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Contents

1 Problem #1: Stark Effect for Hydrogen $n = 3$ Levels.

Work out the Stark effect to linear order in the electric field for the $n = 3$ levels of Hydrogen. Ignore relativistic corrections to the level structure. Sketch the energy level diagram and label each of the levels by the quantum numbers of the unperturbed Rydberg states. Calculate the eigenvectors that diagonalize the perturbation within the subspace of $n = 3$ levels.

Let us denote the $n = 3$ states of the Hydrogen atom as $|\ell, m\rangle$. If the applied electric field $\mathbf{E} = \mathscr{E}\hat{z}$ ($\hat{z}$ is unit vector) is aligned with the z axis, the selection rules are $\Delta\ell = \pm 1$ and $\Delta m = 0$. The electrostatic potential $\phi = -\mathscr{E}z$ (z is the coordinate) is coupled to the electron charge $-e$, so the perturbation is $V' = e\mathscr{E}\hat{z}$, where $\hat{z}$ is now a quantum-mechanical operator. Consider the perturbation matrix defined by the elements $V_{ij} = \langle i| - e\mathscr{E}z|j\rangle$, where $i, j \in \{|\ell, m\rangle\}$:

$$\begin{array}{r} \\ \langle 0,0| \\ \langle 1,-1| \\ \langle 1,0| \\ \langle 1,1| \\ \langle 2,-2| \\ \langle 2,-1| \\ \langle 2,0| \\ \langle 2,1| \\ \langle 2,2| \end{array} \begin{array}{c} \begin{array}{ccccccccc} |0,0\rangle & |1,-1\rangle & |1,0\rangle & |1,1\rangle & |2,-2\rangle & |2,-1\rangle & |2,0\rangle & |2,1\rangle & |2,2\rangle \end{array} \\ \left(\begin{array}{ccccccccc} 0 & 0 & \alpha^* & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \gamma^* & 0 & 0 & 0 \\ \alpha & 0 & 0 & 0 & 0 & 0 & \beta^* & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \delta^* & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \gamma & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \delta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right) \end{array} \tag{1}$$

note the kets are just there as labels and are obviously not included in the perturbation matrix. This leaves only four matrix elements to be calculated:

$$\alpha = e\mathscr{E}\,\langle 1,0|\hat{z}|0,0\rangle \tag{2}$$

$$\beta = e\mathscr{E}\,\langle 2,0|\hat{z}|1,0\rangle \tag{3}$$

$$\gamma = e\mathscr{E}\,\langle 2,-1|\hat{z}|1,-1\rangle \tag{4}$$

$$\delta = e\mathscr{E}\,\langle 2,1|\hat{z}|1,1\rangle \ . \tag{5}$$

The $n = 3$ states of the Hydrogen atom, represented in the spherical coordinate basis, are

$$|\ell, m\rangle = \sqrt{\left(\frac{2}{3a_0}\right)^3 \frac{(2-\ell)!}{6[(3+\ell)!]}} e^{-r/3a_0} \left(\frac{2r}{3a_0}\right)^{\ell} L_{2-\ell}^{2l+1}\left(\frac{2r}{3a_0}\right) Y_\ell^m(\theta,\phi) \equiv R_\ell(r) Y_\ell^m(\theta,\phi) \ , \tag{6}$$

where $L_a^b(x)$ are the generalized Laguerre polynomials and $Y_\ell^m(\theta,\phi)$ are the spherical harmonics, and a_0 is the Bohr radius. Consider the $\hat{z} = r\cos\theta$ operator, in the spherical coordinate basis, acting on the states indicated:

$$\hat{z}\,|0,0\rangle = R_0(r) r\cos(\theta) Y_0^0(\theta,\phi) = \frac{r}{\sqrt{3}} R_0(r) Y_1^0(\theta,\phi) \tag{7}$$

$$\hat{z}\,|1,0\rangle = R_1(r) r\cos(\theta) Y_1^0(\theta,\phi) = r R_1(r) Y_2^0(\theta,\phi) \left(2\sqrt{\frac{3}{5}} \frac{1}{3-\sec^2\theta}\right) \tag{8}$$

$$\hat{z}\,|1,-1\rangle = R_1(r) r\cos(\theta) Y_1^{-1}(\theta,\phi) = \frac{r}{\sqrt{5}} R_1(r) Y_2^{-1}(\theta,\phi) \tag{9}$$

$$\hat{z}\,|1,1\rangle = R_1(r) r\cos(\theta) Y_1^1(\theta,\phi) = \frac{r}{\sqrt{5}} R_1(r) Y_2^1(\theta,\phi) \ , \tag{10}$$

of which three are easily obtained[1]. The first matrix element is

$$\alpha = -e\mathscr{E}\,\langle 1,0|\hat{z}|0,0\rangle = -e\mathscr{E}\int_0^\infty\int_0^\pi\int_0^{2\pi}(r^2\sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi)R_1^*(r)Y_1^{0*}(\theta,\phi)\frac{r}{\sqrt{3}}R_0(r)Y_1^0(\theta,\phi) \tag{11}$$

$$= -\frac{e\mathscr{E}}{\sqrt{3}}\int_0^\infty rR_1^*(r)R_0(r)(r^2\mathrm{d}r)\int Y_1^{0*}(\theta,\phi)Y_1^0(\theta,\phi)\mathrm{d}\Omega \tag{12}$$

$$= -\frac{e\mathscr{E}}{\sqrt{3}}\int_0^\infty rR_1^*(r)R_0(r)(r^2\mathrm{d}r)\ , \tag{13}$$

where the angular integral is unity due to orthonormality (note that $\mathrm{d}\Omega = \sin\theta\mathrm{d}\theta\mathrm{d}\phi$). Similarly, for the $m \neq 0$ matrix elements:

$$\gamma = -e\mathscr{E}\,\langle 2,-1|\hat{z}|1,-1\rangle = -\frac{e\mathscr{E}}{\sqrt{5}}\int_0^\infty rR_2^*(r)R_1(r)(r^2\mathrm{d}r) \tag{14}$$

$$\delta = -e\mathscr{E}\,\langle 2,1|\hat{z}|1,1\rangle = -\frac{e\mathscr{E}}{\sqrt{5}}\int_0^\infty rR_2^*(r)R_1(r)(r^2\mathrm{d}r)\ , \tag{15}$$

and finally

$$\beta = -e\mathscr{E}\,\langle 2,0|\hat{z}|1,0\rangle \tag{16}$$

$$= -e\mathscr{E}\int_0^\infty\int_0^\pi\int_0^{2\pi}(r^2\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi)R_2^*(r)Y_2^{0*}(\theta,\phi)rR_1(r)\left(2\sqrt{\frac{3}{5}}\frac{1}{3-\sec^2\theta}\right)Y_2^0(\theta,\phi) \tag{17}$$

$$= -2\sqrt{\frac{3}{5}}e\mathscr{E}\int_0^\infty\int_0^\pi\int_0^{2\pi}(r^2\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi)R_2^*(r)Y_2^{0*}(\theta,\phi)rR_1(r)\left(\frac{1}{3-\sec^2\theta}\right)Y_2^0(\theta,\phi) \tag{18}$$

$$= -2\sqrt{\frac{3}{5}}e\mathscr{E}\int_0^\infty(r^2\mathrm{d}r)R_2^*(r)rR_1(r)\int\mathrm{d}\Omega\frac{|Y_2^0|^2}{3-\sec^2\theta} \tag{19}$$

$$= -\frac{2}{\sqrt{15}}e\mathscr{E}\int_0^\infty(r^2\mathrm{d}r)R_2^*(r)rR_1(r)\ , \tag{20}$$

so all that remains is to calculate two integrals:

$$I_{01} = \int_0^\infty rR_1^*(r)R_0(r)(r^2\mathrm{d}r) \tag{21}$$

$$I_{12} = \int_0^\infty rR_2^*(r)R_1(r)(r^2\mathrm{d}r)\ , \tag{22}$$

using Equation 6, and defining $\xi = 2/(3a_0)$, we can write[2] the integrands as

$$r^3R_1(r)R_0(r) = \frac{\xi^4e^{-\xi r}}{12\sqrt{2}}\left(-\frac{1}{6}\xi^3r^7 + \frac{5}{3}\xi^2r^6 - 5\xi r^5 + 4r^4\right) \tag{23}$$

$$r^3R_2(r)R_1(r) = \frac{\xi^6e^{-\xi r}}{12^2\sqrt{5}}\left(-\xi r^7 + 4r^6\right)\ , \tag{24}$$

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[1] Multiply $\cos\theta Y_1^0$ by the factor $\sqrt{\frac{5}{3}}\cdot\frac{1}{2}$, and we obtain

$$\sqrt{\frac{5}{3}}\frac{1}{2}\cos\theta Y_1^0 = \frac{1}{4}\sqrt{\frac{5}{\pi}}(\cos^2\theta)$$

then multiply $3-\sec^2\theta$ on both sides and isolate $\cos\theta Y_1^0$, to obtain the result.

[2] See attached work.

by noting the radial equations are real so $R_\ell^* = R_\ell$. These integrals can be evaluated using the identity[3]:

$$\int_0^\infty x^n e^{-ax} = \frac{n!}{a^{n+1}} \tag{25}$$

which, after some work yields the results

$$I_{01} = -9\sqrt{2}a_0 \tag{26}$$

$$I_{12} = -\frac{9}{2}\sqrt{5}a_0 \ . \tag{27}$$

We note that all the integrals evaluate to real quantities so $\alpha = \alpha^*$, and similarly for β, γ, δ.

We can summarize the perturbation matrix elements as

$$\alpha = e\mathscr{E} \langle 1,0|\hat{z}|0,0\rangle = -3\sqrt{6}a_0 e\mathscr{E} = \alpha^* \tag{28}$$

$$\beta = e\mathscr{E} \langle 2,0|\hat{z}|1,0\rangle = -3\sqrt{3}a_0 \mathscr{E} e = \beta^* \tag{29}$$

$$\gamma = e\mathscr{E} \langle 2,-1|\hat{z}|1,-1\rangle = -\frac{9}{2}a_0 e\mathscr{E} = \gamma^* \tag{30}$$

$$\delta = e\mathscr{E} \langle 2,1|\hat{z}|1,1\rangle = -\frac{9}{2}a_0 e\mathscr{E} = \delta^* \ , \tag{31}$$

and if we define $\eta = 3a_0 e\mathscr{E}$, the perturbation matrix becomes

$$\mathbf{V}_{ij} = -\eta \begin{pmatrix} 0 & 0 & \sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{3}{2} & 0 & 0 & 0 \\ \sqrt{6} & 0 & 0 & 0 & 0 & 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{3}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{3}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{3}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \ . \tag{32}$$

To diagonalize this matrix, we can break it down into smaller subspaces, one for each value of m, because there is no mixing between states with different m values. We will return to writing the matrix elements are $\alpha, \beta, \gamma, \delta$. We can note the $m = 2$ and $m = -2$ subspaces are one state each and cannot mix with any other state, so these states are stable under the perturbation and have an energy shift of zero. Let us begin in the $m = 1$ subspace, which has the basis $\{|1,1\rangle, |2,1\rangle\}$. The perturbation matrix for this subspace is

$$\mathbf{V}_{ij}^{(1)} = \begin{array}{c c} & \begin{array}{cc} |1,1\rangle & |2,1\rangle \end{array} \\ \begin{array}{c} \langle 1,1| \\ \langle 2,1| \end{array} & \begin{pmatrix} 0 & \delta \\ \delta & 0 \end{pmatrix} \end{array} , \tag{33}$$

from which we can easily determine the eigenvalues $\pm\delta$ with the associated eigenvectors

$$|m=1,+\rangle = \frac{1}{\sqrt{2}}\big(|1,1\rangle + |2,1\rangle\big) \ \Rightarrow \ \Delta E = +\delta = -\frac{3}{2}\eta \tag{34}$$

$$|m=1,-\rangle = \frac{1}{\sqrt{2}}\big(|1,1\rangle - |2,1\rangle\big) \ \Rightarrow \ \Delta E = -\delta = \frac{3}{2}\eta \ , \tag{35}$$

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[3] Zwillinger. CRC Standard Mathematical Tables and Formulae, 31 ed. Equation 641.

where the plus or minus in the ket denotes which eigenvalue it is associated with (note that since the matrix elements are all negative, when we insert the values the kets with + will have negative energy shifts). We can repeat this process for the $m = -1$ subspace, with basis $\{|1,-1\rangle, |2,-1\rangle\}$:

$$\mathbf{V}_{ij}^{(-1)} = \begin{array}{c c} & \begin{array}{cc} |1,-1\rangle & |2,-1\rangle \end{array} \\ \begin{array}{c} \langle 1,-1| \\ \langle 2,-1| \end{array} & \begin{pmatrix} 0 & \gamma \\ \gamma & 0 \end{pmatrix} \end{array}, \tag{36}$$

from which we can easily determine the eigenvalues $\pm\gamma$ with the associated eigenvectors

$$|m=-1,+\rangle = \frac{1}{\sqrt{2}}\big(\,|1,-1\rangle + |1,-1\rangle\,\big) \;\Rightarrow\; \Delta E = +\gamma = -\frac{3}{2}\eta \tag{37}$$

$$|m=-1,-\rangle = \frac{1}{\sqrt{2}}\big(\,|1,-1\rangle - |1,-1\rangle\,\big) \;\Rightarrow\; \Delta E = -\gamma = +\frac{3}{2}\eta\ . \tag{38}$$

Finally, we repeat this for $m = 0$, which is the only non-trivial diagonalization. This subspace has the basis $\{|0,0\rangle, |1,0\rangle, |2,0\rangle\}$, and the perturbation matrix is

$$\mathbf{V}_{ij}^{(0)} = \begin{array}{c c} & \begin{array}{ccc} |0,0\rangle & |1,0\rangle & |2,0\rangle \end{array} \\ \begin{array}{c} \langle 0,0| \\ \langle 1,0| \\ \langle 2,0| \end{array} & \begin{pmatrix} 0 & \alpha & 0 \\ \alpha & 0 & \beta \\ 0 & \beta & 0 \end{pmatrix} \end{array}, \tag{39}$$

if we represent the eigenvalues with μ, we can write the characteristic equation

$$0 = \mu(\mu^2 - \beta^2)(-\mu) + \alpha^2\mu\ , \tag{40}$$

which has solutions $\mu = 0, \pm\sqrt{\alpha^2+\beta^2}$. Letting x, y, z represent the elements of the eigenvector: $|0,0\rangle, |1,0\rangle, |2,0\rangle$, respectively, the first eigenvalue, $\mu = 0$ gives the equations

$$\alpha y = 0 \tag{41}$$

$$\alpha x + \beta z = 0 \tag{42}$$

$$\beta y = 0\ , \tag{43}$$

implying $\alpha = -\beta$, $y = 0$. We can write the normalized eigenvector as

$$\frac{1}{\sqrt{\alpha^2+\beta^2}}\big(\beta\,|0,0\rangle - \alpha\,|2,0\rangle\,\big) \;\Rightarrow\; \Delta E = 0\ . \tag{44}$$

The second and third eigenvalues give the equations

$$\alpha y = \pm\sqrt{\alpha^2+\beta^2}x \tag{45}$$

$$\alpha x + \beta z = \pm\sqrt{\alpha^2+\beta^2}y \tag{46}$$

$$\beta y = \pm\sqrt{\alpha^2+\beta^2}z\ , \tag{47}$$

which is solved by

$$z = \frac{\beta}{\pm\sqrt{\alpha^2+\beta^2}}y \qquad x = \frac{\alpha}{\pm\sqrt{\alpha^2+\beta^2}}y \quad \text{so} \quad \begin{cases} x &= \alpha \\ y &= \pm\sqrt{\alpha^2+\beta^2} \\ z &= \beta \end{cases}\ . \tag{48}$$

We can calculate the normalization factor for the resulting eigenvector:

$$N = \frac{1}{\sqrt{\alpha^2 + (\pm\sqrt{\alpha^2+\beta^2})^2 + \beta^2}} = \frac{1}{\sqrt{2}}\frac{1}{\sqrt{\alpha^2+\beta^2}} \ . \tag{49}$$

If we insert the values of the matrix elements $\alpha, \beta, \gamma, \delta$, we get the results

$$|m=0,0\rangle = \frac{1}{3\eta}\big(-\sqrt{3}\eta\,|0,0\rangle + \sqrt{6}\eta\,|2,0\rangle \big) \ \Rightarrow \ \Delta E = 0 \tag{50}$$

$$|m=0,\pm\rangle = \frac{1}{3\sqrt{2}\eta}\big(\sqrt{6}\eta\,|0,0\rangle \mp 3\eta\,|1,0\rangle + \sqrt{3}\eta\,|2,0\rangle \big) \ \Rightarrow \ \Delta E = \mp 3\eta \tag{51}$$

The first-order energy shifts and their corresponding perturbation eigenstates (now normalized) are:

$$\begin{array}{llcl}
\Delta E = -3\eta & \Rightarrow \quad |m=0,+\rangle & = & \frac{1}{\sqrt{3}}|0,0\rangle + \frac{1}{\sqrt{2}}|1,0\rangle + \frac{1}{\sqrt{6}}|2,0\rangle \\
\Delta E = -\frac{3}{2}\eta & \Rightarrow \quad |m=1,+\rangle & = & \frac{1}{\sqrt{2}}\big(|1,1\rangle + |2,1\rangle\big) \\
 & \quad |m=-1,+\rangle & = & \frac{1}{\sqrt{2}}\big(|1,-1\rangle + |2,-1\rangle\big) \\
\Delta E = 0 & \Rightarrow \quad |m=2\rangle & = & |2,2\rangle \\
 & \quad |m=0,0\rangle & = & -\frac{1}{\sqrt{3}}|0,0\rangle + \sqrt{\frac{2}{3}}|2,0\rangle \\
 & \quad |m=-2\rangle & = & |2,-2\rangle \\
\Delta E = \frac{3}{2}\eta & \Rightarrow \quad |m=1,-\rangle & = & \frac{1}{\sqrt{2}}\big(|1,1\rangle - |2,1\rangle\big) \\
 & \quad |m=-1,-\rangle & = & \frac{1}{\sqrt{2}}\big(|1,-1\rangle - |2,-1\rangle\big) \\
\Delta E = 3\eta & \Rightarrow \quad |m=0,-\rangle & = & \frac{1}{\sqrt{3}}|0,0\rangle - \frac{1}{\sqrt{2}}|1,0\rangle + \frac{1}{\sqrt{6}}|2,0\rangle
\end{array} \tag{52}$$

this energy splitting is illustrated in Figure 1, below.

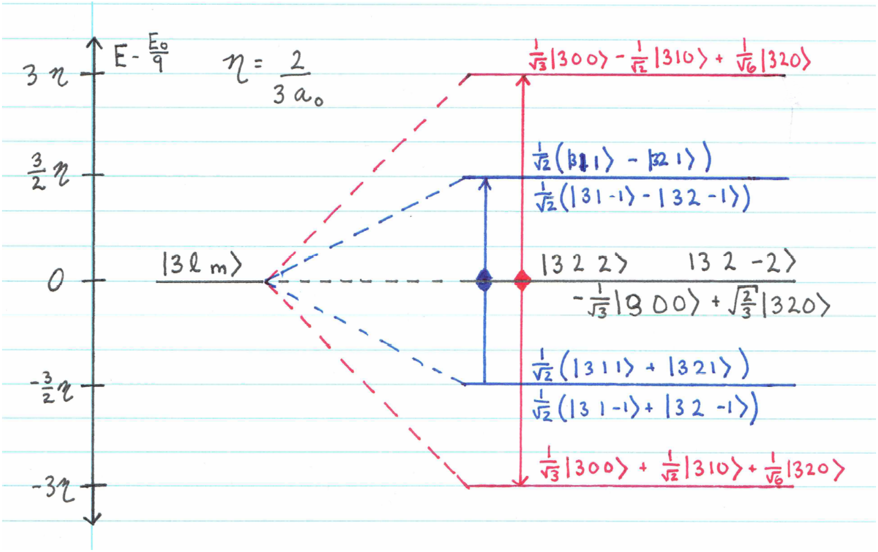

Figure 1: Energy splitting diagram of the $n = 3$ states of the Hydrogen atom due to the Stark effect. E_0 is the Rydberg constant for Hydrogen (-13.6 eV), and $\eta = 3a_0 e\mathscr{E}$. The eigenstates of the unperturbed Hamiltonian are denoted $|n=3,\ell,m\rangle$.

2 Problem #2: Spins in Inhomogeneous Magnetic Field.

In an atomic beam experiment atoms with total angular momentum quantum number j and a definite projection m_j along a specific axis $\mathbf{n}$ pass through an inhomogeneous magnetic field, $\mathbf{B} = B(y)\mathbf{z}$. The magnetic moment operator for the atom is proportional to the total angular momentum operator, $\hat{\mathbf{J}}$,

$$\hat{\mu} = g\frac{|e|}{2mc}\hat{\mathbf{J}} \ , \tag{53}$$

where g is the gyromagnetic ratio for the atom in its ground state, and e and m are the electron charge and mass, respectively, with c being the speed of light. If the direction of the magnetic field is not along the quantization axis of $\hat{\mathbf{J}}$ for the atoms, the beam is observed to separate into $2j + 1$ component beams. For atoms with $j = 1$, determine the relative intensities of the three beams if the incident atoms have a definite value of $\mathbf{n} \cdot \hat{\mathbf{J}} = \hbar$ along an axis $\mathbf{n}$, that makes an angle ϑ with respect to the direction of the field.

For $j = 1$ we can express the vector of total angular momentum operator[4] in matrix form as

$$\hat{\mathbf{J}} = \frac{\hbar}{\sqrt{2}}\left(\begin{bmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{bmatrix}\mathbf{x} + \begin{bmatrix}0 & -i & 0\\ i & 0 & -i\\ 0 & i & 0\end{bmatrix}\mathbf{y} + \begin{bmatrix}\sqrt{2} & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -\sqrt{2}\end{bmatrix}\mathbf{z}\right) \ , \tag{54}$$

and an arbitrary unit vector $\mathbf{n}$ can be written

$$\mathbf{n} = \sin\varphi\cos\varphi\mathbf{x} + \sin\vartheta\sin\varphi\mathbf{y} + \cos\varphi\mathbf{z} \ , \tag{55}$$

so their dot product, the total angular momentum projected along the axis $\mathbf{n}$, is[5]

$$\hat{\mathbf{S}}_{\mathbf{n}} = \mathbf{n} \cdot \hat{\mathbf{J}} = \frac{\hbar}{\sqrt{2}}\begin{bmatrix}\sqrt{2}\cos\vartheta & \sin\theta e^{-i\varphi} & 0\\ \sin\vartheta e^{i\varphi} & 0 & \sin\vartheta e^{-i\varphi}\\ 0 & \sin\vartheta e^{i\varphi} & -\sqrt{2}\cos\vartheta \ .\end{bmatrix} \tag{56}$$

Since, for $j = 1$, there are three possible projections $m_{\mathbf{n}}$ of the total angular momentum along the axis $\mathbf{n}$, the three eigenvalues of this matrix are $\pm\hbar$ and 0. If we consider atoms in a state with a definite projection in this axis of $\hbar$, the state of the atoms is the eigenvector corresponding to this eigenvalue. To find this vector, we solve the equation

$$\frac{\hbar}{\sqrt{2}}\begin{bmatrix}\sqrt{2}\cos\vartheta - \sqrt{2} & \sin\vartheta e^{-i\varphi} & 0\\ \sin\vartheta e^{i\varphi} & -\sqrt{2} & \sin\vartheta e^{-i\varphi}\\ 0 & \sin\vartheta e^{i\varphi} & -\sqrt{2}\cos\vartheta - \sqrt{2} \ .\end{bmatrix}\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} = 0 \ , \tag{57}$$

for the elements α, β, γ. We can see this results in the conditions

$$0 = \alpha\sqrt{2}\left(\cos\vartheta - 1\right) + \beta\sin\vartheta e^{-i\varphi} \tag{58}$$

$$0 = \alpha\sin\vartheta e^{i\varphi} - \beta\sqrt{2} + \gamma\sin\vartheta e^{-i\varphi} \tag{59}$$

$$0 = \beta\sin\vartheta e^{i\varphi} - \gamma\sqrt{2}\left(\cos\vartheta + 1\right) \ . \tag{60}$$

Solving the first and second equations we find

$$\alpha e^{i\varphi} = \frac{-\beta\sin\vartheta}{\sqrt{2}(\cos\vartheta - 1)} \quad \text{and} \quad \gamma e^{-i\varphi} = \frac{\beta\sin\vartheta}{\sqrt{2}(\cos\vartheta + 1)} \ , \tag{61}$$

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[4] In the form of the spin operators for $s = 1$. The basis for the matrices is $\{|m_{\mathbf{z}} = -1\rangle, |m_{\mathbf{z}} = 0\rangle, |m_{\mathbf{z}} = 1\rangle\}$.

[5] To get to this form, we note $\sin\vartheta\cos\varphi \pm i\sin\vartheta\sin\varphi = \sin\vartheta(\cos\varphi \pm i\sin\varphi) = \sin\vartheta e^{\pm i\varphi}$.

which we can plug into Equation 59, to find

$$0 = -\beta \frac{\sin^2\vartheta}{\sqrt{2}(\cos\vartheta - 1)} - \beta\sqrt{2} + \beta\frac{\sin^2\vartheta}{\sqrt{2}(\cos\vartheta + 1)} \tag{62}$$

$$0 = \beta\left(-\frac{\sin^2\vartheta}{\cos\vartheta - 1}\frac{\cos\vartheta + 1}{\cos\vartheta + 1} - 2 + \frac{\sin^2\vartheta}{\cos\vartheta + 1}\frac{\cos\vartheta - 1}{\cos\vartheta - 1}\right) \ , \tag{63}$$

and we note

$$(\cos\vartheta - 1)(\cos\vartheta + 1) = \cos^2\vartheta - 1 = -\sin^2\vartheta \ , \tag{64}$$

so the equation for β reduces to

$$0 = \beta\left([\cos\vartheta + 1] - 2 - [\cos\vartheta - 1]\right) = \beta(0) \ , \tag{65}$$

so β is a free parameter, and we can determine α and γ using Equation 61, and setting $\beta = 1$. We can then calculate the normalization factor for this eigenvector:

$$\frac{1}{N^2} = |\alpha|^2 + |\beta|^2 + |\gamma|^2 = \left(\frac{-\sin\vartheta}{\sqrt{2}(\cos\vartheta - 1)}\right)^2 + 1 + \left(\frac{\sin\vartheta}{\sqrt{2}(\cos\vartheta + 1)}\right)^2 \tag{66}$$

$$= \frac{\sin^2\vartheta}{2}\left(\frac{1}{(\cos\vartheta - 1)^2} + \frac{2}{\sin^2\vartheta} + \frac{1}{(\cos\vartheta + 1)^2}\right) \ , \tag{67}$$

using a common denominator, we can express this as

$$\frac{1}{N^2} = \frac{\sin^2\vartheta}{2}\frac{\sin^2\vartheta(\cos\vartheta + 1)^2 + 2(\cos\vartheta - 1)^2(\cos\vartheta + 1)^2 + (\cos\vartheta - 1)^2\sin^2\vartheta}{(\cos\vartheta - 1)^2\sin^2\vartheta(\cos\vartheta + 1)^2} \ , \tag{68}$$

we can cancel the two factors of $\sin^2\vartheta$, and use Equation 64 to write the denominator as $\sin^4\vartheta$. Using the same trick on the middle term, the numerator simplifies to

$$\sin^2\vartheta(\cos^2\vartheta + 1 + 2\cos\vartheta) + 2\sin^4\vartheta + (\cos^2\vartheta + 1 - 2\cos^2\vartheta)\sin^2\vartheta \tag{69}$$

$$\sin^2\vartheta(\cos^2\vartheta + 1) + 2\sin^4\vartheta + (\cos^2\vartheta + 1)\sin^2\vartheta \tag{70}$$

$$2\sin^2\vartheta(\cos^2\vartheta + 1) + 2\sin^4\vartheta \ , \tag{71}$$

which we reinsert to the full expression and find

$$\frac{1}{N^2} = \frac{1}{2}\frac{2\sin^2\vartheta(\cos^2\vartheta + 1) + 2\sin^4\vartheta}{\sin^4} = \frac{(\cos^2\vartheta + 1) + \sin^2\vartheta}{\sin^2\vartheta} = \frac{2}{\sin^2\vartheta} \ , \tag{72}$$

therefore the normalization constant is $N = \frac{1}{\sqrt{2}}\sin\vartheta$. We now obtain the eigenvector for the $m_{\mathbf{n}} = \hbar$ state in the $m_{\mathbf{z}}$ basis:

$$|m_{\mathbf{n}} = \hbar\rangle = \frac{1}{\sqrt{2}}\sin\vartheta\left(\frac{-e^{-i\varphi}\sin\vartheta}{\sqrt{2}(\cos\vartheta - 1)}|m_{\mathbf{z}} = -1\rangle + |m_{\mathbf{z}} = 0\rangle + \frac{e^{i\varphi}\sin\vartheta}{\sqrt{2}(\cos\vartheta + 1)}|m_{\mathbf{z}} = 1\rangle\right) \ . \tag{73}$$

The probabilities of an atom with $m_{\mathbf{n}} = \hbar$ to have a spin $m_{\mathbf{z}}$ are given by

$$P(m_{\mathbf{z}} = -1) = |\alpha|^2/N^2 = \frac{1}{2}\sin^2\vartheta\left(\frac{\sin^2\vartheta}{2(\cos\vartheta - 1)^2}\right) = \frac{1}{2}\sin^2\vartheta\left(\frac{1}{2}\tan^2\frac{\vartheta}{2}\right) \tag{74}$$

$$P(m_{\mathbf{z}} = 0) = |\beta|^2/N^2 = \frac{1}{2}\sin^2\vartheta \tag{75}$$

$$P(m_{\mathbf{z}} = 1) = |\gamma|^2/N^2 = \frac{1}{2}\sin^2\vartheta\left(\frac{\sin^2\vartheta}{2(\cos\vartheta + 1)^2}\right) = \frac{1}{2}\sin^2\vartheta\left(\frac{1}{2}\cot^2\frac{\vartheta}{2}\right) \ . \tag{76}$$

Since the inhomogeneous magnetic field (in the z direction) splits the incident beam into three beams based on their $m_{\mathbf{z}}$ values, the relative intensity of the three beams is given by the probability of an incoming atom with a definite $m_{\mathbf{n}}$.

3 Problem #3: Spin of Electron.

Spin is an observable property of the electron described by a set of three Hermitian operators, $\hat{\mathbf{S}} \equiv (\hat{S}_x, \hat{S}_y, \hat{S}_z)$, corresponding to the three orthogonal directions in space. The spin operator acts on a two-dimensional subspace of the Hilbert space of the states of the electron. Experiment demonstrates that there are only two possible values, $\pm\frac{\hbar}{2}$, for the spin $\hat{S}_{\mathbf{n}}$ along any axis $\mathbf{n}$ in space, and two associated states which we denote by $|\mathbf{n}+\rangle$ corresponding to the value $+\frac{\hbar}{2}$ and $|\mathbf{n}-\rangle$ corresponding to the value $-\frac{\hbar}{2}$. Experiment shows that if we prepare the electron in a state $|\mathbf{n}+\rangle$ then measure spin along a different axis $\mathbf{m}$, the probability of measuring the electron with spin $+\frac{\hbar}{2}$ along $\mathbf{m}$ is $|\langle \mathbf{m}+|\mathbf{n}+\rangle|^2 = \cos^2\vartheta/2$, where $\mathbf{m}\cdot\mathbf{n} = \cos\vartheta$.

3.1 Projection Operators to $\mathscr{B}_z$.

Let $\mathscr{B}_z = \{|\mathbf{z}+\rangle, |\mathbf{z}-\rangle\}$ denote the eigenvectors of $\hat{S}_z$ corresponding to $\pm\frac{\hbar}{2}$. Construct the projection operators $\hat{P}_{\pm\mathbf{z}}$ corresponding to these two eigenvectors, and the operator $\hat{S}_{\mathbf{z}}$ in the $\mathscr{B}_z$ basis.

Any state that exists in the two-dimensional subspace of Hilbert space the spin operators act on, can be expressed in the basis $\mathscr{B}_z$ as

$$|m\rangle = \begin{pmatrix}\alpha \\ \beta\end{pmatrix} , \tag{77}$$

where the basis vectors are the states with spins aligned and anti-aligned with the z-axis:

$$|\mathbf{z}+\rangle = \begin{pmatrix}1 \\ 0\end{pmatrix} \qquad |\mathbf{z}-\rangle = \begin{pmatrix}0 \\ 1\end{pmatrix} . \tag{78}$$

Let us define $\hat{P}_{+\mathbf{z}}$ as the operator that projects a state onto the $|\mathbf{z}+\rangle$ basis vector. Operators in the two dimensional subspace are 2×2 matrices. Therefore the action of this operator on the basis vetor is the identity,

$$\hat{P}_{+\mathbf{z}}|\mathbf{z}+\rangle = |\mathbf{z}+\rangle , \tag{79}$$

which can be represented in matrix form as

$$\hat{P}_{+\mathbf{z}}|\mathbf{z}+\rangle = \begin{bmatrix}a & b \\ c & d\end{bmatrix}\begin{pmatrix}1 \\ 0\end{pmatrix} = \begin{pmatrix}1 \\ 0\end{pmatrix} , \tag{80}$$

from which we see $a = 1$ and $c = 0$. The projection of $|\mathbf{z}-\rangle$ onto the orthonormal vector $|\mathbf{z}+\rangle$ is zero:

$$\hat{P}_{+\mathbf{z}}|\mathbf{z}+\rangle = \begin{bmatrix}1 & b \\ 0 & d\end{bmatrix}\begin{pmatrix}1 \\ 0\end{pmatrix} = \begin{pmatrix}0 \\ 0\end{pmatrix} , \tag{81}$$

and we see $b = d = 0$. A similar process can be used to determine $\hat{P}_{-\mathbf{z}}$:

$$\hat{P}_{-\mathbf{z}}|\mathbf{z}+\rangle = \begin{bmatrix}e & f \\ g & h\end{bmatrix}\begin{pmatrix}1 \\ 0\end{pmatrix} = \begin{pmatrix}0 \\ 0\end{pmatrix} \quad \Rightarrow \quad \begin{cases} e &= 0 \\ g &= 0\end{cases} \tag{82}$$

$$\hat{P}_{-\mathbf{z}}|\mathbf{z}-\rangle = \begin{bmatrix}0 & f \\ 0 & h\end{bmatrix}\begin{pmatrix}0 \\ 1\end{pmatrix} = \begin{pmatrix}0 \\ 1\end{pmatrix} \quad \Rightarrow \quad \begin{cases} f &= 0 \\ h &= 1\end{cases} \tag{83}$$

Therefore the operators that project vectors onto the basis vectors are

$$\hat{P}_{+\mathbf{z}} = \begin{bmatrix}1 & 0 \\ 0 & 0\end{bmatrix} \qquad \hat{P}_{-\mathbf{z}} = \begin{bmatrix}0 & 0 \\ 0 & 1\end{bmatrix} \tag{84}$$

Let us now consider the action of the spin operator $\hat{S}_z$ on the basis vectors. Using the eigenvalues of this operator for the states with spin parallel to the z axis, we see

$$\hat{S}_z \left|\mathbf{z}+\right\rangle = \frac{\hbar}{2} \left|\mathbf{z}+\right\rangle = \frac{\hbar}{2} \hat{P}_{+\mathbf{z}} \left|\mathbf{z}+\right\rangle \ , \tag{85}$$

using the fact that the eigenvalue of the $+z$ projection operator is one for $\left|\mathbf{z}+\right\rangle$. Let $\hat{\Omega}$ be any arbitrary operator that has an eigenvalue of zero for the vector $\left|\mathbf{z}+\right\rangle$. Then we can express the spin z-projection operator as $\hat{S}_z = (\hbar/2)\hat{P}_{+\mathbf{z}} + \hat{\Omega}$, so its action on the other basis vector is

$$\hat{S}_z \left|\mathbf{z}+\right\rangle = \left(\frac{\hbar}{2}\hat{P}_{+\mathbf{z}} + \hat{\Omega}\right) \left|\mathbf{z}+\right\rangle = -\frac{\hbar}{2} \left|\mathbf{z}+\right\rangle \tag{86}$$

$$0 + \hat{\Omega} \left|\mathbf{z}+\right\rangle = -\frac{\hbar}{2} \hat{P}_{-\mathbf{z}} \left|\mathbf{z}+\right\rangle \ , \tag{87}$$

We have only enforced that $\left|\mathbf{z}+\right\rangle$ is not an eigenvector of $\hat{\Omega}$, which does not restrict its action on $\left|\mathbf{z}-\right\rangle$.Using this, we see

$$\hat{S}_z = \frac{\hbar}{2}\left(\hat{P}_{+\mathbf{z}} - \hat{P}_{-\mathbf{z}}\right) = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \ , \tag{88}$$

which is the spin projection operator for the z-axis. The eigenvalues of this operator are the magnitudes of the z component of the state's total spin angular momentum $s = \frac{1}{2}$.

3.2 Spin Aligned with Perpendicular Axis: x-axis.

For an electron in the state $\left|\mathbf{z}+\right\rangle$ the probability of measuring $\pm\frac{\hbar}{2}$ along the orthogonal $\mathbf{x}$ axis is $\left|\left\langle \mathbf{x}\pm \middle|\mathbf{z}+\right\rangle\right|^2 = \frac{1}{2}$. Construct the projection operators $\hat{P}_{\pm\mathbf{x}}$ assuming that the projectors are real (this amounts to a choice of the phases of the matrix elements of the projectors in the basis $\mathscr{B}_z$).

Now consider the states with spin aligned along the x axis: $\{\left|\mathbf{x}\pm\right\rangle\}$. We can express these in $\mathscr{B}_z$ as

$$\left|\mathbf{x}+\right\rangle = \begin{pmatrix}\alpha \\ \beta\end{pmatrix} \qquad \left|\mathbf{x}-\right\rangle = \begin{pmatrix}\gamma \\ \delta\end{pmatrix} \ , \tag{89}$$

with $\alpha, \beta, \gamma, \delta \in \mathbb{R}$, and we enforce these also form an orthonormal basis that spans the two dimensional substace of Hilbert space. Using the probability of measurements along perpendicular axes, we see

$$\frac{1}{2} = \left|\left\langle \mathbf{x}+ \middle|\mathbf{z}+\right\rangle\right|^2 \quad \Rightarrow \quad \left\langle \mathbf{x}+ \middle|\mathbf{z}+\right\rangle = \pm\frac{1}{\sqrt{2}} \ , \tag{90}$$

if we assume the inner product is real (and similarly for $\left|\mathbf{x}-\right\rangle$), additionally we will pick the positive root becuase an overall sign will not effect the results. We then get

$$(\ \alpha\ \beta\ )\begin{pmatrix}1 \\ 0\end{pmatrix} = \frac{1}{\sqrt{2}} \quad \Rightarrow \quad \alpha = \frac{1}{\sqrt{2}} \tag{91}$$

$$(\ \alpha\ \beta\ )\begin{pmatrix}0 \\ 1\end{pmatrix} = \frac{1}{\sqrt{2}} \quad \Rightarrow \quad \beta = \frac{1}{\sqrt{2}} \ , \tag{92}$$

since the negative z axis is also perpendicular to the positive and negative x axes. To find the state with the negative eigenvalue of $\hat{S}_x$, we enforce orthonormality:

$$\left\langle \mathbf{x}- \middle|\mathbf{x}+\right\rangle = (\ \gamma\ \delta\ )\begin{pmatrix}1/\sqrt{2} \\ 1/\sqrt{2}\end{pmatrix} = 0 \quad \Rightarrow \quad \gamma + \delta = 0 \tag{93}$$

$$\left\langle \mathbf{x}- \middle|\mathbf{x}-\right\rangle = (\ \gamma\ \delta\ )\begin{pmatrix}\gamma \\ \delta\end{pmatrix} = 1 \quad \Rightarrow \quad \gamma^2 + \delta^2 = 1 \ , \tag{94}$$

so $\gamma = -\delta = 1/\sqrt{2}$. So we see, in the basis $\mathscr{B}_z$, the eigenstates of $\hat{S}_x$ are

$$|\mathbf{x}+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} \qquad |\mathbf{x}-\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} \ . \tag{95}$$

We now consider the projection operators $\hat{P}_{\pm\mathbf{x}}$, which project a state onto the indicated basis vector. We can determine these projectors in $\mathscr{B}_z$, using the same method as the previous section, noting:

$$\hat{P}_{+\mathbf{x}}|\mathbf{x}+\rangle = |\mathbf{x}+\rangle \qquad \hat{P}_{+\mathbf{x}}|\mathbf{x}+\rangle = 0 \tag{96}$$

$$\hat{P}_{-\mathbf{x}}|\mathbf{x}+\rangle = 0 \qquad \hat{P}_{+\mathbf{x}}|\mathbf{x}-\rangle = |\mathbf{x}-\rangle \ . \tag{97}$$

To project onto the state with the positive eigenvalue, we have

$$\hat{P}_{+\mathbf{x}}|\mathbf{x}+\rangle = \begin{bmatrix}a & b\\c & d\end{bmatrix}\begin{pmatrix}1\\1\end{pmatrix}\frac{1}{\sqrt{2}} = \begin{pmatrix}1\\1\end{pmatrix}\frac{1}{\sqrt{2}} \quad \Rightarrow \quad \begin{cases}a+b &= 1\\c+d &= 1\end{cases} \tag{98}$$

$$\hat{P}_{+\mathbf{x}}|\mathbf{x}-\rangle = \begin{bmatrix}a & b\\c & d\end{bmatrix}\begin{pmatrix}1\\-1\end{pmatrix}\frac{1}{\sqrt{2}} = 0 \quad \Rightarrow \quad \begin{cases}a-b &= 0\\c-d &= 0\end{cases} , \tag{99}$$

and to project onto the state with the negative eigenvalue:

$$\hat{P}_{-\mathbf{x}}|\mathbf{x}+\rangle = \begin{bmatrix}e & f\\g & h\end{bmatrix}\begin{pmatrix}1\\1\end{pmatrix}\frac{1}{\sqrt{2}} = 0 \quad \Rightarrow \quad \begin{cases}e+f &= 0\\g+h &= 0\end{cases} \tag{100}$$

$$\hat{P}_{-\mathbf{x}}|\mathbf{x}-\rangle = \begin{bmatrix}e & f\\g & h\end{bmatrix}\begin{pmatrix}1\\-1\end{pmatrix}\frac{1}{\sqrt{2}} = \begin{pmatrix}1\\-1\end{pmatrix}\frac{1}{\sqrt{2}} \quad \Rightarrow \quad \begin{cases}e-f &= 1\\g-h &= -1\end{cases} . \tag{101}$$

Using the equations for the matrix elements of $\hat{P}_{\pm\mathbf{x}}$, we get the results

$$\hat{P}_{+\mathbf{x}} = \frac{1}{2}\begin{bmatrix}1 & 1\\1 & 1\end{bmatrix} \qquad \hat{P}_{-\mathbf{x}} = \frac{1}{2}\begin{bmatrix}1 & -1\\-1 & 1\end{bmatrix} \ . \tag{102}$$

We can then use the same method as the previous section to determine the spin operator $\hat{S}_z$:

$$\hat{S}_z|\mathbf{x}+\rangle = \frac{\hbar}{2}|\mathbf{x}+\rangle = \frac{\hbar}{2}\hat{P}_{+\mathbf{x}}|\mathbf{x}+\rangle , \tag{103}$$

using Equation 96, to insert a projection operator. Again we introduce an operator that obeys $\hat{\Omega}|\mathbf{x}+\rangle = 0$, so that we may write

$$\hat{S}_x = \frac{\hbar}{2}\hat{P}_{+\mathbf{x}} + \hat{\Omega} \quad \Rightarrow \quad \hat{S}_x|\mathbf{x}-\rangle = \frac{\hbar}{2}|\mathbf{x}-\rangle \tag{104}$$

$$\frac{\hbar}{2}\hat{P}_{+\mathbf{x}}|\mathbf{x}-\rangle + \hat{\Omega}|\mathbf{x}-\rangle = \frac{\hbar}{2}\hat{P}_{-\mathbf{x}}|\mathbf{x}-\rangle \tag{105}$$

$$\hat{\Omega}|\mathbf{x}-\rangle = \frac{\hbar}{2}\hat{P}_{-\mathbf{x}}|\mathbf{x}-\rangle \ , \tag{106}$$

using Equation 97. We see that if $\hat{\Omega} = (\hbar/2)\hat{P}_{-\mathbf{x}}$, the eigenvalue associated with $|\mathbf{x}-\rangle$ is indeed zero, as we required. Therefore, the spin z component projection operator is

$$\hat{S}_x = \frac{\hbar}{2}\left(\hat{P}_{+\mathbf{x}} - \hat{P}_{-\mathbf{x}}\right) = \frac{\hbar}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} \ . \tag{107}$$

3.3 Spin Aligned with Second Perpendicular Axis: y-axis.

From the measured probabilities: $|\langle \mathbf{y}+|\mathbf{z}+\rangle|^2 = \frac{1}{2}$ and $|\langle \mathbf{y}+|\mathbf{x}+\rangle|^2 = \frac{1}{2}$ find the projection operator $\hat{P}_{+\mathbf{y}}$. Eliminate the ambiguity in the matrix elements by choosing the phase angle of $\langle \mathbf{z}+|\hat{P}_{+\mathbf{y}}|\mathbf{z}-\rangle$ to lie between 0 and π. Construct the projector for the state $|\mathbf{y}-\rangle$.

We now consider states that have spins perpendicular to both previous axes: y. Since we are in the basis $\mathscr{B}_z$, the derivation of these states should be similar to the derivation of the states for the x direction. Let us assume we can now allow complex projections of the $|\mathbf{y}\pm\rangle$ states onto $|\mathbf{z}\pm\rangle$. We can then factor out and overall phase to write the eigenstate of $\hat{S}_z$ with the positive eigenvalue as

$$|\mathbf{y}+\rangle = \begin{pmatrix} \alpha \\ \beta e^{i\phi} \end{pmatrix} , \tag{108}$$

where ϕ is the relative phase angle of $\langle \mathbf{z}+|\hat{P}_{+\mathbf{y}}|\mathbf{z}-\rangle$, and $\alpha, \beta \in \mathbb{R}$. Applying orthonormality, we enforce $\alpha^2 + \beta^2 = 1$. From the measured probabilities we see

$$|\langle \mathbf{y}+|\mathbf{z}+\rangle|^2 = \frac{1}{2} \quad \Rightarrow \quad \frac{1}{\sqrt{2}} = \langle \mathbf{y}+|\mathbf{z}+\rangle = (\ \alpha\ \beta^{-i\phi}\ ) \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \alpha \tag{109}$$

so we see $\alpha = \beta = 1/\sqrt{2}$. We can then write the projection of $|\mathbf{y}+\rangle$ on $|\mathbf{x}+\rangle$ in the measured probability as

$$\frac{1}{2} = |\langle \mathbf{y}+|\mathbf{x}+\rangle|^2 = |\langle \mathbf{y}+|\mathbf{z}+\rangle\langle \mathbf{z}+|\mathbf{x}+\rangle + \langle \mathbf{y}+|\mathbf{z}-\rangle\langle \mathbf{z}-|\mathbf{x}+\rangle|^2 \tag{110}$$

by inserting a completeness relation $\mathbb{1} = \sum_i |i\rangle\langle i|$. We can insert the appropriate inner products to obtain

$$\frac{1}{2} = \left|\alpha\frac{1}{\sqrt{2}} + \beta e^{i\phi}\frac{1}{\sqrt{2}}\right|^2 = \frac{1}{2}(\alpha + \beta e^{i\phi})(\alpha + \beta e^{-i\phi}) \tag{111}$$

$$= \frac{1}{2}(\alpha^2 + \beta^2 + \alpha\beta e^{i\phi} + \alpha\beta e^{-i\phi}) \tag{112}$$

$$= \frac{1}{2}(\alpha^2 + \beta^2 + 2\alpha\beta\cos\phi) \tag{113}$$

$$= \frac{1}{2}\left(\frac{1}{2} + \frac{1}{2} + 2\frac{1}{2}\cos\phi\right) \tag{114}$$

$$1 = 1 + \cos\phi , \tag{115}$$

so we must have that $\phi = (2n+1)\frac{\pi}{2}$, where $n \in \mathbb{Z}$. However, if we restrict the phase angle to the domain $(0, \pi)$, we get $\phi = \pi/2$. The eigenstate of $\hat{S}_z$ associated with the positive eigenvalue is

$$|\mathbf{y}+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ e^{i\pi/2} \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} . \tag{116}$$

We can now determine the state with the negative eigenvalue: $|\mathbf{y}-\rangle = \gamma|\mathbf{z}+\rangle + i\delta|\mathbf{z}-\rangle$ with $\gamma, \delta \in \mathbb{R}$, by enforcing orthonormality:

$$\langle \mathbf{y}-|\mathbf{y}+\rangle = 0 = (\gamma\langle \mathbf{z}+| - i\delta\langle \mathbf{z}-|)\left(\frac{1}{\sqrt{2}}|\mathbf{z}+\rangle + i\frac{1}{\sqrt{2}}|\mathbf{z}-\rangle\right) = \frac{1}{\sqrt{2}}\left(\gamma - \delta(i)^2\right) = \gamma + \delta = 0 \tag{117}$$

$$\langle \mathbf{y}-|\mathbf{y}-\rangle = 1 = \gamma^2 + \delta^2 , \tag{118}$$

from which we see $\gamma = -\delta = 1/\sqrt{2}$. So we can write the eigenvectors of $\hat{S}_y$ in the basis $\mathscr{B}_z$:

$$|\mathbf{y}+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ i\end{pmatrix} \qquad |\mathbf{y}+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ -i\end{pmatrix} \ . \tag{119}$$

Now that the eigenvectors have been determined, we can use the method applied in the previous two sections to determine the projection operators $\hat{P}_{+\mathbf{x}}$. We use the equivalents of Equations 96 and 97 for the y direction to write, for the state with the positive eigenvalue:

$$\hat{P}_{+\mathbf{y}}\,|\mathbf{y}+\rangle = \begin{bmatrix}a & b\\ c & d\end{bmatrix}\begin{pmatrix}1\\ i\end{pmatrix}\frac{1}{\sqrt{2}} = \begin{pmatrix}1\\ i\end{pmatrix}\frac{1}{\sqrt{2}} \quad\Rightarrow\quad \begin{cases} a+ib &= 1\\ c+id &= i\end{cases} \tag{120}$$

$$\hat{P}_{+\mathbf{y}}\,|\mathbf{y}-\rangle = \begin{bmatrix}a & b\\ c & d\end{bmatrix}\begin{pmatrix}1\\ -i\end{pmatrix}\frac{1}{\sqrt{2}} = 0 \quad\Rightarrow\quad \begin{cases} a-ib &= 0\\ c-id &= 0\end{cases} , \tag{121}$$

from which we see $a = ib$ and $c = id$, yielding $b = -i/2$ and $d = 1/2$. For the state with the negative eigenvalue:

$$\hat{P}_{-\mathbf{y}}\,|\mathbf{y}+\rangle = \begin{bmatrix}e & f\\ g & h\end{bmatrix}\begin{pmatrix}1\\ i\end{pmatrix}\frac{1}{\sqrt{2}} = 0 \quad\Rightarrow\quad \begin{cases} e+if &= 0\\ g+ih &= 0\end{cases} \tag{122}$$

$$\hat{P}_{-\mathbf{y}}\,|\mathbf{y}-\rangle = \begin{bmatrix}e & f\\ g & h\end{bmatrix}\begin{pmatrix}1\\ -i\end{pmatrix}\frac{1}{\sqrt{2}} = \begin{pmatrix}1\\ -i\end{pmatrix}\frac{1}{\sqrt{2}} \quad\Rightarrow\quad \begin{cases} e-if &= 1\\ g-ih &= -i\end{cases} , \tag{123}$$

so $e = -if$ and $g = -id$ giving the result $f = i/2$ and $h = 1/2$. The projection operators are then

$$\hat{P}_{+\mathbf{y}} = \frac{1}{2}\begin{bmatrix}1 & i\\ -i & 1\end{bmatrix} \qquad \hat{P}_{-\mathbf{y}} = \frac{1}{2}\begin{bmatrix}1 & -i\\ i & 1\end{bmatrix} , \tag{124}$$

from which we can form the spin operator in the exact same fashion as the previous sections. In the $\mathscr{B}_z$ basis this is

$$\hat{S}_y = \frac{\hbar}{2}(\hat{P}_{+\mathbf{y}} - \hat{P}_{-\mathbf{y}}) = \frac{\hbar}{2}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix} , \tag{125}$$

with eigenvalues that are the magnitude of the projection of the spin angular momentum onto the y axis.

3.4 Spin Matrices in $\mathscr{B}_z$.

From the above, construct matrices for the spin operators: $\hat{S}_\mathbf{x}, \hat{S}_\mathbf{y}, \hat{S}_\mathbf{z}$ in the $\mathscr{B}_z$ basis.

The method used in section 1.1 to find $\hat{S}_z$ was applied for $\hat{S}_x$ and $\hat{S}_y$ to find the spin operators expressed in the basis $\mathscr{B}_z = \{|\mathbf{z}+\rangle, |\mathbf{z}-\rangle\}$. The general result for an arbitrary axis is

$$\hat{S}_n = \frac{\hbar}{2}(\hat{P}_{+\mathbf{n}} - \hat{P}_{-\mathbf{n}}) , \tag{126}$$

so the spin operators are

$$\hat{S}_x = \frac{\hbar}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix} \tag{127}$$

$$\hat{S}_y = \frac{\hbar}{2}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix} \tag{128}$$

$$\hat{S}_z = \frac{\hbar}{2}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix} . \tag{129}$$

4 Problem #4: Hydrogen in Magnetic Field.

Consider the non-relativistic theory of the Hydrogen atom and initially omit the spin of the electron.

4.1 Ground State Energy Shift.

Calculate the shift in the ground state energy for Hydrogen in a uniform magnetic field. Compare this shift with the relativistic shift of the ground-state energy. At what field strength are they equal?

The Hamiltonian for a charged particle of mass m, charge e, in the Coulomb potential is

$$\hat{H} = \frac{1}{2m}\left[\hat{\mathbf{p}} - \frac{e}{c}\mathbf{A}(\hat{\mathbf{r}})\right]^2 - \frac{e^2}{\hat{r}} \ , \tag{130}$$

where, for a uniform magnetic field, the vector potential can be expressed as $\mathbf{A} = -\frac{1}{2}\hat{\mathbf{r}} \times \mathbf{B}$, where $\mathbf{B}$ is the magnetic field, which is a constant, and therefore commutes with all observables. Let us multiply out the kinetic energy term:

$$\left[\hat{\mathbf{p}} - q\mathbf{A}(\hat{\mathbf{r}})\right]^2 = \hat{p}^2 + \frac{e^2}{c^2}\mathbf{A}^2 - \frac{e}{c}\hat{\mathbf{p}} \cdot \mathbf{A} - \frac{e}{c}\hat{\mathbf{A}} \cdot \hat{\mathbf{p}} \ , \tag{131}$$

since the momentum operator commutes with the vector potential (just a function of position). Substituting in the vector potential, we see

$$\begin{aligned}
\left[\hat{\mathbf{p}} - q\mathbf{A}(\hat{\mathbf{r}})\right]^2 &= \hat{p}^2 + \frac{e^2}{4c^2}(\hat{\mathbf{r}} \times \mathbf{B})^2 + \frac{e}{c}\left[\hat{\mathbf{p}} \cdot (\hat{\mathbf{r}} \times \mathbf{B}) + (\hat{\mathbf{r}} \times \mathbf{B}) \cdot \hat{\mathbf{p}}\right] & (132)\\
&= \hat{p}^2 + \frac{e^2}{4c^2}(\hat{\mathbf{r}}^2\mathbf{B}^2 - (\hat{\mathbf{r}} \cdot \mathbf{B})^2) + \frac{e}{c}\left[\mathbf{B} \cdot (\hat{\mathbf{p}} \times \hat{\mathbf{r}}) + (\hat{\mathbf{p}} \times \hat{\mathbf{r}}) \cdot \mathbf{B}\right] & (133)\\
&= \hat{p}^2 + \frac{e^2}{4c^2}(\hat{\mathbf{r}}^2\mathbf{B}^2 - (\hat{\mathbf{r}} \cdot \mathbf{B})^2) + \frac{e}{c}\left[\mathbf{B} \cdot (\hat{\mathbf{p}} \times \hat{\mathbf{r}}) - (\hat{\mathbf{r}} \times \hat{\mathbf{p}}) \cdot \mathbf{B}\right] & (134)\\
&= \hat{p}^2 + \frac{e^2}{4c^2}(\hat{\mathbf{r}}^2\mathbf{B}^2 - (\hat{\mathbf{r}} \cdot \mathbf{B})^2) + \frac{e}{c}\left[\mathbf{B} \cdot -(\hat{\mathbf{L}}) - (\hat{\mathbf{L}}) \cdot \mathbf{B}\right] \ , & (135)
\end{aligned}$$

we can now define three components of the Hamiltonian:

$$\begin{aligned}
\hat{H}_0 &= \frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}} & (136)\\
\hat{H}_1 &= \frac{e^2\mathbf{B}^2}{8mc^2}\hat{\mathbf{r}}_\perp^2 & (137)\\
\hat{H}_2 &= -\frac{e}{2mc}\hat{\mathbf{L}} \cdot \mathbf{B} = -\frac{\mu_B}{\hbar}\hat{\mathbf{L}} \cdot \mathbf{B} \ , & (138)
\end{aligned}$$

where, $\mu_B = e\hbar/2mc$ is the Bohr magneton. The component of $\hat{\mathbf{r}}$ which is perpendicular to $\mathbf{B}$ is denoted $\hat{\mathbf{r}}_\perp$. In the case in which the magnetic field is aligned along the z axis, the perpendicular component is

$$\hat{\mathbf{r}}_\perp^2 = \hat{x}^2 + \hat{y}^2 = r^2 \sin^2\theta \cos^2\phi + r^2 \sin^2\theta \sin^2\phi = r^2 \sin^2\theta \ , \tag{139}$$

which is clearly perpendicular to $\hat{z}^2 = r^2 \cos^2\theta$.

The wave function for the electron in the ground state of a Hydrogen atom, ignoring spin, is

$$|100\rangle = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0} \ , \tag{140}$$

which has angular momentum quantum numbers $l = m_l = 0$. This wave function does not interact with the $\hat{H}_2$ term in the Hamiltonian, so to find the first-order correction to the energy of the ground state, we simply calculate

$$\epsilon_1^{(1)} = \langle 100| \frac{e^2\mathbf{B}^2}{8mc^2} r^2 \sin^2\theta |100\rangle = \frac{1}{\pi a_0^3}\frac{e^2\mathbf{B}^2}{8mc^2}\int_0^\infty\int_0^\pi\int_0^{2\pi} r^2\sin^2\theta e^{-2r/a_0} r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi \tag{141}$$

$$= \frac{e^2\mathbf{B}^2}{4mc^2a_0^3}\int_0^\infty\int_0^\pi r^2\sin^2\theta e^{-2r/a_0} r^2\sin\theta\mathrm{d}r\mathrm{d}\theta \ , \tag{142}$$

after evaluating the azimuthal integral. The radial integral is

$$I_r = \int_0^\infty r^4 e^{-2r/a_0}\mathrm{d}r = \frac{4!}{(2/a_0)^5} = a_0^5\left(\frac{2^3(3)}{2^5}\right) = \frac{3}{4}a_0^5 \ , \tag{143}$$

and the polar integral is

$$I_\theta = \int_0^\pi (1-\cos^2\theta)\sin\theta\mathrm{d}\theta = \int_1^{-1}(1-x^2)(-\mathrm{d}x) = \left(x - \frac{1}{3}x^3\right)\Big|_{-1}^{1} = \frac{2}{3} - \left((-1)+\frac{1}{3}\right) = \frac{4}{3} \ , \tag{144}$$

which we can combine for a factor of a_0^5. Therefore, the energy shift of the ground state due to the presence of a magnetic field $\mathbf{B} = B\mathbf{z}$, is

$$\epsilon_1^{(1)} = a_0^5\frac{e^2B^2}{4mc^2a_0^3} = \frac{e^2a_0^2B^2}{4mc^2} = \frac{e^2a_0^2\alpha^2}{8\epsilon_0}B^2 = \frac{1}{4}\left(\frac{e^2}{2\epsilon_0}\right)a_0^2\alpha^2B^2 = \frac{1}{4}a_0^3\alpha^2B^2 \tag{145}$$

$$\simeq (1.97\text{e}{-30})B^2 \text{ erg} = (1.23\text{e}{-18})B^2 \text{ eV} \ , \tag{146}$$

when B is measured in gauss[6], and using the Rydberg constant for Hydrogen, $\epsilon_0 = \frac{1}{2}mc^2\alpha^2$, and $a_0 = e^2/(2\epsilon_0)$. From the results of problem 6, the energy shift due to the relativistic correction is

$$|\epsilon_{\mathrm{R}}^{(1)}| = \epsilon_0\alpha^2\left[2 - \frac{3}{4}\right] = \frac{5}{4}\epsilon_0\alpha^2 = \frac{5}{2}\frac{\epsilon_0^2}{mc^2} \simeq \frac{5}{2}\frac{13.6^2}{511\text{e}3}\text{eV} = 1.45\text{e}{-15} \text{ erg} = 9\text{e}{-4} \text{ eV} \ . \tag{147}$$

For these effects to be comparable in magnitude[7], it must be that

$$1 \sim \frac{|\epsilon_{\mathrm{R}}^{(1)}|}{|\epsilon_1^{(1)}|} = \frac{\frac{5}{4}\epsilon_0\alpha^2}{\frac{1}{4}a_0^3\alpha^2B^2} = 5\frac{\epsilon_0}{a_0^3}\frac{1}{B^2} \simeq \frac{7.34\text{e}14 \ (\mathrm{G})^2}{B^2} \quad \Rightarrow \quad B = \sqrt{5\frac{\epsilon_0}{a_0^3}} \simeq 2.7\text{e}7 \ \mathrm{G} \ , \tag{148}$$

which is incredibly large. We note the term ϵ_0/a_0^3 is the expectation value of the energy density: it is the energy of the unperturbed ground state divided by the mean volume of the Hydrogen atom in the ground state.

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[6] Dimenionally:

$$\left[\left[\frac{e^2a_0^2B^2}{4mc^2}\right]\right] = \frac{(\mathrm{esu})^2(\mathrm{cm})^2\left(\frac{\mathrm{esu}}{\mathrm{cm}^2}\right)^2}{\mathrm{g}(\mathrm{cm}/\mathrm{s})^2} = \frac{((\mathrm{cm})^{3/2}(\mathrm{g})^{1/2}(\mathrm{s})^{-1})^4}{\mathrm{g}(\mathrm{cm})^4(\mathrm{s})^{-2}} = (\mathrm{cm})^2\mathrm{g}(\mathrm{s})^{-2} = \mathrm{erg}$$

$$\left[\left[\frac{1}{4}a_0^3\alpha^2B^2\right]\right] = (\mathrm{cm})^3\left(\frac{\mathrm{esu}}{(\mathrm{cm})^2}\right)^2 = \frac{((\mathrm{cm})^{3/2}(\mathrm{g})^{1/2}(\mathrm{s})^{-1})^2}{\mathrm{cm}} = (\mathrm{cm})^2\mathrm{g}(\mathrm{s})^{-2} = \mathrm{erg}$$

[7] Dimensionally:

$$\left[\left[\frac{\epsilon_0}{a_0^3}\right]\right] = \frac{\mathrm{erg}}{(\mathrm{cm})^3} = \frac{\mathrm{g}(\mathrm{s})^{-2}}{\mathrm{cm}} = \frac{\mathrm{g}(\mathrm{cm})^3(\mathrm{s})^{-2}}{(\mathrm{cm})^4} = \left(\frac{\mathrm{esu}}{(\mathrm{cm})^2}\right)^2 = (\mathrm{G})^2$$

4.2 Hydrogen Atom Magnetic Susceptibility.

Based on the above ground state energy calculate the magnetic susceptibility of the Hydrogen atom and discuss the implications of your result.

Consider the term $\hat{H}_1$ in the Hamiltonian:

$$\hat{H}_1 = \frac{e^2\mathbf{B}^2}{8mc^2}\hat{\mathbf{r}}_\perp^2 = \frac{e^2}{8mc^2}(r^2\mathbf{B}^2 - (\hat{\mathbf{r}}\cdot\mathbf{B})^2) = \frac{e^2}{8mc^2}\big(r^2B_iB_i - (r_iB_i)(r_jB_j)\big) \ , \tag{149}$$

using Einstein notation. By introducing the Kronecker delta, we can write the interaction term as

$$\hat{H}_1 = \frac{e^2}{8mc^2}\big(r^2B_iB_j\delta_{ij} - (r_iB_i)(r_jB_j)\big) = -\frac{e^2}{8mc^2}\big(B_ir_ir_jB_j - B_ir^2\delta_{ij}B_j\big) \ , \tag{150}$$

which leads to the definition of the magnetic susceptibility,

$$\hat{\chi}_{ij} = \frac{e^2}{4mc^2}\left(r_ir_j - r^2\delta_{ij}\right) \ , \tag{151}$$

so the interaction can be written

$$\hat{H}_1 = -\frac{1}{2}B_i\hat{\chi}_{ij}B_j \ . \tag{152}$$

Since we have $\mathbf{B}$ pointing along the z axis, the only component that contributes to the interaction is

$$\hat{\chi}_{33} = \frac{e^2}{4mc^2}\left(z^2 - r^2\right) = \frac{e^2}{4mc^2}\left(r^2\cos^2\theta - r^2\right) = -\frac{e^2}{4mc^2}r^2\sin^2\theta \ . \tag{153}$$

The ground state has a magnetic susceptibility given by

$$\chi_{100} = \langle 100|\hat{\chi}_{ij}|100\rangle = -\frac{e^2}{4mc^2}\langle 100|r^2\sin^2\theta|100\rangle \ , \tag{154}$$

the inner product is given by

$$\langle 100|r^2\sin^2\theta|100\rangle = -\frac{1}{\pi a_0^3}\int_0^\infty\int_0^\pi\int_0^{2\pi}(r^2\sin^2\theta)e^{-2r/a_0}(r^2\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi) \tag{155}$$

$$= -\frac{2}{a_0^3}\int_0^\infty r^4e^{-2r/a_0}\mathrm{d}r\int_0^\pi\sin^3\theta\mathrm{d}\theta = \frac{2}{a_0^3}\left(\frac{3}{4}a_0^5\right)\left(\frac{4}{3}\right) = 2a_0^2 \ , \tag{156}$$

and the magnetic susceptibility of the spin-less ground state is then

$$\chi_{100} = -\frac{e^2}{4mc^2}(2a_0^2) = -\frac{e^2a_0^2}{2mc^2} = -\frac{e^2a_0^2\alpha^2}{4\epsilon_0} = -\frac{(2a_0)a_0^2\alpha^2}{4} = -\frac{1}{2}\alpha^2a_0^3 = 3.95\text{e}{-30}\text{cm}^3 \ , \tag{157}$$

which because the susceptibility of the ground state is negative, it is diamagnetic. Note we can alternatively express the susceptibility as

$$\chi_{100} = -2\frac{\epsilon_1^{(1)}}{B^2} \ . \tag{158}$$

4.3 Spin Magnetic Moment.

Now include the spin of the electron. Calculate the mean magnetic moment for the Hydrogen in its ground state in a field **B**. Is the ground state paramagnetic or diamagnetic?

If we now include spin, the an additional term is added to the Hamiltonian:

$$\hat{H}_s = -g_e \frac{\mu_B}{\hbar} \hat{\mathbf{S}} \cdot \mathbf{B} = -2\frac{\mu_B}{\hbar} B \hat{S}_z \ , \tag{159}$$

because the magnetic field is aligned with the z axis. This contributes a first-order energy shift

$$\epsilon_s^{(1)} = -2\frac{\mu_B}{\hbar} B \langle 100 m_s | \hat{S}_z | 100 m_s \rangle \ , \tag{160}$$

where m_s is the spin angular momentum z-projection quantum number (note the total spin angular momentum quantum number $s = \frac{1}{2}$, so $m_s = \pm\frac{1}{2}$). The energy shift is then

$$\epsilon_s^{(1)} = -2\frac{\mu_B}{\hbar} B(\hbar m_s) = \mp \mu_B B \ , \tag{161}$$

which is simply the Bohr magneton times the magnitude of the applied magnetic field. The negative energy shift corresponds to $m_s = \frac{1}{2}$ term and the positive shift corresponds to the $m_s = -\frac{1}{2}$. The energy of a magnetic dipole moment is given by

$$\hat{H} = -\boldsymbol{\mu} \cdot \mathbf{B} \ , \tag{162}$$

which if we bra- and -ket with the ground state, we see

$$\langle 100 | \hat{H} | 100 \rangle = \langle 100 | -\boldsymbol{\mu} \cdot \mathbf{B} | 100 \rangle = -\langle 100 | \boldsymbol{\mu} | 100 \rangle \cdot \mathbf{B} = -\langle \boldsymbol{\mu} \rangle \cdot \mathbf{B} \ , \tag{163}$$

where the term on the left hand side is just the energy shift due to the spin interaction with the magnetic field plus the correction from the term from section 4.1. Substituting in these two values, we see

$$\epsilon_s^{(1)} + \epsilon_1^{(1)} = \mp \mu_B B + \frac{1}{4} a_0^3 \alpha^2 B^2 = -\langle \boldsymbol{\mu} \rangle \cdot \mathbf{B} \ , \tag{164}$$

Therefore the mean magnetic moment of Hydrogen in the ground state is

$$\langle \boldsymbol{\mu} \rangle = \left(\pm \mu_B + \frac{1}{4} a_0^3 \alpha^2 B \right) \mathbf{z} \ , \tag{165}$$

where **z** is a unit vector in the z direction. If the magnetic moment is negative, the energy is greater than zero, and the moment is anti-aligned with the magnetic field and is therefore diamagnetic. If it is positive, the energy is less than zero, and the moment is aligned with the magnetic field, and is paramagnetic. The spin term dominates the expression and the dia-/para- magnetism of the ground state is determined by the spin of the electron: it is diamagnetic if $m_s = -\frac{1}{2}$ and paramagnetic if $m_s = +\frac{1}{2}$. For the spin of the electron not to matter, we have

$$\mu_B < \frac{1}{4} a_0^2 \alpha^2 B \quad \Rightarrow \quad B > \frac{4\mu_B}{a_0^3 \alpha^2} \simeq 2.95\text{e}10 \text{ G} \ , \tag{166}$$

which is incredibly large. It is safe to say, that on earth, the dia-/para- magnetism of the ground state of Hydrogen is determined only by the spin projection quantum number m_s.

4.4 Hydrogen Gas Magnetic Susceptibility.

Consider a gas of atomic Hydrogen at temperature T in a magnetic field of strength B. Calculate the magnetic susceptibility of the gas including both the first- and second- order field terms in the Hamiltonian. Note: you need to calculate the equilibrium occupation of each level of the magnetic doublet. Plot your result as a function of B/T. Comment on the sign and magnitude of your results.

Since the correction due to the magnetic field without spin is much lower than the correction due to the spin interaction, we can neglect that and say the energy of a state is (from Equation 161) $\epsilon \equiv \mp\mu_B B$. Consider an ensemble of N Hydrogen atoms, where N_+ of them have electrons with $m_s = +\frac{1}{2}$ and N_- of them have electrons with $m_s = -\frac{1}{2}$, so $N = N_+ + N_-$. The occupancy ratio for each spin projection is

$$\frac{N_+}{N} = \frac{e^{-(-\mu_B B)\beta}}{\mathscr{Z}} \qquad \frac{N_-}{N} = \frac{e^{-(\mu_B B)\beta}}{\mathscr{Z}} \ , \tag{167}$$

where $\beta = 1/k_b T$ is the inverse temperature, and $\mathscr{Z}$ is the partition function, given by

$$\mathscr{Z} = \sum_{\epsilon} e^{-\beta\epsilon} = e^{-\mu_B B\beta} + e^{\mu_B B\beta} = 2\cosh(\mu_B B\beta) \ . \tag{168}$$

The net magnetization of the ensemble is the net spin projection times the Bohr magneton:

$$M = (-\mu_B)N_+ + (\mu_B)N_- = \mu_B\frac{N}{\mathscr{Z}}\left(e^{\mu_B B\beta} - e^{-\mu_B B\beta}\right) = N\frac{2\sinh(\mu_B B\beta)}{2\cosh(\mu_B B\beta)} \tag{169}$$

$$= N\mu_B\tanh(\mu_B B\beta) = N\mu_B\tanh\left(\frac{\mu_B B}{k_B T}\right) \tag{170}$$

note the magnetization is either along the positive or negative z axis (sign determined by above equation). The magnitude of the result makes sense. Each atom contributes a Bohr magneton to the total magnetic moment, and the maximum and minimum mangetizations are $\pm N\mu_B$, which correspond to all the spins aligned, either up or down. For some combination where the spins are not all aligned, we only get some fraction of this maximum magnetic moment, see the plot of the magnetization in Figure 2.

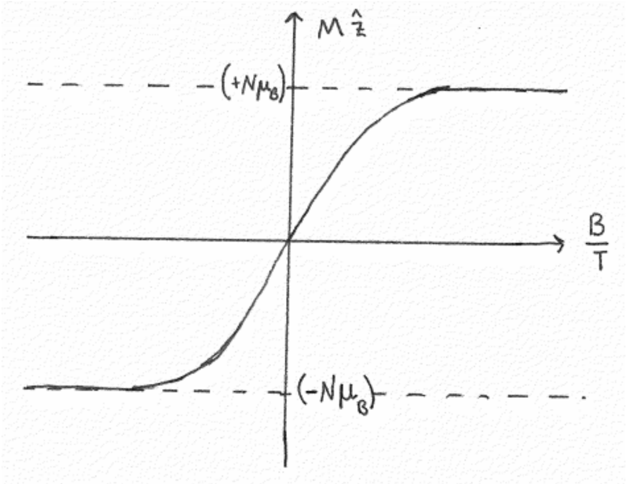

Figure 2: The net magnetization of a gas of N Hydrogen atoms, each with magnetic moment $\pm\mu_B$, where μ_B is the Bohr magneton.

5 Shankar ∼15.2.4: Total Angular Momentum of Electron.

Consider an electron moving in the Coulomb field of a proton. The Hamiltonian commutes with $\hat{S}^2, \hat{L}^2, \hat{J}^2$ and $\hat{J}_z = \hat{L}_z + \hat{S}_z$, where $\hat{S}_z = \frac{\hbar}{2}\sigma_z$. Find the two-component Pauli spinor eigenfunctions of the form

$$\hat{\Psi}(\mathbf{r}) = \begin{pmatrix} \psi_1(\mathbf{r}) \\ \psi_2(\mathbf{r}) \end{pmatrix} \ , \tag{171}$$

for this set of commuting observables. For an electron in a state with angular momentum quantum numbers, (ℓ, j, m_j) calculate the possible values of the orbital and spin angular momentum projections (L_z and S_z), and the probabilities for observing the electron with these spin and orbital projections. Calculate the mean values of L_z and S_z for an electron in the state $|\ell, j, m_j\rangle$.

For an electron, $s = \frac{1}{2}$, so for any value of l, there are only two values of $j = l \pm \frac{1}{2}$ (since j must have integer steps between levels). We know the total j states: $|j, m_j\rangle = |l \pm \frac{1}{2}, m_j\rangle$, but we want these in terms of states with definite m_l and m_s: $|l, m_l; s, m_s\rangle = |l, m_l; \frac{1}{2}, m_s\rangle \equiv |l, m_l; m_s\rangle$. For a given m, there are only two values of m_l that can give $j = l \pm \frac{1}{2}$:

$$|l + \tfrac{1}{2}, m_j\rangle = \alpha\,|l, m - \tfrac{1}{2}; \tfrac{1}{2}\rangle + \beta\,|l, m + \tfrac{1}{2}; -\tfrac{1}{2}\rangle \equiv \alpha\,|\alpha\rangle + \beta\,|\beta\rangle \tag{172}$$

$$|l - \tfrac{1}{2}, m_j\rangle = \gamma\,|l, m - \tfrac{1}{2}; \tfrac{1}{2}\rangle + \delta\,|l, m + \tfrac{1}{2}; -\tfrac{1}{2}\rangle \equiv \gamma\,|\gamma\rangle + \delta\,|\delta\rangle \ . \tag{173}$$

We can use orthonormality to show

$$\langle l + \tfrac{1}{2}, m_j | l + \tfrac{1}{2}, m_j\rangle = 1 = |\alpha|^2 + |\beta|^2 \tag{174}$$

$$\langle l - \tfrac{1}{2}, m_j | l - \tfrac{1}{2}, m_j\rangle = 1 = |\gamma|^2 + |\delta|^2 \tag{175}$$

$$\langle l + \tfrac{1}{2}, m_j | l - \tfrac{1}{2}, m_j\rangle = 0 = \alpha^*\gamma + \beta^*\delta \ , \tag{176}$$

but to uniquely determine the constants $\alpha, \beta, \gamma, \delta$ we need a fourth constraint. Consider the action of the total angular momentum operator:

$$\hat{J}^2\,|j, m\rangle = \hbar^2 j(j+1)\,|j, m\rangle \quad \Rightarrow \quad \hat{J}^2\,|l \pm \tfrac{1}{2}, m\rangle = \hbar^2(l \pm \tfrac{1}{2})(l + (1 \pm \tfrac{1}{2}))\,|l \pm \tfrac{1}{2}, m\rangle \tag{177}$$

$$\hat{J}^2\,|l + \tfrac{1}{2}, m\rangle = \hbar^2(l + \tfrac{1}{2})(l + \tfrac{3}{2})\,|l + \tfrac{1}{2}, m\rangle \tag{178}$$

$$\hat{J}^2\,|l - \tfrac{1}{2}, m\rangle = \hbar^2(l - \tfrac{1}{2})(l + \tfrac{1}{2})\,|l - \tfrac{1}{2}, m\rangle \ . \tag{179}$$

Additionally, if we write $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, we can express the total angular momentum operator $\hat{J}^2$ as

$$\hat{J}^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \hat{L}^2 + \hat{S}^2 + 2\hat{L}_z\hat{S}_z + \hat{L}_-\hat{S}_+ + \hat{L}_+\hat{S}_- \ , \tag{180}$$

let us act each of the composite operators on the $j = l + \frac{1}{2}$ state:

$$\hat{L}^2\,|l + \tfrac{1}{2}, m\rangle = \hbar^2 l(l+1)(\alpha\,|\alpha\rangle + \beta\,|\beta\rangle) \tag{181}$$

$$\hat{S}^2\,|l + \tfrac{1}{2}, m\rangle = \hbar^2 s(s+1) = \frac{3}{4}\hbar^2(\alpha\,|\alpha\rangle + \beta\,|\beta\rangle) \tag{182}$$

$$2\hat{L}_z\hat{S}_z\,|l + \tfrac{1}{2}, m\rangle = 2\hat{L}_z\hat{S}_z\alpha\,|l, m - \tfrac{1}{2}; \tfrac{1}{2}\rangle + 2\hat{L}_z\hat{S}_z\beta\,|l, m + \tfrac{1}{2}; -\tfrac{1}{2}\rangle \tag{183}$$

$$= 2\hbar\left(\alpha(m - \tfrac{1}{2})(\tfrac{1}{2})\,|l, m - \tfrac{1}{2}; \tfrac{1}{2}\rangle + \beta(-\tfrac{1}{2})(m + \tfrac{1}{2})\,|l, m + \tfrac{1}{2}; -\tfrac{1}{2}\rangle\right) \tag{184}$$

$$= \hbar\left[(m - \tfrac{1}{2})\alpha\,|\alpha\rangle - (m + \tfrac{1}{2})\beta\,|\beta\rangle\right] \tag{185}$$

$$= \hbar\left[m(\alpha\,|\alpha\rangle - \beta\,|\beta\rangle) - \tfrac{1}{2}\left(\alpha\,|\alpha\rangle + \beta\,|\beta\rangle\right)\right] \ . \tag{186}$$

It is now useful to note the eigenvalues of spin raising and lowering operators: $\hat{J}_\pm = \sqrt{j(j+1) - m(m \pm 1)}$, and $\hat{S}_+ \left|m_s = \tfrac{1}{2}\right\rangle = 0 = \hat{S}_- \left|m_s = -\tfrac{1}{2}\right\rangle$. Therefore:

$$\begin{aligned}
\hat{L}_-\hat{S}_+ \left|l + \tfrac{1}{2}, m\right\rangle &= \alpha\hat{L}_-\hat{S}_+ \left|l, m - \tfrac{1}{2}; \tfrac{1}{2}\right\rangle + \beta\hat{L}_-\hat{S}_+ \left|l, m + \tfrac{1}{2}; -\tfrac{1}{2}\right\rangle && (187)\\
&= 0 + \beta\sqrt{\tfrac{3}{4} - (-\tfrac{1}{2})(-\tfrac{1}{2} + 1)}\hat{L}_- \left|l, m + \tfrac{1}{2}; +\tfrac{1}{2}\right\rangle && (188)\\
&= \beta\sqrt{l(l+1) - (m + \tfrac{1}{2})(m - \tfrac{1}{2})} \left|l, m - \tfrac{1}{2}; \tfrac{1}{2}\right\rangle && (189)\\
&= \beta\sqrt{l(l+1) - (m^2 - \tfrac{1}{4})} \left|\beta\right\rangle && (190)
\end{aligned}$$

$$\begin{aligned}
\hat{L}_+\hat{S}_- \left|l + \tfrac{1}{2}, m\right\rangle &= \alpha\hat{L}_+\hat{S}_- \left|l, m - \tfrac{1}{2}; \tfrac{1}{2}\right\rangle + \beta\hat{L}_+\hat{S}_- \left|l, m + \tfrac{1}{2}; -\tfrac{1}{2}\right\rangle && (191)\\
&= \alpha\sqrt{\tfrac{3}{4} - (\tfrac{1}{2})(\tfrac{1}{2} - 1)}\hat{L}_+ \left|l, m - \tfrac{1}{2}; -\tfrac{1}{2}\right\rangle + 0 && (192)\\
&= \beta\sqrt{l(l+1) - (m - \tfrac{1}{2})(m + \tfrac{1}{2})} \left|l, m - \tfrac{1}{2}; \tfrac{1}{2}\right\rangle && (193)\\
&= \beta\sqrt{l(l+1) - (m^2 - \tfrac{1}{4})} \left|\alpha\right\rangle && (194)
\end{aligned}$$

Summing these up, we have

$$\begin{aligned}
\hat{J}^2(\alpha\left|\alpha\right\rangle + \beta\left|\beta\right\rangle) = &\left\{\hbar^2 l(l+1) + \frac{3}{4}\hbar^2 + \hbar\left(m - \frac{1}{2}\right) + \sqrt{l(l+1) - (m^2 - \tfrac{1}{4})}\frac{\beta}{\alpha}\right\}\alpha\left|\alpha\right\rangle && (195)\\
&+ \left\{\hbar^2 l(l+1) + \frac{3}{4}\hbar^2 - \hbar\left(m - \frac{1}{2}\right) + \sqrt{l(l+1) - (m^2 - \tfrac{1}{4})}\frac{\alpha}{\beta}\right\}\beta\left|\beta\right\rangle \ , && (196)
\end{aligned}$$

which simplifies to

$$\hat{J}^2(\alpha\left|\alpha\right\rangle + \beta\left|\beta\right\rangle) = \hbar^2 l(l+1)(\alpha\left|\alpha\right\rangle + \beta\left|\beta\right\rangle + \frac{3}{4}\hbar^2(\alpha\left|\alpha\right\rangle + \beta\left|\beta\right\rangle) \qquad (197)$$

6 Shankar ∼17.3.4: Hydrogen Fine Structure.

The fine structure of atomic levels is determined by the leading order relativistic correction to the kinetic energy of the orbital motion of the electron about the nucleus and the spin-orbit interaction between the intrinsic magnetic moment of the electron ($g = 2$) and magnetic field in the rest frame of the electron. For Hydrogen

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}} - \frac{1}{2mc^2}\left(\frac{\hat{p}^2}{2m}\right)^2 + (g-1)\frac{1}{2m^2c^2}\left(\frac{e^2}{\hat{r}^3}\right)\hat{\mathbf{S}}\cdot\hat{\mathbf{L}} \ . \tag{198}$$

The first two terms are the kinetic and potential energy of Hydrogen in the non-relativistic limit. The second term is the leading order (in v/c) correction to the kinetic energy, and the third term is the spin-orbit interaction, also of order v/c. Show that the energy levels of Hydrogen to leading order in v/c are given by

$$\epsilon_{nlj} = -\epsilon_n\left\{1 + \left(\frac{\alpha}{n}\right)^2\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right\}, \quad j = l \pm \frac{1}{2}, \quad j \geq \frac{1}{2}, \quad \text{and } l = 0, 1, \ldots, (n-1) \ , \tag{199}$$

with $\epsilon_n = \frac{1}{2}\alpha^2 mc^2/n^2$, where $\alpha = e^2/\hbar c$ is the fine structure constant. Specifically evaluate the relevant radial integrals, sketch the level structure for the the $n = 2$ shell and label each level with the quantum numbers n, l, j. What is the wavelength of radiation associated with a ${}^2p_{\frac{3}{2}} \leftrightarrow {}^2p_{\frac{1}{2}}$ transition?

Lettuce begin by defining the the total Hamiltonian as the sum of three components, as follows

$$\hat{H} = \hat{H}_0 + \hat{H}_{\mathrm{R}} + \hat{H}_{\mathrm{S0}} \ , \tag{200}$$

where $\hat{H}_0$ is the Hamiltonian for an electron a coulomb potential created by a proton, $\hat{H}_{\mathrm{R}}$ is the relativistic correction to the kinetic energy, and $\hat{H}_{\mathrm{SO}}$ is the potential energy due to the spin-orbit interaction of the electron. The eigenvalues of the Hamiltonian, to first-order are then

$$\epsilon_{nlj} = \langle\psi^{(0)}_{nlmjm_j}|\hat{H}_0|\psi^{(0)}_{nlmjm_j}\rangle + \langle\psi^{(0)}_{nlmjm_j}|\hat{H}_{\mathrm{R}}|\psi^{(0)}_{nlmjm_j}\rangle + \langle\psi^{(0)}_{nlmjm_j}|\hat{H}_{\mathrm{SO}}|\psi^{(0)}_{nlmjm_j}\rangle \ , \tag{201}$$

where $|\psi^{(0)}_{nlmjm_j}\rangle$ are the unperturbed states of Hydrogen. The first matrix element is just the energies of the Hydrogen spectrum, $-\epsilon_n = -\epsilon_0/n^2$ where ϵ_0 is the Rydberg constant for Hydrogen: $\epsilon_0 = \frac{1}{2}\alpha^2 mc^2$.

6.1 Relativistic Correction.

The relativistic correction to the kinetic energy is given by the third term in Equation 198,

$$\hat{H}_{\mathrm{R}} = -\frac{1}{2mc^2}\left(\frac{\hat{p}^2}{2m}\right)^2 \ , \tag{202}$$

which gives (noting that since this correction does not depend on spin we can ignore it and the quantum numbers (l, m) and (j, m_j) are redundant, so we are free to relabel our eigenstates as $|\psi^{(0)}_{nlm}\rangle$) first order corrections to the energy of

$$\epsilon^{(1)}_{\mathrm{R}} = \langle\psi^{(0)}_{nlm}|\hat{H}_{\mathrm{R}}|\psi^{(0)}_{nlm}\rangle = -\frac{1}{(2m)^3c^2}\langle\psi^{(0)}_{nlm}|\hat{p}^4|\psi^{(0)}_{nlm}\rangle \ , \tag{203}$$

but using the unperturbed Hamiltonian $\hat{H}_0$, we can write[8] the momentum operator as

$$\hat{p^4} = (2m)^2 \left(\frac{\hat{p}^2}{2m} \right)^2 = 4m^2 \left(\hat{H}_0 + \frac{e^2}{r} \right)^2 \ , \tag{204}$$

so the relativistic correction becomes

$$\epsilon_{\mathrm{R}}^{(1)} = -\frac{1}{2mc^2} \langle \psi_{nlm}^{(0)} | \left(\hat{H}_0 + \frac{e^2}{r} \right)^2 | \psi_{nlm}^{(0)} \rangle = -\frac{1}{2mc^2} \langle \psi_{nlm}^{(0)} | \left(\hat{H}_0 \right)^2 + 2\hat{H}_0 \frac{e^2}{r} + \left(\frac{e^2}{r} \right)^2 | \psi_{nlm}^{(0)} \rangle \tag{205}$$

after expanding the square. Using the fact that we know the eigenvalues of the unperturbed Hamiltonian we can write this as

$$\epsilon_{\mathrm{R}}^{(1)} = -\frac{1}{2mc^2} \left[(\epsilon_n)^2 + 2\epsilon_n e^2 \langle \psi_{nlm}^{(0)} | r^{-1} | \psi_{nlm}^{(0)} \rangle + e^4 \langle \psi_{nlm}^{(0)} | r^{-2} | \psi_{nlm}^{(0)} \rangle \right] \ , \tag{206}$$

which is easily evaluated if the expectation values of r^{-1} and r^{-2} are known. The first is easy to calculate using the viral theorem[9], which yields

$$-2\epsilon_n = e^2 \langle \psi_{nlm}^{(0)} | r^{-1} | \psi_{nlm}^{(0)} \rangle \ , \tag{207}$$

reducing the first order relativistic correction to

$$\epsilon_{\mathrm{R}}^{(1)} = -\frac{\epsilon_n^2}{2mc^2} \left[1 - 4 + \frac{e^4}{\epsilon_n^2} \langle \psi_{nlm}^{(0)} | r^{-2} | \psi_{nlm}^{(0)} \rangle \right] \ . \tag{208}$$

The final expectation value can be calculated by considering a perturbation to the Coulomb Hamiltonian of the form λ/r^2:

$$\hat{H}'(\lambda) = \hat{H}_0 + \frac{\lambda}{r^2} \ , \tag{209}$$

which we note has the same r dependence as the centrifugal term in the radial wave function of Hydrogen[10], which means we can express the Hamilton including the perturbation as

$$\hat{H}' = \left\{ \frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2m}{\hbar^2} \left[E + \frac{e^2}{r} - \frac{1}{r^2} \left(\frac{\hbar^2 l(l+1)}{2m} + \lambda \right) \right] \right\} U_{El} = 0 \ , \tag{210}$$

so the exact eigenstates are those of Hydrogen, but with a modified centrifugal term. For this to be the case, we must have the coefficient of r^{-2} in the form $(\hbar^2/2m)\tilde{l}(\tilde{l}+1)$, so we have the condition

$$\frac{\hbar^2}{2m} \tilde{l}(\tilde{l}+1) = \frac{\hbar^2}{2m} \left(l(l+1) + \frac{2m\lambda}{\hbar^2} \right) \tag{211}$$

$$\tilde{l}(\tilde{l}+1) = l(l+1) + \frac{2m\lambda}{\hbar^2} \ , \tag{212}$$

so if we write $\tilde{l}$ as a function of λ, we have the energy spectrum[11]:

$$E(\lambda) = -\frac{me^4}{2\hbar^2 (k + \tilde{l}(\lambda) + 1)^2} = E^{(0)} + E^{(1)} + \dots \ , \tag{213}$$

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[8] Following the treatment in Shankar, page 466 to 471.

[9] Shankar, Principles of Quantum Mechanics, 2 ed. Equation 13.1.34.

[10] Shankar, Principles of Quantum Mechanics, 2 ed. Equation 13.1.2.

[11] Using the energy spectrum of Hydrogen, Shankar equation 13.1.14.

where k is the number of nodes in the eigenfunction, with $k, \tilde{l}(\lambda) \in \mathbb{Z}$. The above expression for energy, is the exact result, be we are only interested in the first order correction due to the perturbation λ/r^2, so we can Taylor expand this around $\lambda = 0$, and consider the second term (linear in λ)

$$\left\langle \frac{\lambda}{r^2} \right\rangle = E^{(1)} = \lambda \left(\frac{\partial E(\lambda)}{\partial \lambda} \right) \Big|_{\lambda=0} = \lambda \left(\frac{\partial E(\lambda)}{\partial \tilde{l}} \frac{\partial \tilde{l}}{\partial \lambda} \right) \Big|_{\lambda=0} \tag{214}$$

using the chain rule. Let us calculate these derivatives:

$$\frac{\partial E(\lambda)}{\partial \tilde{l}} = \left(-\frac{me^4}{2\hbar^2} \right) \left(\frac{(-2)}{(k + \tilde{l}(\lambda) + 1)^3} \right) \tag{215}$$

$$2\tilde{l} \frac{\mathrm{d}\tilde{l}}{\mathrm{d}\lambda} + \frac{\mathrm{d}\tilde{l}}{\mathrm{d}\lambda} = \frac{2m}{\hbar} \ \Rightarrow \ \frac{\mathrm{d}\tilde{l}}{\mathrm{d}\lambda} = \frac{2m}{\hbar^2 (2\tilde{l}(\lambda) + 1)} \ , \tag{216}$$

and we can note that $\tilde{l}(\lambda = 0) = l$. We can now write

$$\left\langle \frac{\lambda}{r^2} \right\rangle = \lambda \left(\frac{me^4}{\hbar^2 (k + l + 1)^3} \right) \frac{2m}{\hbar^2 (2l + 1)} = \lambda \left(\frac{2m^2 e^4}{\hbar^4} \frac{1}{(k + l + 1)^3 (2l + 1)} \right) \ , \tag{217}$$

but we have the principal quantum number n defined as $k + l + 1$, and define the Bohr radius $a_0 = \hbar^2/me^2$, so we have

$$\left\langle \frac{\lambda}{r^2} \right\rangle = \lambda \left(\frac{me^4}{\hbar^2 (k + l + 1)^3} \right) \frac{2m}{\hbar^2 (2l + 1)} = \lambda \left(\frac{m^2 e^4}{\hbar^4} \frac{1}{n^3 (l + \frac{1}{2})} \right) = \lambda a_0^{-2} \frac{1}{n^3 (l + \frac{1}{2})} \ . \tag{218}$$

We can now write Equation 208 as

$$\epsilon_{\mathrm{R}}^{(1)} = -\frac{\epsilon_n^2}{2mc^2} \left[1 - 4 + \frac{e^4}{\epsilon_n^2} \left(\frac{1}{a_0^2} \frac{1}{n^3 (l + \frac{1}{2})} \right) \right] \ . \tag{219}$$

An alternate expression of the Rydberg constant for Hydrogen is $\epsilon_0 = \frac{1}{2} \frac{e^2}{a_0}$, so that $e^4/a_0^2 = (2\frac{1}{2} e^2/a_0^2)^2 = 4\epsilon_0^2$. This makes simplifies the final term to

$$\epsilon_{\mathrm{R}}^{(1)} = -\frac{\epsilon_n^2}{2mc^2} \left[-3 + \frac{\epsilon_0^2/n^4}{\epsilon_n^2} \left(\frac{4n}{(l + \frac{1}{2})} \right) \right] = -\frac{\epsilon_n^2}{2mc^2} \left[-3 + \frac{4n}{(l + \frac{1}{2})} \right] \ , \tag{220}$$

using the fine structure constant, we can write the unperturbed energy levels of Hydrogen as

$$\epsilon_n^2 = \frac{1}{4n^2} \alpha^4 m^2 c^4 \ , \tag{221}$$

which we can insert into our result to obtain

$$\epsilon_{\mathrm{R}}^{(1)} = -\frac{1}{2} (mc^2)^2 \alpha^4 \left[-\frac{3}{4n^4} + \frac{1}{n^3 (l + \frac{1}{2})} \right] = -\epsilon_n \frac{\alpha^2}{n^2} \left[\frac{n}{(l + \frac{1}{2})} - \frac{3}{4} \right] \ . \tag{222}$$

6.2 Spin-Orbit Correction.

Consider the total angular momentum operator $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, the square of this operator is

$$\hat{J}^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \ , \tag{223}$$

by noting that $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ commute. We can write the spin-orbit perturbation as

$$\hat{H}_{\text{SO}} = (2-1)\frac{1}{2m^2c^2}\left(\frac{e^2}{\hat{r}^3}\right)\hat{\mathbf{S}} \cdot \hat{\mathbf{L}} = \frac{e^2}{4m^2c^2\hat{r}^3}[\hat{J}^2 - \hat{L}^2 - \hat{S}^2] \ , \tag{224}$$

and the basis that diagonalizes this perturbation is $|n, lsjm_j\rangle$, where m_j is the total angular momentum projection onto the z axis, and since we are dealing with an electron, $s = \frac{1}{2}$. We can note for $l = 0$ this term vanishes, because the eigenvalue of $\hat{\mathbf{L}} = 0$, furthermore this means $l = 0$, and so $j = s$, and the term vanishes regardless of the expression chosen. The first order correction to the energy due to this perturbation is

$$\begin{aligned}\epsilon^{(1)}_{\text{SO}} &= \frac{e^2}{4m^2c^2}\langle n, l, \tfrac{1}{2}, j, m_j|\frac{1}{\hat{r}^3}[\hat{J}^2 - \hat{L}^2 - \hat{S}^2]|n, l, \tfrac{1}{2}, j, m_j\rangle && (225)\\ &= \frac{e^2}{4m^2c^2}\langle n, l|r^{-3}|n, l\rangle\left(\langle j|\hat{J}^2|j\rangle - \langle l|\hat{L}^2|l\rangle - \langle\tfrac{1}{2}|\hat{S}^2|\tfrac{1}{2}\rangle\right) && (226)\\ &= \frac{e^2}{4m^2c^2}\hbar^2\left[j(j+1) - l(l+1) - \tfrac{1}{2}(\tfrac{3}{2})\right]\langle r^{-3}\rangle \ , && (227)\end{aligned}$$

where only the relevant quantum numbers are listen on each inner product. Again since $s = \frac{1}{2}$, we have $j = l \pm \frac{1}{2}$, so, the angular momentum sum becomes

$$(l \pm \tfrac{1}{2})^2 + (l \pm \tfrac{1}{2}) - l^2 - l - \tfrac{3}{4} = \pm l - (\tfrac{1}{2} \mp \tfrac{1}{2}) \ , \tag{228}$$

which give the results l, and $-(l+1)$. These give upper and lower bounds on j, but it can take any value in between these, in integer steps. In this case, we have that j must be an integer.

Now we must calculate the expectation value of r^{-3} for a state with arbitrary n, l. First consider the radial momentum

$$\begin{aligned}\hat{p}_r = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \ \Rightarrow \ \hat{p}_r^2 &= -\hbar\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \frac{1}{r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right) && (229)\\ &= -\hbar^2\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) \ , && (230)\end{aligned}$$

and if we note

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} = \frac{1}{r^2}\left(2r\frac{\partial}{\partial r} + r^2\frac{\partial^2}{\partial r^2}\right) = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \ , \tag{231}$$

we can write the radial kinetic energy as

$$\frac{\hat{p}_r^2}{2m} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} \ . \tag{232}$$

If we substitute the definition of the total orbital angular momentum operator[12] and the radial kinetic energy into the Schrödinger equation in spherical coordinates[13], we find

$$\hat{H} = \frac{\hat{p}_r^2}{2m} + \frac{\hat{L}^2}{2mr^2} - \frac{e^2}{r} \ , \tag{233}$$

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[13] Shankar, Principles of Quantum Mechanics, 2 ed. Equation 12.5.36.

[13] Shankar, Principles of Quantum Mechanics, 2 ed. Equation 12.6.1.

for the Coulomb potential. We now consider the commutator of the Hamiltonian and the radial momentum, in the energy eigenstates $|nl\rangle$:

$$\langle nl|[\hat{H},\hat{p}_r]|nl\rangle = \langle nl|\hat{H}\hat{p}_r|nl\rangle - \langle nl|\hat{p}_r\hat{H}|nl\rangle = \epsilon_n \langle nl|\hat{p}_r|nl\rangle - \langle nl|\hat{p}_r|nl\rangle \epsilon_n = 0 \ , \tag{234}$$

so these operators commute in the hydrogen energy eigenbasis. We can now explicitly calculate the commutator:

$$[\hat{H},\hat{p}_r] = \left[\frac{\hat{p}_r^2}{2m} + \frac{\hat{L}^2}{2mr^2} - \frac{e^2}{r}, \hat{p}_r\right] \sim \left[\frac{\hat{L}^2}{r^2},\hat{p}_r\right] - \left[\frac{1}{r},\hat{p}_r\right] \ , \tag{235}$$

where the first commutator is zero, because every operator commutes with itself. Since the angular momentum operator only depends on angular coordinates and the radial momentum only depends on the radial coordinate, $[\hat{L}^2,\hat{p}_r]=0$, so we just need to know the commutator,

$$[r^{-n},\hat{p}_r] = r^{-n}\hat{p}_r - \hat{p}_r r^{-n} \ , \tag{236}$$

we can compare this to $[f(x),\hat{p}_x]$, where $f(x)$ is an arbitrary function. The canonical commutation relation tells us $[f(x),\hat{p}_x] = i\hbar\frac{\partial f}{\partial x}$, so

$$[r^{-n},\hat{p}_r] = i\hbar\frac{\partial}{\partial r}\left(r^{-n}\right) = -i\hbar n r^{-(n+1)} \ . \tag{237}$$

With this information, Equation 235 becomes

$$[\hat{H},\hat{p}_r] = \frac{\hat{L}^2}{2m}(-2i\hbar r^{-3}) - e^2(-i\hbar^{-2}) = -i\hbar\left(\frac{1}{m}\frac{\hat{L}^2}{r^3} - e^2\frac{1}{r^2}\right) \ , \tag{238}$$

which we know in the energy eigenbasis is zero, so

$$0 = -i\hbar \langle nl|\frac{1}{m}\frac{\hat{L}^2}{r^3} - e^2\frac{1}{r^2}|nl\rangle = \frac{1}{m}\langle nl|\frac{\hat{L}^2}{r^3}|nl\rangle - e^2\langle nl|\frac{1}{r^2}|nl\rangle \tag{239}$$

$$e^2\langle nl|r^{-2}|nl\rangle = \frac{\hbar^2 l(l+1)}{m}\langle nl|r^{-3}|nl\rangle \ , \tag{240}$$

which if we substitute in Equation 218, we see

$$\langle r^{-3}\rangle = \frac{me^2}{\hbar^2}\frac{\langle r^{-2}\rangle}{l(l+1)} = \frac{1}{a_0 l(l+1)}\frac{1}{a_0^2 n^3(l+\frac{1}{2})} = \frac{1}{a_0^3 n^3}\frac{1}{l(l+1)(l+\frac{1}{2})} \ . \tag{241}$$

We can insert this to Equation 227 to obtain the result

$$\epsilon_{\mathrm{SO}}^{(1)} = \frac{e^2\hbar^2}{4m^2c^2}\frac{1}{a_0^3 n^3}\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+1)(l+\frac{1}{2})} \ , \tag{242}$$

we can express the constants as follows:

$$\frac{e^2\hbar^2}{4m^2c^2}\frac{1}{a_0^3n^3} = \frac{1}{n^3}\frac{e^2\hbar^2}{4m^2c^2a_0^2}\left(\frac{me^2}{\hbar^2}\right) = \frac{n}{n^4}\frac{e^4}{a_0^2}\frac{1}{mc^2} = \frac{n\epsilon_n^2}{mc^2} = \frac{1}{4}\alpha^4 mc^2\frac{1}{n^3} \ . \tag{243}$$

If we choose the expression in terms of the Hydrogen energy levels, we find the first-order energy correction due to the spin orbit interaction is

$$\epsilon_{\mathrm{SO}}^{(1)} = \epsilon_n^2\frac{n}{mc^2}\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+1)(l+\frac{1}{2})} = \frac{1}{2}\epsilon_n\frac{\alpha^2}{n}\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+1)(l+\frac{1}{2})} \tag{244}$$

6.3 Total First-Order Energy.

The total energy for a state $|nlj\rangle$, to first-order, is given by the sum of the three contributions

$$\epsilon_{nlj} = -\epsilon_n + \epsilon_{\mathrm{R}}^{(1)} + \epsilon_{\mathrm{SO}}^{(1)} \ , \tag{245}$$

which, gathering our results is

$$\epsilon_{nlj} = \epsilon_n - \epsilon_n \frac{\alpha^2}{n^2}\left[\frac{n}{(l+\frac{1}{2})} - \frac{3}{4}\right] + \frac{1}{2}\epsilon_n \frac{\alpha^2}{n}\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+1)(l+\frac{1}{2})} \ , \tag{246}$$

which we can evaluate for the upper and lower bounds $j = l \pm \frac{1}{2}$.

6.3.1 Electron with $j = l + \frac{1}{2}$

For $j = l + \frac{1}{2}$, the numerator in the spin orbit term is simply l, but we have $l = j - \frac{1}{2}$, so Equation 246 becomes

$$\epsilon_{nlj} = -\epsilon_n - \epsilon_n \frac{\alpha^2}{n^2}\left[\frac{n}{j} - \frac{3}{4}\right] + \frac{1}{2}\epsilon_n \frac{\alpha^2}{n}\frac{j - \frac{1}{2}}{j(j^2 - \frac{1}{4})} \tag{247}$$

$$= -\epsilon_n \left\{1 + \frac{\alpha^2}{n}\left(\left[\frac{1}{j} - \frac{3}{4n}\right] - \frac{1}{2}\frac{j - \frac{1}{2}}{j(j^2 - \frac{1}{4})}\right)\right\} \tag{248}$$

$$= -\epsilon_n \left\{1 + \frac{\alpha^2}{n}\left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4n}\right)\right\} \ , \tag{249}$$

which is the expected result, from Equation 199 (just pull out a facgtor of $1/n$ from the inner parenthesis). Note Mathematica was used only for simplification in the final step, because I have more of this assignment to finish, and algebra is a waste of my time.

6.3.2 Electron with $j = l + \frac{1}{2}$

For $j = l - \frac{1}{2}$, the numerator in the spin orbit term is $-(l+1)$, but we have $l = j + \frac{1}{2}$, so Equation 246 becomes

$$\epsilon_{nlj} = -\epsilon_n - \epsilon_n \frac{\alpha^2}{n^2}\left[\frac{n}{j+1} - \frac{3}{4}\right] + \frac{1}{2}\epsilon_n \frac{\alpha^2}{n}\frac{-(j + \frac{3}{2})}{(j + \frac{1}{2})(j + \frac{3}{2})(j+1)} \tag{250}$$

$$= -\epsilon_n \left\{1 + \frac{\alpha^2}{n}\left(\left[\frac{1}{j+1} - \frac{3}{4n}\right] - \frac{1}{2}\frac{-(j + \frac{3}{2})}{j^3 + 3j^2 + \frac{11j}{4} + \frac{3}{4}}\right)\right\} \tag{251}$$

$$= -\epsilon_n \left\{1 + \frac{\alpha^2}{n}\left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4n}\right)\right\} \ , \tag{252}$$

which is the expected result, from Equation 199.

6.4 First Excited State.

For the $n = 2$ shell, the first excited state, we have, for both $j = l \pm \frac{1}{2}$

$$\epsilon_{2lj} = -\frac{\epsilon_0}{4}\left\{1 + \frac{\alpha^2}{4}\left(\frac{1}{j + \frac{1}{2}} - \frac{3}{16}\right)\right\} \ , \tag{253}$$

with $l = 0, 1$, we see the possible energies for this level are

$$\epsilon_{20\frac{1}{2}} = \epsilon_{21\frac{1}{2}} = -\frac{\epsilon_0}{4}\left\{1 + \frac{\alpha^2}{2}\left(\frac{1}{\frac{1}{2}+\frac{1}{2}} - \frac{3}{8}\right)\right\} = -\frac{\epsilon_0}{4}\left(\frac{5\alpha^2}{16} + 1\right) \tag{254}$$

$$\epsilon_{21\frac{3}{2}} = -\frac{\epsilon_0}{4}\left\{1 + \frac{\alpha^2}{2}\left(\frac{1}{\frac{3}{2}+\frac{1}{2}} - \frac{3}{8}\right)\right\} = -\frac{\epsilon_0}{4}\left(\frac{\alpha^2}{16} + 1\right) \ , \tag{255}$$

so we see both states are shifted down. These shifts are plotted in Figure 3. The difference in energy between these states is

$$\Delta\epsilon = \epsilon_{21\frac{3}{2}} - \epsilon_{21\frac{1}{2}} = \frac{\alpha^2\epsilon_0}{16} \ . \tag{256}$$

A photon with this energy will mediate a transition between the ${}^2p_{\frac{3}{2}}$ and ${}^2p_{1/2}$ states. Using the relationship between wavelength and energy, we have

$$\lambda = \frac{hc}{|\Delta\epsilon|} = 16\frac{hc}{\alpha^2\epsilon_0} = 16\frac{(6.626\text{e}{-27}\text{erg}\cdot\text{s})(3\text{e}10\text{cm}\cdot\text{s}^{-1})(137^2)}{(13.6)\text{eV}} \tag{257}$$

$$= 16\frac{(6.626\text{e}{-27}\text{erg}\cdot\text{s})(3\text{e}10\text{cm}\cdot\text{s}^{-1})(137^2)}{(2.18\text{e}{-11}\text{erg})} \tag{258}$$

$$= 2.73\text{cm} \ , \tag{259}$$

which is in the microwave regime.

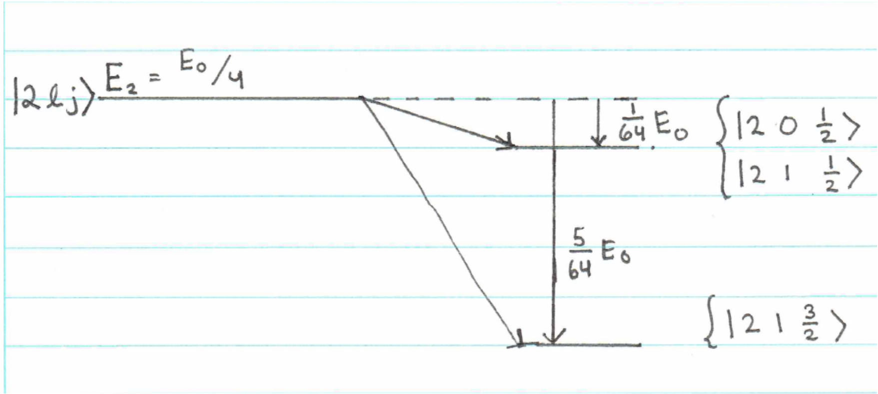

Figure 3: Energy splitting diagram of the $n = 2$ states of the Hydrogen atom, due to fine structure. E_0 is the Rydberg constant for Hydrogen (-13.6 eV). The eigenstates of the unperturbed Hamiltonian are denoted $|n = 2, l, j\rangle$.