(20) Perturbations and Spin

1 Last Time

- Hydrogen, almost...

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2 This Time

- How to make small corrections
- Zeeman effect (almost)
- Introduction to Spin

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3 Perturbations

- Gr. 6, Ga 11.1, Li 13.1, Sh 17.1, Sc 9

Last time we saw that our model of hydrogen was close, but not quite right. If you look closely at the emission spectrum of hydrogen, you will find that many of the lines have structure (e.g., are actually made of 2 or more lines very close in wavelength). Unfortunately, solving exactly a more complicated energy operator, or Hamiltonian, which includes many small effects is not feasible. So, how do we include these small effects in our model?

Perturbed Hamiltonian and Eigenstate

$$\begin{aligned} \hat{E}' &= \hat{E} + \lambda\, \Delta\hat{E} \\ \phi'_n &= \phi_n + \lambda\, \Delta\phi_n \end{aligned}$$

With these new energy eigenstates we can compute the new eigenvalues

Perturbed Eigenstates

$$\begin{aligned} E'_n|\phi'_n\rangle &= \hat{E}'|\phi'_n\rangle \quad \text{eigenvalue equation} \\ &= (\hat{E} + \lambda\Delta\hat{E})|\phi_n + \lambda\,\Delta\phi_n\rangle \\ &= \hat{E}|\phi_n\rangle + \lambda\left(\Delta\hat{E}|\phi_n\rangle + \hat{E}|\Delta\phi_n\rangle\right) + \lambda^2\cdots \\ &\simeq E_n|\phi_n\rangle + \lambda\left(\Delta\hat{E}|\phi_n\rangle + \hat{E}|\Delta\phi_n\rangle\right) \end{aligned}$$

We will only keep the terms which are first order in λ for this analysis. We can similarly expand on the left side of the equation.

Perturbed Eigenvalues

$$\begin{aligned} E'_n|\phi'_n\rangle &= (E_n + \lambda\,\Delta E_n)|\phi_n + \lambda\,\Delta\phi_n\rangle \\ &= E_n|\phi_n\rangle + \lambda(\Delta E_n|\phi_n\rangle + E_n|\Delta\phi_n\rangle) + \lambda^2\cdots \end{aligned}$$

Setting the first order terms equal, and then taking the inner-product with $\langle\phi_n|$ gives:

Perturbed Energies

$$\begin{aligned} \langle\phi_n|\Delta E_n|\phi_n\rangle + \langle\phi_n|E_n|\Delta\phi_n\rangle &= \langle\phi_n|\Delta\hat{E}|\phi_n\rangle + \langle\phi_n|\hat{E}|\Delta\phi_n\rangle \\ \Delta E_n + E_n\langle\phi_n|\Delta\phi_n\rangle &= \langle\phi_n|\Delta\hat{E}|\phi_n\rangle + \langle\hat{E}^\dagger\phi_n|\Delta\phi_n\rangle \\ &= \langle\phi_n|\Delta\hat{E}|\phi_n\rangle + E_n\langle\phi_n|\Delta\phi_n\rangle \\ \Rightarrow \Delta E_n &= \langle\phi_n|\Delta\hat{E}|\phi_n\rangle \end{aligned}$$

This let's us estimate, to first order, the change in the energy of the n^{th} eigenstate *without computing new eigenstates*.

In case you find this proof more appealing...

Perturbed Energies

$$
\begin{aligned}
\langle\phi_n|\Delta E_n|\phi_n\rangle + \langle\phi_n|E_n|\Delta\phi_n\rangle &= \langle\phi_n|\Delta\hat{E}|\phi_n\rangle + \langle\phi_n|\hat{E}|\Delta\phi_n\rangle \\
\text{with } \Delta\phi_n &= \sum_m c_m\phi_m \\
\langle\phi_n|\hat{E}|\Delta\phi_n\rangle &= \sum_m c_m\langle\phi_n|\hat{E}|\phi_m\rangle \\
&= \sum_m c_m E_m\langle\phi_n|\phi_m\rangle \\
&= c_n E_n \\
&= \sum_m c_m E_n\langle\phi_n|\phi_m\rangle \\
&= \langle\phi_n|E_n|\Delta\phi_n\rangle \\
\Rightarrow \Delta E_n &= \langle\phi_n|\Delta\hat{E}|\phi_n\rangle
\end{aligned}
$$

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4 Example: Dented Well

Let's work through a simple example of how to apply this "perturbation theory". Consider a slightly modified infinite square well potential.

Dented Well

$$
V(x) = \begin{cases} U_0\,\delta(x-x_0) & 0 < x < L \\ \infty & \text{otherwise} \end{cases}
$$

$$
0 < x_0 < L \qquad \text{and} \quad U_0 \ll E_0\,L
$$

Recall from the infinite square well,

Infinite Square Well

$$\begin{aligned} \phi_n(x) &= \sqrt{\frac{2}{L}}\sin(k_n x) \\ k_n &= \frac{(n+1)\pi}{L} \quad n \in \{0, 1, \ldots\} \\ E_n &= \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 (n+1)^2 \pi^2}{2mL^2} \end{aligned}$$

To compute the change in the energy eigenvalues of the system for small U_0, we use the linear perturbation calculation derived above.

Energies of Dented Well

$$\begin{aligned} \Delta E_n &\simeq \langle \phi_n | U_0\, \delta(x - x_0) | \phi_n \rangle \\ &\simeq U_0 \frac{2}{L} \sin^2(k_n x_0) \end{aligned}$$

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5 Example: Zeeman Effect

Let's move to an example closer to our original motivation. Imagine that we put our model hydrogen atom, which is really just a charged particle in a Coulomb potential, in a small magnetic field. To compute the change in energy we have to be a little clever, since we don't just have a point particle, but no matter. A simple classical argument will get us the right answer for the dipole moment of the "orbiting electron".

Start by considering the current associated with the electron traveling at some radius.

Magnetic Moment of Orbiting e^-

$$\begin{aligned} I &= -\frac{e}{T} = -\frac{ev}{2\pi r} = -\frac{e}{2\pi r}\,\frac{L}{r m_e} \\ \mu &= IA = -\frac{e}{2\pi r}\,\frac{L}{r m_e}\left(2\pi r^2\right) = -\frac{eL}{2m_e} \end{aligned}$$

Fortunately, the radial dependence drops out, so we don't have to worry about the shape of our energy eigenfunction. All we need to compute the magnetic dipole moment is the angular momentum, the mass and the charge.

The potential energy associated with a magnetic dipole in a magnetic field is our perturbing potential. (The potential is negative so that a dipole aligned with the B-field is in the lowest energy state.)

Perturbation

$$\begin{aligned} \Delta\hat{E} &= -\hat{\vec{\mu}} \cdot \vec{B} \\ & \quad \text{choose coordinates such that } \vec{B} = \hat{e}_z B_z \\ \Rightarrow \Delta\hat{E} &= -\hat{\mu_z}\, B_z = \frac{eB_z}{2m_e}\hat{L}_z \end{aligned}$$

Finally, the change in energy due to our perturbing field is:

Zeeman Splitting

$$\begin{aligned} \Delta E_{nlm} &\simeq \langle\phi_{nlm}|\frac{eB_z}{2m_e}\hat{L}_z|\phi_{nlm}\rangle \\ &\simeq \frac{e\hbar}{2m_e}B_z\, m = m\,\mu_B B_z \quad m \in \{-l, \cdots, l\} \end{aligned}$$

where $\mu_B = e\hbar/2m_e$ is known as the "Bohr Magneton" since an electron in a Bohr orbit has an integer multiple of this dipole moment. (This is another example of something that Bohr was "accidentally" right about.)

From this simple analysis, one concludes that in an applied magnetic field the $2l+1$ degeneracy of the states with a given total orbitally angular momentum will be broken. The total energy becomes

Energy with B-field

$$E'_{nlm} = -\frac{E_{Ry}}{n^2} + m\,\mu_B B_z$$

From this you might imagine that the emission line which result from $E_2 \rightarrow E_1$ transitions will split into 3 lines (one for each value of m).

Draw ground state and 3 excited states with transition arrows.

It turns out that while the math here is correct, this result works for some emission lines, but not for others. Back when Zeeman did this experiment in 1896, physicists had no explanation for the failures of the theory, and so there was a great deal of consternation about the "anomalous Zeeman effect".

Pauli: A colleague who met me strolling rather aimlessly in the beautiful streets of Copenhagen said to me in a friendly manner, "You look very unhappy," whereupon I answered fiercely, "How can one look happy when he is thinking about the anomalous Zeeman effect?!?" [Science 103 (1946)]

The answer to this puzzle, and others, is called "spin".

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6 Spin

Spin is an intrinsic angular momentum carried by a fundamental particle, which despite the name and association with angular momentum has nothing to do with something spinning. Spin is like mass, or charge, or color, in that it is the same for all particles of the same type (e.g., all electrons, or muons, or photons). With that rather enigmatic introduction, let's take a few steps back and try to figure out what is meant by "spin".

We start with a classical thought experiment: consider a hard sphere which has some charge on the surface (e.g., a baseball which you just rubbed on a cat). As we saw above, if you set the ball rotating it will have a magnetic dipole moment proportional to its angular momentum, where the constant of proportionality is given by the geometry of the ball and charge distribution.

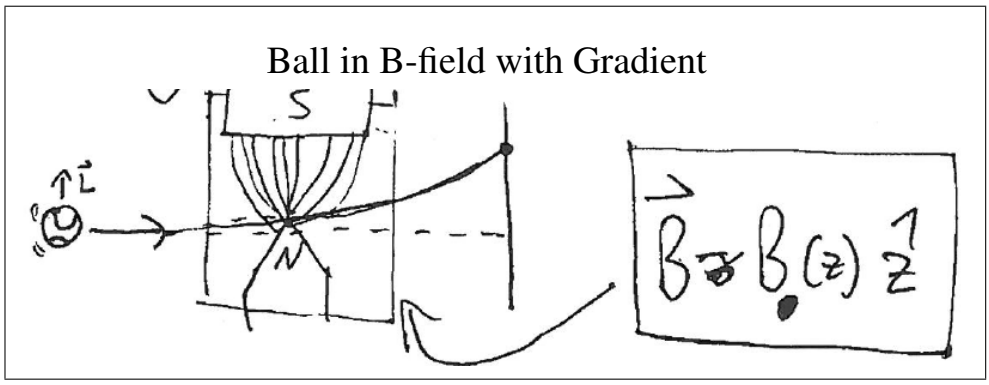
Magnetic Dipole of Charged Ball

$$\vec{\mu} = \gamma \vec{L}$$

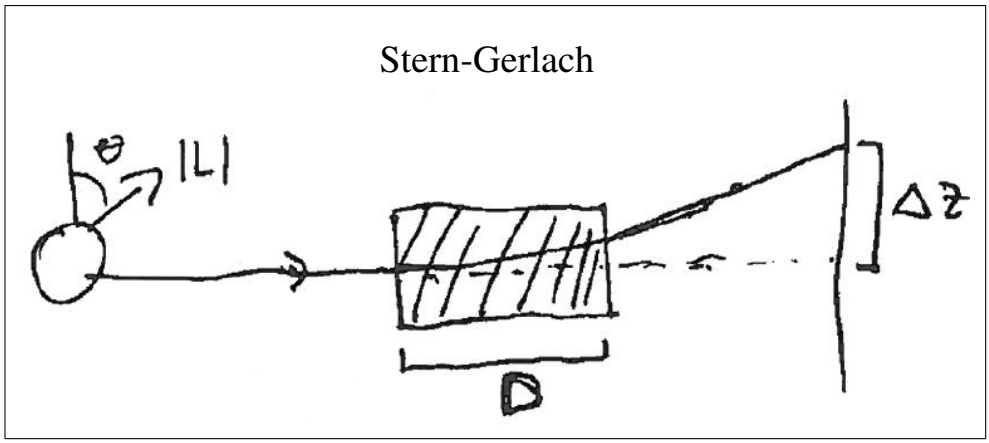
The force on such a charged ball, if placed in a magnetic field is given by

Forced on Charged Ball

$$\begin{aligned} \vec{F} &= -\vec{\nabla}V = \vec{\nabla}\left(\vec{\mu}\cdot\vec{B}\right) \\ &\text{given} \quad \vec{B} = B_z(z)\,\hat{e}_z \\ \vec{F} &= \vec{\nabla}\left(\mu_z B_z(z)\right) = \mu_z\,\partial_z B_z(z)\,\hat{e}_z \\ \Rightarrow \hat{F}_z &= B'_z\,\gamma\hat{L}_z \quad \text{where} \quad B'_z = \partial_z B_z(z) \end{aligned}$$



In an experimental setup, we control B'_z, and γ is fixed by the geometry of the charged ball, so this gives us a good measure of L_z. If the ball enters the magnetic field with velocity $v_x\,\hat{e}_x$ and the field acts over a distance D, we will have $\Delta z = \frac{1}{2}\,(F_z/m)\,(D/v_x)^2$ at the exit. Small distance from exit to screen!



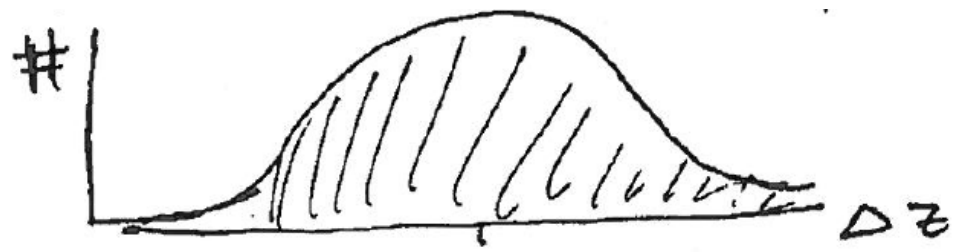
Assume that the ball enters with some angular momentum $\vec{L}$. Where does it land?

Shift at Output

$$\Delta z = \frac{B'_z D^2}{2mv_x^2}\,\gamma L_z = \frac{B'_z D^2}{2mv_x^2}\,\gamma \cos\theta\,|L|$$

Assume also that we do the experiment many times with the same total angular momentum, but in random orientations. What distribution of results will we get?

Distribution at Output



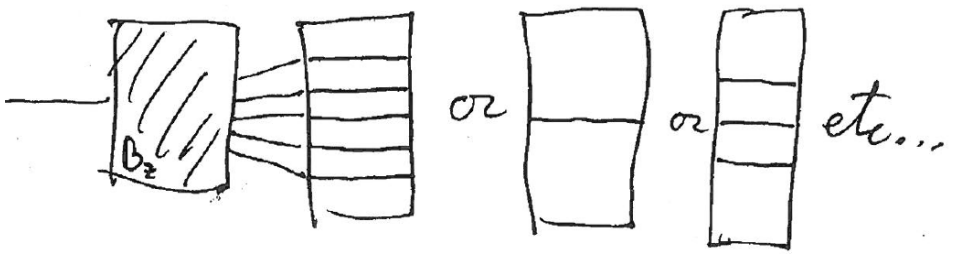
Ok, now let's return to QM, and assert that our ball has total angular momentum $|L|^2 = \hbar^2 l(l+1)$, and $L_z = \hbar m$.

Shift at Output, QM

$$\Delta z = \frac{B'_z D^2}{2mv_x^2}\,\gamma \hbar m \quad \text{with} \quad m \in \{-l, \cdots, l\}$$

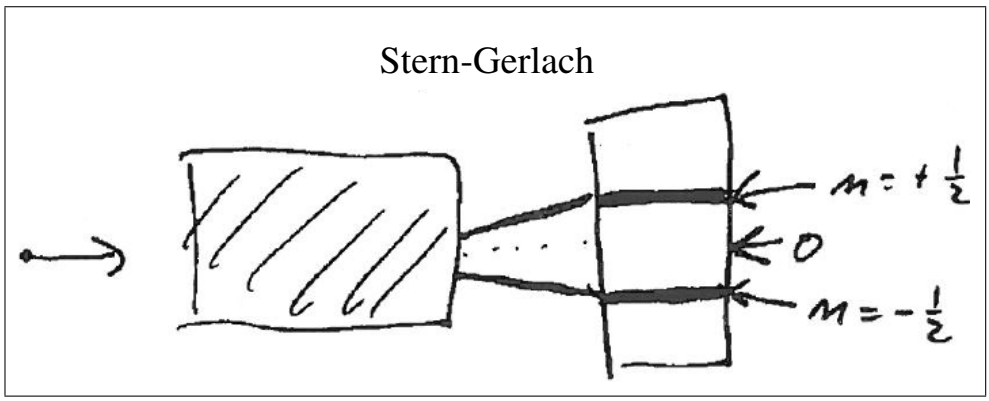
So, we should get a discrete set of shifts at the output corresponding to integer values of m.

Distribution at Output, QM



This works *perfectly* for any sort of orbital angular momentum, but what happens if you send in an electron though such a device? Does it have angular momentum? Can you "spin-up" an electron to have an arbitrary value of l?

The experimental result, performed by Stern and Gerlach in 1922 (!!), is this:



$$\Delta z = \frac{B'_z D^2}{2mv_x^2}\, g_s \mu_b\, m \quad \text{with} \quad m = \pm\tfrac{1}{2}\,, \quad g_s \simeq 2$$

This is always true. You can't make an electron have more or less angular momentum in one direction than $\hbar/2$, and the total angular momentum of an electron is fixed.

$$S_z = \pm\tfrac{1}{2}\hbar, \quad |S|^2 = \tfrac{1}{2}(\tfrac{1}{2}+1)\hbar^2 = \tfrac{3}{4}\hbar^2$$

We know that this cannot correspond to a physical rotation, because a half-integer value of m corresponds to a Y_{lm} which changes sign when you turn it around by 2π. It is also true that any rotating charge distribution would have $g_s = 1$, as we showed previously, but the electron has $g_s = 2.00232\ldots$ (It is interesting to note that spin is *required* by relativistic quantum theory, and that the value of g_s is exactly as predicted by quantum electrodynamics.)

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7 Spin and Angular Momentum

If it isn't rotating, some of you must be wondering why we think spin has anything to do with angular momentum. Maybe it is just a quantized magnetic dipole moment of magnitude $\mu_e = g_s\mu_b m$, right? The evidence to the contrary comes from the fact that orbital angular momentum, L, is *not* conserved in atomic experiments, but rather the sum of orbital and spin angular momentum is conserved.

Total Angular Momentum

$$\vec{J} = \vec{L} + \vec{S}$$

It is also true that spin obeys all of the commutation relations which apply to the orbital angular momentum operators.

Spin Commutators

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

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y \qquad \left[\hat{S}^2, \hat{S}_z\right] = 0 \qquad \left[\hat{S}^2, \hat{S}_\pm\right] = 0$$

For notational convenience, let's define up and down spin states as eigenstates of $\hat{S}_z$

Spin along Z

$$\hat{S}_z|\uparrow\rangle = \tfrac{1}{2}\hbar|\uparrow\rangle\ , \quad \hat{S}_z|\downarrow\rangle = -\tfrac{1}{2}\hbar|\downarrow\rangle$$

From the up and down along Z states we can also easily see that superpositions of states with fixed S_z can be used to make states with spin in the x or y directions.

Spin along X and Y

$$\begin{aligned}
\hat{S}_x|\tfrac{1}{\sqrt{2}}(\uparrow + \downarrow)\rangle &= \tfrac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right)|\tfrac{1}{\sqrt{2}}(\uparrow + \downarrow)\rangle \\
&= \tfrac{1}{2}\hbar|\tfrac{1}{\sqrt{2}}(\downarrow + \uparrow)\rangle \\
&= \tfrac{1}{2}\hbar|\uparrow_x\rangle
\end{aligned}$$

$$\begin{aligned}
\hat{S}_y|\tfrac{1}{\sqrt{2}}(\uparrow + i\downarrow)\rangle &= \tfrac{1}{2i}\left(\hat{S}_+ - \hat{S}_-\right)|\tfrac{1}{\sqrt{2}}(\uparrow + i\downarrow)\rangle \\
&= \tfrac{1}{2i}\hbar|\tfrac{1}{\sqrt{2}}(-\downarrow + i\uparrow)\rangle \\
&= \tfrac{1}{2}\hbar|\tfrac{1}{\sqrt{2}}(i\downarrow + \uparrow)\rangle \\
&= \tfrac{1}{2}\hbar|\uparrow_y\rangle
\end{aligned}$$

Which is just to say that there is nothing fundamentally special about the z-axis.

Note that these superposition states have the same magnitude of angular momentum as the individual Z-axis states. The superposition is a sum of *states*, not a sum of angular momenta.

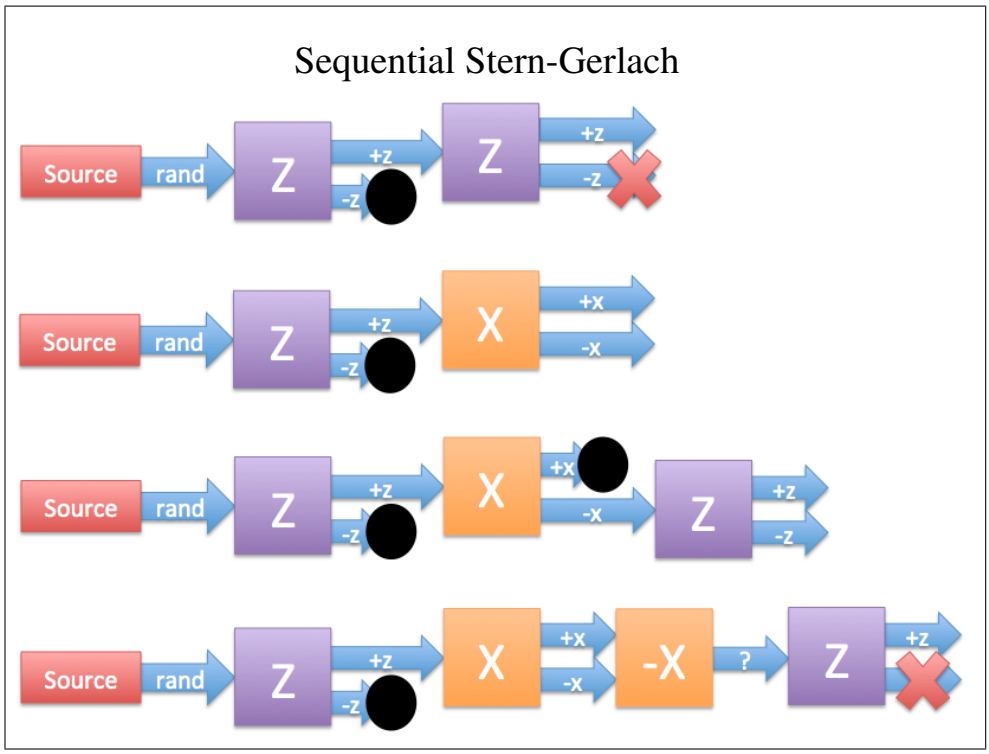
Spin Magnitude

$$\hat{S}^2|\tfrac{1}{\sqrt{2}}(\uparrow+\downarrow)\rangle \;=\; \tfrac{3}{4}\hbar^2|\tfrac{1}{\sqrt{2}}(\uparrow+\downarrow)\rangle$$

This state is not an eigenstate of $\hat{S}_z$ and does not have definite m_s.

Using the above facts about spin, we can explore the Stern-Gerlach experiment in more detail.

Consider the following experiments:



Check out the great PHET simulation at
http://phet.colorado.edu/en/simulation/stern-gerlach

8 Next Time

- Adding Angular Momentum
- Hydrogen with Spin
- Two particle systems
- Entanglement

Pset10 is posted! (This Pset will not be graded.)