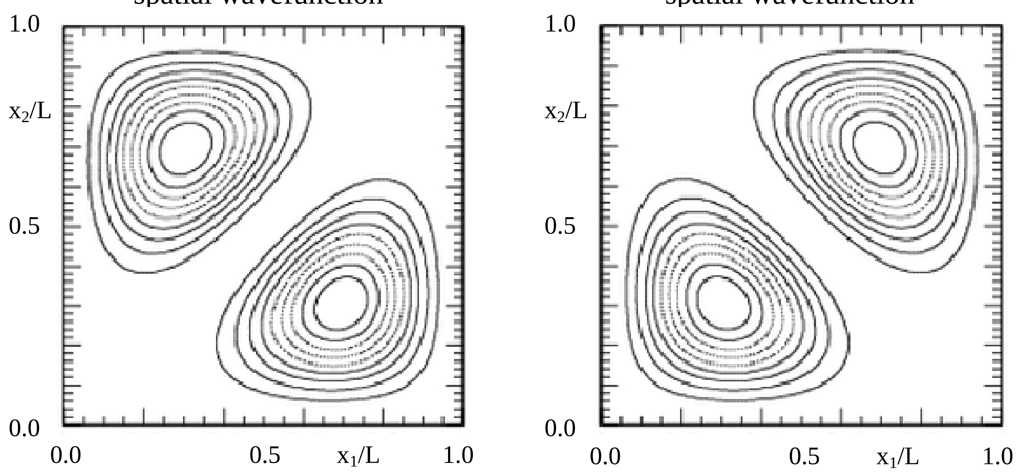
(c) In the triplet case, the spin wavefunction is symmetric, and hence the spatial wavefunction must be antisymmetric, i.e.

$$\begin{aligned}&\sin(\pi x_1/L)\sin(2\pi x_2/L) - \sin(2\pi x_1/L)\sin(\pi x_2/L)\\&= 2\sin(\pi x_1/L)\sin(\pi x_2/L)\left[\cos(\pi x_1/L) - \cos(\pi x_2/L)\right]\end{aligned}$$

Clearly, this has zeroes when $x_1 = 0, L$, when $x_2 = 0, L$ and when $x_1 = x_2$.

Contour plots of the probability density for these two wavefunctions are shown below.

Triplet – antisymmetric spatial wavefunction   Singlet – symmetric spatial wavefunction



If the particles were charged, they would repel through the Coulomb interaction. Therefore, in the spin-$\frac{1}{2}$ case, the triplet state would have the lower energy, because the particles tend to be further apart. This is an example of the *exchange interaction*, and is a simplified model of what happens in the Helium atom.

7 Variational Method

Trial wavefunction is $\psi = A(a^2 - x^2)$, for $|x| < a$ only. First determine A from normalization:

$$1 = \int |\psi|^2 \, dx = A^2 \int_{-a}^{a} (x^4 - 2a^2x^2 + a^4) dx = \frac{16}{15} A^2 a^5$$

Next, the expectation value of the Hamiltonian.

$$\hat{H}\psi = \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \tfrac{1}{2} m\omega^2 x^2 \right) \psi = A \left[\frac{\hbar^2}{m} + \tfrac{1}{2} m\omega^2 (a^2x^2 - x^4) \right]$$

and thus,

$$\begin{aligned} \langle \psi | \hat{H} | \psi \rangle &= A^2 \int_{-a}^{a} (a^2 - x^2) \left[\frac{\hbar^2}{m} + \tfrac{1}{2} m\omega^2 (a^2x^2 - x^4) \right] dx \\ &= \frac{15}{8} \left[\frac{2\hbar^2}{3ma^2} + \frac{4m\omega^2 a^2}{105} \right] \end{aligned}$$

Minimising with respect to a we obtain

$$a^2 = \left(\frac{35}{2} \right)^{\frac{1}{2}} \frac{\hbar}{m\omega}$$

Substituting this value of a into our expression for $\langle \psi | \hat{H} | \psi \rangle$ we obtain the upper bound on the ground state energy

$$\langle \psi | \hat{H} | \psi \rangle = \sqrt{\frac{5}{14}} \hbar\omega = 0.598\hbar\omega$$

which is greater than the true ground state energy ($\tfrac{1}{2}\hbar\omega$) as expected.

8 Variational Method

Trial wavefunction $Ae^{-\beta r}$. First normalise it:

$$1 = A^2 \int_0^\infty 4\pi r^2 e^{-2\beta r} dr = \frac{4\pi A^2}{4\beta^3} \quad \Rightarrow \quad A^2 = \frac{\beta^3}{\pi}$$

We need to work out $\nabla^2 \psi$ before evaluating the matrix element of the Hamiltonian:

$$\nabla^2 \psi = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \frac{1}{r^2} \frac{d}{dr} \left(-\beta r^2 e^{-\beta r} \right) = \beta^2 e^{-\beta r} - \frac{2\beta}{r} e^{-\beta r}$$

Thus, using standard integrals, we can compute

$$\langle \psi | \hat{H} | \psi \rangle = A^2 \int_0^\infty 4\pi r^2 dr \left[-\frac{\hbar^2}{2m} \left(\beta^2 e^{-2\beta r} - \frac{2\beta}{r} e^{-2\beta r} \right) - \frac{e^2}{4\pi\varepsilon_0 r} e^{-2\beta r} \right]$$

$$= \frac{\hbar^2 \beta^2}{2m} - \frac{e^2 \beta}{4\pi\varepsilon_0}$$

Minimising with respect to β we obtain

$$\beta = \frac{me^2}{4\pi\varepsilon_0 \hbar^2} = a_0^{-1}$$

which is the inverse of the Bohr radius and thus

$$\langle \psi | \hat{H} | \psi \rangle = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2 = -13.6\, eV.$$

This is the correct value for the ground state energy of the Hydrogen atom, as expected, because we chose the correct functional form for the trial function.

9 Variational Method

(a) Suppose the two Hamiltonians are $\hat{H}_1$ and $\hat{H}_2$ with ground state wavefunctions ψ_1 and ψ_2, i.e.

$$\hat{H}_1\psi_1 = E_1\psi_1 \quad ; \quad \hat{H}_2\psi_2 = E_2\psi_2$$

Given that $V_1 \le V_2$, we have

$$\hat{H}_1 = \hat{H}_2 - V_2(r) + V_1(r) \equiv \hat{H}_2 + \Delta V(r)$$

From the variational principle,

$$E_1 \le \langle \psi_2 | \hat{H}_1 | \psi_2 \rangle = \langle \psi_2 | \hat{H}_2 | \psi_2 \rangle + \langle \psi_2 | \Delta V | \psi_2 \rangle = E_2 + \langle \psi_2 | \Delta V | \psi_2 \rangle \le E_2$$

where the last inequality follows because $\Delta V(r) \le 0$. Thus $E_2 \ge E_1$.

(b) The Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

and the normalised trial function is

$$\psi = \left(\frac{2\lambda}{\pi}\right)^{\frac{1}{4}} e^{-\lambda x^2}$$

Using standard integrals, we obtain

$$\langle \psi | \hat{H} | \psi \rangle = \frac{\hbar^2}{2m}\lambda + \sqrt{\frac{2\lambda}{\pi}} \int V(x) e^{-2\lambda x^2} dx \equiv \frac{\hbar^2}{2m}\lambda + I$$

Minimising w.r.t. λ we obtain:

$$0 = \frac{\hbar^2}{2m} + \frac{1}{2\lambda} I + \sqrt{\frac{2\lambda}{\pi}} \int V(x)(-2x^2) e^{-2\lambda x^2} dx$$

where the second term arises from differentiating the normalization in I and the third term from differentiating the integrand. This is an implicit equation for λ and if we solve for I and substitute into the equation from above:

$$\langle \psi | \hat{H} | \psi \rangle = \frac{\hbar^2}{2m}\lambda + I$$

we obtain

$$\langle \psi | \hat{H} | \psi \rangle = -\frac{\hbar^2}{2m}\lambda + 2\lambda\sqrt{\frac{2\lambda}{\pi}} \int V(x) 2x^2 e^{-2\lambda x^2} dx$$

This is our upper bound on the ground state energy, and since $V(x) \le 0$, both terms are manifestly negative. Hence the ground state energy is negative, and at least one bound state must exist.

10 Molecular bonding

Taking the 1s Hydrogen wavefunctions as our basis, we apply the Rayleigh-Ritz variational method. The elements of the Hamiltonian matrix are given in the question, so the matrix is:

$$\begin{pmatrix} \alpha & \beta & \beta\gamma \\ \beta & \alpha & \beta \\ \beta\gamma & \beta & \alpha \end{pmatrix}$$

Neglecting the overlap integrals, the upper bound E on the energy levels is given, according to Rayleigh-Ritz, by setting the determinant of the matrix $H - EI$ to zero, i.e.

$$\begin{vmatrix} \alpha - E & \beta & \beta\gamma \\ \beta & \alpha - E & \beta \\ \beta\gamma & \beta & \alpha - E \end{vmatrix}$$

Multiplying out:

$$(\alpha - E)^3 + 2\gamma\beta^3 - 2\beta^2(\alpha - E) - \gamma^2\beta^2(\alpha - E) = 0$$

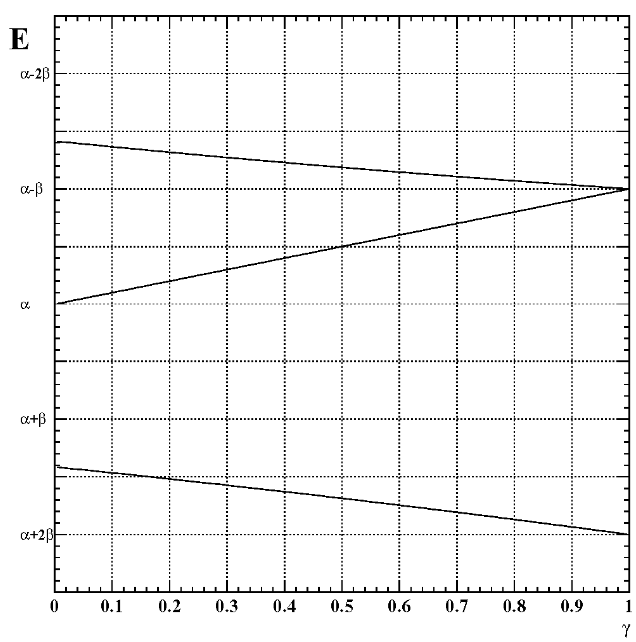
which factorises as:

$$(\alpha - E - \gamma\beta)\left[(\alpha - E)^2 + \gamma\beta(\alpha - E) - 2\beta^2\right] = 0$$

This readily leads to the three solutions:

$$E = \alpha - \gamma\beta\,; \quad E = \alpha + \tfrac{1}{2}\beta\left(\gamma \pm \sqrt{\gamma^2 + 8}\right)$$

As a function of γ the energies look like this:



As $\theta \to 60^\circ$ we expect $\gamma \to 1$, as all the bond lengths become equal. The solutions in this limit are:

$$E = \alpha - \beta\,,\ \alpha - \beta\,,\ \alpha + 2\beta\,.$$

As $\theta \to 180^\circ$ we expect $\gamma \to 0$, as atoms 1 and 3 become separated. The solutions in this limit are:

$$E = \alpha\,,\ \alpha \pm \sqrt{2}\beta\,.$$

Noting that $\beta < 0$, the lowest energy is $\alpha + 2\beta$ corresponding to $\theta = 60^\circ$. Since this state is non-degenerate, it can only accommodate the two electrons of the H_3^+ ion if they are in an antisymmetric singlet ($S = 0$) spin state.

11 Molecular bonding

Write (with obvious notation):

$$|VB\rangle = C\{|a_1\rangle|b_2\rangle + |b_1\rangle|a_2\rangle\}$$

(a) Normalizing $|VB\rangle$:

$$\langle VB|VB\rangle = 1 = C^2\{\langle a_1|a_1\rangle\langle b_2|b_2\rangle + 2\langle a_1|b_1\rangle\langle b_2|a_2\rangle + \langle b_1|b_1\rangle\langle a_2|a_2\rangle\} = C^2(2+2SS^*)$$

and hence $C^2 = 1/2(1+SS^*)$.

(b) We have

$$|g\rangle = (|a\rangle + |b\rangle)/\sqrt{2(1+S)} \quad ; \quad |u\rangle = (|a\rangle - |b\rangle)/\sqrt{2(1-S)}$$

which we can rearrange to get expressions for $|a\rangle$ and $|b\rangle$:

$$|a\rangle = \sqrt{(1+S)/2}\,|g\rangle + \sqrt{(1-S)/2}\,|u\rangle \quad ; \quad |b\rangle = \sqrt{(1+S)/2}\,|g\rangle - \sqrt{(1-S)/2}\,|u\rangle$$

which we substitute into $|VB\rangle$ yielding

$$|VB\rangle = C\{(1+S)|g_1\rangle|g_2\rangle - (1-S)|u_1\rangle|u_2\rangle\}$$

(c) The orthogonal state must be

$$|\perp\rangle = C\{(1-S)|g_1\rangle|g_2\rangle + (1+S)|u_1\rangle|u_2\rangle\}$$

Rewriting this in the $|a\rangle$, $|b\rangle$ basis, after a little algebra we arrive at:

$$\frac{C(1+S^2)}{(1-S^2)}\{|a_1\rangle|a_2\rangle + |b_1\rangle|b_2\rangle\} - \frac{2CS}{(1-S^2)}\{|a_1\rangle|b_2\rangle + |b_1\rangle|a_2\rangle\}$$

of which the first term is ionic and the second covalent, i.e.

$$\frac{(1+S^2)}{(1-S^2)}|IB\rangle - \frac{2S}{(1-S^2)}|VB\rangle$$

(d) Inserting the given value of ρ gives $S = 0.697$, and hence the ratio of IB and VB probabilities in the state $|\perp\rangle$:

$$IB/VB = \left[\frac{(1+S^2)}{2S}\right]^2 = 1:0.88$$

12 Perturbation Theory

The unperturbed ground state wavefunction is

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-m\omega x^2/2\hbar}$$

with energy $\frac{1}{2}\hbar\omega$. The first order shift in energy is

$$\int \psi_0^* \lambda x^4 \psi_0 dx = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} \lambda x^4 e^{-m\omega x^2/\hbar} dx = \frac{3\hbar^2\lambda}{4m^2\omega^2} \text{ (standard Integral)}$$

and hence the energy is

$$E = \tfrac{1}{2}\hbar\omega + \frac{3\hbar^2\lambda}{4m^2\omega^2} + O(\lambda^2)$$

13 Perturbation Theory

The normal treatment of the Hydrogen atom with a point nucleus has potential energy

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

A hollow spherical shell will have the same potential for $r > b$, but $V(r) = V(b)$ for $r < b$, by Gauss' theorem, and thus its effect can be regarded as adding a perturbation

$$\hat{H}' = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r} - \frac{1}{b}\right)$$

to the Hamiltonian for $r < b$, and zero for $r > b$.

For the 2s wavefunction, the energy shift induced by the perturbation is

$$\Delta E = \langle\psi|\hat{H}'|\psi\rangle = \frac{1}{8\pi a_0^3}\frac{e^2}{4\pi\varepsilon_0}\int_0^b 4\pi r^2 dr\left(\frac{1}{r} - \frac{1}{b}\right)\left(1 - \frac{r}{2a_0}\right)^2 e^{-r/a_0}$$

Since $b \ll a_0$, the terms involving r/a_0 are negligible in the region of integration, so we can simplify the integral to

$$\Delta E = \frac{e^2}{8\pi\varepsilon_0 a_0^3}\int_0^b r^2 dr\left(\frac{1}{r} - \frac{1}{b}\right) = \frac{b^2}{6a_0^2}R_\infty \qquad R_\infty = \frac{e^2}{8\pi\varepsilon_0 a_0}$$

Likewise for the 2p$_0$ wavefunction, making the same approximation, we obtain

$$\Delta E = \frac{e^2}{128\pi^2\varepsilon_0 a_0^5}\int_0^b r^4 dr\left(\frac{1}{r} - \frac{1}{b}\right)\int_0^\pi 2\pi\sin\theta\cos^2\theta d\theta = \frac{b^4}{240a_o^4}R_\infty$$

Both energy shifts are very small, but that for the 2p state is much smaller, because the 2p wavefunction vanishes at the origin.

Not a good method because other effects, such as spin-orbit interaction and other relativistic corrections would swamp the nuclear size effect. It is more effective for heavy atoms, with larger nuclei and smaller Bohr radii, and especially for "muonic" atoms, where the greater mass of the muon again reduces the Bohr radius.

14 Perturbation Theory

Without loss of generality, take the electric field, $\mathcal{E}$, to lie in the z direction. The perturbation is thus $\hat{H}' = e\mathcal{E}z$. The first order perturbation theory result is therefore

$$\Delta E = -\langle 0|e\mathcal{E}z|0\rangle = 0$$

since the state $|0\rangle$ is an eigenstate of parity. The leading contribution to ΔE is therefore the second order term

$$\Delta E = \sum_{k\neq 0} \frac{|\langle k|e\mathcal{E}z|0\rangle|^2}{E_0 - E_k} = e^2\mathcal{E}^2 \sum_{k\neq 0} \frac{|\langle k|z|0\rangle|^2}{E_0 - E_k}$$

If the induced dipole moment is $d = \alpha\varepsilon_0\mathcal{E}$, its energy of interaction with the electric field is $-\frac{1}{2}d\mathcal{E} = -\frac{1}{2}\alpha\varepsilon_0\mathcal{E}^2 \equiv \Delta E$, so by comparing with our perturbation theory result we obtain

$$\alpha = \frac{2e^2}{\varepsilon_0} \sum_{k\neq 0} \frac{|\langle k|z|0\rangle|^2}{E_k - E_0}$$

An alternative derivation of this result starts from the first order perturbation theory expression for the perturbed wavefunction:

$$|\psi\rangle = |0\rangle + \sum_{k\neq 0} c_k|k\rangle \quad where \quad c_k = \frac{\langle k|-e\mathcal{E}z|0\rangle}{E_0 - E_k}$$

The dipole moment operator for the electron is ez, and its expectation value in this state is (neglecting small terms of order (c_k^2)):

$$\begin{aligned}\langle\psi|ez|\psi\rangle &= \langle 0|ez|0\rangle + \sum_{k\neq 0}[c_k\langle 0|ez|k\rangle + c_k^*\langle k|ez|0\rangle] + O(c_k^2)\\ &= 0 + 2\mathcal{E}\sum_{k\neq 0}\frac{|\langle k|ez|0\rangle|^2}{E_k - E_0}\\ &\equiv \alpha\varepsilon_0\mathcal{E}\end{aligned}$$

from which the value of α follows as before.

Since $E_k \geq E_1\ \forall k$, we obtain

$$\alpha \leq \frac{2e^2}{\varepsilon_0}\sum_{k\neq 0}\frac{|\langle k|z|0\rangle|^2}{E_1 - E_0} = \frac{2e^2}{\varepsilon_0}\sum_{k\neq 0}\frac{\langle 0|z|k\rangle\langle k|z|0\rangle}{E_1 - E_0} = \frac{2e^2}{\varepsilon_0}\frac{\langle 0|z^2|0\rangle}{E_1 - E_0}$$

where we have used the completeness relation $\sum_k |k\rangle\langle k| = 1$. Note that the sum now includes the $k = 0$ term. Using the explicit form for the Hydrogen ground state,

$$|0\rangle = \left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-r/a_0}$$

we evaluate the matrix element:

$$\langle 0|z^2|0\rangle = \langle 0|r^2\cos^2\theta|0\rangle = \frac{1}{\pi a_0^3}\int_0^\pi 2\pi\sin\theta\cos^2\theta d\theta\int_0^\infty r^2dr\, r^2e^{-2r/a_0} = a_0^2$$

We also need the energy difference,

$$E_1 - E_0 = (1-\tfrac{1}{4})R_\infty = \frac{3}{4}\cdot\frac{e^2}{8\pi\varepsilon_0 a_0}$$

from which we obtain:

$$\alpha \le \frac{64\pi a_0^3}{3} = 9.9\,10^{-30}\ m^3$$

Not too far from experiment, and higher as expected.

15 Degenerate Perturbation Theory:2D harmonic oscillator

(a) The Hamiltonian for the system is: $\hat{H} = \frac{1}{2m}\left(\hat{p}_x^2 + \hat{p}_y^2\right) + \frac{1}{2}k\left(\hat{x}^2 + \hat{y}^2\right) + \lambda\hat{x}\hat{y}$

For $\lambda = 0$ we have a 2D harmonic oscillator and can split the Hamiltonian into two parts for *x* and *y*.

$$\hat{H}^0 = \hat{H}_x^0 + \hat{H}_y^0 \Rightarrow \hat{H}_x^0 = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}k\hat{x}^2, \quad \hat{H}_y^0 = \frac{\hat{p}_y^2}{2m} + \frac{1}{2}k\hat{y}^2$$

From the definitions of the raising and lowering operators for *x*

$$\hat{a}^\dagger = \frac{1}{\sqrt{2m\hbar\omega}}\left(-i\hat{p} + m\omega\hat{x}\right), \quad \hat{a} = \frac{1}{\sqrt{2m\hbar\omega}}\left(i\hat{p} + m\omega\hat{x}\right)$$

we have $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a} + \hat{a}^\dagger\right)$ and $\hat{p} = i\sqrt{\frac{m\hbar\omega}{2}}\left(\hat{a}^\dagger - \hat{a}\right)$

Substituting into the Hamiltonian we can find the eigenenergies for *x*:

$$\hat{H}_x^0 = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}k\hat{x}^2 = -\frac{\hbar\omega}{4}\left(\hat{a}^\dagger - \hat{a}\right)^2 + \frac{\hbar\omega}{4}\left(\hat{a} + \hat{a}^\dagger\right)^2 = \frac{\hbar\omega}{2}\left[\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger\right]$$

$$E_{n_x}^0\left|n_x\right\rangle = \hat{H}_x^0\left|n_x\right\rangle = \frac{\hbar\omega}{2}\left(\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger\right)\left|n_x\right\rangle = \frac{\hbar\omega}{2}\left(n_x + \left(n_x + 1\right)\right)\left|n_x\right\rangle = \hbar\omega\left(n_x + \tfrac{1}{2}\right)\left|n_x\right\rangle$$

$$\Rightarrow E_{n_x}^0 = \hbar\omega\left(n_x + \tfrac{1}{2}\right)$$

With a similar result for $E_{n_y}^0$ the eigenenergies of $\hat{H}^0$ are: $E_{n_x,n_y}^0 = \hbar\omega\left(n_x + n_y + 1\right)$

(b) The eigenstates of $\hat{H}^0$ are:

If $E^0 = \hbar\omega$ we have one eigenstate: $\left|n_x = 0\right\rangle\left|n_y = 0\right\rangle$

$E^0 = 2\hbar\omega$, two degenerate eigenstates $\left|n_x = 1\right\rangle\left|n_y = 0\right\rangle$, $\left|n_x = 0\right\rangle\left|n_y = 1\right\rangle$

$E^0 = 3\hbar\omega$, three degenerate eigenstates $\left|n_x = 2\right\rangle\left|n_y = 0\right\rangle$, $\left|n_x = 0\right\rangle\left|n_y = 2\right\rangle$, $\left|n_x = 1\right\rangle\left|n_y = 1\right\rangle$

(c)

For the 2 fold degenerate level with $E^0 = 2\hbar\omega$

$\hat{H}' = \lambda\hat{x}\hat{y}$ and the secular determinent is: $\begin{vmatrix} H'_{11} - E_2^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E_2^{(1)} \end{vmatrix} = 0$

$$H'_{11} = \left\langle n_x = 1, n_y = 0\right|\lambda\hat{x}\hat{y}\left|n_x = 1, n_y = 0\right\rangle = \lambda\left\langle n_x = 1\right|\hat{x}\left|n_x = 1\right\rangle\left\langle n_y = 0\right|\hat{y}\left|n_y = 0\right\rangle = 0$$

$$H'_{22} = \left\langle n_x = 0, n_y = 1\right|\lambda\hat{x}\hat{y}\left|n_x = 0, n_y = 1\right\rangle = \lambda\left\langle n_x = 0\right|\hat{x}\left|n_x = 0\right\rangle\left\langle n_y = 1\right|\hat{y}\left|n_y = 1\right\rangle = 0$$

$$H'_{12} = \left\langle n_x = 1, n_y = 0 \middle| \lambda \hat{x}\hat{y} \middle| n_x = 0, n_y = 1 \right\rangle = \lambda \left\langle n_x = 1 \middle| \hat{x} \middle| n_x = 0 \right\rangle \left\langle n_y = 0 \middle| \hat{y} \middle| n_y = 1 \right\rangle$$
$$= \lambda \frac{\hbar}{2m\omega} \left\langle n_x = 1 \middle| \hat{a} + \hat{a}^\dagger \middle| n_x = 0 \right\rangle \left\langle n_y = 0 \middle| \hat{b} + \hat{b}^\dagger \middle| n_y = 1 \right\rangle = \lambda \frac{\hbar}{2m\omega}(0+1)(1+0) = \lambda \frac{\hbar}{2m\omega}$$

where we have used $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a} + \hat{a}^\dagger\right)$ and $\hat{y} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{b} + \hat{b}^\dagger\right)$.

In a similar way:

$$H'_{21} = \left\langle n_x = 0, n_y = 1 \middle| \lambda \hat{x}\hat{y} \middle| n_x = 1, n_y = 0 \right\rangle = \lambda \left\langle n_x = 0 \middle| \hat{x} \middle| n_x = 1 \right\rangle \left\langle n_y = 1 \middle| \hat{y} \middle| n_y = 0 \right\rangle$$
$$= \lambda \frac{\hbar}{2m\omega} \left\langle n_x = 0 \middle| \hat{a} + \hat{a}^\dagger \middle| n_x = 1 \right\rangle \left\langle n_y = 1 \middle| \hat{b} + \hat{b}^\dagger \middle| n_y = 0 \right\rangle = \lambda \frac{\hbar}{2m\omega}(1+0)(0+1) = \lambda \frac{\hbar}{2m\omega}$$

Hence we have $\begin{vmatrix} -E_2^{(1)} & \frac{\lambda\hbar}{2m\omega} \\ \frac{\lambda\hbar}{2m\omega} & -E_2^{(1)} \end{vmatrix} = 0 \quad \Rightarrow E_2^{(1)} = \pm \frac{\lambda\hbar}{2m\omega}$

To solve for the eigenfunctions: $\begin{pmatrix} -E_2^{(1)} & \frac{\lambda\hbar}{2m\omega} \\ \frac{\lambda\hbar}{2m\omega} & -E_2^{(1)} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$

For $E_2^{(1)} = +\frac{\lambda\hbar}{2m\omega}$ we have $c_1 = c_2 = \frac{1}{\sqrt{2}}$, for $E_2^{(1)} = -\frac{\lambda\hbar}{2m\omega}$ we have $c_1 = -c_2 = \frac{1}{\sqrt{2}}$.

So the first order wavefunctions are given by:

$$\phi_1 = \frac{1}{\sqrt{2}}\left[\left|n_x = 1, n_y = 0\right\rangle + \left|n_x = 0, n_y = 1\right\rangle\right], \qquad E_2^{(1)} = +\frac{\lambda\hbar}{2m\omega}$$
$$\phi_2 = \frac{1}{\sqrt{2}}\left[\left|n_x = 1, n_y = 0\right\rangle - \left|n_x = 0, n_y = 1\right\rangle\right], \qquad E_2^{(1)} = -\frac{\lambda\hbar}{2m\omega}$$

16 Magnetic fields; time dependence; precession

Taking as basis the $\hat{S}_z$ eigenstates, the $\hat{S}_x$ operator is (c.f. question 5 for $\hat{L}_x$):

$$\hat{S}_x = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

whose eigenstates are:

$$\begin{array}{ccc} m_x = 1 & m_x = 0 & m_x = -1 \\ \frac{1}{2}\begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} & \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} & \frac{1}{2}\begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix} \end{array}$$

When placed in a magnetic field, B, the molecules will acquire an energy $\mu B m_z$, where μ is the magnetic moment of the molecule, which in this case equals twice the magnetic moment of the proton, and $m_z\hbar$ is the eigenvalue of $\hat{S}_z$. At $t = 0$, the molecules enter the magnetic field in the $m_x = 1$ state, after which their wavefunction evolves with time in the usual way, i.e.

$$\psi(t) = \frac{1}{2}\begin{pmatrix} e^{-i\mu Bt/\hbar} \\ \sqrt{2} \\ e^{\,i\mu Bt/\hbar} \end{pmatrix}$$

Thus, if $\mu Bt/\hbar = (2n+1)\pi$, with n an integer, the molecules will be in a pure $m_x = -1$ state, and none will pass the second filter. The time is given by $t = L/v = L\sqrt{m/2E}$, where $L = 20$ mm and m and E are the mass and energy of the molecules respectively. We thus have

$$\mu = \frac{(2n+1)\pi\hbar}{BL}\left(\frac{2E}{m}\right)^{\frac{1}{2}} = 2.84\,10^{-26}\ JT^{-1}$$

and hence the proton magnetic moment is $1.42\,10^{-26}$ JT^{-1}.

Note that the result can also be obtained by treating the problem as one of classical precession. The couple $= \mu B = L\Omega$, where $L = \hbar$ is the angular momentum and Ω the angular frequency of precession. If $\Omega t = (2n+1)\pi$, the molecules have precessed into the $m_x = -1$ state, and the result readily follows.

17 Magnetic fields; the Aharonov-Bohm effect

The phase of the electron wavefunction changes as the electron moves through regions of magnetic vector potential. As the magnetic field changes, the vector potential changes and the phase of the electron wave taking one path around the ring varies with respect to the phase of the electron taking the other path. When the phase difference between the two paths is $\delta\Lambda = 2\pi n$,where n is an integer, constructive inteference will occur with a maximum in conductance. When the phase difference between the two paths is $\pi(2n+1)$, destructive inteference occurs and the conductance is a minimum. As a result oscillations in conductance are observed as the magnetic field varies.

The wavefunction in a magnetic vector potential $\mathbf{A}$ is given by:

$$\psi(\mathbf{r}) = \psi(\mathbf{r}_0)\exp\left(-i\frac{q}{\hbar}\int_a^b \mathbf{A}(\mathbf{r}')\cdot d\,\mathbf{r}'\right) = \psi(\mathbf{r}_0)\exp(-i\Lambda)$$

and the phase difference between an electron moving along path 1 on one side of the ring and moving via path 2 on the other side of the ring is:

$$\delta\Lambda = \frac{e}{\hbar}\int\limits_{path1}\mathbf{A}\cdot d\,\mathbf{r}' - \frac{e}{\hbar}\int\limits_{path2}\mathbf{A}\cdot d\,\mathbf{r}' = \frac{e}{\hbar}\oint\limits_{ring}\mathbf{A}\cdot d\,\mathbf{r}'.$$

Given that;

$$\oint\limits_{ring}\mathbf{A}\cdot d\,\mathbf{r}' = \iint\limits_{\substack{enclosed\\surface}}\nabla\times\mathbf{A}\cdot d\mathbf{S} = \iint\limits_{\substack{enclosed\\surface}}\mathbf{B}\cdot d\mathbf{S} = \Phi$$

the total phase change corresponds to: $\delta\Lambda = \frac{e}{\hbar}\Phi = \frac{e}{\hbar}BS$ where Φ is the magnetic flux enclosed by the ring, B the perpendicular magnetic field and S the area of the ring. Between maxima there is a phase change of 2π , so the change in magnetic field is given by:

$$\Delta B = \frac{2\pi\hbar}{eS} = \frac{h}{eS}$$

Hence the area S and diameter of the ring, d are given by:

$$S = \frac{h}{e\Delta B} = \pi\left(\frac{d}{2}\right)^2 \Rightarrow d = 2\sqrt{\frac{h}{\pi e\Delta B}}$$

From the graph there are 12.5 oscillations in 400Gauss (=0.4T) which gives,

$$\Delta B = 3.2\times10^{-3}T/osc. \Rightarrow d = 2\sqrt{\frac{h}{\pi e\Delta B}} = 2\sqrt{\frac{6.63\times10^{34}}{\pi\times1.60\times10^{-19}\times3.2\times10^{-3}}} = 1.28\times10^{-6}m$$

A result that agrees well with the value of $0.65\times10^{-6}m$ for the radius of the ring quoted in the paper.

20 Magnetic fields

The classical Hamiltonian for an electron in an electromagnetic field described by potentials $(\mathbf{A},\phi)$ is:

$$H = \frac{1}{2m}(\mathbf{p}+e\mathbf{A})^2 - e\phi$$

A uniform field in the z direction can be described by potentials (in cylindrical polars)

$$A_\phi = \tfrac{1}{2}Br \quad ; \quad \phi = 0$$

The Hamiltonian therefore becomes:

$$\begin{aligned}(-i\hbar\nabla + e\mathbf{A})^2 &= (-i\hbar\nabla + e\mathbf{A})(-i\hbar\nabla + e\mathbf{A}) \\ &= -\hbar^2\nabla^2 + e^2A^2 - 2ie\hbar\mathbf{A}.\nabla - ie\hbar\nabla.\mathbf{A}\end{aligned}$$

With our choice of potential, $\nabla.\mathbf{A} = 0$ (Coulomb gauge). The perturbation terms in the Hamiltonian are therefore:

$$\begin{aligned}&\frac{1}{2m}(e^2A^2 + 2e\mathbf{A}.\hat{\mathbf{p}}) \\ &= \frac{e^2}{2m}\cdot\frac{B^2(x^2+y^2)}{4} + \frac{e}{2m}Br\,\hat{p}_\phi \\ &= \frac{e^2}{8m}B^2(x^2+y^2) + \frac{e}{2m}B.\hat{L}_z + \frac{e}{m}B.\hat{S}_z\end{aligned}$$

where we have added by hand the final term representing the intrinsic magnetic moment of the electron, $\frac{e}{m}\hat{S}_z$, interacting with the field. To calculate the energy shift to second order in B, we need to use the first order perturbation theory result for the term quadratic in B and the second order perturbation theory result for the term linear in B, obtaining:

$$\Delta E = \underbrace{B\frac{e}{2m}\langle i|\hat{L}_z + 2\hat{S}_z|i\rangle}_{paramagnetism} + \underbrace{B^2\frac{e^2}{8m}\langle i|x^2+y^2|i\rangle}_{diamagnetism} + \underbrace{B^2\frac{e^2}{4m^2}\sum_{j\neq i}\frac{\langle i|\hat{L}_z + 2\hat{S}_z|j\rangle^2}{E_i - E_j}}_{van\,Vleck\;\;paramagnetism}$$

The first term represents paramagnetism, the energy of alignment of the permanent dipole moment of the atom with the field. The second term represents diamagnetism, which arises owing to induced dipoles, and is therefore quadratic in the field. The third term, by a process of elimination, must be van Vleck paramagnetism; being the second order energy shift caused by the permanent dipoles.

21 Magnetic fields; Landau levels

The Hamiltonian for an electron in an electromagnetic field described by potentials $(\mathbf{A},\phi)$ is:

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\phi$$

If the magnetic field $\mathbf{B} = (0,0,B)$ and we use the Landau gauge: $\mathbf{A} = (0, Bx, 0)$, $\phi = 0$ .The eigenvalue equation is:

$$\hat{H}\Psi = \frac{1}{2m}\begin{pmatrix} -i\hbar\frac{\partial}{\partial x} \\ -i\hbar\frac{\partial}{\partial y} - qB\hat{x} \\ -i\hbar\frac{\partial}{\partial z} \end{pmatrix}^2 \Psi = \frac{1}{2m}\left(-\hbar^2\frac{\partial^2}{\partial x^2} + \left(-i\hbar\frac{\partial}{\partial y} - qB\hat{x}\right)^2 - \hbar^2\frac{\partial^2}{\partial z^2}\right)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Because the particle is confined in the z direction it is in an eigenfunction of $\hat{p}_z$ with eigenvalue zero so we can write:

$$\hat{H}\Psi = \frac{1}{2m}\left(-\hbar^2\frac{\partial^2}{\partial x^2} + \left(-i\hbar\frac{\partial}{\partial y} - qB\hat{x}\right)^2\right)\Psi = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \left(\frac{\partial}{\partial y} - i\frac{qB}{\hbar}\hat{x}\right)^2\right) = i\hbar\frac{\partial\Psi}{\partial t} = E\Psi(x,y)$$

If $\Psi(x,y) = e^{iky}u(x-a)$

We can write the equation above as:

$$\hat{H}\Psi = \frac{1}{2m}\left(-\hbar^2\frac{\partial^2}{\partial x^2} + \left(-i\hbar\frac{\partial}{\partial y} - qB\hat{x}\right)^2\right)e^{iky}u(x-a)$$

$$= \frac{1}{2m}\left(-\hbar^2\frac{\partial^2}{\partial x^2} - \hbar^2\frac{\partial^2}{\partial y^2} + q^2B^2\hat{x}^2 + 2i\hbar qB\hat{x}\frac{\partial}{\partial y}\right)e^{iky}u(x-a)$$

$$= \frac{e^{iky}}{2m}\left(-\hbar^2\frac{\partial^2}{\partial x^2} + \hbar^2k^2 + q^2B^2\hat{x}^2 - 2\hbar kqB\hat{x}\right)u(x-a) = Ee^{iky}u(x-a)$$

$$\Rightarrow \frac{1}{2m}\left(-\hbar^2\frac{\partial^2}{\partial x^2} + q^2B^2\left(\hat{x} - \frac{\hbar k}{qB}\right)^2\right)u(x-a) = Eu(x-a)$$

This equation is that for a traveling wave in the y-direction and 1D simple harmonic oscillator in the x-direction with a potential centred at $x = a = \frac{\hbar k}{qB} \Rightarrow \boxed{k = \frac{qBa}{\hbar}}$. The functions *u* will be Hermite polynomials multiplied by a Gaussian.

A comparison with the usual potential $\frac{1}{2}m\omega^2(x-a)^2 = \frac{q^2B^2}{2m}(x-a)^2$ gives $\omega = \frac{qB}{m}$.

The energy eigenvalues for a harmonic oscillator are given by:

$$E = \left(n+\tfrac{1}{2}\right)\hbar\omega, n = 0,1,2,3.... \Rightarrow E = \left(n+\tfrac{1}{2}\right)\frac{\hbar qB}{m}.$$

The particles are confined to an area of length X in the x-direction and Y in the y-direction. The boundary condition in the y-direction will be $\Psi(y) = \Psi(y+Y)$ so $kY = \frac{qBaY}{\hbar} = 2\pi n^*, \quad n^* = 0,1,2,3...$ and since $0 \le a \le X$ then $0 \le n^* \le \frac{qB}{2\pi\hbar} XY$ so the maximum number of states per unit area is: $\frac{qB}{2\pi\hbar}$.

The Landau gauge produces a solution of traveling waves in the y-direction, and simple harmonic motion in the x-direction, the x and y directions could easily be swopped.

The symmetric gauge produces solutions which describe simple harmonic motion in both the x and y directions.

These discrepancies can be resolved by realizing that this system is highly degenerate – the electrons have a great deal of freedom and wavefunctions can easily be constructed to meet the boundary conditions.

22 Magnetic fields;Hyperfine interaction

$$\hat{H} = B(\mu_e \sigma_{ze} + \mu_p \sigma_{zp}) + W \vec{\sigma}_e \cdot \vec{\sigma}_p \,,$$

(a) First two terms represent interaction between the magnetic moments of electron and proton respectively with the external field B; the final term is the spin-spin (hyperfine) interaction between electron and proton.

(b) The Pauli matrices are:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

and thus we have

$$\sigma_x \uparrow = \downarrow \quad \sigma_x \downarrow = \uparrow \quad \sigma_y \uparrow = i \downarrow \quad \sigma_y \downarrow = -i \uparrow$$

Using this we can evaluate

$$\vec{\sigma}_e \cdot \vec{\sigma}_p \left| \uparrow_e \uparrow_p \right\rangle \equiv \sigma_e^x \sigma_p^x \left| \uparrow_e \uparrow_p \right\rangle + \sigma_e^y \sigma_p^y \left| \uparrow_e \uparrow_p \right\rangle + \sigma_e^z \sigma_p^z \left| \uparrow_e \uparrow_p \right\rangle = \left| \downarrow_e \downarrow_p \right\rangle - \left| \downarrow_e \downarrow_p \right\rangle + \left| \uparrow_e \uparrow_p \right\rangle = \left| \uparrow_e \uparrow_p \right\rangle$$

$$\vec{\sigma}_e \cdot \vec{\sigma}_p \left| \uparrow_e \downarrow_p \right\rangle = \left| \downarrow_e \uparrow_p \right\rangle + \left| \downarrow_e \uparrow_p \right\rangle - \left| \uparrow_e \downarrow_p \right\rangle = 2 \left| \downarrow_e \uparrow_p \right\rangle - \left| \uparrow_e \downarrow_p \right\rangle \quad etc.$$

The terms in the Hamiltonian can thus be evaluated straightforwardly

$$\begin{pmatrix} b+W & 0 & 0 & 0 \\ 0 & b-W & 2W & 0 \\ 0 & 2W & -b-W & 0 \\ 0 & 0 & 0 & -b+W \end{pmatrix}$$

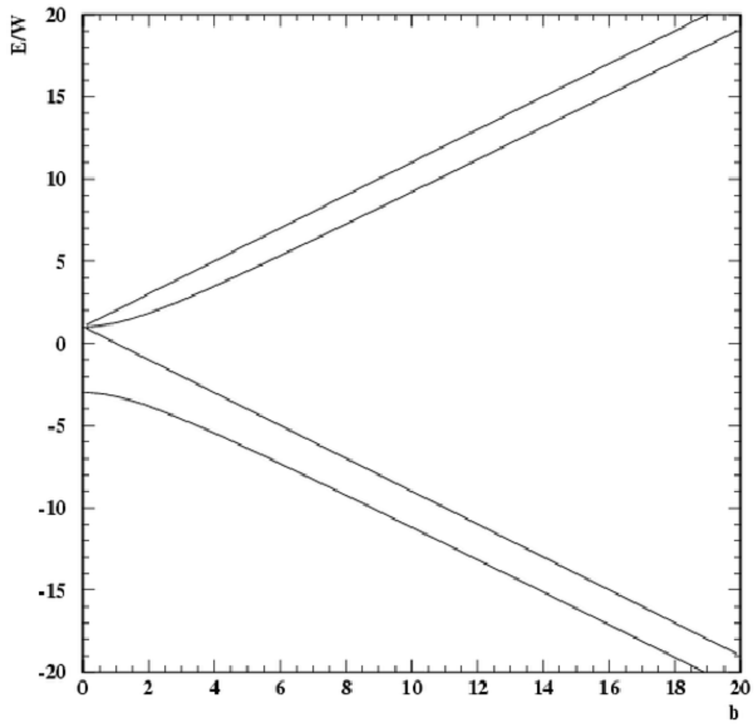
(c) By inspection, the states $\left| \uparrow_e \uparrow_p \right\rangle$ and $\left| \downarrow_e \downarrow_p \right\rangle$ are energy eigenstates with energies $W+b$ and $W-b$ respectively. The other two energy eigenvalues are given by the solutions of

$$\begin{vmatrix} b-W-E & 2W \\ 2W & -b-W-E \end{vmatrix} = 0$$

which leads to

$$E = -W \pm \sqrt{4W^2 + b^2}$$

As a function of b these energies look like:



In the case where $b \ll W$, i.e. where the external magnetic field is very weak, these reduce to $W + b^2/2W$ and $-3W - b^2/2W$, so there is a triplet of $S = 1$ states with energy close to W, and the singlet $S = 0$ state with energy close to $-3W$. In the other limit where $b \gg W$, i.e. where the external magnetic field is very strong, this expression reduces to $\pm b$, so we have two states with energy close to $+b$ and two close to $-b$, corresponding to the two possible orientations of the electron spin.

23 Transitions:Two state system

The Hamiltonian for an interaction between a magnetic moment $\hat{\boldsymbol{\mu}}$ and magnetic field $\mathbf{B}$ is given by: $\hat{H} = -\hat{\boldsymbol{\mu}}\cdot\mathbf{B}$.
In this case $\hat{\boldsymbol{\mu}} = \gamma\hat{\mathbf{S}} = \gamma\frac{\hbar}{2}\hat{\boldsymbol{\sigma}}$ in terms of the Pauli spin matrices, so $\hat{H} = -\gamma\frac{\hbar}{2}\hat{\boldsymbol{\sigma}}\cdot\mathbf{B}$.
Substituting into the time dependent Schrodinger equation, $\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$, we have:

$$-\tfrac{1}{2}\gamma\mathbf{B}\cdot\hat{\boldsymbol{\sigma}}\left|\psi(t)\right\rangle = i\frac{\partial\psi}{\partial t}$$

If $\mathbf{B} = \begin{pmatrix}0 & 0 & B_0\end{pmatrix}$ and $\psi(t) = \begin{bmatrix}a\\ b\end{bmatrix}$ then: $-\tfrac{1}{2}\gamma B_0\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\begin{bmatrix}a\\ b\end{bmatrix} = i\frac{\partial}{\partial t}\begin{bmatrix}a\\ b\end{bmatrix}$
So
$$-\tfrac{1}{2}\gamma B_0 a = i\frac{\partial a}{\partial t} \Rightarrow a = A\exp(i\gamma B_0 t/2) = A\exp(i\omega_0 t/2)$$
$$\tfrac{1}{2}\gamma B_0 b = i\frac{\partial b}{\partial t} \Rightarrow b = B\exp(-i\gamma B_0 t/2) = B\exp(-i\omega_0 t/2)$$

We can normalize this by writing $A = \cos(\theta/2)$, $B = \sin(\theta/2)$
So $\left|\psi(t)\right\rangle = \cos(\theta/2)\exp(i\omega_0 t/2)\begin{bmatrix}1\\ 0\end{bmatrix} + \sin(\theta/2)\exp(-i\omega_0 t/2)\begin{bmatrix}0\\ 1\end{bmatrix}$ as required.

$$\langle\mu_x\rangle = \langle\psi|\mu_x|\psi\rangle = \gamma\frac{\hbar}{2}\begin{bmatrix}a^* & b^*\end{bmatrix}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\begin{bmatrix}a\\ b\end{bmatrix} = \gamma\frac{\hbar}{2}\left(a^*b + b^*a\right)$$
$$= \gamma\frac{\hbar}{2}\cos(\theta/2)\sin(\theta/2)\left[\exp(-i\omega_0 t) + \exp(i\omega_0 t)\right] = \underline{\gamma\frac{\hbar}{2}\sin\theta\cos(\omega_0 t)}$$
$$\langle\mu_y\rangle = \langle\psi|\mu_y|\psi\rangle = \gamma\frac{\hbar}{2}\begin{bmatrix}a^* & b^*\end{bmatrix}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}\begin{bmatrix}a\\ b\end{bmatrix} = \gamma\frac{\hbar}{2}\left(-ia^*b + ib^*a\right)$$
$$= \gamma\frac{\hbar}{2}\cos(\theta/2)\sin(\theta/2)\left[-i\exp(-i\omega_0 t) + i\exp(i\omega_0 t)\right] = \underline{-\gamma\frac{\hbar}{2}\sin\theta\sin(\omega_0 t)}$$
$$\langle\mu_z\rangle = \langle\psi|\mu_z|\psi\rangle = \gamma\frac{\hbar}{2}\begin{bmatrix}a^* & b^*\end{bmatrix}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\begin{bmatrix}a\\ b\end{bmatrix} = \gamma\frac{\hbar}{2}\left(a^*a - b^*b\right)$$
$$= \gamma\frac{\hbar}{2}\left[\cos^2(\theta/2) - \sin^2(\theta/2)\right] = \underline{\gamma\frac{\hbar}{2}\cos\theta}$$

These equations represent precession of the magnetic moment vector about the z-axis with angular frequency ω_0. The magnetic moment is at an angle of θ to the z-axis.

$$\hat{H} = -\hat{\boldsymbol{\mu}}\cdot\mathbf{B} = -\gamma\hat{\mathbf{S}}\cdot\mathbf{B}, \qquad \left(\hat{\boldsymbol{\mu}} = \gamma\hat{\mathbf{S}}\right)$$
$$\frac{d}{dt}\langle\hat{\boldsymbol{\mu}}\rangle = \frac{i}{\hbar}\left\langle\left[\hat{H},\hat{\boldsymbol{\mu}}\right]\right\rangle = \frac{i}{\hbar}\left\langle\left[\left(-\gamma\hat{\mathbf{S}}\cdot\mathbf{B}\right)\gamma\hat{\mathbf{S}} + \gamma\hat{\mathbf{S}}\left(\gamma\hat{\mathbf{S}}\cdot\mathbf{B}\right)\right]\right\rangle = \frac{i\gamma^2}{\hbar}\left\langle\left[\hat{\mathbf{S}}\left(\hat{\mathbf{S}}\cdot\mathbf{B}\right) - \left(\hat{\mathbf{S}}\cdot\mathbf{B}\right)\hat{\mathbf{S}}\right]\right\rangle$$

$$\frac{d}{dt}\langle\hat{\boldsymbol{\mu}}\rangle=\frac{i\gamma^2}{\hbar}\left\langle\left[\left(\hat{S}_x\mathbf{i}+\hat{S}_y\mathbf{j}+\hat{S}_z\mathbf{k}\right)\left(\hat{S}_xB_x+\hat{S}_yB_y+\hat{S}_zB_z\right)-\left(\hat{S}_xB_x+\hat{S}_yB_y+\hat{S}_zB_z\right)\left(\hat{S}_x\mathbf{i}+\hat{S}_y\mathbf{j}+\hat{S}_z\mathbf{k}\right)\right]\right\rangle$$

$$=\frac{i\gamma^2}{\hbar}\left\langle\begin{array}{l}\mathbf{i}\left[\hat{S}_x\left(\hat{S}_yB_y+\hat{S}_zB_z\right)-\left(\hat{S}_yB_y+\hat{S}_zB_z\right)\hat{S}_x\right]+\mathbf{j}\left[\hat{S}_y\left(\hat{S}_xB_x+\hat{S}_zB_z\right)-\left(\hat{S}_xB_x+\hat{S}_zB_z\right)\hat{S}_y\right]\\+\mathbf{k}\left[\hat{S}_z\left(\hat{S}_xB_x+\hat{S}_yB_y\right)-\left(\hat{S}_xB_x+\hat{S}_yB_y\right)\hat{S}_z\right]\end{array}\right\rangle$$

Since $\left[\hat{S}_x,\hat{S}_x\right]=0$ etc.

and given $\left[\hat{S}_x,\hat{S}_y\right]=i\hbar\hat{S}_z$, $\quad\left[\hat{S}_y,\hat{S}_z\right]=i\hbar\hat{S}_x\quad\left[\hat{S}_z,\hat{S}_x\right]=i\hbar\hat{S}_y$

$$\frac{d}{dt}\langle\hat{\boldsymbol{\mu}}\rangle=\frac{i\gamma^2}{\hbar}\left\langle\mathbf{i}\left[\left[\hat{S}_x,\hat{S}_y\right]B_y-\left[\hat{S}_z,\hat{S}_x\right]B_z\right]+\mathbf{j}\left[-\left[\hat{S}_x,\hat{S}_y\right]B_x+\left[\hat{S}_y,\hat{S}_z\right]B_z\right]+\mathbf{k}\left[\left[\hat{S}_z,\hat{S}_x\right]B_x-\left[\hat{S}_y,\hat{S}_z\right]B_y\right]\right\rangle$$

$$=-\gamma^2\left\langle\mathbf{i}\left[\hat{S}_zB_y-\hat{S}_yB_z\right]+\mathbf{j}\left[-\hat{S}_zB_x+\hat{S}_xB_z\right]+\mathbf{k}\left[\hat{S}_yB_x-\hat{S}_xB_y\right]\right\rangle$$

$$=\gamma^2\left\langle\hat{\mathbf{S}}\times\mathbf{B}\right\rangle=\gamma^2\left\langle\hat{\mathbf{S}}\right\rangle\times\mathbf{B}=\gamma\langle\hat{\boldsymbol{\mu}}\rangle\times\mathbf{B}$$

$\frac{d}{dt}\langle\hat{\boldsymbol{\mu}}\rangle=\gamma\langle\hat{\boldsymbol{\mu}}\rangle\times\mathbf{B}$ as required.

From above:

$\left\langle\mu_x\right\rangle=\gamma\frac{\hbar}{2}\sin\theta\cos\left(\omega_0t\right)\qquad\left\langle\mu_y\right\rangle=-\gamma\frac{\hbar}{2}\sin\theta\sin\left(\omega_0t\right)\qquad\left\langle\mu_z\right\rangle=\gamma\frac{\hbar}{2}\cos\theta\qquad\mathbf{B}=B_0\mathbf{j}$

So:

$\left\langle\hat{\boldsymbol{\mu}}\right\rangle=\gamma\frac{\hbar}{2}\sin\theta\cos\left(\omega_0t\right)\mathbf{i}-\gamma\frac{\hbar}{2}\sin\theta\sin\left(\omega_0t\right)\mathbf{j}+\gamma\frac{\hbar}{2}\cos\theta\mathbf{k}$

And therefore:

$\left\langle\hat{\boldsymbol{\mu}}\right\rangle\times\gamma B_0\mathbf{k}=\gamma\left\langle\mu_y\right\rangle B_0\mathbf{i}-\gamma\left\langle\mu_x\right\rangle B_0\mathbf{j}=-\gamma^2\frac{\hbar}{2}\sin\theta\sin\left(\omega_0t\right)B_0\mathbf{i}-\gamma^2\frac{\hbar}{2}\sin\theta\cos\left(\omega_0t\right)B_0\mathbf{j}$

Also

$$\frac{d}{dt}\langle\hat{\boldsymbol{\mu}}\rangle=-\gamma\omega_0\frac{\hbar}{2}\sin\theta\sin\left(\omega_0t\right)\mathbf{i}-\gamma\omega_0\frac{\hbar}{2}\sin\theta\cos\left(\omega_0t\right)\mathbf{j}$$

$$=-\gamma^2B_0\frac{\hbar}{2}\sin\theta\sin\left(\omega_0t\right)\mathbf{i}-\gamma^2B_0\frac{\hbar}{2}\sin\theta\cos\left(\omega_0t\right)\mathbf{j}$$

Hence $\frac{d}{dt}\langle\hat{\boldsymbol{\mu}}\rangle=\gamma\langle\hat{\boldsymbol{\mu}}\rangle\times\mathbf{B}$ is satisfied.

The cross product of magnetic moment and magnetic field produces a torque which causes the magnetic moment to precess around the magnetic field.

25 Time Dependence

Standard bookwork allows us to derive the amplitude for being in state ψ_n at time t:

$$c_n(t) = \frac{1}{i\hbar}\int_0^t dt' e^{i(E_n - E_0)t'/\hbar} \langle \psi_n | \hat{H}'(t') | \psi_0 \rangle .$$

In the present instance,

$$\hat{H}'(t) = e\mathcal{E}_0 z e^{-t/\tau}$$

The matrix element $\langle \psi_{2s} | z | \psi_{1s} \rangle$ is zero, since the 1s and 2s wavefunctions both have even parity while z has odd parity, and hence the integrand has odd parity. Therefore the probability of finding the atom in the 2s state is zero.

The matrix elements $\langle \psi_{2p\pm1} | z | \psi_{1s} \rangle$ are zero, since the ϕ part of the integral will vanish:

$$\langle \psi_{2p\pm1} | z | \psi_{2s} \rangle = \int dr \cdots \int d\theta \cdots \int_0^{2\pi} d\phi e^{\pm i\phi} = 0$$

The only non-zero matrix element is:

$$\begin{aligned}\langle \psi_{2p_0} | z | \psi_{1s} \rangle &= \left(\frac{1}{32\pi a_0^5}\right)^{\frac{1}{2}} \left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} \int r^2 dr\, r^2 e^{-r/a_0} e^{-r/2a_0} \int 2\pi \sin\theta d\theta \cos^2\theta \\ &= \frac{1}{4\sqrt{2}\pi a_0^4} \cdot \frac{4!}{(3/2a_0)^5} \cdot \frac{4\pi}{3} \\ &= \frac{256 a_0}{243\sqrt{2}}\end{aligned}$$

The t' integral, taking the limit as $t \to \infty$, is:

$$\int_0^\infty dt' e^{-t'/\tau} e^{i(E_{2p} - E_{1s})t'/\hbar} = \frac{1}{1/\tau - i\Delta E/\hbar}$$

where $\Delta E = E_{2p} - E_{1s} = \frac{3}{4} R_\infty$. Putting all this together we obtain the probability of being in the 2p $_0$ state after a long time as

$$| c_{2p_0}(\infty) |^2 = \frac{e^2 \mathcal{E}_0^2 a_0^2 2^{15}}{3^{10}} \cdot \frac{1}{\Delta E^2 + \hbar^2/\tau^2}$$

26 Time dependence

From the previous question $c_n(t) = \frac{1}{i\hbar}\int_0^t dt' e^{i(E_n - E_0)t'/\hbar} \langle \psi_n | \hat{H}'(t') | \psi_0 \rangle$.

The perturbation is:

$$\hat{H}' = \lambda x(1 - t/T) \qquad 0 \le t \le T, \qquad \hbar\omega_n = (n + 1/2)\hbar\omega$$

$$\Rightarrow c_n(t \ge T) = \frac{\lambda}{i\hbar}\int_0^T \exp(in\omega t')\left(1 - \frac{t'}{T}\right)\langle \psi_n | x | \psi_0 \rangle dt'$$

$$n = 1 \Rightarrow c_1 = \frac{\lambda}{i\hbar}\int_0^T \exp(i\omega t')\left(1 - \frac{t'}{T}\right)\langle \psi_1 | x | \psi_0 \rangle dt'$$

Integrating by parts:

$$c_1 = \frac{\lambda}{i\hbar}\langle \psi_1 | x | \psi_0 \rangle \left\{ \left[\frac{\exp(i\omega t')}{i\omega}\left(1 - \frac{t'}{T}\right) \right]_0^T + \int_0^T \frac{\exp(i\omega t')}{i\omega T} dt' \right\}$$

$$c_1 = \frac{\lambda}{i\hbar}\langle \psi_1 | x | \psi_0 \rangle \left\{ -\frac{1}{i\omega} + \frac{1}{i\omega T}\cdot\frac{1}{i\omega}\left(\exp(i\omega T) - 1\right) \right\} = \frac{\lambda}{\hbar\omega}\langle \psi_1 | x | \psi_0 \rangle \left\{ 1 + \frac{1 - \exp(i\omega T)}{i\omega T} \right\}$$

$$\langle \psi_1 | x | \psi_0 \rangle = \sqrt{\frac{\hbar}{2m\omega}}\langle \psi_1 | \psi_1 \rangle, \qquad \left(\psi_1 = \sqrt{\frac{2m\omega}{\hbar}}\, x\psi_0 \right)$$

$$\Rightarrow |c_1|^2 = \left(\frac{\lambda}{\hbar\omega}\right)^2 \frac{\hbar}{2m\omega}\left\{ 1 + \frac{1 - \exp(i\omega t)}{i\omega T} \right\}^2$$

Which is the probability of being in the first excited state at time $t > T$.

For $\omega T \gg 1$, $\quad |c_1|^2 = \left(\frac{\lambda}{\hbar\omega}\right)^2 \frac{\hbar}{2m\omega} = \frac{\lambda^2}{2m\hbar\omega^3}$

We have $\hat{H}_0 + \lambda x = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2 x^2 + \lambda x = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\left(x + \frac{\lambda}{m\omega^2}\right)^2 - \frac{1}{2}\frac{\lambda^2}{m\omega^2}$

So for the new ground state we can use $x' = x + \frac{\lambda}{m\omega^2}$

And: $\langle \psi_1 | \psi_0' \rangle = \left(\frac{2m\omega}{\hbar}\cdot\frac{m\omega}{\pi\hbar}\right)^{1/2}\int_{-\infty}^{\infty} x\exp\left(-\alpha x^2 - \alpha x'^2\right)dx$ where $\alpha = \frac{m\omega}{2\hbar}$

Now

$$\alpha x^2 + \alpha x'^2 = \alpha\left(x^2 + \left(x + \frac{\lambda}{m\omega^2}\right)^2\right) = 2\alpha\left(\left(x + \frac{\lambda}{2m\omega^2}\right)^2 + \left(\frac{\lambda}{2m\omega^2}\right)^2\right)$$

$$\Rightarrow \langle \psi_1 | \psi_0' \rangle = \left(\frac{2m\omega}{\hbar}\cdot\frac{m\omega}{\pi\hbar}\right)^{1/2}\int_{-\infty}^{\infty}\left[\left(x + \frac{\lambda}{m\omega^2}\right) - \frac{\lambda}{m\omega^2}\right]\exp\left\{-2\alpha\left(\left(x + \frac{\lambda}{2m\omega^2}\right)^2 + \left(\frac{\lambda}{2m\omega^2}\right)^2\right)\right\}dx$$

$$= \left(\frac{2m\omega}{\hbar}\right)^{1/2}\left(-\frac{\lambda}{2m\omega^2}\right)\exp\left(-2\alpha\left(\frac{\lambda}{2m\omega^2}\right)^2\right)$$

So to first order in λ $\quad \left|\langle \psi_1 | \psi_0' \rangle\right|^2 = \frac{2m\omega}{\hbar}\frac{\lambda^2}{4m^2\omega^4} = \frac{\lambda^2}{2m\hbar\omega^3}$

(Or: find an expression for ψ_0' in terms of ψ_0, ψ_1 using 1st order perturbation theory)

27 The Fermi golden rule

We can expand the wavefunction:

$$\left|\psi(t)\right\rangle = \sum_n c_n \left|\psi_n\right\rangle \exp(-i\omega_n t), \qquad i\hbar\frac{\partial\left|\psi(t)\right\rangle}{\partial t} = \left[\hat{H}_0 + \hat{V}\exp(-i\omega t)\right]\left|\psi(t)\right\rangle$$

$$\Rightarrow i\hbar\sum_n \frac{\partial c_n}{\partial t}\left|\psi_n\right\rangle \exp(-i\omega_n t) = \sum_n \hat{V}\exp(-i\omega t)c_n\left|\psi_n\right\rangle\exp(-i\omega_n t)$$

Cancelling terms from the unperturbed Schrodinger equation.
On the rhs we can approximate $c_1 = 1, c_{n\neq 1} = 0$ and left multiplying by $\left\langle\psi_n\right|$

$$\Rightarrow i\hbar\frac{\partial c_n}{\partial t} = \left\langle\psi_n\right|\hat{V}\left|\psi_1\right\rangle \exp\left(i(\omega_n - \omega - \omega_1)t\right)$$

$$\Rightarrow c_n = \frac{1}{i\hbar}\int_0^t \left\langle\psi_n\right|\hat{V}\left|\psi_1\right\rangle \exp\left(i(\omega_n - \omega - \omega_1)t'\right)dt' = -\frac{1}{\hbar}\left\langle\psi_n\right|\hat{V}\left|\psi_1\right\rangle \frac{\exp\left(i(\omega_n - \omega - \omega_1)t\right) - 1}{\omega_n - \omega - \omega_1}$$

Substituting into above:

$$\left|\psi(t)\right\rangle = \left|\psi_1\right\rangle\exp(-i\omega_1 t) - \sum_{n\neq 1}\frac{1}{\hbar}\left\langle\psi_n\right|\hat{V}\left|\psi_1\right\rangle \frac{\exp\left(i(\omega_n - \omega - \omega_1)t\right) - 1}{\omega_n - \omega - \omega_1}\left|\psi_n\right\rangle\exp(-i\omega_n t)$$ as

required.

(i) if $E_n = E_1 + \hbar\omega$ then $\omega_n = \omega_1 + \omega$ and expanding the exponential

$$\frac{\exp\left(i(\omega_n - \omega - \omega_1)t\right) - 1}{\omega_n - \omega - \omega_1} \approx \frac{1 + i(\omega_n - \omega - \omega_1)t - 1}{\omega_n - \omega - \omega_1} = it$$

$$\Rightarrow \text{prob} = \left|\mathrm{c_n}\right|^2 = \frac{t^2}{\hbar^2}\left|\left\langle\psi_n\right|\hat{V}\left|\psi_1\right\rangle\right|^2 \propto t^2$$

$$\text{rate} = \frac{d\left|\mathrm{c_n}\right|^2}{dt} = \frac{2t}{\hbar^2}\left|\left\langle\psi_n\right|\hat{V}\left|\psi_1\right\rangle\right|^2$$

(ii) If $E_n \neq E_1 + \hbar\omega$

$$\text{prob} = \left|c_n\right|^2 = \frac{1}{\hbar^2}\left|\left\langle\psi_n\right|\hat{V}\left|\psi_1\right\rangle\right|^2\left[\frac{\exp\left(i(\omega_n - \omega - \omega_1)t\right) - 1}{\omega_n - \omega - \omega_1}\right]^2$$

$$= \frac{1}{\hbar^2}\left|\left\langle\psi_n\right|\hat{V}\left|\psi_1\right\rangle\right|^2\left|\frac{\exp\left(\frac{i\delta\omega t}{2}\right)\left(\exp\left(\frac{i\delta\omega t}{2}\right) - \exp\left(-\frac{i\delta\omega t}{2}\right)\right)}{\delta\omega}\right|^2 = \frac{4}{\hbar^2}\left|\left\langle\psi_n\right|\hat{V}\left|\psi_1\right\rangle\right|^2\frac{\sin^2\left(\frac{\delta\omega t}{2}\right)}{\delta\omega^2}$$

$$\text{rate} = \frac{d\left|\mathrm{c_n}\right|^2}{dt} = \frac{4}{\hbar^2}\left|\left\langle\psi_n\right|\hat{V}\left|\psi_1\right\rangle\right|^2\frac{\sin\left(\frac{\delta\omega t}{2}\right)\cos\left(\frac{\delta\omega t}{2}\right)}{\delta\omega} = \frac{2}{\hbar^2}\left|\left\langle\psi_n\right|\hat{V}\left|\psi_1\right\rangle\right|^2\frac{\sin(\delta\omega t)}{\delta\omega}$$

To calculate the overall transition rate we integrate the probability of a transition over all energies

$$P = \frac{4}{\hbar^2}\int\left|\left\langle\psi_n\right|\hat{V}\left|\psi_1\right\rangle\right|^2\frac{\sin^2\left(\frac{\delta\omega t}{2}\right)}{\delta\omega^2}g(E_n)\hbar d(\delta\omega)$$

Making the substitution: $x = \frac{1}{2}\delta\omega t,\ dx = \frac{t}{2} d\left(\delta\omega\right)$

$$P = \frac{2}{\hbar}\int \left|\langle\psi_n|\hat{V}|\psi_1\rangle\right|^2 \frac{t\sin^2 x}{x^2} g\left(E_n\right)dx$$

The $\dfrac{\sin^2 x}{x^2}$ is only significantly different from zero over the range $-2\pi < x < 2\pi$ so for large t we can assume that the density of states and the matrix element are constant.

Since $\int_{-\infty}^{\infty} \dfrac{\sin^2 x}{x^2} = \pi$ we get for the probability:

$$P = \frac{2}{\hbar}\left|\langle\psi_n|\hat{V}|\psi_1\rangle\right|^2 g\left(E_n\right)\int_{-\infty}^{\infty}\frac{t\sin^2 x}{x^2}dx = \frac{2\pi}{\hbar}\left|\langle\psi_n|\hat{V}|\psi_1\rangle\right|^2 g\left(E_n\right)t$$

And the transition rate:

$$T = \frac{dP}{dt} = \frac{2\pi}{\hbar}\left|\langle\psi_n|\hat{V}|\psi_1\rangle\right|^2 g\left(E_n\right)$$

Assumptions

Includes a continuum of final states – ok for large systems with lots of states

Density of states is a constant in the integral – as time increases the $\sin^2 x/x^2$ function becomes more and more sharply peaked.

$\left|\langle\psi_n|\hat{V}|\psi_1\rangle\right|^2$ is a constant for all final states…….?

28 Scattering

From lectures, Born Approximation gives:

$$\frac{d\sigma}{d\Omega} = \left(\frac{m}{2\pi\hbar^2}\right)^2 \left|\int V(r) e^{i\mathbf{K}.\mathbf{r}} dr^3\right|^2$$

where $\mathbf{K}$ is the difference beween incoming and outgoing wave vectors, of magnitude $2k\sin\frac{1}{2}\theta$. In the case where $V(\mathbf{r}) = V(r)$, i.e. where the potential is centrally symmetric, it is convenient to take $\mathbf{K}$ as the axis of polar coordinates for the purpose of integration, so that $\mathbf{K}.\mathbf{r} = Kr\cos\theta'$. The integral thus becomes

$$\begin{aligned}
\int V(r) e^{i\mathbf{K}.\mathbf{r}} d^3r &= \int V(r) e^{iKr\cos\theta'} 2\pi \sin\theta' d\theta' r^2 dr \\
&= 2\pi \int V(r) r^2 dr \left[\frac{e^{iKr\cos\theta'}}{iKr}\right]_0^{\pi} \\
&= \frac{4\pi}{K}\int V(r) r dr \sin Kr
\end{aligned}$$

and hence

$$\frac{d\sigma}{d\Omega} = \left(\frac{2m}{K\hbar^2}\right)^2 \left|\int V(r) r dr \sin Kr\right|^2$$

Taking $V(r) = -V_0$ for $r \le a$, and $V(r) = 0$ otherwise, the integral becomes (integrating by parts):

$$-V_0\int_0^a r\sin Kr dr = -V_0\left\{\left[-r\frac{\cos Kr}{K}\right]_0^a + \int_0^a \frac{\cos Kr}{K} dr\right\} = -\frac{V_0}{K^2}(\sin Ka - Ka\cos Ka)$$

and thus

$$\frac{d\sigma}{d\Omega} = \left[\frac{2mV_0}{\hbar^2 K^3}(\sin Ka - Ka\cos Ka)\right]^2$$

In the low energy limit, $K \to 0$,

$$\sin Ka - Ka\cos Ka \approx Ka - \frac{1}{3!}(Ka)^3 - Ka(1 - \tfrac{1}{2}(Ka)^2) = \tfrac{1}{3}(Ka)^3$$

and hence

$$\frac{d\sigma}{d\Omega} = \left(\frac{2mV_0 a^3}{3\hbar^2}\right)^2$$

This is independent of K and hence independent of θ, so isotropic, as required. The total cross-section is obtained by integrating over solid angles, which simply involves multiplying by 4π in this case

$$\sigma_{tot} = 4\pi\left(\frac{2mV_0 a^3}{3\hbar^2}\right)^2$$

29 Spontaneous emission
From lectures decay rate is:

$$A = \frac{\omega^3 \, | \, d_{k\,j} \, |^2}{3\pi\varepsilon_0 c^3 \hbar}$$

and the lifetime is thus $\tau = 1/A$. Take for example the $2p_0$ state of Hydrogen decaying to 1s (the other 2p states must have the same lifetime, but the $2p_0$ to 1s decay depends on the matrix elements that we computed in question 25). Only the z component of d is non-zero for this transition, (the ϕ integral yields zero if you compute the matrix elements of x or y) giving:

$$\langle 2p_0 | ez | 1s \rangle = \frac{256 e a_0}{243\sqrt{2}} = 6.31 \times 10^{-30} \ Cm$$

The energy of the emitted photon is

$$\hbar\omega = \frac{3}{4} R_\infty = \frac{3}{4} \cdot \frac{me^4}{2(4\pi\varepsilon_0)^2 \hbar^2} \quad \Rightarrow \quad \omega = 1.56 \times 10^{16} \ Hz$$

Hence, the lifetime of the state is

$$\tau = 1.56 \times 10^{-9} \ s$$

The only lower lying state to which 3s can decay is 2p according to the selection rules. We can expect the matrix element $\langle 3s | ez | 2p \rangle \sim ea_0$ on dimensional grounds, and thus not very different from $\langle 2p | ez | 1s \rangle$. The main difference between the lifetimes of the 3s and 2p levels will arise from the difference in ω^3. For the 3s$\rightarrow$2p transition,

$$\hbar\omega = (\tfrac{1}{4} - \tfrac{1}{9}) R_\infty = \tfrac{5}{36} R_\infty$$

The ratio of the lifetimes is therefore approximately

$$\frac{\tau(3s)}{\tau(2p)} \sim \left(\frac{3}{4} \cdot \frac{36}{5} \right)^3 \sim 150$$

The only state lying below 2s is 1s, but the decay 2s$\rightarrow$1s is not allowed by the electric dipole selection rules. The 2s state is “metastable”. The dominant decay is actually via two-photon emission, a process which can be described by second order perturbation theory, and occurs very slowly. In practice, atoms may well make transitions from 2s to 2p (for example) before decay takes place as a result of collision processes. Alternatively, decay of the 2s state may be induced by the application of an external electric field, which mixes 2s and 2p through the Stark effect.

30 Spontaneous emission

At some juncture midway through the transition process, the wavefunction will be

$$|\psi\rangle = \alpha e^{-iE_{2p}t/\hbar}|2p_1\rangle + \beta e^{-iE_{1s}t/\hbar}|1s\rangle$$

In principle, the coefficients α and β are time varying, but the lifetime of the state (question 20) is much greater than the period of the emitted radiation, so we can neglect this. The expectation value of the x dipole moment is

$$\begin{aligned}\langle d_x\rangle &= e\langle\psi|x|\psi\rangle \\ &= e[|\alpha^2|\langle 2p_1|x|2p_1\rangle + \alpha^*\beta e^{i\omega t}\langle 2p_1|x|1s\rangle + \alpha\beta^* e^{-i\omega t}\langle 1s|x|2p_1\rangle + |\beta^2|\langle 1s|x|1s\rangle]\end{aligned}$$

where $\omega = (E_{2p} - E_{1s})/\hbar$ is the frequency of the emitted radiation. The first and fourth terms are zero from parity, and thus we have

$$\langle d_x\rangle = 2e\Re[\alpha^*\beta e^{i\omega t}\langle 2p_1|x|1s\rangle]$$

The x dipole moment thus oscillates with frequency ω.

Next, evaluate $\langle 2p_1|x|1s\rangle$, noting that $x = r\sin\theta\cos\phi$:

$$\begin{aligned}\langle 2p_1|x|1s\rangle &= \left(\frac{1}{64\pi a_0^5}\right)^{\frac{1}{2}}\left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}}\int d\phi e^{i\phi}\cos\phi\int d\theta\sin^3\theta\int dr\, r^4 e^{-r/a_0}e^{-r/2a_0} \\ &= \frac{\pi}{8\pi a_0^4}\cdot\frac{4}{3}\cdot\frac{256a_0^5}{81} \\ &= \frac{128a_0}{243}\end{aligned}$$

To evaluate $\langle d_y\rangle$, the calculation is identical, except that $\cos\phi$ becomes $\sin\phi$ in the ϕ integral. The upshot is that

$$\langle 2p_1|y|1s\rangle = i\langle 2p_1|x|1s\rangle$$

Hence the y dipole moment oscillates at the same frequency as the x dipole, but $\pi/2$ out of phase, i.e. the atom has a rotating dipole moment, which yields circularly polarised radiation. The magnitude of the dipole moment is $2\Re[\alpha^*\beta]128ea_0/243$, which is of order ea_0 as required, and indeed as it must be on dimensional grounds.

From classical electrodynamics, the rate of power emission from a dipole d oscilating at frequency ω is

$$W = \frac{\omega^4 d^2}{3\pi\varepsilon_0 c^3}$$

According to quantum mechanics, the rate of transition is given by the Einstein A coefficient, which we multiply by $\hbar\omega$ to get the power radiated:

$$A\hbar\omega = \frac{\omega^3 \mathbf{d}_{kj}^2}{3\pi\varepsilon_0 \hbar c^3}\hbar\omega = \frac{\omega^4 \mathbf{d}_{kj}^2}{3\pi\varepsilon_0 c^3}$$

in accordance with the classical result, where the matrix element of the dipole operator $\mathbf{d}_{kj} = \langle k|\mathbf{d}|\,j\rangle$ plays the rôle of the classical dipole moment.

31 Coherent states

To generate a coherent state we make an expansion in number states, which form a complete set. $|\alpha\rangle = \sum_n c_n |n\rangle$

To find the coefficients in this expansion - $c_n = \langle n|\alpha\rangle$ we use the definition of the coherent state – that it should be unchanged when operated on with an annihilation operator:

$$\hat{a}|\alpha\rangle = \alpha|\alpha\rangle$$

The eigenvalue α may be complex since $\hat{a}$ is not hermitian. If we left multiply by $\langle n|$ we obtain $\langle n|\hat{a}|\alpha\rangle = \alpha\langle n|\alpha\rangle$ and since $\langle n|\hat{a} = \sqrt{n+1}\langle n+1|$ we have:

$$\alpha\langle n|\alpha\rangle = \langle n|\hat{a}|\alpha\rangle = \sqrt{n+1}\langle n+1|\alpha\rangle$$

Which is a recursion relation between successive number states.

If we apply this to the successive states**:**

$$\alpha\langle 0|\alpha\rangle = \sqrt{1}\langle 1|\alpha\rangle, \quad \alpha\langle 1|\alpha\rangle = \sqrt{2}\langle 2|\alpha\rangle, \quad \alpha\langle 2|\alpha\rangle = \sqrt{3}\langle 3|\alpha\rangle$$

We find that : $\langle 3|\alpha\rangle = \frac{\alpha}{\sqrt{3}}\langle 2|\alpha\rangle = \frac{\alpha^2}{\sqrt{3}\sqrt{2}}\langle 1|\alpha\rangle = \frac{\alpha^3}{\sqrt{3}\sqrt{2}\sqrt{1}}\langle 0|\alpha\rangle$ so:

$$c_n = \langle n|\alpha\rangle = \frac{\alpha^n}{\sqrt{n!}}\langle 0|\alpha\rangle \qquad \Rightarrow \qquad |\alpha\rangle = \langle 0|\alpha\rangle\sum_n \frac{\alpha^n}{\sqrt{n!}}|n\rangle$$

To normalize we can use: $\langle\alpha|\alpha\rangle = |\langle 0|\alpha\rangle|^2 \sum_n \frac{\alpha^{2n}}{n!}\langle n|n\rangle = |\langle 0|\alpha\rangle|^2 e^{|\alpha|^2}$ giving:

$$|\alpha\rangle = e^{-|\alpha|^2/2}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}|n\rangle$$

To assess the orthogonality of the states we can derive an expression for $|\langle\alpha|\beta\rangle|^2$.

Substituting the expression for the coherent states into $\langle\alpha|\beta\rangle$ we get:

$$\langle\alpha|\beta\rangle = e^{-|\alpha|^2/2}e^{-|\beta|^2/2}\sum_{n,m}^{\infty}\frac{(\alpha^*)^n}{\sqrt{n!}}\frac{(\beta)^m}{\sqrt{m!}}\langle n|m\rangle = e^{-|\alpha|^2/2}e^{-|\beta|^2/2}\sum_{n}^{\infty}\frac{(\alpha^*\beta)^n}{n!} = e^{-|\alpha|^2/2}e^{-|\beta|^2/2}e^{\alpha^*\beta}$$

Since $\langle n|m\rangle = \delta_{nm}$ and hence

$$|\langle\alpha|\beta\rangle|^2 = e^{-|\alpha|^2}e^{-|\beta|^2}e^{\alpha^*\beta}e^{\beta^*\alpha} = e^{-\left(|\alpha|^2+|\beta|^2-\alpha^*\beta-\beta^*\alpha\right)} = e^{-|\alpha-\beta|^2} > 0 \quad \forall\alpha,\beta.$$

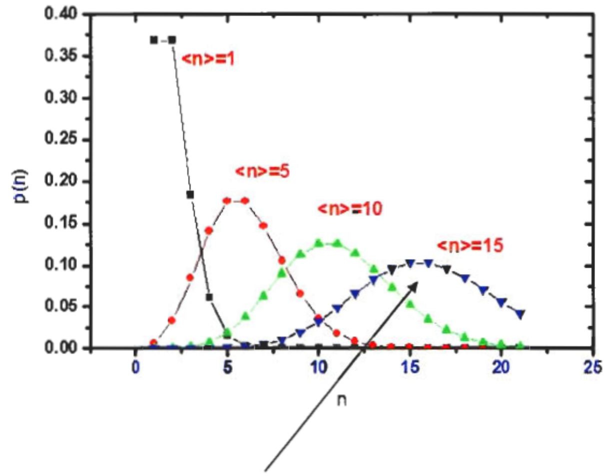
Hence coherent states are not orthogonal to one another.

The probability of having n photons in a coherent state is given by:

$$p(n) = |\langle n|\alpha\rangle|^2 = \left|e^{-|\alpha|^2/2}\sum_{j=0}^{\infty}\frac{\alpha^j}{\sqrt{j!}}\langle n|j\rangle\right|^2 = \frac{\alpha^{2n}e^{-|\alpha|^2}}{n!}$$

Which is a Poisson distribution with a mean value of n: $\langle n\rangle = |\alpha|^2$ where we have:

$$p(n) = \frac{\langle n\rangle^n e^{-\langle n\rangle}}{n!}$$



The distribution tends to a Gaussian for large $\langle n \rangle$

(figure taken from “lasers,atoms and light” R T Phillips)

32 Lasers

B_{12} describes the stimulated transition between levels 1 and 2 with the transition rate per atom being given by $B_{12}u(\omega)$ where $u(\omega)$ is the energy density of radiation per unit frequency. B_{21} describes the stimulated transition between levels 2 and 1. A_{21} is the coefficient for spontaneous transitions between level 2 and level 1 it is the transition rate per atom.

Suppose we have many atoms in a black body radiation field $u(\omega)$ at a temperature T with the numbers of atoms in state 1 being n_1 and in state 2, n_2.
In thermodynamic equilibrium the transition rates $2 \to 1$ and $1 \to 2$ must balance:
$n_2\left[A_{21} + B_{21}u(\omega)\right] = n_1 B_{12} u(\omega)$.
In thermal equilibrium relative populations of two states are given by the Boltzmann factor: $\frac{n_1}{n_2} = \frac{g_1 e^{-E_1/kT}}{g_2 e^{-E_2/kT}} = e^{\hbar\omega/kT}$ where $\hbar\omega = E_2 - E_1$ and so: $g_2 A_{21} = \left[g_1 B_{12} e^{\hbar\omega/kT} - g_2 B_{21}\right]u(\omega)$

The energy density per unit ω is given by Planck's black body formula: $u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\hbar\omega/kT} - 1}$

and so: $g_2 A_{21} = \left[g_1 B_{12} e^{\hbar\omega/kT} - g_2 B_{21}\right]\frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\hbar\omega/kT} - 1}$. The A coefficient (spontaneous emission) cannot depend on temperature so T must cancel on the RHS and hence:

$$g_2 B_{21} = g_1 B_{12}, g_2 A_{21} = g_2 B_{21}\frac{\hbar\omega^3}{\pi^2 c^3} = g_1 B_{12}\frac{\hbar\omega^3}{\pi^2 c^3}$$

$$\frac{dN_2}{dt} = RN_0 - A_{21}N_2 - B_{21}u(\omega)N_2 + B_{12}u(\omega)N_1$$

$$\frac{dN_1}{dt} = A_{21}N_2 - A_{10}N_1 + B_{21}u(\omega)N_2 - B_{12}u(\omega)N_1$$

In equilibrium rates are zero:

$$0 = RN_0 - A_{21}N_2 - B_{21}u(\omega)N_2 + B_{12}u(\omega)N_1 \quad 0 = A_{21}N_2 - A_{10}N_1 + B_{21}u(\omega)N_2 - B_{12}u(\omega)N_1$$

Since $g_1 B_{12} = g_2 B_{21}$ [2]we have

$$0 = RN_0 - A_{21}N_2 - B_{21}u(\omega)\left(N_2 - \tfrac{g_2}{g_1}N_1\right) \qquad 0 = A_{21}N_2 - A_{10}N_1 + B_{21}u(\omega)\left(N_2 - \tfrac{g_2}{g_1}N_1\right)$$

Adding these equations gives: $RN_0 = A_{10}N_1$ and from the RH equation above

$$N_2\left(A_{21} + B_{21}u(\omega)\right) = N_1\left(A_{10} + \tfrac{g_2}{g_1}B_{21}u(\omega)\right) \Rightarrow \frac{N_2}{N_1} = \frac{\left(A_{10} + \tfrac{g_2}{g_1}B_{21}u(\omega)\right)}{\left(A_{21} + B_{21}u(\omega)\right)}$$ as required

$$\frac{N_2}{N_1} - \frac{g_2}{g_1} = \frac{\left(A_{10} + \tfrac{g_2}{g_1}B_{21}u(\omega)\right) - \tfrac{g_2}{g_1}\left(A_{21} + B_{21}u(\omega)\right)}{\left(A_{21} + B_{21}u(\omega)\right)} = \frac{A_{10} - \tfrac{g_2}{g_1}A_{21}}{A_{21} + B_{21}u(\omega)}$$

$$\Rightarrow \Delta N = N_1\frac{A_{10} - \tfrac{g_2}{g_1}A_{21}}{A_{21} + B_{21}u(\omega)} = \frac{RN_0}{A_{10}}\frac{A_{10} - \tfrac{g_2}{g_1}A_{21}}{A_{21} + B_{21}u(\omega)}$$

If the spontaneous emission from level 1 to level 0 is much greater than that from level 2 to level 1 a population inversion can be maintained. If the degeneracy of the lower level is greater than that of the upper level, $g_1 > g_2$, it is easier to achieve $\Delta N > 0$, since $g_2 B_{21} = g_1 B_{12} \Rightarrow B_{21} > B_{12}$ and the stimulated $2 \to 1$ emission rate is greater than the stimulated $1 \to 2$ rate, giving rise to a net emission of power even though $N_2 < N_1$.

34 Spectroscopic Terms

2s3p Allowed values of L and S quantum numbers are $S = 0,1$ $L = 1$. Non-equivalent electrons, so all combinations of L and S are allowed, so terms are:

$$^1P_1,\ ^3P_{0,1,2}$$

(2p)^2 Equivalent electrons, so take $S = 0$ (antisymmetric) with symmetric spatial wavefunction $L = 0, 2$, or alternatively $S = 1$ (symmetric) with antisymmetric spatial wavefunction $L = 1$, so terms are:

$$^1S_0,\ ^1D_2,\ ^3P_{0,1,2}$$

(3d)^2 Equivalent electrons, so take $S = 0$ (antisymmetric) with symmetric spatial wavefunction $L = 0, 2, 4$, or alternatively $S = 1$ (symmetric) with antisymmetric spatial wavefunction $L = 1, 3$, so terms are:

$$^1S_0,\ ^1D_2,\ ^1G_4,\ ^3P_{0,1,2},\ ^3F_{2,3,4}$$

(3d)^{10} Completely filled shell, so $L = S = J = 0$, term is

$$^1S_0$$

(3d)^9 Shell has just one unoccupied state, so the values of L, S and J are just those for a single electron in the shell, i.e. $L = 2$, $S = \frac{1}{2}$ and the terms are

$$^2D_{\frac{3}{2},\frac{5}{2}}$$

(4f)^6 first Hund rule says maximise S, $\Rightarrow S = 3$. This spin state is totally symmetric with respect to interchange of electrons, so the spatial state must be totally antisymmetric. Hence the six electrons must occupy six different m_ℓ values out of the seven $(2\ell + 1)$ available. Hence the total M_L of the atom is $M_L = \pm 3, \pm 2, \pm 1, 0$, and so $L = 3$ is the only possibility. The shell is less than half full, so Hund's third rule says $J = |L - S| = 0$. The term is

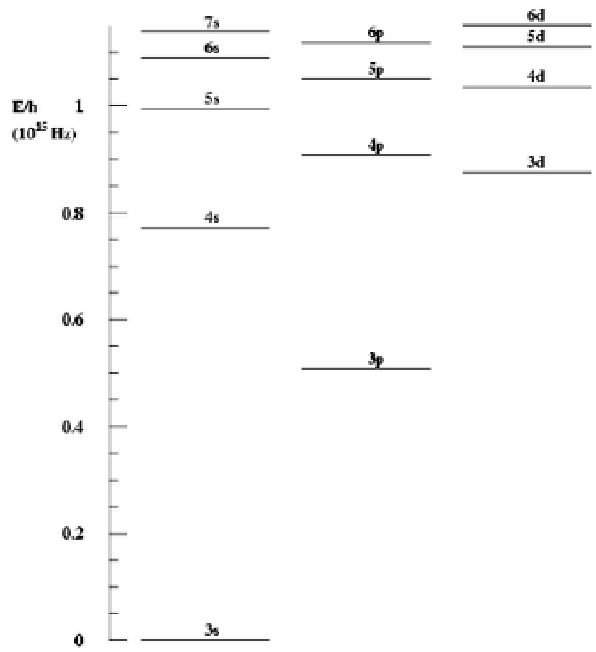
$$^7F_0$$

35 Single electron spectra

Answers to introductory questions:

- Sodium has a single electron outside closed shells. All the excited states involve excitation of this electron. Appropriate quantum numbers are ℓ, s and j (the quantum numbers for the whole atom being the same as for the unpaired electron. The allowed states for the electron are [3s (ground state), 3p, 3d], [4s, 4p, 4d, 4f], [5s, 5p, 5d, 5f, 5g] etc.
- The spin-orbit interaction splits each level into a doublet according to $j = \ell \pm \frac{1}{2}$, except for the s-states for which $j = \frac{1}{2}$ only.
- The spin-orbit effect decreases with n, since the electrons in higher energy levels see a smaller magnetic field, because the nucleus is better screened.
- Selection rules $\Delta J = \pm 1, 0$, parity change, $\Delta \ell = \pm 1$.

Doublets involve s$\leftrightarrow$p transitions. Those in group **II** all have the same doublet spacing, so they all involve the same p-state. They are likely to be 4s$\rightarrow$3p, 5s$\rightarrow$3p, 6s$\rightarrow$3p and 7s$\rightarrow$3p respectively. Those in group I are probably several p-states decaying to the same s-state. Note that the first one has the same splitting as group **II**. They are therefore likely to be 3p$\rightarrow$3s, 4p$\rightarrow$3s, 5p$\rightarrow$3s and 6p$\rightarrow$3s respectively, with spin-orbit splitting decreasing with n as expected. The group **III** triplets must involve d$\leftrightarrow$p or higher values of ℓ. The splittings are the same as in group **II**, telling us that 3p is involved again. They must be 3d$\rightarrow$3p, 4d$\rightarrow$3p, 5d$\rightarrow$3p and 6d$\rightarrow$3p. You can check with the Grotrian diagram in the lecture notes that your diagram looks about right with these assignments. It should look something like this:



(a) 5p$_{\frac{1}{2}}$, 5p$_{\frac{3}{2}}$ are involved in the transitions of frequency 1.05086 and $1.05079 \times 10^{15}\,Hz$, which differ by $7 \times 10^{10}\,Hz$. The energy splitting is thus $7 \times 10^{10} h = 4.6 \times 10^{-23}\,J = 0.29\,meV$.

(b) We expect the Sodium energy levels to converge to the Hydrogen levels for large n, and thus to scale like $1/n^2$. To test this, note that the ratio of the energy differences (6s-5s)/(7s-6s)=1.9, compared with the expected ratio $(\frac{1}{25} - \frac{1}{36})/(\frac{1}{36} - \frac{1}{49}) = 1.65$, which is not too bad. The energy difference between 7s and ionisation may be estimated as the energy difference between 7s and 6s (Planck's constant h times $0.049\,10^{15}$ Hz) times $(\frac{1}{49}-\frac{1}{\infty})/(\frac{1}{36}-\frac{1}{49})$, which yields $h\times 0.135\,10^{15}$ Hz. We add this to the energy difference between 7s and 3s, inferred from the sum of the $0.63142\,10^{15}$ Hz (7s$\to$3p) and $0.50899\,10^{15}$ Hz (3p$\to$3s) transitions to obtain $h\times 1.27\,10^{15}$ Hz, i.e. 5.2 eV. You could use other states instead in a similar way.

(c) The spin-orbit energy in the p-states can be estimated from the splittings of the corresponding doublets in group I. The Coulomb effect is given by the difference between the p- and s-levels for a given n. The ratios in the $n=3$ and $n=6$ cases are:

$$n=3: \quad \frac{spin-orbit}{coulomb}=\frac{0.00052}{0.51}=1.02\,10^{-3}$$

$$n=6: \quad \frac{spin-orbit}{coulomb}=\frac{0.00003}{0.028}=1.07\,10^{-3}$$

i.e. both effects decrease with n at about equal rates.

36 Atomic Spectra

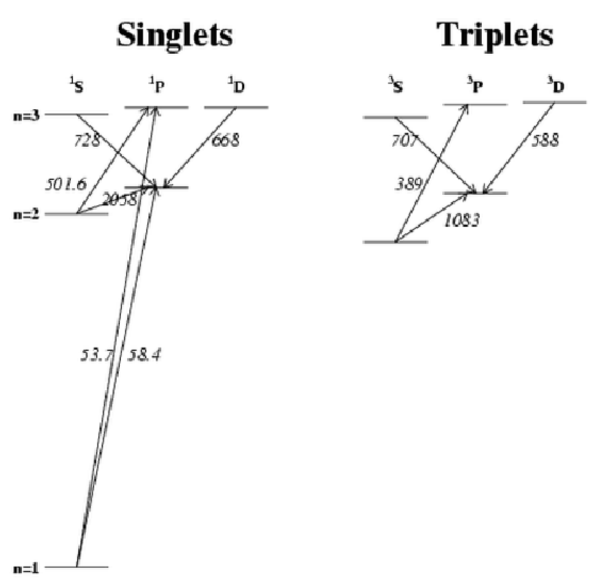
Selection rules in the electric dipole approximation:

Always valid	**in L-S Coupling regime**
Parity changes	$\Delta S = 0$
$\Delta J = \pm 1, 0$ not $(0 \to 0)$	$\Delta L = \pm 1, 0$
$\Delta M_J = \pm 1, 0$	$\Delta M_S = 0$
$\lvert \Delta \ell \rvert = \pm 1$ if only one electron involved	$\Delta M_L = \pm 1, 0$

Terms:

Configuration	**Singlets**	**Triplets**
$(1s)^2$	${}^1S_0$	
(1s)(2s)	${}^1S_0$	${}^3S_1$
(1s)(2p)	${}^1P_1$	${}^3P_{2,1,0}$
(1s)(3s)	${}^1S_0$	${}^3S_1$
(1s)(3p)	${}^1P_1$	${}^3P_{2,1,0}$
(1s)(3d)	${}^1D_2$	${}^3D_{3,2,1}$

Absorption spectrum will involve transitions starting from $(1s)^2$ only, so the two of lowest energy will be $1s \to 2p$ (${}^1P_1$) and $1s \to 3p$ (${}^1P_1$), corresponding to 58.4 nm and 53.7 nm respectively. If the atoms are excited by a discharge, they can get into any of the excited states. The two (1s)(2s) states are metastable, because the selection rules debar their decay, and hence a significant population will build up in these two states. The new absorption lines will start from these levels, so the singlets at 2058 and 501.6 nm are $2s \to 2p$ and $2s \to 3p$ in the singlet system. The multiplets at 1083 and 389 nm are $2s \to 2p$ and $2s \to 3p$ in the triplet system. The singlet emission lines not covered above are probably $3s \to 2p$ and $3d \to 2p$. The multiplet emission lines not covered above are likewise $3s \to 2p$ and $3d \to 2p$. The energy level diagram is therefore as shown below



Going to heavier atoms, Be, Mg, Ca, the same general picture should emerge, with the principal quantum numbers n increasing by one in each case. The relative importance of the spin-orbit interaction will increase with atomic number, meaning that the L-S coupling approximation may become less valid. In Ca, the ground state $(4s)^2$ has term ${}^1S_0$, and the first excited state (4s)(4p) has a singlet ${}^1P_1$ and a triplet ${}^3P_{2,1,0}$ term. Transition from the ground to the ${}^3P_{2,0}$ states are forbidden by the stringent ΔJ selection rule, but transition to ${}^3P_1$ is only forbidden by the weaker ΔS selection rule. The fact that this transition is seen tells us that the L-S coupling approximation is not terribly good in this case.

38 Zeeman effect

In the LS coupling regime we have

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i)\hat{\mathbf{L}}_{\mathbf{i}}\cdot\hat{\mathbf{S}}_{\mathbf{i}}}_{\hat{H}_2} \qquad \text{where} \quad \hat{H}_1 \gg \hat{H}_2$$

For the eigenstates of $\hat{H} \approx \hat{H}_0 + \hat{H}_1$, the Hamiltonian must commute with $\hat{\mathbf{J}}^2$ because of invariance under rotation, it also commutes with $\hat{\mathbf{S}}^2$. Since $\hat{H}_1$ only involves internal interactions and is invariant under rotation of all electrons then $\hat{H} \approx \hat{H}_0 + \hat{H}_1$ must commute with $\hat{\mathbf{L}}^2$. Given $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ we have $\hat{\mathbf{J}}^2 = \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + 2\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$ and eigenstates of $\hat{\mathbf{J}}^2$, $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$ are eigenstates of $\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$. So the energy levels are characterized by the quantum numbers L,S,J. and m_J .

Since $m_J = m_L + m_S$ and we only have one possible combination for $m_L + m_S = 3$ where $m_L = 2,\ m_S = 1,\ m_J = 3$ then we can write $\left|\phi_{L=2,S=1,J=3,m_J=3}\right\rangle = \left|\psi_{L=2,m_L=2}\right\rangle \left|\chi_{S=1,m_S=1}\right\rangle$.

Given:

$$\Delta E_{L,S,J,m_J} = \left\langle \phi_{L,S,J,m_J} \left| \frac{Be}{2m_e}\left(\hat{L}_z + 2\hat{S}_z\right) \right| \phi_{L,S,J,m_J} \right\rangle$$

$$= \frac{Be}{2m_e}\left[\left\langle \psi_{L=2,m_L=2}\left|\hat{L}_z\right|\psi_{L=2,m_L=2}\right\rangle + \left\langle \chi_{S=1,m_S=1}\left|2\hat{S}_z\right|\chi_{S=1,m_S=1}\right\rangle\right] = \frac{Be}{2m_e}\left[2\hbar + 2\hbar\right] = \underline{4\mu_B B}$$

Since $g = \frac{3}{2} - \frac{L(L+1) - S(S+1)}{2J(J+1)}$ we have $g = \frac{3}{2} - \frac{2(2+1) - 1(1+1)}{2.3(3+1)} = \frac{3}{2} - \frac{4}{24} = \frac{4}{3}$

$\Delta E = g\mu_B B m_J = \frac{4}{3}\mu_B B \times 3 = \underline{4\mu_B B}$ - so this is consistent.

Now: $\hat{J}_-\left|\phi_{L=2,S=1,J=3,m_J=3}\right\rangle = \left(\hat{L}_- + \hat{S}_-\right)\left|\psi_{L=2,m_L=2}\right\rangle\left|\chi_{S=1,m_S=1}\right\rangle$

since $\hat{L}_\pm\left|\psi_{L,m_L}\right\rangle = \hbar\sqrt{L(L+1) - m_L(m_L \pm 1)}\left|\psi_{L,m_L\pm 1}\right\rangle$ we can write

$$\hbar\sqrt{6}\left|\phi_{L=2,S=1,J=3,m_J=2}\right\rangle = \hbar\left[2\left|\psi_{L=2,m_L=1}\right\rangle\left|\chi_{S=1,m_S=1}\right\rangle + \sqrt{2}\left|\psi_{L=2,m_L=2}\right\rangle\left|\chi_{S=1,m_S=0}\right\rangle\right]$$

$$\left|\phi_{L=2,S=1,J=3,m_J=2}\right\rangle = \left[\sqrt{\frac{2}{3}}\left|\psi_{L=2,m_L=1}\right\rangle\left|\chi_{S=1,m_S=1}\right\rangle + \sqrt{\frac{1}{3}}\left|\psi_{L=2,m_L=2}\right\rangle\left|\chi_{S=1,m_S=0}\right\rangle\right]$$

So: $\Delta E_{2,1,3,2} = \frac{Be}{2m_e}\left[\frac{2}{3}\left(\hbar + 2\hbar\right) + \frac{1}{3}\cdot 2\hbar\right] = \underline{\frac{8}{3}\mu_B B}$ and calculating the g factor

$L = 2, S = 1, J = 3, m_J = 2,\ \ g = \frac{3}{2} - \frac{6-2}{24} = \frac{4}{3} \Rightarrow \Delta E = g\mu_B B m_J = \frac{4}{3}\mu_B B \times 2 = \underline{\frac{8}{3}\mu_B B}$,

Which is consistent with the previous calculation.

The orthogonal state:

$$\left|\phi_{L=2,S=1,J=3,m_J=2}\right\rangle = \left[\sqrt{\frac{1}{3}}\left|\psi_{L=2,m_L=1}\right\rangle\left|\chi_{S=1,m_S=1}\right\rangle - \sqrt{\frac{2}{3}}\left|\psi_{L=2,m_L=2}\right\rangle\left|\chi_{S=1,m_S=0}\right\rangle\right]$$

Which gives: $\Delta E_{2,1,2,2} = \dfrac{Be}{2m_e}\left[\dfrac{1}{3}(\hbar + 2\hbar) + \dfrac{2}{3}\cdot 2\hbar\right] = \underline{\dfrac{7}{3}\mu_B B}$

and $L = 2, S = 1, J = 2, m_J = 2,\ g = \dfrac{3}{2} - \dfrac{6-2}{12} = \dfrac{7}{6} \Rightarrow \Delta E = g\mu_B B m_J = \dfrac{7}{6}\mu_B B \times 2 = \underline{\dfrac{7}{3}\mu_B B}$

again consistent with previous calculation.

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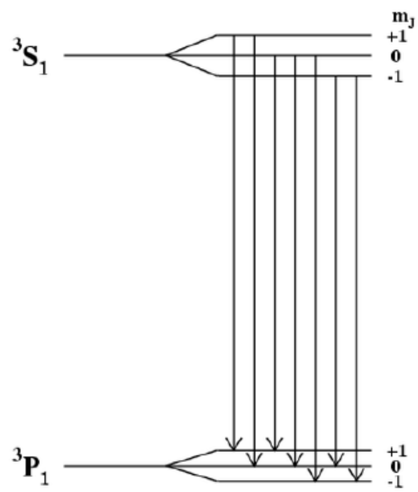
The $^3\mathrm{S}_1$ level has $g = 2$ and $^3\mathrm{P}_1$ level has $g = \frac{3}{2}$. Bearing in mind the selection rules, $\Delta M_J = \pm 1, 0$, the shifts in the energy levels are:

$$^3S_1\begin{cases} M_J & \Delta E \\ 1 & 2\mu_B B \\ 0 & 0 \\ -1 & -2\mu_B B \end{cases} \qquad ^3P_1\begin{cases} M_J & \Delta E \\ 1 & \frac{3}{2}\mu_B B \\ 0 & 0 \\ -1 & -\frac{3}{2}\mu_B B \end{cases}$$

and thus the shifts in the energies of the allowed transitions are

$\mathbf{M_J}$	**ΔE**
$1 \to 1$	$+\frac{1}{2}\mu_B B$
$1 \to 0$	$+2\mu_B B$
$0 \to 1$	$-\frac{3}{2}\mu_B B$
$0 \to 0$	0
$0 \to -1$	$+\frac{3}{2}\mu_B B$
$-1 \to 0$	$-2\mu_B B$
$-1 \to -1$	$-\frac{1}{2}\mu_B B$



The line therefore splits into seven components.
Viewing perpendicular to the magnetic field, all seven lines will be seen. The $\Delta M_J = 0$ lines correspond to dipoles parallel to the field, and thus the light will be plane polarised in the direction of the field; these will have energy shifts of $\pm\frac{1}{2}\mu_B B$ and zero. The $\Delta M_J = \pm 1$ lines correspond to dipoles perpendicular to the field, and thus the light will be plane polarised perpendicular to the field; these will have energy shifts of $\pm\frac{3}{2}\mu_B B$ and $\pm 2\mu_B B$.
If the $^3\mathrm{P}_1 \to {}^3\mathrm{S}_1$ transition is excited with circularly polarised light, the photons carry angular momentum $+\hbar$ along their direction of propagation, and hence only the $\Delta M_J = +1$ transitions are excited (or only $\Delta M_J = -1$ if the other sense of polarization is used). So only two transitions are possible, namely $-1 \to 0$ and $0 \to 1$.
In this process, only the $M_J = 1, 0$ sub-states of the $^3\mathrm{S}_1$ level get excited. Viewing the fluorescence along the magnetic field direction, only the $\Delta M_J = \pm 1$ transitions can be seen, of which those starting from the $M_J = 1, 0$ states are $1 \to 0$ and $0 \to -1$ (both circularly polarised) and $0 \to 1$ (with the opposite sense of circular polarisation).