NST Part II Physics Michaelmas Term 2022

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ADVANCED QUANTUM PHYSICS

Examples Sheet Solutions

1. **Operator methods and measurement**

(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 $E_1 \neq E_2$. Therefore

$$\langle\psi_1|\hat{H}|\psi_2\rangle = \int \psi_1^* \hat{H}\psi_2 \,\mathrm{d}x = \int \psi_1^* E_2 \psi_2 \,\mathrm{d}x = E_2\langle\psi_1|\psi_2\rangle \,.$$

Since $\hat{H}$ is Hermitian, the eigenvalues E_1 and E_2 are real, and we can write

$$\langle\psi_1|\hat{H}|\psi_2\rangle = \int (\hat{H}\psi_1)^* \psi_2 \,\mathrm{d}x = \int (E_1\psi_1)^* \psi_2 \,\mathrm{d}x = E_1^*\langle\psi_1|\psi_2\rangle = E_1\langle\psi_1|\psi_2\rangle \,.$$

Therefore $(E_1 - E_2)\langle\psi_1|\psi_2\rangle = 0$ and, if $E_1 \neq E_2$ we must have $\langle\psi_1|\psi_2\rangle = 0$.

(b) Adding and subtracting the relations $\hat{A}|\psi_1\rangle = |\psi_2\rangle$ and $\hat{A}|\psi_2\rangle = |\psi_1\rangle$ gives

$$\hat{A}(|\psi_1\rangle + |\psi_2\rangle) = |\psi_1\rangle + |\psi_2\rangle \,, \qquad \hat{A}(|\psi_1\rangle - |\psi_2\rangle) = -(|\psi_1\rangle - |\psi_2\rangle) \,.$$

Hence $\hat{A}$ has an eigenvalue $a = +1$ corresponding to a normalized eigenvector $(|\psi_1\rangle + |\psi_2\rangle)/\sqrt{2}$ and an eigenvalue $a = -1$ corresponding to eigenvector $(|\psi_1\rangle - |\psi_2\rangle)/\sqrt{2}$.

(c) The initial measurement of $\hat{A}$, giving the result $a = -1$, puts the system into the corresponding eigenstate of $\hat{A}$:

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}\big[|\psi_1\rangle - |\psi_2\rangle\big] \,.$$

The time-dependent Schrödinger equation is $\hat{H}\psi = E\psi = i\hbar(\partial\psi/\partial t)$; hence the eigenstates of $\hat{H}$ evolve with time dependence $e^{-iEt/\hbar}$. Thus the system evolves as

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left[|\psi_1\rangle e^{-iE_1 t/\hbar} - |\psi_2\rangle e^{-iE_2 t/\hbar}\right] \,.$$

The probability that a measurement of $\hat{A}$ again gives the result $a = -1$ is then

$$\begin{aligned} P(t) = |\langle\psi(0)|\psi(t)\rangle|^2 &= \frac{1}{4}\Big|\big[\langle\psi_1| - \langle\psi_2|\big]\left[|\psi_1\rangle e^{-iE_1 t/\hbar} - |\psi_2\rangle e^{-iE_2 t/\hbar}\right]\Big|^2 \\ &= \frac{1}{2}\big[1 + \cos((E_1 - E_2)t/\hbar)\big] = \cos^2((E_1 - E_2)t/2\hbar) \,. \end{aligned}$$

2. **Ladder operators**

(a) From the definitions of $\hat{a}$ and $\hat{a}^\dagger$, we have

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

Using $\langle n|\hat{a}|n\rangle = \sqrt{n}\langle n|n-1\rangle = 0$ and $\langle n|\hat{a}^\dagger|n\rangle = \sqrt{n+1}\langle n|n+1\rangle = 0$ then gives

$$\boxed{\langle n|\hat{x}|n\rangle = \langle n|\hat{p}|n\rangle = 0}.$$

(b) The expectation value of the potential $V(x) = (1/2)m\omega^2 x^2$ requires $\langle \hat{x}^2\rangle$:

$$\hat{x}^2 = \frac{\hbar}{2m\omega}(\hat{a} + \hat{a}^\dagger)^2 = \frac{\hbar}{2m\omega}(\hat{a}^2 + \hat{a}^{\dagger 2} + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}) \ ,$$

$$\begin{aligned}
\langle n|\hat{x}^2|n\rangle &= \frac{\hbar}{2m\omega}\langle n|(\hat{a}^2 + \hat{a}^{\dagger 2} + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a})|n\rangle \\
&= \frac{\hbar}{2m\omega}\left[\sqrt{n}\sqrt{n-1}\langle n|n-2\rangle + \sqrt{n+1}\sqrt{n+2}\langle n|n+2\rangle + (n+1)\langle n|n\rangle + n\langle n|n\rangle\right] \\
&= \frac{\hbar}{2m\omega}(2n+1) \ .
\end{aligned}$$

Hence

$$\langle n|V(\hat{x})|n\rangle = \frac{1}{2}m\omega^2\,\frac{\hbar}{2m\omega}(2n+1) = \frac{1}{2}(n+1/2)\hbar\omega \ .$$

(c) The uncertainties Δx and Δp are given by

$$(\Delta x)^2 \equiv \langle \hat{x}^2\rangle - \langle \hat{x}\rangle^2 = \frac{\hbar}{2m\omega}(2n+1) - 0 = \frac{\hbar}{2m\omega}(2n+1)$$

$$(\Delta p)^2 \equiv \langle \hat{p}^2\rangle - \langle \hat{p}\rangle^2 = \frac{m\hbar\omega}{2}(2n+1) - 0 = \frac{m\hbar\omega}{2}(2n+1)$$

Hence

$$\boxed{\Delta x \Delta p = \hbar(n+1/2)} \ .$$

3. **Heisenberg picture**

The time derivative of a Heisenberg picture operator $\hat{A}(t) \equiv e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}$ is

$$\frac{\mathrm{d}\hat{A}(t)}{\mathrm{d}t} = \frac{i\hat{H}}{\hbar}e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar} - e^{i\hat{H}t/\hbar}\hat{A}\frac{i\hat{H}}{\hbar}e^{-i\hat{H}t/\hbar} = \frac{i}{\hbar}e^{i\hat{H}t/\hbar}[H,A]e^{-i\hat{H}t/\hbar} \ ,$$

giving the equation of motion

$$\frac{\mathrm{d}\hat{A}(t)}{\mathrm{d}t} = \frac{i}{\hbar}[H,\hat{A}(t)] \ .$$

For the one-dimensional harmonic oscillator, the Hamiltonian is

$$\hat{H} = \left(\hat{a}^\dagger \hat{a} + \frac{1}{2}\right) \hbar\omega \ ,$$

where the ladder operators $\hat{a}$ and $\hat{a}^\dagger$ satisfy the commutation relation $[\hat{a}, \hat{a}^\dagger] = 1$. Therefore $[\hat{a}^\dagger \hat{a}, \hat{a}] = -\hat{a}$, and the commutator of the Hamiltonian with $\hat{a}$ is given by

$$[\hat{H}, \hat{a}] = -\hbar\omega \hat{a} \ .$$

Thus also

$$[\hat{H}, \hat{a}(t)] = -\hbar\omega \hat{a}(t) \ ,$$

and the Heisenberg equation of motion for $\hat{a}(t)$ is therefore

$$\frac{\mathrm{d}\hat{a}(t)}{\mathrm{d}t} = \frac{i}{\hbar}[\hat{H}, \hat{a}(t)] = -i\omega \hat{a}(t) \ .$$

We can integrate this to find that

$$\boxed{\hat{a}(t) = e^{-i\omega t}\hat{a}(0) \ , \qquad \hat{a}^\dagger(t) = e^{i\omega t}\hat{a}^\dagger(0)} .$$

From the definition of the ladder operators, the position operator is

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

This relation holds also for the operators in the Heisenberg picture. We have

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

For a more general Hamiltonian of the form

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) \ ,$$

the Heisenberg equation of motion gives

$$\frac{\mathrm{d}\hat{x}(t)}{\mathrm{d}t} = \frac{i}{\hbar}[\hat{H}, \hat{x}(t)] = \frac{i}{\hbar}\left[\frac{\hat{p}^2}{2m}, \hat{x}(t)\right] \ .$$

Repeatedly using $[\hat{x}, \hat{p}] = i\hbar$, the commutator $[\hat{p}^2, \hat{x}]$ is

$$[\hat{p}^2, \hat{x}] = \hat{p}\hat{p}\hat{x} - \hat{x}\hat{p}\hat{p} = \hat{p}(\hat{x}\hat{p} - i\hbar) - (i\hbar + \hat{p}\hat{x})\hat{p} = -2i\hbar\hat{p} \ .$$

Hence we again obtain

$$\boxed{\frac{\mathrm{d}\hat{x}(t)}{\mathrm{d}t} = \frac{\hat{p}(t)}{m}} \ .$$

4. **Addition of angular momenta**

(a) For the case $\ell_1 = 2$, $\ell_2 = 1$, the possible ways of forming each value of $M = m_1 + m_2$ can be tabulated as

M	(m_1, m_2)		
3	$(2,1)$		
2	$(2,0)$	$(1,1)$	
1	$(2,-1)$	$(1,0)$	$(0,1)$
0	$(1,-1)$	$(0,0)$	$(-1,1)$
-1	$(0,-1)$	$(-1,0)$	$(-2,1)$
-2	$(-1,-1)$	$(-2,0)$	
-3	$(-2,-1)$		

The largest value of M is $M = 3$, so the largest value of L must be $L = 3$. There must also be a state with $M = 2$ corresponding to $L = 3$, but the table contains two states with $M = 2$. Therefore there must be a state with $L = 2$ as well. We need two states with $M = 1$, one for each of the $L = 3, 2$ multiplets, but the table lists three states with $M = 1$, so there must be an $L = 1$ state as well. With $L = 3, 2, 1$, all of the M states are now accounted for.

For the case $\ell_1 = 3$, $\ell_2 = 1$, we can again form a table:

M	(m_1, m_2)		
4	$(3,1)$		
3	$(3,0)$	$(2,1)$	
2	$(3,-1)$	$(2,0)$	$(1,1)$
1	$(2,-1)$	$(1,0)$	$(0,1)$
0	$(1,-1)$	$(0,0)$	$(-1,1)$
-1	$(0,-1)$	$(-1,0)$	$(-2,1)$
-2	$(-1,-1)$	$(-2,0)$	$(-3,1)$
-3	$(-2,-1)$	$(-3,0)$	
-4	$(-3,-1)$		

Following the same logic as before, we see that sets of states with $L = 4, 3, 2$ just account for all the entries in the table.

(b) To construct the states explicitly, we start with the $|L, M\rangle = |3, 3\rangle$ state, which can be formed in only one way, viz. $|3, 3\rangle = |2, 2\rangle \otimes |1, 1\rangle$. Operating with the lowering operator $\hat{L}_- = (\hat{L}_1)_- + (\hat{L}_2)_-$, and recalling that

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

we then obtain

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

where the first term on the right hand side comes from lowering the $\ell_2 = 1$ state with $(\hat{L}_2)_-$ and the second from lowering the $\ell_1 = 2$ state with $(\hat{L}_1)_-$. Hence

$$\boxed{|3, 2\rangle = \sqrt{1/3}|2, 2\rangle \otimes |1, 0\rangle + \sqrt{2/3}|2, 1\rangle \otimes |1, 1\rangle}\,. \tag{1}$$

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

$$\boxed{|2,2\rangle = \sqrt{2/3}|2,2\rangle \otimes |1,0\rangle - \sqrt{1/3}|2,1\rangle \otimes |1,1\rangle}. \tag{2}$$

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

(c) The column headed $J = 3, M = +2$ in the 2×1 table of Clebsch-Gordan coefficients contains two entries, $1/3$ and $2/3$, corresponding to $\langle \ell_1 m_1; \ell_2 m_2 | JM \rangle = \langle 22; 10|32\rangle = \sqrt{1/3}$ and $\langle 21; 11|32\rangle = \sqrt{2/3}$, respectively. This is in agreement with equation (1) above.

The neighbouring column, headed $J = 2, M = +2$, contains entries $2/3$ and $-1/3$, corresponding to the Clebsch-Gordan coefficients $\langle 22; 10|22\rangle = \sqrt{2/3}$ and $\langle 21; 11|22\rangle = -\sqrt{1/3}$, respectively. This is in agreement with equation (2) above.

(d) The column headed $J = 1, M = -1$ in the 2×1 table gives the state $|J, M\rangle = |1, -1\rangle$ as

$$\boxed{|1,-1\rangle = \sqrt{\frac{1}{10}}|20\rangle|1,-1\rangle - \sqrt{\frac{3}{10}}|2,-1\rangle|10\rangle + \sqrt{\frac{3}{5}}|2,-2\rangle|11\rangle}. \tag{3}$$

(e) Expressing the operators $\hat{L}_x$ and $\hat{L}_y$ in terms of ladder operators as $\hat{L}_x = (1/2)(\hat{L}_+ + \hat{L}_-)$ and $\hat{L}_y = (1/2i)(\hat{L}_+ - \hat{L}_-)$, the scalar product $\hat{\boldsymbol{L}}_1 \cdot \hat{\boldsymbol{L}}_2$ can be written as

$$\begin{aligned}\hat{\boldsymbol{L}}_1 \cdot \hat{\boldsymbol{L}}_2 &= (\hat{L}_1)_x(\hat{L}_2)_x + (\hat{L}_1)_y(\hat{L}_2)_y + (\hat{L}_1)_z(\hat{L}_2)_z \\ &= \tfrac{1}{4}[(\hat{L}_1)_+ + (\hat{L}_1)_-][(\hat{L}_2)_+ + (\hat{L}_2)_-] - \tfrac{1}{4}[(\hat{L}_1)_+ - (\hat{L}_1)_-][(\hat{L}_2)_+ - (\hat{L}_2)_-] + (\hat{L}_1)_z(\hat{L}_2)_z \ .\end{aligned}$$

This tidies up to give the result required:

$$\boxed{\hat{\boldsymbol{L}}_1 \cdot \hat{\boldsymbol{L}}_2 = \tfrac{1}{2}(\hat{L}_1)_+(\hat{L}_2)_- + \tfrac{1}{2}(\hat{L}_1)_-(\hat{L}_2)_+ + (\hat{L}_1)_z(\hat{L}_2)_z}.$$

To verify that the linear combination of product states on the right-hand side of equation (3),

$$|\psi\rangle \equiv \sqrt{\frac{1}{10}}|20\rangle|1,-1\rangle - \sqrt{\frac{3}{10}}|2,-1\rangle|10\rangle + \sqrt{\frac{3}{5}}|2,-2\rangle|11\rangle \ , \tag{4}$$

truly is the total angular momentum state $|L, M\rangle = |1, -1\rangle$, we need to show that

$$(\hat{\boldsymbol{L}}_1 + \hat{\boldsymbol{L}}_2)^2|\psi\rangle = L(L+1)\hbar^2|\psi\rangle = 2\hbar^2|\psi\rangle \ , \tag{5}$$

$$\big((\hat{L}_1)_z + (\hat{L}_2)_z\big)|\psi\rangle = M\hbar|\psi\rangle = -\hbar|\psi\rangle \ . \tag{6}$$

The second of these, equation (6), follows immediately from the general property

$$\big((\hat{L}_1)_z + (\hat{L}_2)_z\big)|\ell_1 m_1\rangle|\ell_2 m_2\rangle = (m_1 + m_2)\hbar|\ell_1 m_1\rangle|\ell_2 m_2\rangle \ ,$$

together with the fact that all terms on the right-hand side of equation (4) have $m_1 + m_2 = -1$. Equation (5) can be verified by writing $(\hat{\boldsymbol{L}}_1 + \hat{\boldsymbol{L}}_2)^2 = \hat{\boldsymbol{L}}_1^2 + \hat{\boldsymbol{L}}_2^2 + 2\hat{\boldsymbol{L}}_1 \cdot \hat{\boldsymbol{L}}_2$ as

$$(\hat{\boldsymbol{L}}_1 + \hat{\boldsymbol{L}}_2)^2 = \hat{\boldsymbol{L}}_1^2 + \hat{\boldsymbol{L}}_2^2 + (\hat{L}_1)_+(\hat{L}_2)_- + (\hat{L}_1)_-(\hat{L}_2)_+ + 2(\hat{L}_1)_z(\hat{L}_2)_z \, .$$

Since all three terms on the right-hand side of equation (4) have $\ell_1 = 2$, $\ell_2 = 1$, we have

$$\hat{\boldsymbol{L}}_1^2|\psi\rangle = \ell_1(\ell_1+1)\hbar^2|\psi\rangle = 6\hbar^2|\psi\rangle$$
$$\hat{\boldsymbol{L}}_2^2|\psi\rangle = \ell_2(\ell_2+1)\hbar^2|\psi\rangle = 2\hbar^2|\psi\rangle \ .$$

Using $(\hat{L}_1)_z(\hat{L}_2)_z|\ell_1 m_1\rangle|\ell_2 m_2\rangle = m_1 m_2\hbar^2|\ell_1 m_1\rangle|\ell_2 m_2\rangle$, the $(\hat{L}_1)_z(\hat{L}_2)_z$ contribution is

$$(\hat{L}_1)_z(\hat{L}_2)_z|\psi\rangle = -2\sqrt{\frac{3}{5}}\hbar^2|2,-2\rangle|11\rangle \ .$$

Finally, applying products of ladder operators gives the non-zero contributions

$$(\hat{L}_1)_+(\hat{L}_2)_-|2,-1\rangle|10\rangle = \sqrt{6}\sqrt{2}\hbar^2|20\rangle|1,-1\rangle$$
$$(\hat{L}_1)_+(\hat{L}_2)_-|2,-2\rangle|11\rangle = 2\sqrt{2}\hbar^2|2,-1\rangle|10\rangle$$
$$(\hat{L}_1)_-(\hat{L}_2)_+|20\rangle|1,-1\rangle = \sqrt{6}\sqrt{2}\hbar^2|2,-1\rangle|10\rangle$$
$$(\hat{L}_1)_-(\hat{L}_2)_+|2,-1\rangle|10\rangle = 2\sqrt{2}\hbar^2|2,-2\rangle|11\rangle \ .$$

Summing the various contributions above then establishes equation (5).

(f) For each table, the absolute values of the entries in each row or column (ie the moduli-squared of the Clebsch-Gordan coefficients) sum to unity. Also, remembering to take the signed square root of each table entry, each pair of rows in the table is orthogonal, as is each pair of columns. Hence each table corresponds to a unitary matrix of Clebsch-Gordan coefficients, $UU^\dagger = I$. In the standard convention, the Clebsch-Gordan coefficients are all real, so the matrix is in fact orthogonal: $UU^T = I$.

For the tables $(1/2)\otimes(1/2)$, $1\otimes 1$, $(3/2)\otimes(3/2)$, $2\otimes 2$, the coefficients in each column $|j,m\rangle$ are the same for the rows (m_1,m_2) and (m_2,m_1), except possibly for a change in sign. The relative sign gives the symmetry of the $|j,m\rangle$ state under interchange $1\leftrightarrow 2$.

For $(1/2)\otimes(1/2)$, the states are symmetric for $j=1$ and antisymmetric for $j=0$.

For $1\otimes 1$, the states are symmetric for $j=2,0$ and antisymmetric for $j=1$.

For $(3/2)\otimes(3/2)$, the states are symmetric for $j=3,1$ and antisymmetric for $j=2,0$.

For $2\otimes 2$, the states are symmetric for $j=4,2,0$ and antisymmetric for $j=3,1$.

In general, the $j_1\leftrightarrow j_2$ exchange symmetry is given by $(-1)^{J-j_1-j_2}$. This quantity appears in the box about half-way down the right-hand side of the page of Clebsch-Gordan coefficient tables.

5. **Matrix methods**

The basis states $|\phi_1\rangle = |Y_{11}\rangle$, $|\phi_0\rangle = |Y_{10}\rangle$, $|\phi_{-1}\rangle = |Y_{1,-1}\rangle$ are eigenstates of $\hat{L}_z$, with eigenvalues $+\hbar$, 0, $-\hbar$. Therefore the matrix representation of $\hat{L}_z$ is diagonal:

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

The ladder operators $\hat{L}_\pm$ act on the basis states as

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

from which we can straightforwardly obtain the matrix representations

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

From these we can infer

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

Using these results, the operator

$$\hat{H} = \frac{\hat{L}_x^2}{2I_x} + \frac{\hat{L}_y^2}{2I_y} + \frac{\hat{L}_z^2}{2I_z}$$

can then be written in matrix form as

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

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:

$$\begin{array}{ccc} \frac{\hbar^2}{2}\left(\frac{1}{I_x} + \frac{1}{I_y}\right) & \frac{\hbar^2}{2}\left(\frac{1}{I_x} + \frac{1}{I_z}\right) & \frac{\hbar^2}{2}\left(\frac{1}{I_y} + \frac{1}{I_z}\right) \\ \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} & \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} & \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \end{array}$$

6. **Spin**

The spin operator in the (θ, ϕ) direction, $\hat{\boldsymbol{S}}_{\theta\phi}$, can be found by forming the scalar product $\hat{\boldsymbol{S}} \cdot \boldsymbol{n}$ of the spin operator $\hat{\boldsymbol{S}}$ with a unit vector $\boldsymbol{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ in the (θ, ϕ) direction. In the basis of states $|\uparrow\rangle_z$, $|\downarrow\rangle_z$, the operator $\hat{\boldsymbol{S}}$ has matrix representation $\hat{\boldsymbol{S}} = (\hbar/2)\boldsymbol{\sigma}$, where the σ_i are the Pauli matrices. Therefore

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

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

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

Eliminating u and v, we find $\lambda^2=1$ and hence the eigenvalues of $\hat{\boldsymbol{S}}_{\theta\phi}$ are $\pm\hbar/2$, as expected. Substituting the values $\lambda=\pm1$ back into the equations relating u and v, we can infer the ratios, $u/v=e^{-i\phi}\cot(\theta/2)$ and $-e^{-i\phi}\tan(\theta/2)$. So, in matrix notation, the eigenstates are

$$|\uparrow\rangle_{\theta\phi}=\begin{pmatrix}\cos(\theta/2)\\ e^{i\phi}\sin(\theta/2)\end{pmatrix},\qquad |\downarrow\rangle_{\theta\phi}=\begin{pmatrix}\sin(\theta/2)\\ -e^{i\phi}\cos(\theta/2)\end{pmatrix},$$

(up to multiplication by arbitrary overall phases) for eigenvalues $+\hbar/2$ and $-\hbar/2$ respectively.

The spin states in the x-direction are obtained by setting $\theta=\pi/2$, $\phi=0$:

$$|\uparrow\rangle_x=\frac{1}{\sqrt2}\begin{pmatrix}1\\1\end{pmatrix}=\frac{1}{\sqrt2}\big(|\uparrow\rangle_z+|\downarrow\rangle_z\big),\qquad |\downarrow\rangle_x=\frac{1}{\sqrt2}\begin{pmatrix}1\\-1\end{pmatrix}=\frac{1}{\sqrt2}\big(|\uparrow\rangle_z-|\downarrow\rangle_z\big).$$

The spin states in the y-direction are obtained by setting $\theta=\pi/2$, $\phi=\pi/2$:

$$|\uparrow\rangle_y=\frac{1}{\sqrt2}\begin{pmatrix}1\\i\end{pmatrix}=\frac{1}{\sqrt2}\big(|\uparrow\rangle_z+i|\downarrow\rangle_z\big),\qquad |\downarrow\rangle_y=\frac{1}{\sqrt2}\begin{pmatrix}1\\-i\end{pmatrix}=\frac{1}{\sqrt2}\big(|\uparrow\rangle_z-i|\downarrow\rangle_z\big).$$

7. **Perturbation theory**

From Gauss' theorem, the potential due to a hollow spherical shell of radius b carrying charge $+e$ is $V(r)=-e^2/4\pi\epsilon_0 r$ in the region $r>b$, and $V(r)=V(b)$ in the region $r<b$. Compared to a pointlike charge $+e$, the effect can be regarded as adding a perturbation

$$\hat H'=\begin{cases}\dfrac{e^2}{4\pi\epsilon_0}\left(\dfrac1r-\dfrac1b\right) & (r<b)\\ 0 & (r>b)\end{cases}.$$

For the $2s$ state, the energy shift induced by the perturbation $\hat H'$ is

$$(\Delta E)_{2s}=\langle 2\mathrm{s}|\hat H'|2\mathrm{s}\rangle=\frac{1}{8\pi a_0^3}\frac{e^2}{4\pi\epsilon_0}\int_0^b 4\pi r^2\,\mathrm{d}r\left(\frac1r-\frac1b\right)\left(1-\frac{r}{2a_0}\right)^2 e^{-r/a_0}.$$

Since $b\ll a_0$, the terms involving r/a_0 are negligible throughout the region of integration $0<r<b$, so we can simplify the integral to

$$(\Delta E)_{2s}=\frac{e^2}{8\pi\epsilon_0 a_0^3}\int_0^b r^2\,\mathrm{d}r\left(\frac1r-\frac1b\right)=\frac{b^2}{6a_0^2}R_\infty,\qquad R_\infty=\frac{e^2}{8\pi\epsilon_0 a_0}.$$

Likewise, for the $2p_0$ state, making the same approximation, we obtain

$$(\Delta E)_{2p_0}=\frac{e^2}{128\pi^2\epsilon_0 a_0^5}\int_0^b r^4\left(\frac1r-\frac1b\right)\mathrm{d}r\int_{-1}^{+1}\mathrm{d}\cos\theta\,2\pi\cos^2\theta=\frac{b^4}{240a_0^4}R_\infty.$$

The energy correction for the $2p_{\pm1}$ states is the same as for the $2p_0$ state:

$$(\Delta E)_{2p_{\pm1}} = \frac{e^2}{256\pi^2\epsilon_0 a_0^5}\int_0^b r^4\left(\frac{1}{r}-\frac{1}{b}\right)\,\mathrm{d}r\int_{-1}^{+1}\mathrm{d}\cos\theta\,2\pi\sin^2\theta = \frac{b^4}{240a_0^4}R_\infty\,.$$

A common energy correction for all the $2p_m$ states is to be expected; the perturbation $\hat{H}'$ is isotropic, so the energy shift cannot depend on a quantum number such as m whose definition depends on a particular choice of quantisation axis (the z-axis).

The states $\{2s,\ 2p_0,\ 2p_{\pm1}\}$ are degenerate in energy, $E = -R_\infty/4$, so we really need to use degenerate perturbation theory. However it is easy to see that the matrix representation of $\hat{H}'$ in the basis of states $\{2s,\ 2p_0,\ 2p_{+1},\ 2p_{-1}\}$ is diagonal just by considering the angular components of the matrix elements of $\hat{H}'$. The angular component of each 2s or 2p wavefunction is a spherical harmonic, Y_{00} or Y_{1m}, but the operator $\hat{H}'$ is independent of angle. Orthogonality of the spherical harmonics then ensures that all the off-diagonal matrix elements, $\langle 2p_0|\hat{H}'|2s\rangle$, $\langle 2p_{\pm1}|\hat{H}'|2s\rangle$, $\langle 2p_{\pm1}|\hat{H}'|2p_0\rangle$ and $\langle 2p_{+1}|\hat{H}'|2p_{-1}\rangle$, are zero. The energy corrections are therefore given simply by the diagonal matrix elements of $\hat{H}'$, as above.

The 2s energy shift is small, of order $(b/a_0)^2$, but the 2p energy shift is even smaller, of order $(b/a_0)^4$. This is because the 2p wavefunction vanishes at the origin (where the perturbation is) whereas the 2s wavefunction remains finite.

For light atoms, trying to measure these small energy shifts is not a good method to explore the nucleus because other effects, such as spin-orbit interactions and relativistic corrections swamp the nuclear size effect. Measuring the energy shifts is a more effective method for heavy atoms, due to the larger nuclear radius and smaller Bohr radius, and is especially effective for "muonic" atoms, where the greater mass of the muon reduces the Bohr radius by a factor ~ 200.

8. **Perturbation Theory: Polarizability of Hydrogen**

If, without loss of generality, we take the electric field to lie along z, the perturbation is given by $\hat{H}' = eEz$. At first-order in perturbation theory, $\Delta E = \langle 0|eEz|0\rangle$ vanishes since the ground state of the hydrogen atom $|0\rangle$ is an eigenstate of parity. The leading contribution to ΔE is therefore the second order term

$$\Delta E = \sum_{k\neq0}\frac{|\langle k|eEz|0\rangle|^2}{E_0 - E_k}\,.$$

If the induced dipole moment is $\boldsymbol{d} = \alpha\epsilon_0\boldsymbol{E}$, its energy of interaction with the electric field is given by $\Delta E = -\frac{1}{2}\boldsymbol{d}\cdot\boldsymbol{E} = -\frac{1}{2}\alpha\epsilon_0 E^2$. Comparing with the perturbation theory result above then gives the polarisibility as

$$\boxed{\alpha = \frac{2e^2}{\epsilon_0}\sum_{k\neq0}\frac{|\langle k|z|0\rangle|^2}{E_k - E_0}}\,.$$

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

$$|\psi\rangle = |0\rangle + \sum_{k\neq0}\frac{\langle k|eEz|0\rangle}{E_0 - E_k}|k\rangle\,.$$

The dipole moment operator for the electron is $-ez$, and the expectation value in this state is

$$\langle\psi|ez|\psi\rangle = \langle 0|ez|0\rangle + \sum_{k\neq 0}\left[\frac{\langle k|eEz|0\rangle}{E_0 - E_k}\langle 0|ez|k\rangle + \frac{\langle k|eEz|0\rangle^*}{E_0 - E_k}\langle k|ez|0\rangle\right] + \mathcal{O}(E^2)\,.$$

The first term on the right-hand side above vanishes, giving

$$\langle\psi|ez|\psi\rangle = 2E\sum_{k\neq 0}\frac{|\langle k|eEz|0\rangle|^2}{E_0 - E_k} + \mathcal{O}(E^2)\,.$$

Comparing with $\langle\psi|-ez|\psi\rangle \equiv \alpha\epsilon_0 E$, the value of the polarisibilty α follows as before.

Since $E_k \geq E_1$ for all k, we obtain

$$\alpha \leq \frac{2e^2}{\epsilon_0}\sum_{k\neq 0}\frac{|\langle k|z|0\rangle|^2}{E_1 - E_0} = \frac{2e^2}{\epsilon_0}\sum_{k\neq 0}\frac{\langle 0|z|k\rangle\langle k|z|0\rangle}{E_1 - E_0} = \frac{2e^2}{\epsilon_0}\frac{\langle 0|z^2|0\rangle}{E_1 - E_0}\,,$$

where we have used the completeness relation $\hat{I} = \sum_k |k\rangle\langle k|$ in the last step. Note that the completeness relation sum includes a $k = 0$ term, but this doesn't contribute because $\langle 0|z|0\rangle = 0$. Using the explicit form for the hydrogen ground state, $|0\rangle = (\pi a_0^3)^{-1/2}e^{-r/a_0}$, we obtain

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

We also need the energy difference,

$$E_1 - E_0 = \left(1 - \frac{1}{4}\right)R_\infty = \frac{3}{4}\frac{e^2}{8\pi\epsilon_0 a_0}\,,$$

from which we obtain $\alpha \leq 64\pi a_0^3/3 = 9.9\times 10^{-30}\,\mathrm{m}^3$, not too far from experiment.

9. **Degenerate perturbation theory**

(a) For $\lambda = 0$, the Hamiltonian separates into two independent components,

$$\hat{H}^{(0)} = \hat{H}_x^{(0)} + \hat{H}_y^{(0)}\ ,$$

each of which is a 1D harmonic oscillator of angular frequency ω. Introducing ladder operators for x and y, the Hamiltonian can be written as

$$\hat{H}^{(0)} = \hbar\omega\left(\hat{a}_x^\dagger\hat{a}_x + \hat{a}_y^\dagger\hat{a}_y + 1\right)\ .$$

The overall eigenstates of $\hat{H}^{(0)}$ are products $|n_x, n_y\rangle \equiv |n_x\rangle|n_y\rangle$ of the individual eigenstates $|n_x\rangle$ and $|n_y\rangle$ of $\hat{H}_x^{(0)}$ and $\hat{H}_y^{(0)}$:

$$\hat{H}^{(0)}|n_x, n_y\rangle = (\hat{H}_x^{(0)} + \hat{H}_y^{(0)})|n_x\rangle|n_y\rangle = (E_x + E_y)|n_x\rangle|n_y\rangle = (E_x + E_y)|n_x, n_y\rangle\ ,$$

where $E_x = (n_x + 1/2)\hbar\omega$ and $E_y = (n_y + 1/2)\hbar\omega$. Hence the eigenvalues of $\hat{H}^{(0)}$ are

$$\boxed{E^{(0)}_{(n_x,n_y)} = (n_x + n_y + 1)\hbar\omega}\,.$$

(b) The unperturbed spectrum is

$E^{(0)}_0 = \hbar\omega$ with one state: $|n_x\rangle|n_y\rangle = |0\rangle|0\rangle$
$E^{(0)}_1 = 2\hbar\omega$ with two states: $|n_x\rangle|n_y\rangle = |1\rangle|0\rangle, |0\rangle|1\rangle$
$E^{(0)}_2 = 3\hbar\omega$ with three states: $|n_x\rangle|n_y\rangle = |2\rangle|0\rangle, |1\rangle|1\rangle, |0\rangle|2\rangle$.

(c) The perturbation is

$$\hat{H}' = \lambda\hat{x}\hat{y} = \lambda\frac{\hbar}{2m\omega}\left(\hat{a}^\dagger_x + \hat{a}_x\right)\left(\hat{a}^\dagger_y + \hat{a}_y\right)\,.$$

For the unperturbed 2-fold degenerate level with $E^{(0)}_1 = 2\hbar\omega$, in the basis $\{|1,0\rangle, |0,1\rangle\}$, the perturbation has matrix representation

$$H' = \begin{pmatrix} H'_{11} & H'_{12} \\ H'_{21} & H'_{22} \end{pmatrix} = \lambda\begin{pmatrix} \langle 1,0|\hat{x}\hat{y}|1,0\rangle & \langle 1,0|\hat{x}\hat{y}|0,1\rangle \\ \langle 0,1|\hat{x}\hat{y}|1,0\rangle & \langle 0,1|\hat{x}\hat{y}|0,1\rangle \end{pmatrix}\,.$$

Each matrix element factorises into separate x and y matrix element components:

$$H' = \lambda\begin{pmatrix} \langle 1|\hat{x}|1\rangle\langle 0|\hat{y}|0\rangle & \langle 1|\hat{x}|0\rangle\langle 0|\hat{y}|1\rangle \\ \langle 0|\hat{x}|1\rangle\langle 1|\hat{y}|0\rangle & \langle 0|\hat{x}|0\rangle\langle 1|\hat{y}|1\rangle \end{pmatrix}\,.$$

The only non-zero components are

$$\langle 1|\hat{x}|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}\big(\langle 1|\hat{a}_x|0\rangle + \langle 1|\hat{a}^\dagger_x|0\rangle\big) = \sqrt{\frac{\hbar}{2m\omega}} = \langle 0|\hat{x}|1\rangle\,,$$

and similarly for y. Hence

$$H' = \lambda\frac{\hbar}{2m\omega}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\,.$$

The first-order energy corrections are given by the eigenvalues of H'. The zeroth-order eigenstates which should be used in perturbation theory are given by the eigenstates of $\hat{H}'$. Thus the first-order energy corrections and zeroth-order eigenstates are

$$\boxed{\Delta E^{(1)}_1 = \pm\frac{\lambda\hbar}{2m\omega}\,; \qquad |\phi^{(0)}_\pm\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\big(|1,0\rangle \pm |0,1\rangle\big)}\,.$$

In perturbation theory, the first-order eigenstate corresponding to the unperturbed eigenstate $|n^{(0)}\rangle$ is obtained as

$$|n^{(0)}\rangle + \sum_{E^{(0)}_m \neq E^{(0)}_n} |m^{(0)}\rangle\frac{\langle m^{(0)}|\hat{H}'|n^{(0)}\rangle}{E^{(0)}_n - E^{(0)}_m}\,.$$

Thus the first-order eigenstates corresponding to the unperturbed (zeroth-order) eigenstates $|\phi_\pm^{(0)}\rangle$, both with unperturbed energy $2\hbar\omega$, are

$$|\phi_\pm^{(0)}\rangle + \sum_{(n_x+n_y)\neq 1} |n_x, n_y\rangle \frac{\langle n_x, n_y|\lambda\hat{x}\hat{y}|\phi_\pm^{(0)}\rangle}{2\hbar\omega - E^{(0)}_{(n_x,n_y)}} \ .$$

Substituting for $|\phi_\pm^{(0)}\rangle$, the matrix element in the numerator is

$$\frac{\lambda}{\sqrt{2}}\big(\langle n_x, n_y|\hat{x}\hat{y}|1,0\rangle \pm \langle n_x, n_y|\hat{x}\hat{y}|0,1\rangle\big) = \frac{\lambda}{\sqrt{2}}\big(\langle n_x|\hat{x}|1\rangle\langle n_y|\hat{y}|0\rangle \pm \langle n_x|\hat{x}|0\rangle\langle n_y|\hat{y}|1\rangle\big) \, .$$

Expressing $\hat{x}$ and $\hat{y}$ in terms of ladder operators shows that the only non-zero contributions to the sum, with $n_x + n_y \neq 1$, come from the terms with $(n_x, n_y) = (2,1)$ or $(1,2)$, with unperturbed energy $E^{(0)}_{2,1} = E^{(0)}_{1,2} = 4\hbar\omega$:

$$|\phi_\pm^{(0)}\rangle \to |\phi_\pm^{(0)}\rangle + |2,1\rangle \frac{\lambda}{\sqrt{2}} \frac{\langle 2|\hat{x}|1\rangle\langle 1|\hat{y}|0\rangle}{2\hbar\omega - 4\hbar\omega} \pm |1,2\rangle \frac{\lambda}{\sqrt{2}} \frac{\langle 1|\hat{x}|0\rangle\langle 2|\hat{y}|1\rangle}{2\hbar\omega - 4\hbar\omega} \ .$$

Using

$$\langle 2|\hat{x}|1\rangle = \sqrt{\frac{\hbar}{2m\omega}}\big(\langle 2|\hat{a}_x|1\rangle + \langle 2|\hat{a}_x^\dagger|1\rangle\big) = \sqrt{\frac{\hbar}{m\omega}} \ ,$$

and similarly for y, then gives the first-order eigenstates as

$$\boxed{|\phi_\pm^{(0)}\rangle - \frac{\lambda}{4m\omega^2}\big(|2\rangle|1\rangle \pm |1\rangle|2\rangle\big)}$$

10. **Variational method**

From the trial wavefunction, we can obtain A from the normalization,

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

Using the identity

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

the expectation value of the Hamiltonian is given by

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

Minimising with respect to a we obtain $a^2 = (35/2)^{1/2}(\hbar/m\omega)$. Substituting this value of a into our expression for $\langle\psi|\hat{H}|\psi\rangle$, we obtain an upper bound on the ground state energy,

$$\boxed{\langle\psi|\hat{H}|\psi\rangle = \sqrt{(5/14)}\hbar\omega = 0.598\hbar\omega},$$

which is greater than the true ground state energy $\hbar\omega/2$, as expected.

11. **Variational method**

(a) Suppose that the two Hamiltonians are $\hat{H}_1$ and $\hat{H}_2$ with ground state wavefunctions ψ_1 and ψ_2, i.e. $\hat{H}_1\psi_1 = E_1\psi_1$, and $\hat{H}_2\psi_2 = E_2\psi_2$. We have $\hat{H}_1 = \hat{H}_2 - V_2(\boldsymbol{r}) + V_1(\boldsymbol{r}) = \hat{H}_2 + \Delta V(\boldsymbol{r})$, where $\Delta V(\boldsymbol{r}) \leq 0$ since $V_1(\boldsymbol{r}) \leq V_2(\boldsymbol{r})$. From the variational principle, we then obtain

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

Thus $E_1 \leq E_2$ if $V_1(\boldsymbol{r}) \leq V_2(\boldsymbol{r})$.

(b) The trial wavefunction $\psi(x) = Ae^{-\lambda x^2}$ can be normalised using a standard integral as

$$1 = |A|^2 \int_{-\infty}^{+\infty} e^{-2\lambda x^2}\,\mathrm{d}x = |A|^2\sqrt{\frac{\pi}{2\lambda}}\,,$$

giving $\psi(x) = (2\lambda/\pi)^{1/4}e^{-\lambda x^2}$. The Hamiltonian is $\hat{H} = -(\hbar^2/2m)(\mathrm{d}^2/\mathrm{d}x^2) + V(x)$. Using $\psi''(x) = 4\lambda^2x^2\psi(x) - 2\lambda\psi(x)$, and the standard integral

$$\int_{-\infty}^{+\infty} x^2 e^{-2\lambda x^2}\,\mathrm{d}x = \frac{1}{4\lambda}\sqrt{\frac{\pi}{2\lambda}}\,,$$

we obtain

$$\langle\psi|\hat{H}|\psi\rangle = \frac{\hbar^2}{2m}\lambda + \sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{\infty} V(x)e^{-2\lambda x^2}\,\mathrm{d}x \equiv \frac{\hbar^2}{2m}\lambda + I(\lambda)\,. \tag{7}$$

Minimising with respect to λ, we obtain,

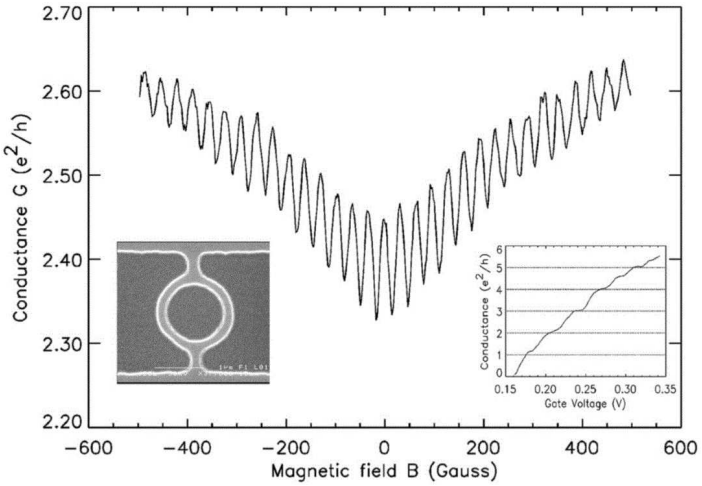
$$0 = \frac{\hbar^2}{2m} + \frac{I(\lambda)}{2\lambda} + \sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{+\infty} V(x)(-2x^2)e^{-2\lambda x^2}\,\mathrm{d}x\,,$$

where the second term arises from differentiating the normalization in $I(\lambda)$, and the third term from differentiating the integrand. Solving for $I(\lambda)$ and substituting back into equation (7), we obtain

$$\langle\psi|\hat{H}|\psi\rangle = -\frac{\hbar^2}{2m}\lambda + 2\lambda\sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{+\infty} V(x)(2x^2)e^{-2\lambda x^2}\,\mathrm{d}x\,.$$

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

12. **Aharonov-Bohm effect**



Electron waves that pass on either side of the ring produce constructive/destructive interference that is periodic in the flux BS through the ring (of area S). Following the discussion of the Aharanov-Bohm effect in lectures, the phase difference accumulated is

$$\Delta\phi = \frac{e}{\hbar} BS \ ,$$

so a period 2π in the phase translates to a period of $2\pi\hbar/e = h/e$ in the flux. The interference leads to oscillations in the conductance with field B, with period

$$\Delta B = \frac{h}{eS} \ .$$

Hence the area S and diamater d of the ring are given by

$$S = \frac{h}{e(\Delta B)} = \pi(d/2)^2 \ , \qquad d = 2\sqrt{\frac{h}{\pi e(\Delta B)}} \ .$$

From the graph, there are 12.5 oscillations in 400 Gauss (= 0.04 T), which gives

$$\Delta B = 3.2 \times 10^{-3}\,\mathrm{T/osc.} \ , \qquad d = 2\sqrt{\frac{h}{\pi e(\Delta B)}} = 1.28 \times 10^{-6}\,\mathrm{m} \ .$$

The results agree well with the value 0.65×10^{-6} m for the radius of the ring quoted in the paper.

13. **Spin precession (Tripos 1999)**

The Hamiltonian for the interaction between a magnetic moment $\hat{\boldsymbol{\mu}}$ and a magnetic field $\boldsymbol{B}$ is

$$\hat{H} = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{B} = -\gamma \hat{\boldsymbol{S}} \cdot \boldsymbol{B} = -\gamma \frac{\hbar}{2} \hat{\boldsymbol{\sigma}} \cdot \boldsymbol{B}$$

Substituting into the time-dependent Schrödinger equation we have

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

For $\boldsymbol{B} = (0, 0, B_0)$, we have

$$-\frac{1}{2}\gamma B_0 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} a(t) \\ b(t) \end{pmatrix} = i\frac{\partial}{\partial t} \begin{pmatrix} a(t) \\ b(t) \end{pmatrix} \ ,$$

with solutions

$$a(t) = A\exp(i\omega_0 t/2) \ , \qquad b(t) = B\exp(-i\omega_0 t/2) \ .$$

Normalise by setting $A = \cos(\theta/2)$, $B = \sin(\theta/2)$, giving

$$|\psi(t)\rangle = \cos(\theta/2)\exp(i\omega_0 t/2)|\uparrow\rangle + \sin(\theta/2)\exp(-i\omega_0 t/2)|\downarrow\rangle \ .$$

The expectation value of μ_x is

$$\begin{aligned} \langle\mu_x\rangle &= \gamma\frac{\hbar}{2}\begin{pmatrix} a^* & b^* \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \gamma\frac{\hbar}{2}(a^*b + b^*a) \\ &= \gamma\frac{\hbar}{2}\cos(\theta/2)\sin(\theta/2)\left[\exp(-i\omega_0 t) + \exp(i\omega_0 t)\right] = \gamma\frac{\hbar}{2}\sin\theta\cos(\omega_0 t) \ . \end{aligned}$$

Similarly,

$$\langle\mu_y\rangle = -\gamma\frac{\hbar}{2}\sin\theta\sin(\omega_0 t) \, ; \qquad \langle\mu_z\rangle = \gamma\frac{\hbar}{2}\cos\theta \, .$$

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

For a general field $\boldsymbol{B}(t)$,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{\boldsymbol{\mu}}\rangle = \frac{i}{\hbar}\langle[-\gamma\hat{\boldsymbol{S}}\cdot\boldsymbol{B}, \hat{\boldsymbol{\mu}}]\rangle = \frac{i\gamma^2}{\hbar}\langle\hat{\boldsymbol{S}}(\hat{\boldsymbol{S}}\cdot\boldsymbol{B}) - (\hat{\boldsymbol{S}}\cdot\boldsymbol{B})\hat{\boldsymbol{S}}\rangle \, .$$

In particular, for the x component,

$$\begin{aligned} \hat{S}_x(\hat{\boldsymbol{S}}\cdot\boldsymbol{B}) - (\hat{\boldsymbol{S}}\cdot\boldsymbol{B})\hat{S}_x &= (\hat{S}_x\hat{S}_y - \hat{S}_y\hat{S}_x)B_y + (\hat{S}_x\hat{S}_z - \hat{S}_z\hat{S}_x)B_z \\ &= (i\hbar\hat{S}_z)B_y + (-i\hbar\hat{S}_y)B_z = -i\hbar(\hat{\boldsymbol{S}}\wedge\boldsymbol{B})_x \, , \end{aligned}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\mu_x\rangle = \frac{i\gamma^2}{\hbar}\times -i\hbar\langle(\hat{\boldsymbol{S}}\wedge\boldsymbol{B})_x\rangle = \gamma^2\langle(\hat{\boldsymbol{S}}\wedge\boldsymbol{B})_x\rangle \, .$$

The same result must apply also to the y and z components, giving

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{\boldsymbol{\mu}}\rangle = \gamma\langle\hat{\boldsymbol{\mu}}\wedge\boldsymbol{B}(t)\rangle} \, .$$

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

14. **Proton magnetic moment**

Taking as a basis the states of the $\hat{S}_z$ operator, we can deduce the form of the $\hat{S}_x$ operator most easily from the action of the spin raising and lower operators. For spin $S = 1$, this is

$$\begin{aligned} \hat{S}_+|1,1\rangle &= 0 & \hat{S}_-|1,1\rangle &= \sqrt{2}\hbar|1,0\rangle \\ \hat{S}_+|1,0\rangle &= \sqrt{2}\hbar|1,1\rangle & \hat{S}_-|1,0\rangle &= \sqrt{2}\hbar|1,-1\rangle \\ \hat{S}_+|1,-1\rangle &= \sqrt{2}\hbar|1,0\rangle & \hat{S}_-|1,-1\rangle &= 0\,. \end{aligned}$$

In the basis $|1,+1\rangle$, $|1,0\rangle$, $|1,-1\rangle$, the matrix representations are

$$\hat{S}_+ = \sqrt{2}\hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \qquad \hat{S}_- = \hat{S}_+^\dagger = \sqrt{2}\hbar \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}.$$

Then, using the relation, $\hat{S}_x = \frac{1}{2}(\hat{S}_+ - \hat{S}_-)$, we obtain the matrix elements of the $\hat{S}_x$ operator and the corresponding eigenstates,

$$S_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \qquad \begin{matrix} m_x = +1 \\ \frac{1}{2}\begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} \end{matrix}, \quad \begin{matrix} m_x = 0 \\ \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \end{matrix}, \quad \begin{matrix} m_x = -1 \\ \frac{1}{2}\begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix} \end{matrix}$$

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 $\hat{S}_z$. (Alternatively, one can write the magnetic moment as $\mu = \gamma\hbar$ where γ is the gyromagnetic ratio.) 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.

$$\psi(t) = e^{i\mu B\hat{S}_z t/\hbar^2}\psi(0) = \frac{1}{2}\begin{pmatrix} e^{i\mu Bt/\hbar} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\mu Bt/\hbar} \end{pmatrix}\begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} e^{i\mu Bt/\hbar} \\ \sqrt{2} \\ e^{-i\mu Bt/\hbar} \end{pmatrix}.$$

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

$$\mu = \frac{(2n+1)\pi\hbar}{BL}\left(\frac{2E}{m}\right)^{1/2} = \frac{2\pi\hbar}{B_0 L}\left(\frac{2E}{m}\right)^{1/2} = 2.84 \times 10^{-26}\ \mathrm{J\,T^{-1}}$$

and hence the proton magnetic moment is 1.42×10^{-26} J T^{-1}.

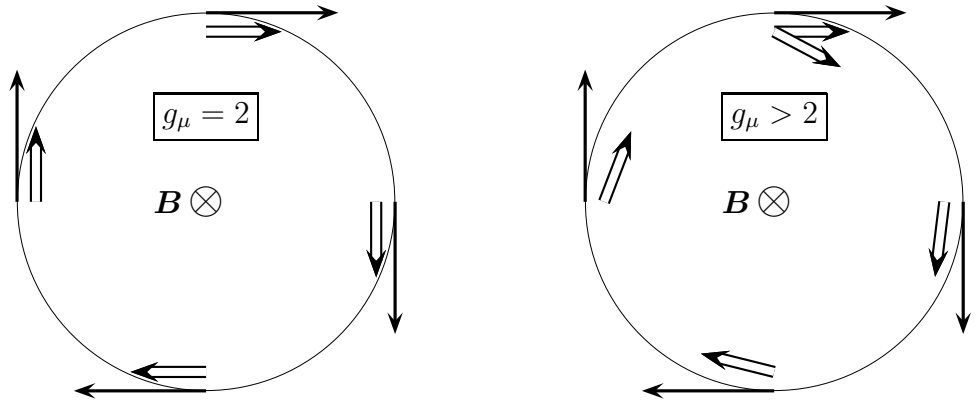
The result can also be obtained by treating the problem as one of classical precession. The couple $= \mu B = L\Omega$, where $L = \hbar$ is the angular momentum and Ω the angular frequency of precession. If $\Omega t = (2n+1)\pi$, the molecules have precessed into the $m_x = -1$ state, and the result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

15. **Muon magnetic moment**

(a) The difference $\omega_{\rm a} = \omega_{\rm s} - \omega_{\rm c}$ between the spin precession and cyclotron frequencies for a particle moving in a plane perpendicular to a magnetic field $\boldsymbol{B}$ is given by

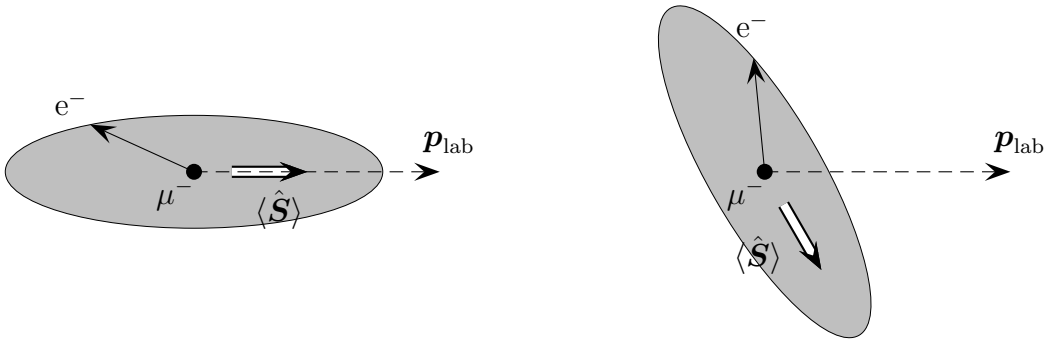
$$\omega_{\rm a} \equiv \omega_{\rm s} - \omega_{\rm c} = \frac{g-2}{2}\frac{qB}{m} = a\frac{qB}{m} \ , \tag{8}$$

where $a \equiv (g-2)/2$ is the anomalous magnetic moment. This expression holds for relativistic as well as non-relativistic particles.



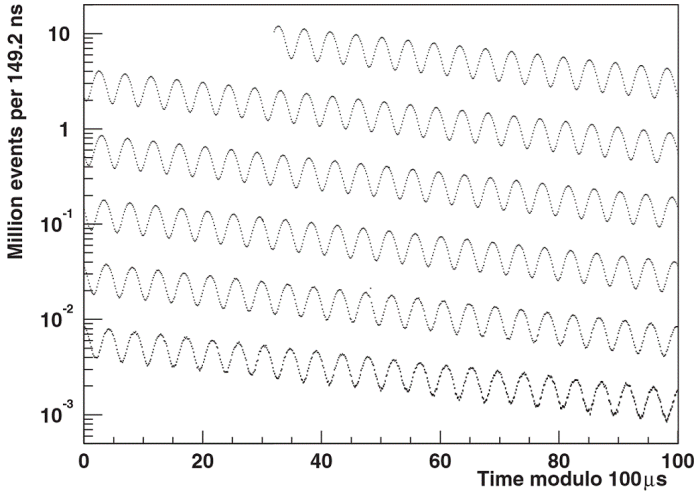
For $g_\mu = 2$ ($a_\mu = 0$), the spin precession and cyclotron frequencies are equal ($\omega_{\rm s} = \omega_{\rm c}$, $\omega_{\rm a} = 0$). The muon momentum and spin vectors precess at the same rate, remaining tangential to the circular orbit at all times (left-hand diagram).

For $g_\mu \approx 2.002$ ($a_\mu \approx 0.001$), we have $\omega_{\rm s} > \omega_{\rm c}$, so the spin vector precesses (slightly) faster than the momentum vector. The spin vector therefore rotates relative to the orbital tangent, with angular frequency $\omega_{\rm s} - \omega_{\rm c} = \omega_{\rm a}$ (right-hand diagram).



In the muon rest frame, electrons from muon decay, $\mu^- \to e^- + \overline{\nu}_e + \nu_\mu$, are emitted non-isotropically with respect to the muon spin direction, as shown schematically by the elliptical probability distribution in the diagrams. (The shape is not in fact elliptical, nor even symmetric, but this doesn't affect the argument.) The electron distribution (the ellipse) rotates with the muon spin vector.

After a Lorentz transformation to the lab frame, the distribution of electron four-momenta depends on the angle of the spin vector relative to the direction of the Lorentz boost. The boost direction is always tangential to the orbital circle, or, equivalently, always lies along the muon three-momentum direction. The electron energy distribution in the lab frame therefore depends on the angle between the muon spin vector and the muon three-momentum. In the lab frame, electrons above a given threshold energy are detected and counted. The number of detected electrons therefore shows a structure which depends on the difference $\omega_a = \omega_s - \omega_c$ between the spin and momentum precession frequencies, with a period $2\pi/\omega_a$ (superimposed on a steady exponential decay of the number of electrons due to the muon lifetime of about $2.2\,\mu$s).



Between the first minimum on the plot, at time $(34.5 \pm 0.5)\,\mu$s, and the penultimate minimum, at time $(593.5 \pm 0.5)\,\mu$s, the plot of $N_e(t)$ versus t contains 128 complete ω_a cycles. The period $T_a = 2\pi/\omega_a$ can then be estimated as

$$T_a = \frac{(593.5 - 34.5)\,\mu s}{128} = 4.367 \pm 0.006\,\mu\text{s}\ .$$

From equation (8), we can estimate the magnetic moment as

$$a_\mu = \frac{\omega_a m_\mu}{eB} = \frac{2\pi \times (206.77 \times 9.11 \times 10^{-31})}{(4.367 \times 10^{-6}) \times (1.6 \times 10^{-19}) \times 1.4513} = \boxed{0.0011690 \pm 0.0000016},$$

which corresponds also to

$$\boxed{g_\mu = 2(a_\mu + 1) = 2.002338 \pm 0.000003}.$$

(b) The two frequencies measured by E821 are (using Equation (8) for ω_a),

$$\omega_a = a_\mu \frac{eB}{m_\mu}\ , \qquad \omega_p = \frac{g_p eB}{2m_p}\,,$$

where $g_p \approx 5.586$ is the proton g-factor. Their ratio $\mathcal{R}$ is independent of B:

$$\mathcal{R} \equiv \frac{\omega_a}{\omega_p} = \frac{2a_\mu}{g_p}\frac{m_p}{m_\mu}\,.$$

The muon and proton magnetic moments are given by

$$\mu_\mu = \frac{g_\mu}{2}\frac{e\hbar}{2m_\mu}\,, \quad \mu_\mathrm{p} = \frac{g_\mathrm{p}}{2}\frac{e\hbar}{2m_\mathrm{p}}\,.$$

Their ratio λ, taken from another experiment, is therefore

$$\lambda \equiv \frac{\mu_\mu}{\mu_\mathrm{p}} = \frac{g_\mu}{g_\mathrm{p}}\frac{m_\mathrm{p}}{m_\mu} = \frac{2(1+a_\mu)}{g_\mathrm{p}}\frac{m_\mathrm{p}}{m_\mu} = (1+a_\mu)\frac{\mathcal{R}}{a_\mu}\,.$$

This rearranges as

$$\boxed{a_\mu = \frac{\mathcal{R}}{\lambda - \mathcal{R}}}.$$

E821 measured $\mathcal{R} = 0.0037072064(20)$, while measurements of hyperfine splitting in muonium (Liu et al., Phys. Rev. Lett. **82** (1999) 711) give $\lambda = 3.18334513(39)$. Standard error propagation,

$$\sigma_a^2 = \left(\frac{\partial a_\mu}{\partial \mathcal{R}}\right)^2 \sigma_\mathcal{R}^2 + \left(\frac{\partial a_\mu}{\partial \lambda}\right)^2 \sigma_\lambda^2 = \frac{1}{(\lambda-\mathcal{R})^4}\left(\lambda^2\sigma_\mathcal{R}^2 + \mathcal{R}^2\sigma_\lambda^2\right)\,,$$

then gives

$$a_\mu = \frac{0.0037072064(20)}{3.18334513(39) - 0.0037072064(20)} = \boxed{0.00116592093(65)}.$$

This is about 3.7 standard deviations from the QED prediction, $a_\mu(\mathrm{QED}) = 0.001165918204(356)$.

(c) (*optional*) Using the same data points as in part (a), we can estimate from the plot that the number of muon decays falls from 5.3 at the first minimum to 10^{-3} at the penultimate minimum. The muon lifetime in the lab frame can then be estimated (exponential decay) as

$$\tau_\mathrm{lab} \approx \frac{593.5 - 34.5}{\ln(5.3/0.001)} = 65.2\,\mu\mathrm{s}.$$

From $\tau_\mathrm{lab} = \gamma\tau_\mu$, where $\tau_\mu = 2.197\,\mu$s is the muon lifetime in its rest frame, we then obtain the Lorentz factor as $\gamma = 29.7$.

With $m_\mu/m_e = 206.77$, the orbital (cyclotron) period is approximately

$$T_\mathrm{c} = \frac{2\pi}{\omega_\mathrm{c}} = \frac{2\pi m_\mu \gamma}{eB} = \frac{2\pi \times (206.77 \times 9.11 \times 10^{-31}) \times 29.7}{(1.6\times 10^{-19}) \times 1.4513} = 151.4\,\mathrm{ns}\,.$$

(A more precise value is 149.2 ns, as in the y-axis label on the figure). Using the estimate of T_a from part (a), muons undergo about $N_\mathrm{c} = 4.367/0.151 = 28.9$ orbits in the time T_a it takes the spin vector to precess once relative to the muon momentum direction.

Consulting the E821 paper: to focus the muon beam in its orbit, a quadrupole electric field must be applied. The dependence of the frequency difference ω_a on an electric field can be eliminated by choosing the muon momentum such that

$$a_\mu = \frac{1}{\gamma^2 - 1}\,.$$

For $a_\mu = 0.00117$, this requires $\gamma = 29.25$, corresponding to a "magic" muon momentum of about $3.1\,\mathrm{GeV}/c$. The number of cyclotron orbits, N_c, undergone in the time taken for one relative precession orbit is

$$N_\mathrm{c} = \frac{T_\mathrm{a}}{T_\mathrm{c}} = \frac{\omega_\mathrm{c}}{\omega_\mathrm{a}} = \frac{eB}{m_\mu \gamma} \frac{m_\mu}{a_\mu eB} = \frac{1}{\gamma a_\mu} \ .$$

For the magic γ, this is

$$N_\mathrm{c} = \frac{\gamma^2 - 1}{\gamma} \approx \gamma \ .$$

Thus it is not a coincidence that $N_\mathrm{c} \approx \gamma$; this choice largely eliminates systematic uncertainties associated with the electric field which must be used to focus the beam.

16. **Landau levels**

Since $\hat{H}$ does not depend on $\hat{y}$, the Schrödinger equation $\hat{H}\psi = E\psi$ has energy eigenstates which are plane waves in the y direction, $\psi(x,y) = e^{ik_y y}\chi(x)$. Using $\hat{p}_y e^{ik_y y} = \hbar k_y e^{ik_y y}$, the function $\chi(x)$ is a solution of $\hat{H}_{k_y}\chi(x) = E\chi(x)$, where the Hamiltonian $\hat{H}_{k_y}$ is

$$\begin{aligned}
\hat{H}_{k_y} &= \frac{\hat{p}_x^2}{2m} + \frac{(\hbar k_y + eBx)^2}{2m} + eEx \\
&= \frac{\hat{p}_x^2}{2m} + \frac{1}{2m}\left[(\hbar k_y)^2 + 2(eB\hbar k_y + meE)x + e^2B^2x^2\right] \\
&= \frac{\hat{p}_x^2}{2m} + \frac{e^2B^2}{2m}\left[\frac{(\hbar k_y)^2}{e^2B^2} + 2\left(\frac{\hbar k_y}{eB} + \frac{mE}{eB^2}\right)x + x^2\right] \ .
\end{aligned}$$

Completing the square, and defining

$$x_0 \equiv -\frac{mE}{eB^2} - \frac{\hbar k_y}{eB}$$

and the cyclotron frequency

$$\omega_c \equiv \frac{eB}{m} \ ,$$

after some algebra one finds

$$\hat{H}_{k_y} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega_c^2(x - x_0)^2 - \frac{mE^2}{2B^2} - \frac{E}{B}\hbar k_y \ .$$

Compared to the case $E = 0$ (in lectures) there is a different position offset x_0, and an additional energy shift $-(mE^2/2B^2) - (E/B)\hbar k_y$. The energy spectrum is therefore

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega_c - \frac{mE^2}{2B^2} - \frac{E}{B}\hbar k_y} \ .$$

For a wavepacket, the group velocity in the y direction is

$$v_y = \frac{1}{\hbar}\frac{\partial E_n}{\partial k_y} = -\frac{E}{B} \ .$$

(This can also be understood by the Lorentz transformations of the electric and magnetic fields; in the frame of reference moving with $v_y = -E/B$ the electric field vanishes.)

17. **Atomic structure (Part IB Advanced Physics 1993)**

(a) For the relativistic energy correction $\hat{H}_1$, the expectation value is

$$\langle\psi|\hat{H}_1|\psi\rangle \sim \int (\psi^*\hat{\boldsymbol{p}}^2)(\hat{\boldsymbol{p}}^2\psi)\,\mathrm{d}^3\boldsymbol{r} \sim \int |\nabla^2\psi|^2\,\mathrm{d}^3\boldsymbol{r}\,.$$

Consider the change of variables $\boldsymbol{u} = Z\boldsymbol{r}/a_0$. Then

$$\nabla^2 = \left(\frac{Z}{a_0}\right)^2 \nabla_u^2\,; \qquad \mathrm{d}^3\boldsymbol{r} = \left(\frac{a_0}{Z}\right)^3 \mathrm{d}^3\boldsymbol{u}\,,$$

giving

$$\langle\psi|\hat{H}_1|\psi\rangle \sim \frac{Z}{a_0}\int |\nabla_u^2\psi|^2\,\mathrm{d}^3\boldsymbol{u}\,.$$

For a wavefunction of the form

$$\psi = \left(\frac{Z}{a_0}\right)^{3/2} G_{n\ell}(u)e^{-u/n}Y_{\ell m}(\theta,\phi)\,,$$

we then have

$$\langle\psi|\hat{H}_1|\psi\rangle \sim \left(\frac{Z}{a_0}\right)^4 \int \left|\nabla_u^2(G_{n\ell}(u)e^{-u/n})\right|^2 u^2\,\mathrm{d}u \sim Z^4.$$

(b) For the spin-orbit interaction $\hat{H}_2$, the scalar product $\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$ contributes a Z-independent factor $\frac{1}{2}[j(j+1) - \ell(\ell+1) - s(s+1)]\hbar^2$ to the expectation value $\langle\psi|\hat{H}_2|\psi\rangle$, so we need only to consider the $(1/r)(\partial V/\partial r)$ component. For the Coulomb interaction, we have

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}\,, \qquad \frac{\partial V}{\partial r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}\,,$$

and hence, since the angular components are Z-independent,

$$\langle\psi|\hat{H}_2|\psi\rangle \sim \int |\psi|^2\frac{Z}{r^3}\,\mathrm{d}^3\boldsymbol{r} \sim \int |\psi|^2\frac{Z}{r^3}\,r^2\,\mathrm{d}r\,.$$

Making the same change of variable, $u = Zr/a_0$, as in part (a) then gives

$$\langle\psi|\hat{H}_2|\psi\rangle \sim \left(\frac{Z}{a_0}\right)^3 \int \frac{Z}{u^3}|G_{n\ell}(u)|^2e^{-2u/n}|Y_{\ell m}|^2\,\mathrm{d}^3\boldsymbol{u} \sim Z^4\,.$$

(c) Making the usual substitution $\boldsymbol{u} = Z\boldsymbol{r}/a_0$, we have $\delta^3(\boldsymbol{r}) = (Z/a_0)^3\delta^3(\boldsymbol{u})$. Thus the expectation value of the $\hat{H}_3$ term in the Hamiltonian is

$$\langle\psi|\hat{H}_3|\psi\rangle \sim \int Z\,\delta^{(3)}(\boldsymbol{r})|\psi|^2\,\mathrm{d}^3\boldsymbol{r} \sim \int Z\left(\frac{Z}{a_0}\right)^3\delta^3(\boldsymbol{u})\left(\frac{Z}{a_0}\right)^3|G_{n\ell}(u)|^2e^{-2u/n}\left(\frac{a_0}{Z}\right)^3\,\mathrm{d}^3\boldsymbol{u}\,,$$

which is proportional to Z^4 again.

18. **Hyperfine structure**

(a) In the Hamiltonian

$$\hat{H} = B\left(\mu_{\rm e}\hat{\sigma}_z^{(\rm e)} + \mu_{\rm p}\hat{\sigma}_z^{(\rm p)}\right) + W\hat{\boldsymbol{\sigma}}^{(\rm e)}\cdot\hat{\boldsymbol{\sigma}}^{(\rm p)}\ ,$$

the first two terms represent the interaction of the magnetic moments of the electron and proton with the external field B, while the final term represents the spin-spin (hyperfine) interaction between the electron and proton.

(b) Introducing $\sigma_\pm = \sigma_x \pm i\sigma_y$ gives the identity

$$\boldsymbol{\sigma}^{(\rm e)}\cdot\boldsymbol{\sigma}^{(\rm p)} = \sigma_z^{(\rm e)}\sigma_z^{(\rm p)} + \frac{1}{2}(\sigma_+^{(\rm e)}\sigma_-^{(\rm p)} + \sigma_-^{(\rm e)}\sigma_+^{(\rm p)}),$$

where

$$\sigma_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\ ,\quad \sigma_+ = \begin{pmatrix}0 & 2\\ 0 & 0\end{pmatrix}\ ,\quad \sigma_- = \begin{pmatrix}0 & 0\\ 2 & 0\end{pmatrix}\ .$$

Using $\sigma_z|\uparrow\rangle = |\uparrow\rangle$, $\sigma_z|\downarrow\rangle = -|\downarrow\rangle$, $\sigma_+|\downarrow\rangle = 2|\uparrow\rangle$, $\sigma_+|\uparrow\rangle = 0$, $\sigma_-|\downarrow\rangle = 0$, $\sigma_-|\uparrow\rangle = 2|\downarrow\rangle$, and using the notation $|\uparrow_{\rm e}\uparrow_{\rm p}\rangle \equiv |\uparrow_{\rm e}\rangle\otimes|\uparrow_{\rm p}\rangle$, we have

$$\begin{aligned}
\boldsymbol{\sigma}^{(\rm e)}\cdot\boldsymbol{\sigma}^{(\rm p)}|\uparrow_{\rm e}\uparrow_{\rm p}\rangle &= |\uparrow_{\rm e}\uparrow_{\rm p}\rangle\\
\boldsymbol{\sigma}^{(\rm e)}\cdot\boldsymbol{\sigma}^{(\rm p)}|\uparrow_{\rm e}\downarrow_{\rm p}\rangle &= -|\uparrow_{\rm e}\downarrow_{\rm p}\rangle + 2|\downarrow_{\rm e}\uparrow_{\rm p}\rangle\\
\boldsymbol{\sigma}^{(\rm e)}\cdot\boldsymbol{\sigma}^{(\rm p)}|\downarrow_{\rm e}\uparrow_{\rm p}\rangle &= -|\downarrow_{\rm e}\uparrow_{\rm p}\rangle + 2|\uparrow_{\rm e}\downarrow_{\rm p}\rangle\\
\boldsymbol{\sigma}^{(\rm e)}\cdot\boldsymbol{\sigma}^{(\rm p)}|\downarrow_{\rm e}\downarrow_{\rm p}\rangle &= |\downarrow_{\rm e}\downarrow_{\rm p}\rangle\ .
\end{aligned}$$

This gives non-zero matrix elements such as

$$\big\langle\uparrow_{\rm e}\downarrow_{\rm p}\big|\boldsymbol{\sigma}^{(\rm e)}\cdot\boldsymbol{\sigma}^{(\rm p)}\big|\uparrow_{\rm e}\downarrow_{\rm p}\big\rangle = -1\,,\qquad \big\langle\downarrow_{\rm e}\uparrow_{\rm p}\big|\boldsymbol{\sigma}^{(\rm e)}\cdot\boldsymbol{\sigma}^{(\rm p)}\big|\uparrow_{\rm e}\downarrow_{\rm p}\big\rangle = 2\,.$$

The term $B\mu_{\rm e}\hat{\sigma}_z^{(\rm e)}$ in the Hamiltonian gives matrix elements such as

$$\big\langle\downarrow_{\rm e}\downarrow_{\rm p}\big|\hat{\sigma}_z^{(\rm e)}\big|\downarrow_{\rm e}\downarrow_{\rm p}\big\rangle = -1\,.\qquad \big\langle\uparrow_{\rm e}\downarrow_{\rm p}\big|\hat{\sigma}_z^{(\rm e)}\big|\downarrow_{\rm e}\downarrow_{\rm p}\big\rangle = 0\,.$$

Working in the basis $\{\ |\uparrow_{\rm e}\uparrow_{\rm p}\rangle,\ |\uparrow_{\rm e}\downarrow_{\rm p}\rangle,\ |\downarrow_{\rm e}\uparrow_{\rm p}\rangle,\ |\downarrow_{\rm e}\downarrow_{\rm p}\rangle,\ \}$, and neglecting the term in $\mu_{\rm p}$, the matrix representation of the Hamiltonian $\hat{H}$ can then be obtained as

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

where $b \equiv \mu_B B$.

(c) By inspection, the states $|\uparrow_{\rm e}\uparrow_{\rm p}\rangle$ and $|\downarrow_{\rm e}\downarrow_{\rm p}\rangle$ are eigenstates of H with eigenvalues $E = W + b$ and $E = W - b$, respectively. The other two eigenvalues are given by the solutions of

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

which leads to $E = -W \pm \sqrt{4W^2 + b^2}$. The (unnormalised) eigenstates corresponding to these eigenvalues are

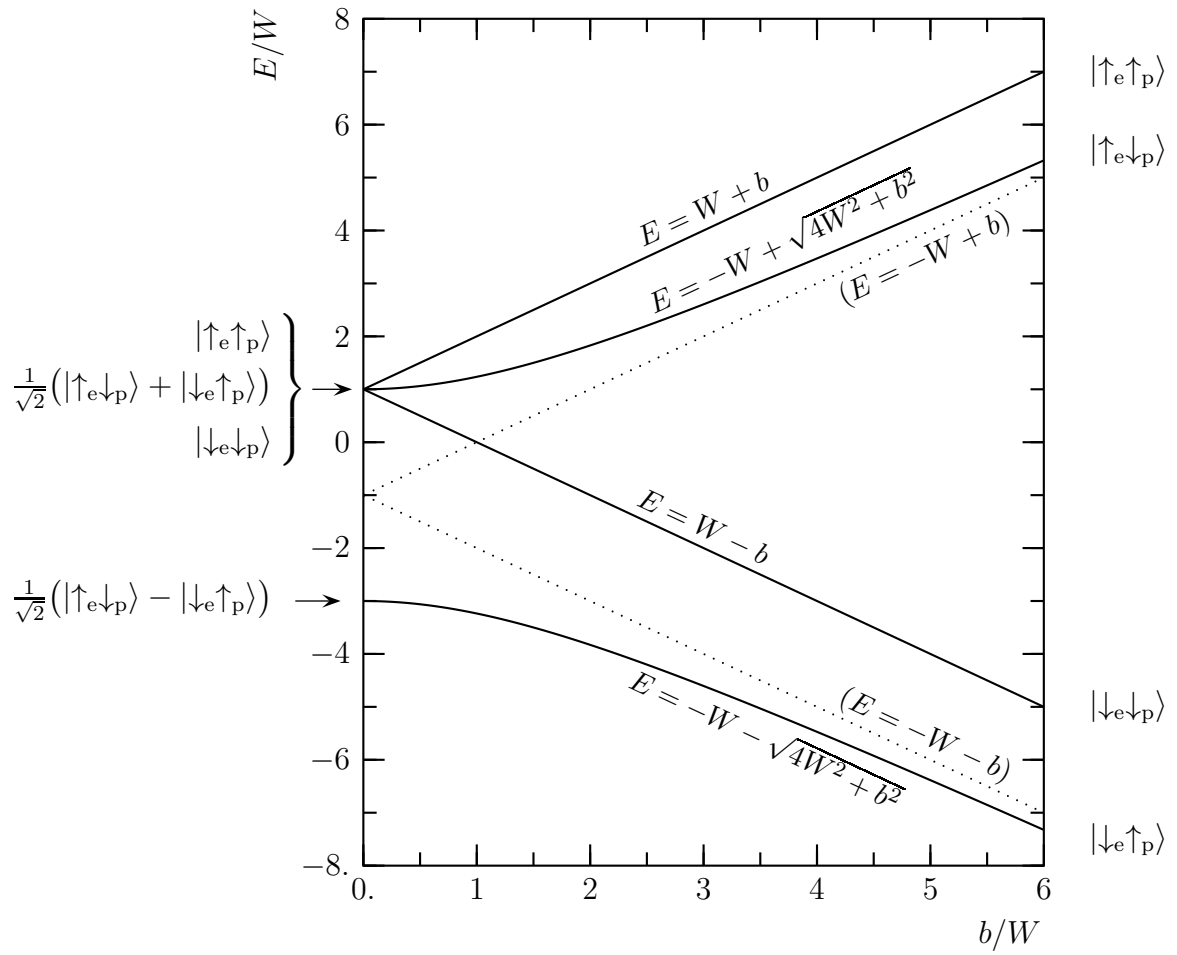
$$\left(b \pm \sqrt{4W^2 + b^2}\right) |{\uparrow_{\rm e}}{\downarrow_{\rm p}}\rangle + 2W |{\downarrow_{\rm e}}{\uparrow_{\rm p}}\rangle \ .$$

For zero field ($b = 0$), the energies become W and $-3W$, and the corresponding eigenstates become $(1/\sqrt{2})(|{\uparrow_{\rm e}}{\downarrow_{\rm p}}\rangle + |{\downarrow_{\rm e}}{\uparrow_{\rm p}}\rangle)$ and $(1/\sqrt{2})(|{\uparrow_{\rm e}}{\downarrow_{\rm p}}\rangle - |{\downarrow_{\rm e}}{\uparrow_{\rm p}}\rangle)$. This corresponds to a triplet of $F = 1$ states with energy W, and a singlet $F = 0$ state with energy $-3W$.

In the high field limit, $b \gg W$, the energies approach $b \pm W$ and $-b \pm W$. We therefore obtain two widely separated pairs of states (energy separation $2b$ growing linearly with the field strength), such that the (small) energy separation within each pair asymptotically approaches the constant value $2W$.

The two pairs of states correspond to the two possible orientations of the electron spin. The two states within each pair correspond to the two possible orientations of the proton spin.

In the low field region, $b \ll W$, the energies of the states with $m_F = 0$ reduce to $W + b^2/4W$ and $-3W - b^2/4W$. The quadratic dependence of energy on b can be understood in terms of perturbation theory around $b = 0$ (the first-order perturbation correction vanishes).



19. **Rotational symmetry**

The Wigner-Eckart theorem for a vector operator $\hat{\boldsymbol{V}}$, with spherical components $\hat{V}_m$, is

$$\langle \alpha_1 j_1 m_1 | \hat{V}_m | \alpha_2 j_2 m_2 \rangle = \langle \alpha_1 j_1 \,\|\, \hat{\boldsymbol{V}} \,\|\, \alpha_2 j_2 \rangle \, \langle 1m; j_2 m_2 | j_1 m_1 \rangle \ .$$

The reduced matrix element $\langle \alpha_1 j_1 \,\|\, \hat{\boldsymbol{V}} \,\|\, \alpha_2 j_2 \rangle$ is a complex constant which is independent of the quantum numbers m_1, m_2 and m. The Clebsch-Gordan coefficient $\langle 1m; j_2 m_2 | j_1 m_1 \rangle$ arises from angular momentum addition $1 \otimes j_2 = j_1$ and is independent of the vector operator $\hat{\boldsymbol{V}}$.

(a) The Clebsch-Gordan coefficient $\langle 1m; j_2 m_2 | j_1 m_1 \rangle$ vanishes unless $m_1 = m + m_2$. Hence the matrix element $\langle \alpha_1 j_1 m_1 | \hat{V}_m | \alpha_2 j_2 m_2 \rangle$ vanishes unless $m_1 = m + m_2$. For the case $j_1 = 1$ and $j_2 = 0$, with $m_1 = \pm 1, 0$ and $m_2 = 0$, the only matrix elements which can be non-zero are those with $m = m_1$:

$$\begin{aligned}
\langle \alpha_1 11 | \hat{V}_{+1} | \alpha_2 00 \rangle &= \langle \alpha_1 1 \,\|\, \hat{\boldsymbol{V}} \,\|\, \alpha_2 0 \rangle \, \langle 11; 00 | 11 \rangle \\
\langle \alpha_1 1, -1 | \hat{V}_{-1} | \alpha_2 00 \rangle &= \langle \alpha_1 1 \,\|\, \hat{\boldsymbol{V}} \,\|\, \alpha_2 0 \rangle \, \langle 1, -1; 00 | 1, -1 \rangle \\
\langle \alpha_1 10 | \hat{V}_0 | \alpha_2 00 \rangle &= \langle \alpha_1 1 \,\|\, \hat{\boldsymbol{V}} \,\|\, \alpha_2 0 \rangle \, \langle 10; 00 | 10 \rangle \, .
\end{aligned}$$

The Clebsch-Gordan coefficients above derive from the "trivial" angular momentum addition $1 \otimes 0 = 1$, and are all unity. Hence, for the spherical components $\hat{V}_m$, the non-vanishing matrix elements are all equal :

$$\boxed{\langle \alpha_1 11 | \hat{V}_{+1} | \alpha_2 00 \rangle = \langle \alpha_1 1, -1 | \hat{V}_{-1} | \alpha_2 00 \rangle = \langle \alpha_1 10 | \hat{V}_0 | \alpha_2 00 \rangle = \langle \alpha_1 1 \,\|\, \hat{\boldsymbol{V}} \,\|\, \alpha_2 0 \rangle} \, .$$

The Cartesian components of $\hat{\boldsymbol{V}}$ are given in terms of the spherical components as

$$\hat{V}_x = \frac{1}{\sqrt{2}} (\hat{V}_{-1} - \hat{V}_{+1}) \ , \qquad \hat{V}_y = \frac{i}{\sqrt{2}} (\hat{V}_{-1} + \hat{V}_{+1}) \ , \qquad \hat{V}_z = \hat{V}_0 \, .$$

The matrix elements of the Cartesian components of $\hat{\boldsymbol{V}}$ are thus of the form

$$\begin{aligned}
\langle \alpha_1 10 | (\hat{V}_x, \hat{V}_y, \hat{V}_z) | \alpha_2 00 \rangle &= A(0, 0, 1) \\
\langle \alpha_1 1, \pm 1 | (\hat{V}_x, \hat{V}_y, \hat{V}_z) | \alpha_2 00 \rangle &= \frac{A}{\sqrt{2}} (\mp 1, i, 0) \ ,
\end{aligned}$$

where $A \equiv \langle \alpha_1 1 \,\|\, \hat{\boldsymbol{V}} \,\|\, \alpha_2 0 \rangle$ is a constant.

(b) For the position operator $\hat{\boldsymbol{V}} = \hat{\boldsymbol{r}} = (r \sin\theta \cos\phi, r \sin\theta \sin\phi, r \cos\theta)$, the matrix elements $\langle \alpha_1 1 m_1 | (x, y, z) | \alpha_2 00 \rangle$ can be evaluated explicitly. Starting with $|\alpha_1 10\rangle$, the z matrix element is

$$\begin{aligned}
\langle \alpha_1 10 | z | \alpha_2 00 \rangle &= \int \psi^*_{\alpha_1 10}(\boldsymbol{r}) \, r \cos\theta \, \psi_{\alpha_2 00}(\boldsymbol{r}) \, \mathrm{d}^3 r \\
&= \int_0^\infty r^3 R_{\alpha_1 1}(r) R_{\alpha_2 0}(r) \, \mathrm{d}r \int_0^{2\pi} \int_{-1}^{+1} \cos\theta \, Y^*_{10} Y_{00} \, \mathrm{d}\cos\theta \, \mathrm{d}\phi \, .
\end{aligned}$$

Writing the radial integral above as K_r, this is

$$\langle \alpha_1 10|z|\alpha_2 00\rangle = K_r \sqrt{\frac{3}{4\pi}}\sqrt{\frac{1}{4\pi}} 2\pi \int_{-1}^{+1} \cos^2\theta \,\mathrm{d}\cos\theta = \frac{1}{\sqrt{3}} K_r \ .$$

The x and y matrix elements vanish:

$$\langle \alpha_1 10|x|\alpha_2 00\rangle \propto \int_0^{2\pi} \cos\phi \,\mathrm{d}\phi = 0 \ , \qquad \langle \alpha_1 10|y|\alpha_2 00\rangle \propto \int_0^{2\pi} \sin\phi \,\mathrm{d}\phi = 0 \ .$$

Similarly, for $|\alpha_1 11\rangle$, the x matrix element is

$$\begin{aligned}
\langle \alpha_1 11|x|\alpha_2 00\rangle &= \int \psi^*_{\alpha_1 11}(\boldsymbol{r})\, r\sin\theta\cos\phi\, \psi_{\alpha_2 00}(\boldsymbol{r})\, \mathrm{d}^3 r \\
&= \int_0^\infty R_{\alpha_1 1}(r) R_{\alpha_2 0}(r) r^3 \,\mathrm{d}r \int_0^{2\pi}\int_{-1}^{+1} \sin\theta\cos\phi\, Y^*_{11} Y_{00} \,\mathrm{d}\cos\theta\,\mathrm{d}\phi \\
&= -K_r \sqrt{\frac{3}{8\pi}}\sqrt{\frac{1}{4\pi}} \int_{-1}^{+1} \sin^2\theta \,\mathrm{d}\cos\theta \int_0^{2\pi} \cos\phi\, e^{-i\phi}\,\mathrm{d}\phi = -\frac{1}{\sqrt{6}} K_r \ .
\end{aligned}$$

The y matrix element is given similarly, but with a ϕ contribution $\int_0^{2\pi} \sin\phi\, e^{-i\phi}\,\mathrm{d}\phi = -i\pi$ in place of $\int_0^{2\pi} \cos\phi\, e^{-i\phi}\,\mathrm{d}\phi = \pi$, and hence with an extra factor of $-i$:

$$\langle \alpha_1 11|y|\alpha_2 00\rangle = \frac{i}{\sqrt{6}} K_r \ .$$

The matrix element for z vanishes:

$$\langle \alpha_1 11|z|\alpha_2 00\rangle \propto \int_0^{2\pi} e^{-i\phi}\,\mathrm{d}\phi = 0 \ .$$

Finally, $|\alpha_1 1,-1\rangle$ is the same as $|\alpha_1 11\rangle$, but with $-e^{i\phi}$ instead of $e^{-i\phi}$.

The matrix elements of $(\hat{x},\hat{y},\hat{z})$ thus take the form expected from the Wigner-Eckart theorem, with the constant A (the reduced matrix element) given by

$$A = \frac{1}{\sqrt{3}} K_r = \frac{1}{\sqrt{3}} \int_0^\infty r^3 R_{\alpha_1 1}(r) R_{\alpha_2 0}(r)\,\mathrm{d}r \ .$$

(c) For the case $j_1 = 0$, $j_2 = 0$ (and hence $m_1 = 0$, $m_2 = 0$), the Wigner-Eckart theorem gives

$$\langle \alpha_1 00|\hat{V}_m|\alpha_2 00\rangle = \langle \alpha_1 0 \,\|\, \hat{\boldsymbol{V}} \,\|\, \alpha_2 0\rangle \, \langle 1m; 00|00\rangle \ .$$

The Clebsch-Gordan coefficients $\langle 1m; 00|00\rangle$ vanish for all $m = \pm 1, 0$ (because $1 \otimes 0 \neq 0$). Hence the matrix elements of all components of a vector operator $\hat{\boldsymbol{V}}$ taken between states with zero total angular momentum must vanish:

$$\boxed{\langle \alpha_1 00|\hat{\boldsymbol{V}}|\alpha_2 00\rangle = 0} \ .$$

20. **Identical particles**

A single particle in the potential well has the (unnormalized) wavefunction $\psi_n(x) = \sin(n\pi x/L)$, and energy $E = (\hbar^2\pi^2/2mL^2)n^2 \equiv \epsilon n^2$. The wavefunction for a system of two indistinguishable particles must be either symmetric or antisymmetric under particle interchange $1 \leftrightarrow 2$, i.e.

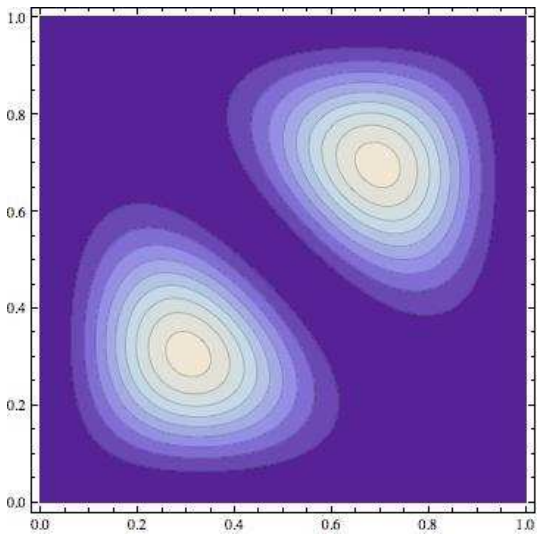
$$\psi(x_1, x_2) = \sin(n_1\pi x_1/L)\sin(n_2\pi x_2/L) \pm \sin(n_2\pi x_1/L)\sin(n_1\pi x_2/L)\,,$$

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

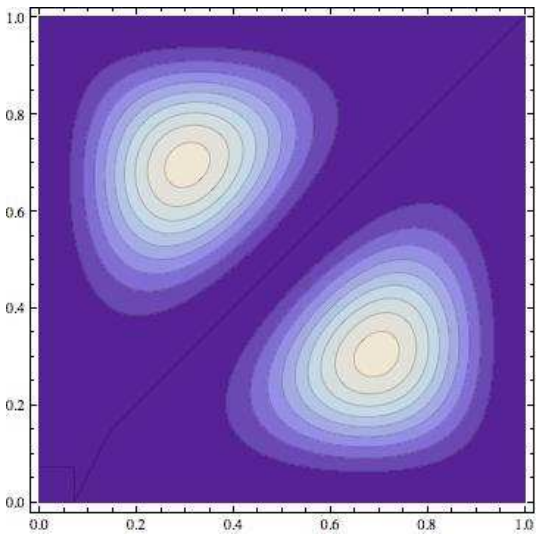
(a) Spin-zero particles are bosons and must have a symmetric wavefunction,

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

This has zeros for $x_1 = 0$, $x_1 = L$, $x_2 = 0$, $x_2 = L$, and $x_1 + x_2 = L$.



Symmetric spatial wavefunction



Antisymmetric spatial wavefunction

(b) Spin 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.

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

This has zeros for $x_1 = 0$, $x_1 = L$, $x_2 = 0$, $x_2 = L$, and $x_1 = x_2$.

If the particles were charged, they would repel each other through the Coulomb interaction. Therefore, in the spin 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.

21. **Hund's rules**

$(2s)(3p)$ The allowed values of L and S are $S = 0, 1$, $L = 1$. Since the electrons are inequivalent, all combinations of L and S are allowed, i.e. ${}^1\mathrm{P}_1$, ${}^3\mathrm{P}_{0,1,2}$.

$(2p)^2$ Since the electrons are equivalent, we are restricted to $S = 0$ (antisymmetric) with $L = 0, 2$ (symmetric), or alternatively $S = 1$ (symmetric) with $L = 1$ (antisymmetric), i.e. ${}^1\mathrm{S}_0$, ${}^1\mathrm{D}_2$, ${}^3\mathrm{P}_{0,1,2}$.

$(3d)^2$ Since the electrons are equivalent, we may take $S = 0$ (antisymmetric) with $L = 0, 2, 4$ (symmetric), or alternatively $S = 1$ (symmetric) with $L = 1, 3$ (antisymmetric), i.e. ${}^1\mathrm{S}_0$, ${}^1\mathrm{D}_2$, ${}^1\mathrm{G}_4$, ${}^3\mathrm{P}_{0,1,2}$, ${}^3\mathrm{F}_{2,3,4}$.

$(3d)^{10}$ This is a completely filled subshell, so $L = S = J = 0$, i.e. ${}^1\mathrm{S}_0$.

$(3d)^9$ The subshell has just one unoccupied state, so the values of L, S and J are the same as for a single electron in the subshell, i.e. $L = 2$, $S = 1/2$ and the terms are ${}^2\mathrm{D}_{3/2,5/2}$.

The $(4\mathrm{f})^6$ configuration consists of six electrons, each with $\ell_i = 3$ and $s_i = 1/2$.

The possible values of the total spin S are $S = 3, 2, 1, 0$. Hund(1) gives the lowest energy state as $S = 3$.

Being the maximal value of S, states in the $S = 3$ multiplet are totally symmetric with respect to the interchange of electrons. This is clearly true for the state $|S, m_S\rangle = |3, 3\rangle = |\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\rangle$, and this exchange symmetry is preserved when downward ladder operators are applied to obtain the $S = 3$ states with lower m_S. For identical fermions, the overall (spin and spatial) wavefunction must be totally antisymmetric. Since the spin state is symmetric, the spatial state for the six electron system must be totally antisymmetric. The only way such a state can be formed is for each of the six electrons to occupy a different $\ell = 3$ state; otherwise the Slater determinant vanishes. The six electrons must therefore occupy six different m_ℓ states out of the seven available ($m_\ell = 0, \pm1, \pm2, \pm3$).

The possible combinations of m_ℓ values can be tabulated as

m_1	m_2	m_3	m_4	m_5	m_6	m_L
$+3$	$+2$	$+1$	0	-1	-2	$+3$
$+3$	$+2$	$+1$	0	-1	-3	$+2$
$+3$	$+2$	$+1$	0	-2	-3	$+1$
$+3$	$+2$	$+1$	-1	-2	-3	0
$+3$	$+2$	0	-1	-2	-3	-1
$+3$	$+1$	0	-1	-2	-3	-2
$+2$	$+1$	0	-1	-2	-3	-3

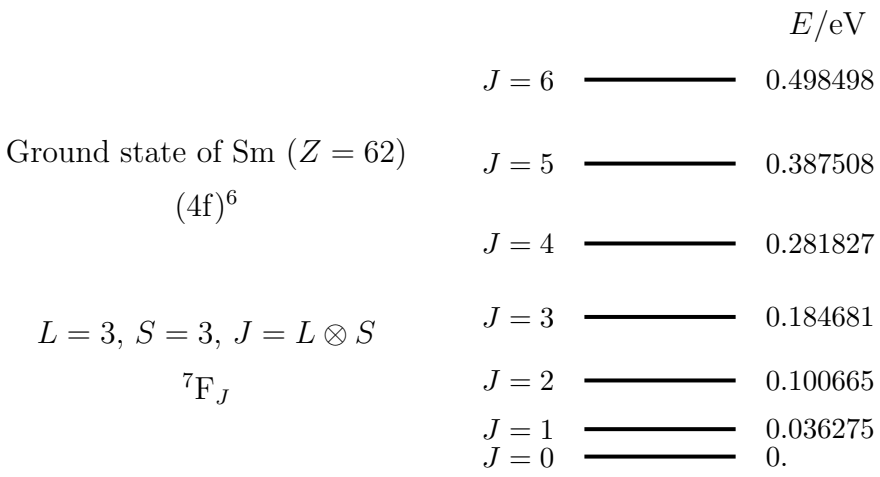
For each row of the table, a single totally antisymmetric spatial state (Slater determinant) can be constructed.

The values of $m_L = \sum_i (m_\ell)_i$ obtained ($m_L = 0, \pm1, \pm2, \pm3$), exactly fill a single angular momentum multiplet with $L = 3$. Thus $L = 3$ is the only value of L consistent with identical particle symmetry, and Hund(2) is not needed.

For $S = 3$ and $L = 3$, the possible values of J are $J = 6, 5, 4, 3, 2, 1, 0$. The (4f) subshell has capacity $2(2\ell + 1) = 14$, so is less than half full. Hund(3) then gives $J = 0$ as the lowest lying state. In order of increasing energy, the Sm ground state is therefore predicted to be

$$\boxed{{}^{(2S+1)}\mathrm{L}_J = {}^7\mathrm{F}_{0,1,2,3,4,5,6}} \, .$$

This is in agreement with observation (https://www.nist.gov/pml/atomic-spectra-database):



For completeness: How can we obtain explicit forms for the *wavefunctions* for each ${}^7\mathrm{F}_J$ level, and how does this relate to the quantum number tabulation argument above?

For example, the ${}^7\mathrm{F}_0$ ground state wavefunction, $|J, m_J\rangle = |0, 0\rangle$, is a linear combination of product states $|L, m_L\rangle|S, m_S\rangle$ with $m_L + m_S = m_J = 0$:

$$|0, 0\rangle = \sum_{m_L=-3}^{+3} C_{m_L} |3, m_L\rangle|3, -m_L\rangle \, ,$$

where the $C_m = \langle 3, m; 3, -m|00\rangle$ are Clebsch-Gordan coefficients from the $L \otimes S = 3 \otimes 3 = 0$ table. Each of the $|L, m_L\rangle = |3, m_L\rangle$ spatial factors is the 6×6 Slater determinant corresponding to the appropriate m_L row in the table of m_ℓ quantum numbers above, and built from six-particle products of $|\ell, m_\ell\rangle = |3, m_\ell\rangle$ single-particle states. Each of the $|S, m_S\rangle = |3, m_S\rangle = |3, -m_L\rangle$ factors is the spin state obtained by starting from the maximal state $|S, m_S\rangle = |3, 3\rangle = |\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\rangle$, and repeatedly applying the downward ladder operator

$$\hat{S}_- = (\hat{S}_1)_- + (\hat{S}_2)_- + (\hat{S}_3)_- + (\hat{S}_4)_- + (\hat{S}_5)_- + (\hat{S}_6)_- \, .$$

The resulting $|J, m_J\rangle = |0, 0\rangle$ wavefunction cannot be expressed as a *single* product of separate spatial and spin factors, but is rather a linear combination of such factors (as is generally the case for systems consisting of three or more particles).

22. **Atomic spectra (Tripos 1997)**

For configurations $(1s)(n\ell)$, the $S = 0$ levels have $J = \ell$ only and hence are singlets (parahelium), while the $S = 1$ levels can have $J = \ell, \ell \pm 1$ and hence are triplets (orthohelium):

Configuration	Singlets ($S=0$)	Triplets ($S=1$)
$(1s)^2$	$^1\mathrm{S}_0$	
$(1s)(2s)$	$^1\mathrm{S}_0$	$^3\mathrm{S}_1$
$(1s)(2p)$	$^1\mathrm{P}_1$	$^3\mathrm{P}_{2,1,0}$
$(1s)(3s)$	$^1\mathrm{S}_0$	$^3\mathrm{S}_1$
$(1s)(3p)$	$^1\mathrm{P}_1$	$^3\mathrm{P}_{2,1,0}$
$(1s)(3d)$	$^1\mathrm{D}_2$	$^3\mathrm{D}_{3,2,1}$

The $\Delta\ell = \pm 1$ selection rule allows E1 transitions $(ns) \leftrightarrow (np)$, $(np) \leftrightarrow (nd)$, $(np) \leftrightarrow (nd)$, ...

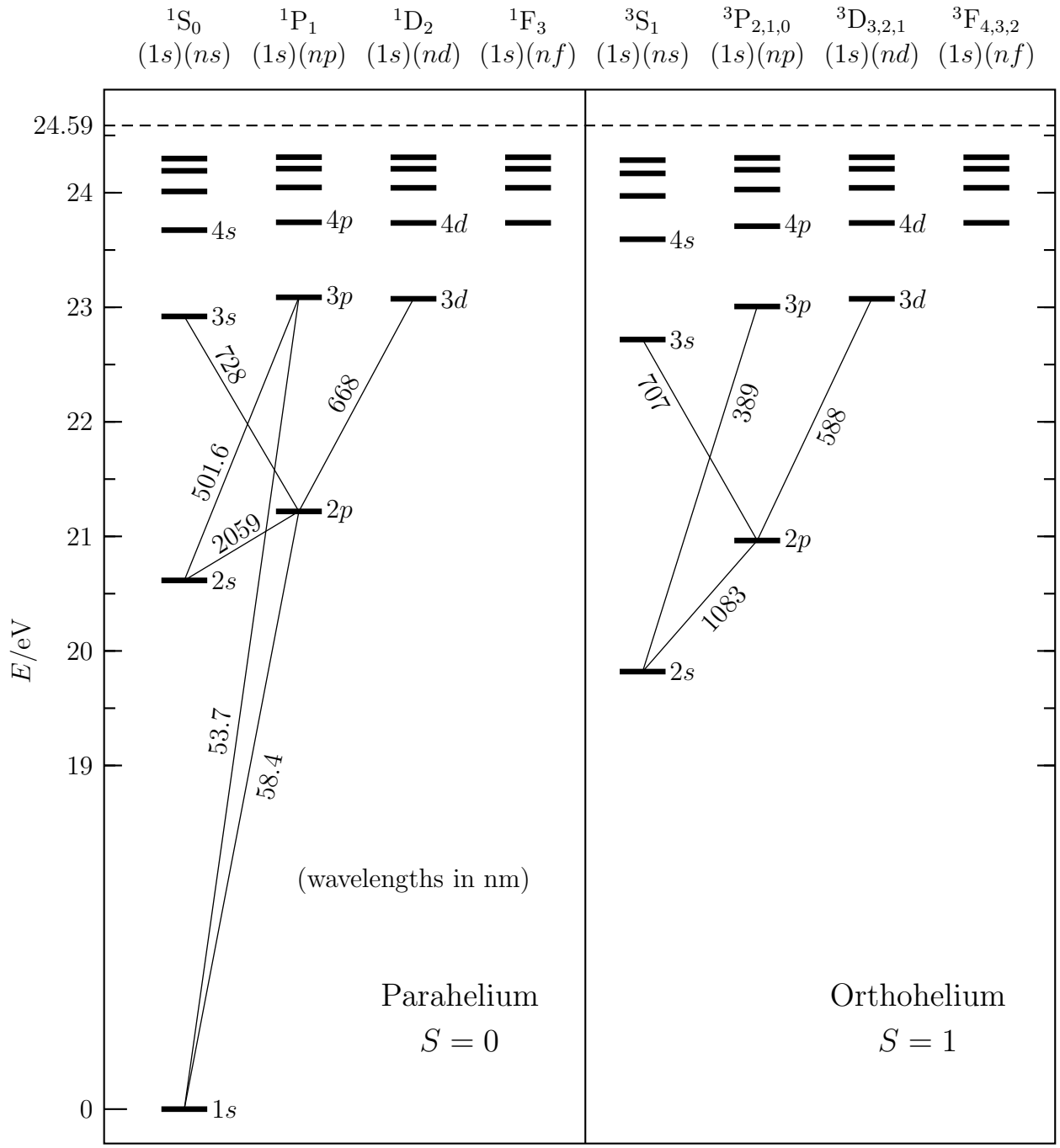
Transitions between two $S = 0$ levels must be singlets. Transitions between two $S = 1$ levels are multiplets (triplets for $3S \leftrightarrow 3P$, and sextets for all other cases; not nonets because of the ΔJ selection rule). To the extent that LS coupling holds, transitions between $S = 0$ and $S = 1$ are forbidden by the $\Delta S = 0$ selection rule.

The absorption spectrum will involve transitions starting from the $(1s)^2$ ground state only. The two of shortest wavelength (highest energy) will be $1s \to 2p$ and $1s \to 3p$ (both $^1\mathrm{S}_0 \to {}^1\mathrm{P}_1$), 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 nm and 501.6 nm are $2s \to 2p$ and $2s \to 3p$ in the singlet system. The multiplets at 1083 nm and 389 nm are $2s \to 2p$ and $2s \to 3p$ in the triplet system.

The singlet emission lines, 728 and 668, not covered above are probably parahelium $3s \to 2p$ and $3d \to 2p$ transitions. The multiplet emission lines, 707 and 588, not covered above are likewise $3s \to 2p$ and $3d \to 2p$ in orthohelium.

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 LS coupling approximation may become less valid. In Ca, the ground state $(4s)^2$ has term $^1\mathrm{S}_0$, and the first excited state $(4s)(4p)$ has a singlet $^1\mathrm{P}_1$ and a triplet $^3\mathrm{P}_{2,1,0}$ term. Transitions from the ground to the $^3\mathrm{P}_{2,0}$ states are forbidden by the stringent ΔJ selection rule, but transition to $^3\mathrm{P}_1$ is only forbidden by the weaker ΔS selection rule. The fact that this transition is seen tells us that the LS coupling approximation is not as good for Ca.



23. **Linear Stark effect**

(a) Matrix elements of the operator z taken between states $|n\ell m_\ell\rangle$ can only be non-zero if the states involved have $\Delta m_\ell = 0$ and opposite parity $(-1)^\ell$. For the $n = 3$ states of hydrogen, the only matrix elements $\langle n\ell' m'_\ell|\hat{H}'|n\ell m_\ell\rangle$ of the perturbation $\hat{H}' = e\mathcal{E}z$ that can possibly be non-zero are therefore

$$\langle 300|\hat{H}'|310\rangle \equiv a \; ; \quad \langle 320|\hat{H}'|310\rangle \equiv b \; ; \quad \langle 321|\hat{H}'|311\rangle \equiv c \; ; \quad \langle 32,-1|\hat{H}'|31,-1\rangle \equiv c' \; ,$$

together with their conjugates. In the basis of states $|n\ell m_\ell\rangle$ ordered as

$$|300\rangle, \quad |310\rangle, \quad |320\rangle, \quad |311\rangle, \quad |321\rangle, \quad |31,-1\rangle, \quad |32,-1\rangle, \quad |322\rangle, \quad |32,-2\rangle \ ,$$

the 9×9 matrix representation of $\hat{H}'$ is therefore block-diagonal, with submatrices H'_0, H'_{+1}, H'_{-1}, $H'_{\pm 2}$ coming from the states with $m_\ell = 0$, $m_\ell = +1$, $m_\ell = -1$ and $m_\ell = \pm 2$:

$$H'_0 = \begin{pmatrix} 0 & a & 0 \\ a^* & 0 & b^* \\ 0 & b & 0 \end{pmatrix} \ , \qquad H'_{+1} = \begin{pmatrix} 0 & c^* \\ c & 0 \end{pmatrix} \ , \qquad H'_{-1} = \begin{pmatrix} 0 & c'^* \\ c' & 0 \end{pmatrix} \ , \qquad H'_{\pm 2} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \ .$$

The reduced matrix elements are given to be

$$\langle 3s \,\|\, \hat{\boldsymbol{r}} \,\|\, 3p\rangle = 9\sqrt{2}\, a_0 \ , \qquad \langle 3d \,\|\, \hat{\boldsymbol{r}} \,\|\, 3p\rangle = -(9/\sqrt{2})\, a_0 \ .$$

Using the Wigner-Eckart theorem, the matrix elements a and b in H'_0 are

$$a = e\mathcal{E}\langle 300|\hat{z}|310\rangle = e\mathcal{E}\langle 3s \,\|\, \hat{\boldsymbol{r}} \,\|\, 3p\rangle \, \langle 10;10|00\rangle = 9\sqrt{2}\, e\mathcal{E}a_0 \times -\sqrt{\frac{1}{3}} = -9\sqrt{\frac{2}{3}} e\mathcal{E}a_0$$

$$b = e\mathcal{E}\langle 320|\hat{z}|310\rangle = e\mathcal{E}\langle 3d \,\|\, \hat{\boldsymbol{r}} \,\|\, 3p\rangle \, \langle 10;10|20\rangle = -9\sqrt{\frac{1}{2}}\, e\mathcal{E}a_0 \times \sqrt{\frac{2}{3}} = -9\sqrt{\frac{1}{3}} e\mathcal{E}a_0 \ .$$

Similarly, the matrix elements c and c' in $H'_{\pm 1}$ are

$$c = e\mathcal{E}\langle 321|\hat{z}|311\rangle = e\mathcal{E}\langle 3d \,\|\, \hat{\boldsymbol{r}} \,\|\, 3p\rangle \, \langle 10;11|21\rangle = -9\sqrt{\frac{1}{2}}\, e\mathcal{E}a_0 \times \sqrt{\frac{1}{2}} = -\frac{9}{2} e\mathcal{E}a_0$$

$$c' = e\mathcal{E}\langle 32,-1|\hat{z}|31,-1\rangle = e\mathcal{E}\langle 3d \,\|\, \hat{\boldsymbol{r}} \,\|\, 3p\rangle \, \langle 10;1,-1|2,-1\rangle = -9\sqrt{\frac{1}{2}}\, e\mathcal{E}a_0 \times \sqrt{\frac{1}{2}} = -\frac{9}{2} e\mathcal{E}a_0 \ .$$

Thus the H' submatrices have the form

$$H'_0 = \begin{pmatrix} 0 & a & 0 \\ a & 0 & b \\ 0 & b & 0 \end{pmatrix} \ , \qquad H'_{+1} = \begin{pmatrix} 0 & c \\ c & 0 \end{pmatrix} \ , \qquad H'_{-1} = \begin{pmatrix} 0 & c \\ c & 0 \end{pmatrix} \ ,$$

where the constants a, b, c are

$$a = \sqrt{2}b = -9\sqrt{\frac{2}{3}} e\mathcal{E}a_0 \ , \qquad c = -\frac{9}{2} e\mathcal{E}a_0 \ .$$

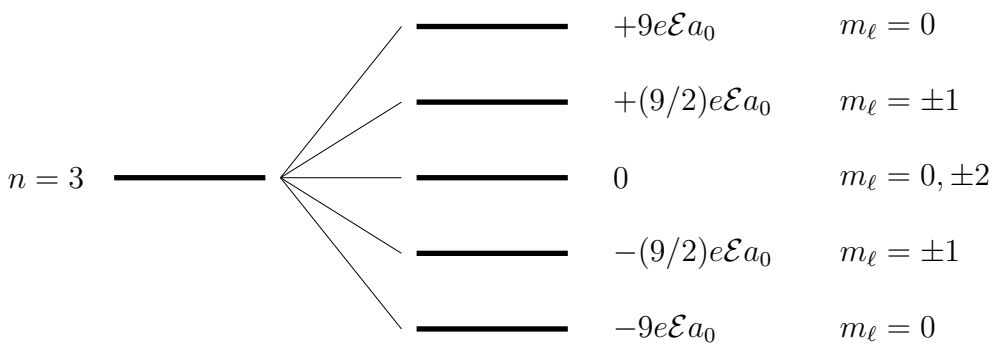
(b) In first-order degenerate perturbation theory, the energy shifts ΔE are obtained as the eigenvalues of the matrix H'. The energy shifts for the $m_\ell = 0$ states are given by the eigenvalues of the matrix H'_0 as

$$\Delta E = 0 \ , \qquad \Delta E = \pm\sqrt{a^2 + b^2} = \pm 2c \ .$$

Similarly, the eigenvalues of the matrices $H'_{\pm 1}$ give the $m_\ell = \pm 1$ energy shifts as $\Delta E = \pm c$.

The states $|322\rangle$ and $|32,-2\rangle$ with $m_\ell = \pm 2$ have no energy correction at first-order: $\Delta E = 0$.

Overall, we obtain energy shifts $\Delta E = 0$, $\pm c$, $\pm 2c$, and hence five equally spaced levels with energy separation $|c| = (9/2) e\mathcal{E}a_0$.



(c) The split state of highest energy has $\Delta E = 9e\mathcal{E}a_0$ and $m_\ell = 0$. The eigenvector of H_0' corresponding to the eigenvalue ΔE is given by the solution of

$$-\frac{9}{\sqrt{3}}\, e\mathcal{E}a_0 \begin{pmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = 9e\mathcal{E}a_0 \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} \ .$$

This gives the (normalised) zeroth-order eigenstate in the electric field as

$$|\psi\rangle = \sqrt{\frac{1}{3}}\,|300\rangle - \sqrt{\frac{1}{2}}\,|310\rangle + \sqrt{\frac{1}{6}}\,|320\rangle \ .$$

Similarly, the eigenstate of H_0' corresponding to the eigenvalue $\Delta E = -9e\mathcal{E}a_0$ is

$$|\psi\rangle = \sqrt{\frac{1}{3}}\,|300\rangle + \sqrt{\frac{1}{2}}\,|310\rangle + \sqrt{\frac{1}{6}}\,|320\rangle \ ,$$

and the eigenstate of H_0' corresponding to $\Delta E = 0$ is

$$|\psi\rangle = \sqrt{\frac{1}{3}}|300\rangle - \sqrt{\frac{2}{3}}|320\rangle \ .$$

The eigenstates of H_{+1}' are

$$\Delta E = \mp\frac{9}{2}e\mathcal{E}a_0 \quad \Rightarrow \quad |\psi\rangle = \frac{1}{\sqrt{2}}\left(|311\rangle \pm |321\rangle\right) \ .$$

The eigenstates of H_{-1}' are

$$\Delta E = \mp\frac{9}{2}e\mathcal{E}a_0 \quad \Rightarrow \quad |\psi\rangle = \frac{1}{\sqrt{2}}\left(|31,-1\rangle \pm |32,-1\rangle\right) \ .$$

In summary (the final column contains the degeneracy g):

$\Delta E/ea_0\mathcal{E}$	$m_\ell = 0$	$m_\ell = \pm 1$	$m_\ell = \pm 2$	g
$+9.0$	$\sqrt{\frac{1}{3}}\,\lvert300\rangle - \sqrt{\frac{1}{2}}\,\lvert310\rangle + \sqrt{\frac{1}{6}}\,\lvert320\rangle$			1
$+4.5$		$\sqrt{\frac{1}{2}}\left(\lvert31,\pm1\rangle - \lvert32,\pm1\rangle\right)$		2
0	$\sqrt{\frac{1}{3}}\lvert300\rangle - \sqrt{\frac{2}{3}}\lvert320\rangle$		$\lvert32,\pm2\rangle$	3
-4.5		$\sqrt{\frac{1}{2}}\left(\lvert31,\pm1\rangle + \lvert32,\pm1\rangle\right)$		2
-9.0	$\sqrt{\frac{1}{3}}\,\lvert300\rangle + \sqrt{\frac{1}{2}}\,\lvert310\rangle + \sqrt{\frac{1}{6}}\,\lvert320\rangle$			1

For completeness: to obtain the values of the reduced matrix elements given in the question, $\langle 3s \parallel \hat{\boldsymbol{r}} \parallel 3p\rangle = 9\sqrt{2}\,a_0$ and $\langle 3d \parallel \hat{\boldsymbol{r}} \parallel 3p\rangle = -(9/\sqrt{2})\,a_0$, it is sufficient to evaluate explicitly a single relevant matrix element in each case, for example the matrix elements $\langle 300|\hat{z}|310\rangle$ and $\langle 320|\hat{z}|310\rangle$:

$$\langle 300|\hat{z}|310\rangle = \langle 3s\,\|\,\hat{\boldsymbol{r}}\,\|\,3p\rangle\,\langle 10;10|00\rangle = -\langle 3s\,\|\,\hat{\boldsymbol{r}}\,\|\,3p\rangle\,\sqrt{(1/3)}\;, \tag{9}$$

$$\langle 320|\hat{z}|310\rangle = \langle 3d\,\|\,\hat{\boldsymbol{r}}\,\|\,3p\rangle\,\langle 10;10|20\rangle = \langle 3d\,\|\,\hat{\boldsymbol{r}}\,\|\,3p\rangle\,\sqrt{(2/3)}\;. \tag{10}$$

The eigenstates involved are $|300\rangle = R_{30}Y_{00}$, $|310\rangle = R_{31}Y_{10}$, $|320\rangle = R_{32}Y_{20}$, where

$$R_{30}(r) = \left(\frac{1}{3a_0}\right)^{3/2}\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}$$

$$R_{31}(r) = \left(\frac{1}{3a_0}\right)^{3/2}\frac{4\sqrt{2}}{9}\left(1 - \frac{r}{6a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$$

$$R_{32}(r) = \left(\frac{1}{3a_0}\right)^{3/2}\frac{4\sqrt{10}}{270}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}\;,$$

$$Y_{00} = \sqrt{\frac{1}{4\pi}}\,; \qquad Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta\,; \qquad Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)\,.$$

With $\hat{z} = r\cos\theta$, the radial components of the matrix elements $\langle 300|\hat{z}|310\rangle$ and $\langle 320|\hat{z}|310\rangle$ are straightforwardly evaluated by repeated use of the standard integral $\int_0^\infty x^n e^{-x}\,\mathrm{d}x = n!$:

$$\int_0^\infty r^3 R_{30}(r)R_{31}(r)\,\mathrm{d}r = -9\sqrt{2}\,a_0\,; \qquad \int_0^\infty r^3 R_{32}(r)R_{31}(r)\,\mathrm{d}r = -\frac{9\sqrt{5}}{2}a_0\,.$$

The angular components are given by the integrals

$$\int \cos\theta\, Y_{00}Y_{10}\,\mathrm{d}\Omega = \frac{1}{\sqrt{3}}\,; \qquad \int \cos\theta\, Y_{20}Y_{10}\,\mathrm{d}\Omega = \sqrt{\frac{4}{15}}\;.$$

The product of the radial and angular components then gives the matrix elements required as

$$\langle 300|\hat{z}|310\rangle = -9\sqrt{2}\,a_0\sqrt{\frac{1}{3}}\,; \qquad \langle 320|\hat{z}|310\rangle = -\frac{9\sqrt{5}}{2}\,a_0\sqrt{\frac{4}{15}}\,.$$

Comparing with Equations (9) and (10), the values of the reduced matrix elements can then be read off directly.

24. **Landé g-factors (Tripos 2004)**

The dominant contributions to the Hamiltonian for a multielectron atom are

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2 = \hat{H}_0 + \sum_{i<j}\frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_i \xi_i(r_i)\hat{\boldsymbol{L}}_i\cdot\hat{\boldsymbol{S}}_i\;.$$

If the spin-orbit contribution $\hat{H}_2$ is relatively small, $\langle\hat{H}_2\rangle \ll \langle\hat{H}_0\rangle, \langle\hat{H}_1\rangle$, as it is for the low-$Z$ region of the periodic table, then LS-coupling provides a good description of atomic eigenstates.

The terms $\hat{H}_0$ and $\hat{H}_1$ commute with (all components of) $\hat{\boldsymbol{L}}$, $\hat{\boldsymbol{S}}$ and $\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}$, and hence also with $\hat{\boldsymbol{L}}^2$, $\hat{\boldsymbol{S}}^2$ and $\hat{\boldsymbol{J}}^2$. Hence L, S, J and m_J are good quantum numbers for $\hat{H}_0 + \hat{H}_1$ (as also are m_L and m_S).

With $\hat{H}_2$ "switched on", the overall Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2$ no longer commutes with $\hat{\boldsymbol{L}}$ or $\hat{\boldsymbol{S}}$, but still commutes with $\hat{\boldsymbol{J}}$ and $\hat{\boldsymbol{J}}^2$, as it must from rotational symmetry. Hence, strictly speaking, only J and m_J remain good quantum numbers. However, provided $\hat{H}_2$ represents only a small perturbation, L and S remain good quantum numbers to good approximation. In perturbation theory terms, the admixture of zeroth-order states with other values of L and S in the perturbed wavefunctions is very small. The spin-orbit perturbation $\hat{H}_2$ breaks the degeneracy in J, producing fine structure consisting of closely spaced levels ordered by J. Thus, to good approximation, the fine-structure levels are characterised by the quantum numbers L, S, and J, and the degenerate states within each level are characterised by m_J.

For $L = 2$, $S = 1$ and $J = 3$, there is a unique combination of m_L and m_S (namely $m_L = 2$, $m_S = 1$) that can combine to give $m_J = m_L + m_S = 3$. Therefore the state $|J, m_J\rangle = |3, 3\rangle$ must be the product state $|L, m_L\rangle \otimes |S, m_S\rangle = |2, 2\rangle \otimes |1, 1\rangle$:

$$\boxed{|3, 3\rangle = |2, 2\rangle|1, 1\rangle} \,. \tag{11}$$

This state, $|\psi\rangle = |3, 3\rangle$, is an eigenstate of $\hat{L}_z$ and $\hat{S}_z$, with $\hat{L}_z|\psi\rangle = m_L\hbar|\psi\rangle = 2\hbar|\psi\rangle$ and $\hat{S}_z|\psi\rangle = m_S\hbar|\psi\rangle = \hbar|\psi\rangle$. Therefore, on application of the magnetic field B, the first-order energy correction for this state is

$$\Delta E = \frac{eB}{2m_\mathrm{e}}\langle\psi|(\hat{L}_z + 2\hat{S}_z)|\psi\rangle = \frac{eB}{2m_\mathrm{e}}(2\hbar + 2\hbar) = \boxed{4\mu_\mathrm{B}B} \,.$$

The Landé g-factor is

$$g = \frac{3}{2} - \frac{L(L+1) - S(S+1)}{2J(J+1)} = \frac{4}{3} \,.$$

Hence the energy correction can be obtained equivalently as

$$\Delta E = g\mu_\mathrm{B}Bm_J = \frac{4}{3}\mu_\mathrm{B}B \times 3 = 4\mu_\mathrm{B}B \,.$$

Applying the ladder operator $\hat{J}_- = \hat{L}_- + \hat{S}_-$ to Equation (11) gives

$$\hat{J}_-|3, 3\rangle = (\hat{L}_- + \hat{S}_-)|2, 2\rangle|1, 1\rangle \,.$$

Using $\hat{J}_-|3, 3\rangle = \sqrt{6}\hbar|3, 2\rangle$, $\hat{L}_-|2, 2\rangle = 2\hbar|2, 1\rangle$ and $\hat{S}_-|1, 1\rangle = \sqrt{2}\hbar|1, 0\rangle$ then determines the state with $J = 3$ and $m_J = 2$:

$$|3, 2\rangle = \sqrt{\frac{2}{3}}|2, 1\rangle|1, 1\rangle + \sqrt{\frac{1}{3}}|2, 2\rangle|1, 0\rangle \,.$$

The energy correction for this state is

$$\Delta E = \frac{eB}{2m_\mathrm{e}}\left[\frac{2}{3}(\hbar + 2\hbar) + \frac{1}{3}(2\hbar)\right] = \boxed{\frac{8}{3}\mu_\mathrm{B}B} \,.$$

The g-factor is $g = 4/3$, and this can also be obtained as

$$\Delta E = g\mu_{\rm B} B m_J = \frac{4}{3}\mu_{\rm B} B \times 2 = \frac{8}{3}\mu_{\rm B} B \ .$$

The state $|J, m_J\rangle = |2, 2\rangle$ must be a linear combination of the same product states as in the state $|J, m_J\rangle = |3, 2\rangle$, and must be orthogonal to it:

$$|2, 2\rangle = \sqrt{\frac{1}{3}}|2, 1\rangle|1, 1\rangle - \sqrt{\frac{2}{3}}|2, 2\rangle|1, 0\rangle \ .$$

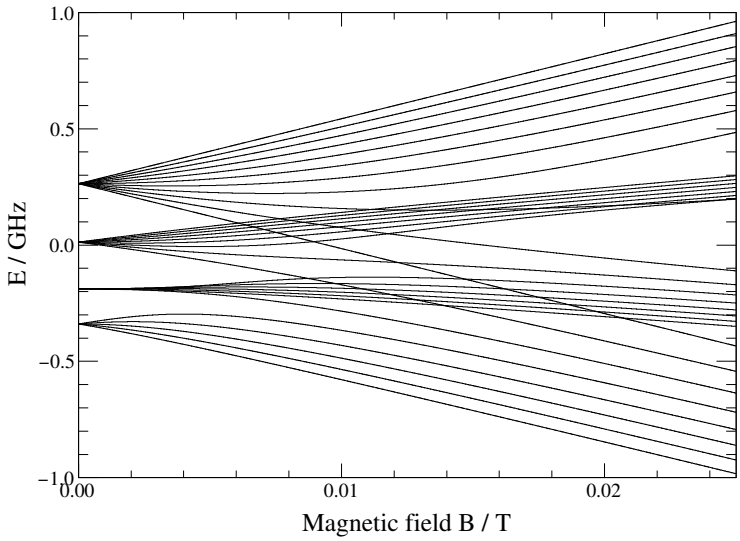
The energy correction for this state is

$$\Delta E = \frac{eB}{2m_e}\left[\frac{1}{3}(\hbar + 2\hbar) + \frac{2}{3}(2\hbar)\right] = \boxed{\frac{7}{3}\mu_{\rm B} B}.$$

The g-factor is $g = 7/6$, and this can also be obtained as

$$\Delta E = g\mu_{\rm B} B m_J = \frac{7}{6}\mu_{\rm B} B \times 2 = \frac{7}{3}\mu_{\rm B} B \ .$$

25. **Zeeman effect for hyperfine levels**



(a) Working upwards, each zero-field hyperfine level is seen to split into $2F+1 = 5, 7, 9, 11$ states; hence these levels have $F = 2, 3, 4, 5$. These values of $F = I \otimes J$ can be produced by either $\{I = 3/2, J = 7/2\}$, or by $\{I = 7/2, J = 3/2\}$.

(b) The level with $F = 3$ has no visible splitting at low field, and hence has $g_F \approx 0$ (since $\Delta E = g_F m_F \mu_{\rm B} B$ is zero for all m_F). Using

$$g_F \approx g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)}$$

then shows that $I = 7/2, J = 3/2$ is the correct assignment (without needing to know the value of g_J).

(c) In the high-field limit, the Zeeman effect gives first-order energy corrections

$$\Delta E = (g_I m_I + g_J m_J)\mu_\mathrm{B} B \approx g_J \mu_\mathrm{B} B m_J \ .$$

The 32 levels are seen to be evolving towards four groups of 8 levels, with each group corresponding to a different value of m_J. Hence $2J + 1 = 4$ and $2I + 1 = 8$, giving $I = 7/2, J = 3/2$ again.

(d) To estimate g_F, the highest hyperfine level ($F = 5$) is the best to use, especially the highest and lowest of the split levels ($m_F = \pm 5$) since they are linear with B and have the largest lever-arm. For $B = 0.025\,\mathrm{T}$, the frequency separation between these two levels can be estimated from the plot to be

$$\Delta\nu \approx 3.47 - 2.07 = 1.40\,\mathrm{GHz} \ .$$

The weak-field Zeeman energy corrections are given by $\Delta E = g_F m_F \mu_\mathrm{B} B$, and the two levels are separated by $\Delta m_F = 10$. We can therefore estimate g_F as

$$g_F = \frac{h\,\Delta\nu}{\mu_\mathrm{B} B\,\Delta m_F} = \frac{(6.626 \times 10^{-34}) \times (1.4 \times 10^9)}{(9.28 \times 10^{-24}) \times (0.025) \times 10} = \boxed{0.40} \ .$$

We can in turn estimate g_J as (with $F = 5$, $J = 3/2$, $I = 7/2$, $g_F = 2/5$)

$$g_J \approx g_F \frac{2F(F+1)}{F(F+1) + J(J+1) - I(I+1)} \approx \boxed{\frac{4}{3}} \ .$$

(e) Assuming $g_L = 1$ and $g_S = 2$, the Landé g-factor g_J is given by

$$g_J = \frac{3}{2} - \frac{L(L+1) - S(S+1)}{2J(J+1)} \ .$$

Hence

$$L(L+1) - S(S+1) = \left(\frac{3}{2} - g_J\right) 2J(J+1) = \frac{5}{4} \ .$$

Since L must be an integer, and since $J = 3/2$, the total spin S must be half-integer. The only solution of $L(L+1) - S(S+1) = 5/4$ with L integer and S half-integer is $L = 1$, $S = 1/2$. The term is therefore $^2\mathrm{P}_{3/2}$.

(The plot in fact corresponds to the $6^2\mathrm{P}_{3/2}$ term of ^{133}Cs.)

(f) For an interaction proportional to $\hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{J}}$, the energy shift $(\Delta E)_F$ for each hyperfine level is expected to be

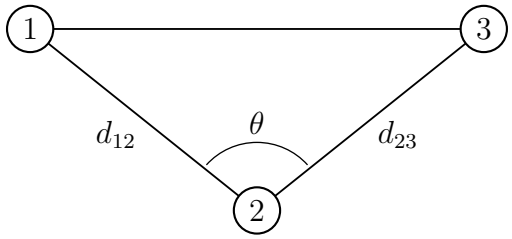
$$(\Delta E)_F \propto F(F+1) - I(I+1) - J(J+1) \ .$$

Since I and J are the same throughout, we expect neighbouring hyperfine levels $F + 1$ and F to be separated by

$$(\Delta E)_{(F+1)} - (\Delta E)_F \propto (F+1)(F+2) - F(F+1) = 2(F+1) \ .$$

Thus, working upwards from the bottom, we expect separations in the ratio $6 : 8 : 10$. This is consistent with the relative separations in the plot of about 0.15, 0.20, 0.25 GHz.

26. **Molecular bonding (Tripos 1998)**



In the basis $\{|\phi_1\rangle,\ |\phi_2\rangle,\ |\phi_3\rangle\}$ of $1s$ hydrogen atom wavefunctions, the matrix elements $H_{ij} \equiv \langle\psi_i|\hat{H}|\psi_j\rangle$ of the Hamiltonian for the H_3^+ ion are given in the question as

$$\begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{pmatrix} = \begin{pmatrix} \alpha & \beta & \beta\gamma \\ \beta & \alpha & \beta \\ \beta\gamma & \beta & \alpha \end{pmatrix} .$$

Neglecting the overlap integrals, the upper bound E on the energy levels is given, according to Rayleigh-Ritz, by solving the secular equation $|H_{ij} - E\delta_{ij}| = 0$, which would require solving a cubic equation for E.

If instead we use the basis $\{|\psi_-\rangle \equiv (|\psi_1\rangle - |\psi_3\rangle)/\sqrt{2},\ |\psi_+\rangle \equiv (|\psi_1\rangle + |\psi_3\rangle)/\sqrt{2},\ |\psi_2\rangle\}$, then the matrix representation of $\hat{H}$ becomes

$$\begin{pmatrix} H_{--} & H_{-+} & H_{-2} \\ H_{+-} & H_{++} & H_{+2} \\ H_{2-} & H_{2+} & H_{22} \end{pmatrix} = \begin{pmatrix} \alpha - \gamma\beta & 0 & 0 \\ 0 & \alpha + \gamma\beta & \beta\sqrt{2} \\ 0 & \beta\sqrt{2} & \alpha \end{pmatrix} .$$

For example,

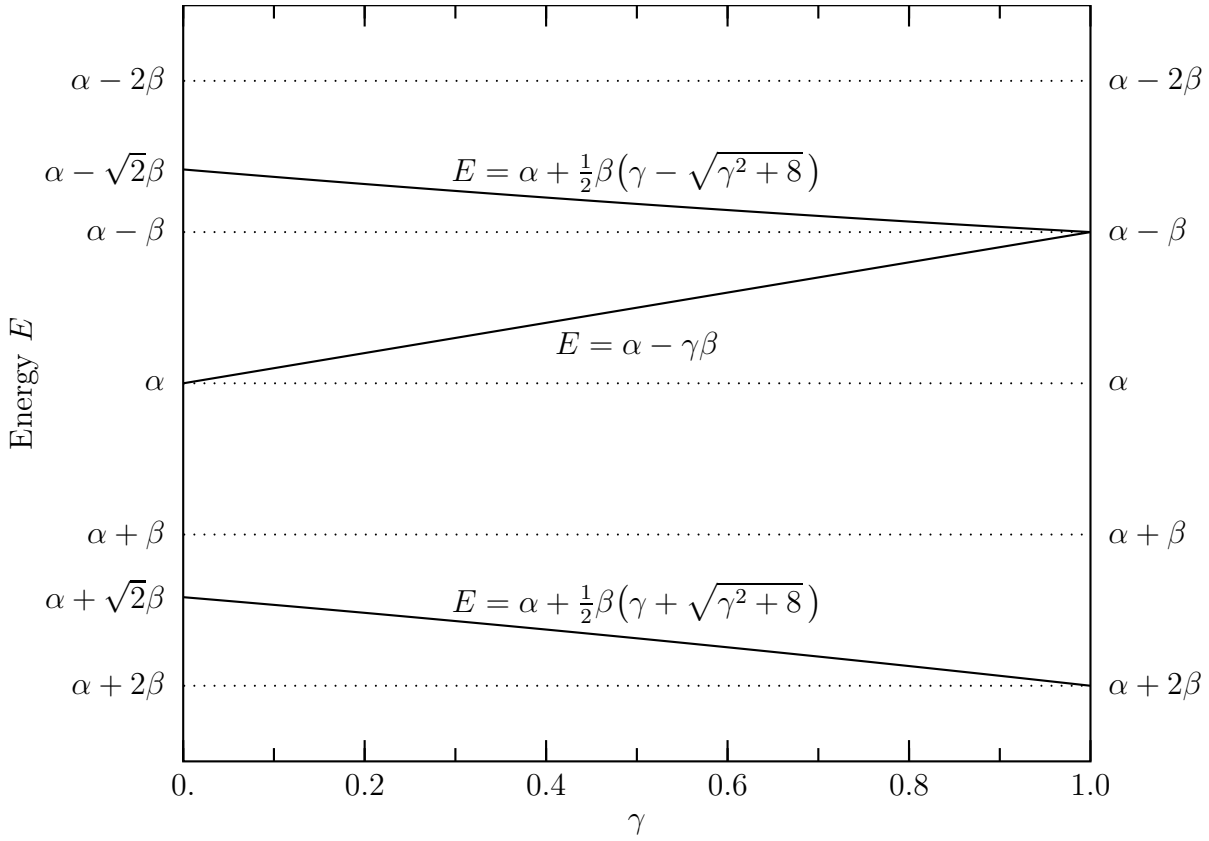
$$H_{--} \equiv \langle\psi_-|\hat{H}|\psi_-\rangle = \frac{1}{2}\langle\psi_1 - \psi_3|\hat{H}|\psi_1 - \psi_3\rangle = \frac{1}{2}\left(H_{11} + H_{33} - H_{13} - H_{31}\right) = \alpha - \beta\gamma \ .$$

The secular equation clearly has $E = \alpha - \gamma\beta$ as one solution, and only a quadratic equation needs to be solved to find the remaining two:

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

Overall, the three solutions are:

$$\boxed{E = \alpha - \gamma\beta, \qquad E = \alpha + \frac{1}{2}\beta\left(\gamma \pm \sqrt{\gamma^2 + 8}\right).}$$



As $\theta \to 60°$ we expect $\gamma \to 1$, as all the bond lengths become equal. The solutions in this limit are: $E = \alpha - \beta$, $\alpha - \beta$, and $\alpha + 2\beta$.

As $\theta \to 180°$ we expect $\gamma \to 0$, as atoms 1 and 3 become highly separated. The solutions in this limit are: $E = \alpha$, and $\alpha \pm \sqrt{2}\beta$.

Since $\beta < 0$, the lowest energy is seen to be $\alpha + 2\beta$, obtained when $\gamma = 1$, corresponding to $\theta = 60°$ (equilateral triangle). The corresponding eigenvector is easily found to be $|\psi_0\rangle = (|\psi_1\rangle + |\psi_2\rangle + |\psi_3\rangle)/\sqrt{3}$.

The ground state of the H_3^+ ion is obtained by placing both electrons into this lowest energy orbital, giving the spatial component $|\psi\rangle = |\psi_0(1)\rangle|\psi_0(2)\rangle$. This is symmetric under particle interchange, so must be combined with the antisymmetric singlet ($S = 0$) spin state.

27. **Time-dependent perturbation theory**

(i) With $V(t) = e\mathcal{E}_0 z e^{-t/\tau}$, the amplitude for a $1s \to 2s$ transition in hydrogen is

$$c_{2s}(t) = \frac{e\mathcal{E}_0}{i\hbar}\int_0^t \mathrm{d}t' e^{i(E_n - E_0)t'/\hbar} e^{-t'/\tau}\langle 2s|z|1s\rangle \ .$$

From question 19(c), the matrix element $\langle 2s|z|1s\rangle = 0$. Alternatively, since the $1s$ and $2s$ wavefunctions both have even parity while z has odd parity, the matrix element must vanish. Therefore the probability of finding the atom in the $2s$ state is identically zero.

(ii) From question 19(a), the matrix elements $\langle 2p_{\pm 1}|z|1s\rangle = 0$ because the relevant C-G coefficients vanish, or equivalently, from question 19(b), because the ϕ component of the integral vanishes. Therefore the probability of finding the atom in the $2p_{\pm 1}$ states is identically zero.

The only non-zero matrix element is:

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

Taking the limit as $t\to\infty$, the t' integral is given by,

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

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

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

28. **Time-dependent perturbation theory (Tripos 2001)**

The amplitude for a transition $0\to n$ from the ground state is

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

where $E_n = (n+1/2)\hbar\omega$. For the perturbation

$$\hat{H}'(t) = \begin{cases} 0 & t<0 \text{ and } t>T \\ \lambda\hat{x}(1-t/T) & 0\le t\le T\end{cases}\,,$$

this gives the amplitude for a transition $0\to 1$ to the first excited state as

$$c_1 = \frac{\lambda}{i\hbar}\int_0^T \exp(i\omega t')\left(1-\frac{t'}{T}\right)\langle\psi_1|x|\psi_0\rangle\,\mathrm{d}t'\;.$$

Integration by parts gives

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

Using

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

then gives the probability of a transition to the first excited state as

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

For $\omega T \gg 1$,

$$|c_1|^2 = \frac{\lambda^2}{2m\hbar\omega^3} \ .$$

We have

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

So for the new ground state, we can use

$$x' = x + \frac{\lambda}{m\omega^2} \ .$$

We have

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

where $\alpha = m\omega/2\hbar$. Hence

$$\langle\psi_1|\psi_0'\rangle = \left(\frac{2m\omega}{\hbar}\right)^{1/2}\left(-\frac{\lambda}{2m\omega^2}\right)\exp\left[-2\alpha\left(\frac{\lambda}{2m\omega^2}\right)^2\right] \ .$$

To first order in λ,

$$|\langle\psi_1|\psi_0'\rangle|^2 = \frac{2m\omega}{\hbar}\frac{\lambda^2}{4m^2\omega^4} = \frac{\lambda^2}{2m\hbar\omega^3} \ .$$

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

29. **Electron-hydrogen elastic scattering in the Born approximation**:

The probability that the atomic electron is found in a volume element $\mathrm{d}^3\boldsymbol{r}'$ at position $\boldsymbol{r}'$ is $|\psi(\boldsymbol{r}')|^2\,\mathrm{d}^3\boldsymbol{r}'$. The corresponding electric charge is $-e|\psi(\boldsymbol{r}')|^2\,\mathrm{d}^3\boldsymbol{r}'$. The potential energy due to the Coulomb interaction of this charge with the incoming beam electron at position $\boldsymbol{r}$ is $(e^2/4\pi\epsilon_0)(|\psi(\boldsymbol{r}')|^2\,\mathrm{d}^3\boldsymbol{r}'/|\boldsymbol{r}-\boldsymbol{r}'|)$. Integrating over all possible atomic electron positions $\boldsymbol{r}'$, and adding the potential energy $-e^2/(4\pi\epsilon_0 r)$ due to the Coulomb interaction between the beam electron and the hydrogen nucleus gives an overall potential energy

$$\boxed{V(\boldsymbol{r}) = \frac{e^2}{4\pi\epsilon_0}\left(-\frac{1}{r} + \int\frac{|\psi(\boldsymbol{r}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\,\mathrm{d}^3\boldsymbol{r}'\right)}.$$

In the Born approximation, the scattering amplitude $f(\theta,\phi)$ is proportional to the FT of $V(\boldsymbol{r})$,

$$f(\theta,\phi) = \frac{m_\mathrm{e}}{2\pi\hbar^2}\int V(\boldsymbol{r})e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\,\mathrm{d}^3\boldsymbol{r} \ ,$$

where $\boldsymbol{q} = \boldsymbol{k} - \boldsymbol{k}'$ is the three-momentum transferred in the scattering. The integral in the expression for $V(\boldsymbol{r})$ is the convolution of $1/r$ with $|\psi(\boldsymbol{r})|^2$. The convolution theorem gives the scattering amplitude as

$$f(\theta,\phi) = \frac{m_{\rm e}}{2\pi\hbar^2}\frac{e^2}{4\pi\epsilon_0}\left[-F(1/r) + F(1/r)F(|\psi|^2)\right] \ .$$

The prefactor above is equal to $a_0/2\pi$. For the hydrogen ground state, $\psi_{1s} = (\pi a_0^3)^{-1/2}e^{-r/a_0}$, we then have

$$f(\theta,\phi) = \frac{a_0}{2\pi}F(1/r)\left[-1 + \frac{1}{(\pi a_0^3)}F(e^{-2r/a_0})\right] \ .$$

Setting $\lambda \equiv 2/a_0$ for convenience, the FT's above are

$$F(1/r) = \int \frac{1}{r}e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\,{\rm d}^3\boldsymbol{r} = \frac{4\pi}{q^2} \ ; \qquad F(e^{-2r/a_0}) = \int e^{-\lambda r}e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\,{\rm d}^3\boldsymbol{r} = \frac{8\pi\lambda}{(\lambda^2+q^2)^2} \ .$$

Hence

$$\boxed{f(\theta,\phi) = \frac{a_0}{2\pi}\frac{4\pi}{q^2}\left[-1 + \frac{1}{(\pi a_0^3)}\frac{8\pi\lambda}{(\lambda^2+q^2)^2}\right] = -2a_0\frac{8+(qa_0)^2}{(4+(qa_0)^2)^2}} \ .$$

For elastic scattering, we have $|\boldsymbol{k}'| = |\boldsymbol{k}| = k$, $\boldsymbol{k} = (0,0,k)$, $\boldsymbol{k}' = k(\sin\theta, 0, \cos\theta)$, and hence

$$q^2 = |\boldsymbol{k}|^2 + |\boldsymbol{k}'|^2 - 2\boldsymbol{k}\cdot\boldsymbol{k}' = 2k^2 - 2k^2\cos\theta \ , \qquad q = 2k\sin(\theta/2) \ .$$

Non-relativistic incoming electrons of energy E have momentum $\hbar k = \sqrt{2m_{\rm e}E}$, and hence

$$qa_0 = 2ka_0\sin(\theta/2) = 2a_0\frac{\sqrt{2m_{\rm e}E}}{\hbar}\sin(\theta/2) \ .$$

For $E = 20\,{\rm eV}$ and $\theta = 100^\circ$, the scattering amplitude is predicted as

$$qa_0 = 2\times(0.53\times10^{-10})\times\frac{\sqrt{2\times(9.11\times10^{-31})\times(20\times1.6\times10^{-19})}}{(1.055\times10^{-34})}\sin(50^\circ) = 1.8585 \ ,$$

$$f(\theta,\phi) = -2\times\frac{8+(1.8585)^2}{(4+(1.8585)^2)^2}a_0 = -(0.4123)a_0 \ .$$

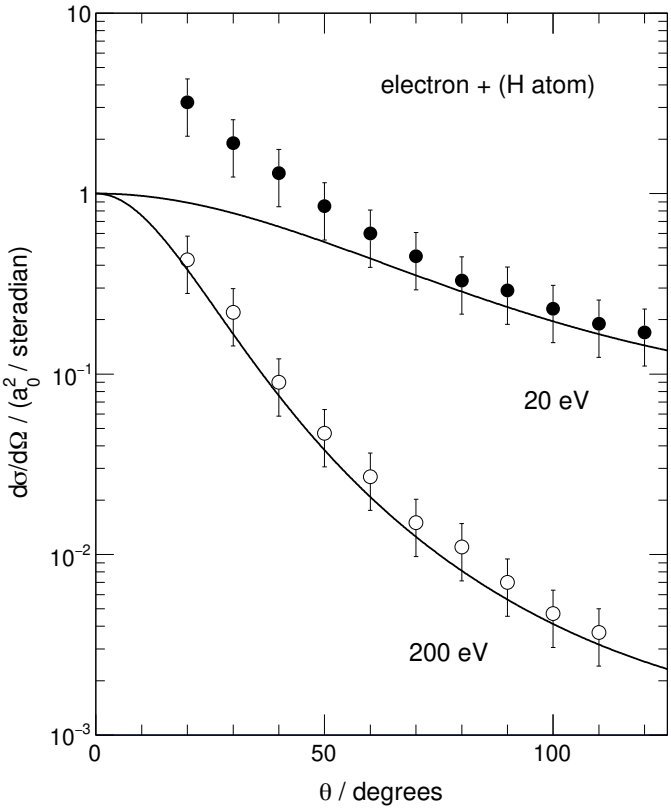
The predicted cross section, ${\rm d}\sigma/{\rm d}\Omega = |f(\theta,\phi)|^2$, is then

$$\boxed{\frac{{\rm d}\sigma}{{\rm d}\Omega} = (0.4123)^2a_0^2 = (0.17)a_0^2} \ .$$

For $E = 200\,{\rm eV}$ and $\theta = 100^\circ$, the equivalent calculation gives

$$\boxed{\frac{{\rm d}\sigma}{{\rm d}\Omega} = (3.3\times10^{-3})a_0^2} \ .$$

Both of these predictions are in good agreement with the data.



At small angles, $\theta \to 0$, we have $q \to 0$, $f(\theta, \phi) \to -a_0$, so the Born approximation prediction (the solid curves in the figure) is $\mathrm{d}\sigma/\mathrm{d}\Omega \to a_0^2$ for all electron energies. This prediction is consistent with the data for $E = 200\,\mathrm{eV}$, but lies below the $20\,\mathrm{eV}$ data. The Born approximation works better at higher energies where the scattering potential becomes a small perturbation.

30. **Photons**

The linear momentum operator for the EM field is

$$\hat{\boldsymbol{P}} = \sum_{\boldsymbol{k},\lambda} \hbar \boldsymbol{k}\, \hat{a}^\dagger_{\boldsymbol{k},\lambda} \hat{a}_{\boldsymbol{k},\lambda} \ .$$

Applying the total momentum operator $\hat{\boldsymbol{P}}$ to a single photon state $|\boldsymbol{k},\lambda\rangle = \hat{a}^\dagger_{\boldsymbol{k},\lambda}|0\rangle$ gives

$$\hat{\boldsymbol{P}}|\boldsymbol{k},\lambda\rangle = \hat{\boldsymbol{P}}\, \hat{a}^\dagger_{\boldsymbol{k},\lambda}|0\rangle = \left(\sum_{\boldsymbol{k}',\lambda'} \hbar \boldsymbol{k}'\, \hat{a}^\dagger_{\boldsymbol{k}',\lambda'} \hat{a}_{\boldsymbol{k}',\lambda'} \right) \hat{a}^\dagger_{\boldsymbol{k},\lambda}|0\rangle \ .$$

The commutation relation $[\hat{a}_{\boldsymbol{k},\lambda}, \hat{a}^\dagger_{\boldsymbol{k}',\lambda'}] = \delta_{\boldsymbol{k}',\boldsymbol{k}}\, \delta_{\lambda'\lambda}$ allows the rightmost pair of operators to be reordered as

$$\hat{a}_{\boldsymbol{k}',\lambda'} \hat{a}^\dagger_{\boldsymbol{k},\lambda} = \delta_{\boldsymbol{k}'\boldsymbol{k}} \delta_{\lambda'\lambda} + \hat{a}^\dagger_{\boldsymbol{k},\lambda} \hat{a}_{\boldsymbol{k}',\lambda'} \ .$$

Since $\hat{a}_{\boldsymbol{k}',\lambda'}|0\rangle = 0$, we then obtain

$$\hat{a}_{\boldsymbol{k}',\lambda'} \hat{a}^\dagger_{\boldsymbol{k},\lambda}|0\rangle = \delta_{\boldsymbol{k}'\boldsymbol{k}} \delta_{\lambda'\lambda}|0\rangle \ .$$

Hence

$$\hat{\boldsymbol{P}}|\boldsymbol{k},\lambda\rangle = \sum_{\boldsymbol{k}',\lambda'} \hbar\boldsymbol{k}'\, \hat{a}^\dagger_{\boldsymbol{k}',\lambda'}\delta_{\boldsymbol{k}'\boldsymbol{k}}\delta_{\lambda'\lambda}|0\rangle = \hbar\boldsymbol{k}\, \hat{a}^\dagger_{\boldsymbol{k},\lambda}|0\rangle \ .$$

Thus photons have linear momentum $\hbar\boldsymbol{k}$:

$$\boxed{\hat{\boldsymbol{P}}|\boldsymbol{k},\lambda\rangle = \hbar\boldsymbol{k}|\boldsymbol{k},\lambda\rangle} \ .$$

The intrinsic angular momentum operator is

$$\hat{\boldsymbol{J}}_{\rm S} = \hbar\sum_{\boldsymbol{k}} \frac{\boldsymbol{k}}{|\boldsymbol{k}|}\left[\hat{a}^\dagger_{\boldsymbol{k},L}\hat{a}_{\boldsymbol{k},L} - \hat{a}^\dagger_{\boldsymbol{k},R}\hat{a}_{\boldsymbol{k},R}\right] \ .$$

Operating with $\hat{\boldsymbol{J}}_{\rm S}$ on a right-handed single photon state $|\boldsymbol{k},R\rangle = \hat{a}^\dagger_{\boldsymbol{k},R}|0\rangle$ gives

$$\hat{\boldsymbol{J}}_{\rm S}|\boldsymbol{k},R\rangle = \hat{\boldsymbol{J}}_{\rm S}\hat{a}^\dagger_{\boldsymbol{k},R}|0\rangle = \hbar\sum_{\boldsymbol{k}'} \frac{\boldsymbol{k}'}{|\boldsymbol{k}'|}\left[\hat{a}^\dagger_{\boldsymbol{k}',L}\hat{a}_{\boldsymbol{k}',L} - \hat{a}^\dagger_{\boldsymbol{k}',R}\hat{a}_{\boldsymbol{k}',R}\right]\hat{a}^\dagger_{\boldsymbol{k},R}|0\rangle \ .$$

The operators $\hat{a}_{\boldsymbol{k}',L}$ and $\hat{a}^\dagger_{\boldsymbol{k},R}$ commute, and $\hat{a}_{\boldsymbol{k}',L}|0\rangle = 0$. Hence the first term on the right-hand side vanishes, leaving just the second term:

$$\hat{\boldsymbol{J}}_{\rm S}|\boldsymbol{k},R\rangle = -\hbar\sum_{\boldsymbol{k}'} \frac{\boldsymbol{k}'}{|\boldsymbol{k}'|}\hat{a}^\dagger_{\boldsymbol{k}',R}\hat{a}_{\boldsymbol{k}',R}\hat{a}^\dagger_{\boldsymbol{k},R}|0\rangle \ .$$

Inverting the order of the rightmost two operators,

$$\hat{a}_{\boldsymbol{k}',R}\hat{a}^\dagger_{\boldsymbol{k},R} = \delta_{\boldsymbol{k}'\boldsymbol{k}}\delta_{\lambda'\lambda} + \hat{a}^\dagger_{\boldsymbol{k},R}\hat{a}_{\boldsymbol{k}',R} \ ,$$

and using $\hat{a}_{\boldsymbol{k}',R}|0\rangle = 0$ then gives

$$\boxed{\hat{\boldsymbol{J}}_{\rm S}|\boldsymbol{k},R\rangle = -\hbar\frac{\boldsymbol{k}}{|\boldsymbol{k}|}\hat{a}^\dagger_{\boldsymbol{k},R}|0\rangle} \ .$$

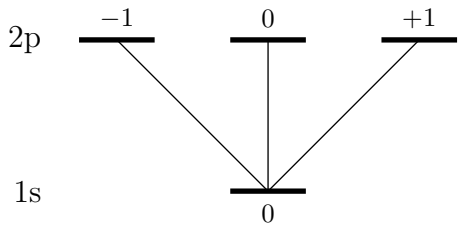
Hence right-handed photons possess an intrinsic angular momentum oriented opposite to the photon direction of motion, with spin projection $-\hbar$ along the photon direction.

For left-handed photons, it is the first term rather than the second term on the right-hand side that survives, giving a change of sign:

$$\boxed{\hat{\boldsymbol{J}}_{\rm S}|\boldsymbol{k},L\rangle = +\hbar\frac{\boldsymbol{k}}{|\boldsymbol{k}|}\hat{a}^\dagger_{\boldsymbol{k},L}|0\rangle} \ .$$

31. **Spontaneous emission lifetimes**

Neglecting electron spin, the $n = 2$ level of hydrogen consists of four degenerate states: a 2s state, $|n\ell m_\ell\rangle = |200\rangle$, and three $2\mathrm{p}_m$ states, $|n\ell m_\ell\rangle = |211\rangle$, $|210\rangle$ and $|21,-1\rangle$. The $n = 1$ ground state is the non-degenerate 1s state $|n\ell m_\ell\rangle = |100\rangle$. The three transitions $2p_m \to 1s$ ($m = 0, \pm 1$) are allowed by the E1 selection rules, but the transition $2s \to 1s$ is not.



From rotational symmetry, all three transitions must have the same decay rate. Equivalently, each $2p_m$ state must have the same lifetime. For an isolated system, with no preferred spatial direction, an observable quantity such as a lifetime cannot depend on a quantum number such as m which is associated with a projection onto an arbitrary choice of spatial direction (the z-axis).

Alternatively, consider an isolated sample of hydrogen atoms which is initially an equal mix of the three $2p_m$ states, and hence is initially unpolarised. Suppose that the lifetime of the $2p_1$ state was less than the lifetimes of the other two states. Then, with the passage of time, the 2p atoms in the sample would become dominated by $2p_1$. The sample would thus spontaneously develop a net polarisation, i.e. a preferred spatial direction, which is not possible for an isolated system.

More quantitatively, from lectures, the decay rate for a spontaneous decay $|Jm_J\rangle \to |J'm'_J\rangle + \gamma$ is given by

$$\Gamma(m_J \to m'_J) = \frac{\omega^3}{3\pi\epsilon_0 c^3\hbar}|d_m|^2\,,$$

where $d_m = \langle Jm_J|\hat{d}_m|J'm'_J\rangle$ is a matrix element involving the spherical component $\hat{d}_m$ of the dipole operator $\hat{\boldsymbol{d}} = -e\hat{\boldsymbol{r}}$, with $m = m_J - m'_J$ (with possible values $m = 0, \pm 1$).

The dipole matrix elements $\langle 21m|\hat{d}_m|100\rangle$ governing each $2p_m \to 1s$ transition are all equal to each other (see question 19(a)):

$$\langle 21m|\hat{d}_m|100\rangle = \langle 2p\,\|\,\hat{\boldsymbol{d}}\,\|\,1s\rangle\,\langle 1m;00|1m\rangle = \langle 2p\,\|\,\hat{\boldsymbol{d}}\,\|\,1s\rangle\,.$$

Explicitly,

$$\langle 21,+1|\hat{d}_{+1}|100\rangle = \langle 210|\hat{d}_0|100\rangle = \langle 21,-1|\hat{d}_{-1}|100\rangle = \langle 2p\,\|\,\hat{\boldsymbol{d}}\,\|\,1s\rangle\,.$$

Hence all three $2p_m$ states, $|nlm\rangle = |210\rangle, |21,\pm 1\rangle$ have the same lifetime:

$$\Gamma(2p_m \to 1s) = \frac{\omega^3}{3\pi\epsilon_0 c^3\hbar}\big|\langle 2p\,\|\,\hat{\boldsymbol{d}}\,\|\,1s\rangle\big|^2\,.$$

To obtain the value of the lifetime, $\tau = 1/\Gamma$, choose the $2p_0$ state. The decay rate depends on $d_0 = \langle 210|z|100\rangle$, which is the same as the matrix element already computed in question 27:

$$ed_0 = \langle 2p_0|ez|1s\rangle = \frac{256\,ea_0}{243\sqrt{2}} = 6.31\times 10^{-30}\,\mathrm{C\,m}\,.$$

The energy of the emitted photon is

$$\hbar\omega = \frac{3}{4}R_\infty = \frac{3}{4}\times\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2} \qquad \Rightarrow \qquad \omega = 1.56\times 10^{16}\,\mathrm{Hz}\,.$$

Hence, the lifetime of the 2p state is

$$\tau(2p) = \frac{1}{\Gamma} = \frac{3\pi\epsilon_0 c^3\hbar}{\omega^3|d_0|^2} = \boxed{1.56\times10^{-9}\,\mathrm{s}}\,.$$

(a) The only lower lying state consistent with the E1 selection rules to which 3s can decay is 2p. We expect $\langle 3s|ez|2p\rangle \sim ea_0$ on dimensional grounds, not very different from $\langle 2p|ez|1s\rangle$. A difference in lifetime for the 3s and 2p states arises primarily from the factor ω^3. For $3s \to 2p$, the transition energy is

$$\hbar\omega = \left(\frac{1}{4} - \frac{1}{9}\right) R_\infty = \frac{5}{36} R_\infty\,.$$

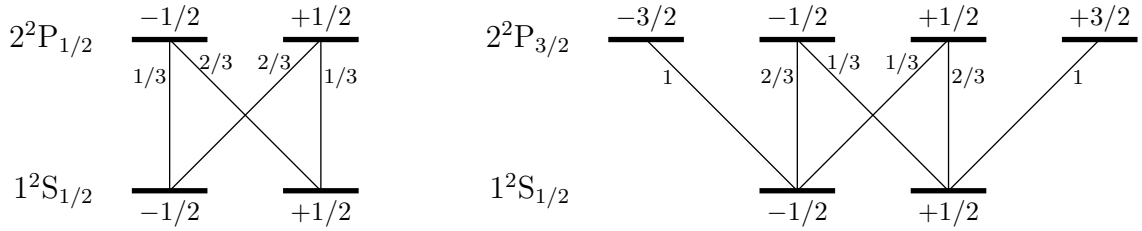
The lifetimes are therefore expected to be approximately in the ratio

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

The 3s lifetime is in fact $\tau(3s) = 1.58\times10^{-7}\,\mathrm{s}$, a factor 100.8 greater than the 2p lifetime.

(b) The decay $2s \to 1s$ is not allowed by the E1 selection rules; the 2s state is accordingly metastable. The 2s decay takes place via two-photon emission, a process which can only arise at second-order in perturbation theory, and thus occurs relatively slowly. In practice, as a result of collision processes, atoms in the metastable 2s state will generally transfer from 2s to 2p (for example), followed by rapid decay $2p \to 1s$, before the slow decay $2s \to 1s$ can occur. Alternatively, a more rapid decay of the 2s state may be induced by the presence of an external electric field, which mixes the 2s and 2p states through the linear Stark effect.

(c) "Switching on" the electron spin, the 2p states become $2^2\mathrm{P}_{3/2}$ and $2^2\mathrm{P}_{1/2}$. Since the dipole operator $\hat{\boldsymbol{d}}$ is independent of spin, we would not expect the lifetime to depend on whether we examine a state at a level which does (2P), or does not (2p), include the electron spin. Therefore we expect the lifetimes for the states $2^2\mathrm{P}_{3/2}$ and $2^2\mathrm{P}_{1/2}$ to be the same as for the "zeroth-order" states $2\mathrm{p}_{0,\pm1}$.



More quantitatively, consider for example the spontaneous decay of the $2^2\mathrm{P}_{3/2}$ state with $m_J = +1/2$. Expressed as a linear combination of $|n\ell m_\ell\rangle \otimes |s, m_s\rangle$ product states, this state is given by

$$|n, J, m_J\rangle = |2, \tfrac{3}{2}, +\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}|211\rangle|\downarrow\rangle + \sqrt{\tfrac{2}{3}}|210\rangle|\uparrow\rangle\ .$$

The $1^2\mathrm{S}_{1/2}$ ground state consists of the two states

$$|n, J, m_J\rangle = |1, \tfrac{1}{2}, +\tfrac{1}{2}\rangle = |100\rangle|\uparrow\rangle\ ; \qquad |n, J, m_J\rangle = |1, \tfrac{1}{2}, -\tfrac{1}{2}\rangle = |100\rangle|\downarrow\rangle\ .$$

The E1 selection rules allow the $2^2\mathrm{P}_{3/2}$ state $|J, m_J\rangle = |\frac{3}{2}, +\frac{1}{2}\rangle$ to decay to both of these ground states. For the decay $|\frac{3}{2}, +\frac{1}{2}\rangle \to |\frac{1}{2}, +\frac{1}{2}\rangle$, the dipole matrix element is

$$\langle 2, \tfrac{3}{2}, +\tfrac{1}{2}|\hat{d}_0|1, \tfrac{1}{2}, +\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\langle 210|\hat{d}_0|100\rangle \ .$$

For the decay $|\frac{3}{2}, +\frac{1}{2}\rangle \to |\frac{1}{2}, -\frac{1}{2}\rangle$, the dipole matrix element is

$$\langle 2, \tfrac{3}{2}, +\tfrac{1}{2}|\hat{d}_{+1}|1, \tfrac{1}{2}, -\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}\langle 211|\hat{d}_{+1}|100\rangle \ .$$

Summing the two transition rates gives the same total decay rate as above

$$\Gamma = \frac{\omega^3}{3\pi\epsilon_0 c^3\hbar}\left[\frac{2}{3}\left|\langle 210|\hat{d}_0|100\rangle\right|^2 + \frac{1}{3}\left|\langle 211|\hat{d}_{+1}|100\rangle\right|^2\right] = \frac{\omega^3}{3\pi\epsilon_0 c^3\hbar}\left|\langle 2p\,\|\,\hat{\boldsymbol{d}}\,\|\,1s\rangle\right|^2 .$$

Similarly for all other allowed $2^2\mathrm{P}_{3/2} \to 1^2\mathrm{S}_{1/2}$ and $2^2\mathrm{P}_{1/2} \to 1^1\mathrm{S}_{1/2}$ transitions. The decay rates involve the same spatial factors as in the 2p lifetime calculation above, multiplied by Clebsch-Gordan coefficients whose squares sum to unity.

Hence all the 2P states $|J, m_J\rangle$ have a lifetime which is the same as the 2p lifetime computed above (1.56×10^{-9} s). Hence the $2^2\mathrm{P}_{1/2}$ and $2^2\mathrm{P}_{3/2}$ levels of hydrogen have equal lifetimes.

A small difference in lifetime of about 2 parts in 10^5 is expected due to relativistic corrections (see V. G. Pal'chikov, Phys. Scr. **57** (1998) 581). The difference in the factor ω^3 arising from the fine structure splitting between $2^2\mathrm{P}_{1/2}$ and $2^2\mathrm{P}_{3/2}$ gives a negligible effect.