Perturbation Theory

Start with a problem we know how to solve. This is the method of finding approximate solutions of a "perturbed" problem. In QM, this means going from $H = H_0$ (solvable) $\rightarrow H = H_0 + H_1$ with H_1 "small"

These ideas are broadly applicable in physics (+ math)

- Time-Independent Perturbation Theory
  - Basic Idea:
    - Hamiltonian $H = H_0 + H_1$ consists of H_0 we know how to solve (find e'states) and a perturbation H_1 which is 1st order in small quantity ϵ. ϵ may be a number in H_1 or a small expectation value for an operator in H_1
    - Want to find e'states + e'values of H as power series in ϵ
      - + full e'states

$$|\psi_n\rangle = \underbrace{|\psi_n^0\rangle}_{\substack{\text{0th order} \\ \text{e'state of } H_0}} + \underbrace{|\psi_n^1\rangle}_{\substack{\text{1st order} \\ \text{1 power of } \epsilon}} + |\psi_n^2\rangle + \cdots$$

      - + full energy e'values

$$E_n = E_n^0 + E_n^1 + E_n^2 + \cdots, \quad E_n^0 = \text{e'value of } H_0$$

    - Want to solve time-indep Schr. eqn order by order in ϵ

$$H|\psi_n\rangle = E_n|\psi_n\rangle \quad \text{expanded}$$

      - + This is

$$(H_0 + H_1)(|\psi_n^0\rangle + |\psi_n^1\rangle + \cdots) = (E_n^0 + E_n^1 + \cdots)(|\psi_n^0\rangle + |\psi_n^1\rangle + \cdots)$$

      - + At 0th order in ϵ

$$H_0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle \quad \text{Solved already!}$$

  - First Order Solution
    - Want to pick out terms with a single power of ϵ

$$H_1|\psi_n^0\rangle + H_0|\psi_n^1\rangle = E_n^1|\psi_n^0\rangle + E_n^0|\psi_n^1\rangle$$

    - The 1st order energy correction comes from the inner product with $\langle\psi_n^0|$. $H_0^\dagger = H_0 \Rightarrow$ 2nd terms cancel

$$E_n^1 = \langle\psi_n^0|H_1|\psi_n^0\rangle \quad (\ast)$$

- Example: Zeeman Effect for Hydrogen (see text)

Consider hydrogen in a magnetic field $B_0 \hat{z}$ (with B_0 bigger than internal magnetic fields)

+ This field acts on the e^- magnetic moment

$$H_1 = -\vec{B}\cdot\vec{\mu} = \frac{e}{2m} B_0 (L_z + 2S_z)$$

L_z term from orbiting current, S_z from intrinsic moment.

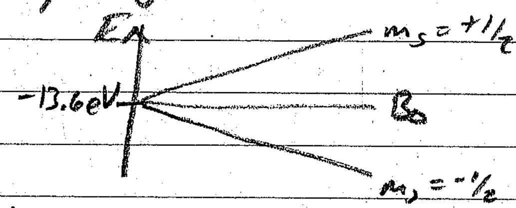
$\mu_B = e\hbar/2m$ = Bohr magneton

+ The 1st order energy shifts are

$$E^1_{n l m_l m_s} = \langle n, l, m_l, m_s | \mu_B B_0/\hbar \, (L_z + S_z) | n, l, m_l, m_s\rangle$$
$$= \mu_B B_0 (m_l + 2 m_s)$$

This is an exact result as far as the Coulomb potential is the full description of hydrogen

+ In the ground state for example, the 2 spin states are no longer degenerate



+ I've actually cheated a little using this example, as we'll see later

- To get the 1st order correction to the state, write

$$|\psi_n^1\rangle = \sum_m c_{nm} |\psi_m^0\rangle \quad b/c \ \{|\psi_m^0\rangle\} \text{ is a basis}$$

+ We can set $c_{nn} = 0$ b/c

$$1 = \langle \psi_n | \psi_n \rangle = \langle \psi_n^0 | \psi_n^0 \rangle + 2\,\mathrm{Re}\langle \psi_n^0 | \psi_n^1 \rangle + \langle \psi_n^1 | \psi_n^1 \rangle + \dots$$
$$= 1 + 2\,\mathrm{Re}(c_{nn}) + \dots \Rightarrow \mathrm{Re}(c_{nn}) = 0 + \dots$$

and $|\psi_n^0\rangle + i\,\mathrm{Im}(c_{nn})|\psi_n^0\rangle + \dots \simeq \exp(i\,\mathrm{Im}(c_{nn}))|\psi_n^0\rangle + \dots$

+ The 1st order Schr eqn is

$$\sum_m c_{nm}(E_m^0 - E_n^0)|\psi_m^0\rangle = (E_n^1 - H_1)|\psi_n^0\rangle$$

+ Take the inner product with $\langle \psi_k^0|$ + use orthonormality

For $k \neq n$

$$C_{nk}(E_k^0 - E_n^0) = -\langle \psi_k^0 | H_1 | \psi_n^0 \rangle$$

$$\Rightarrow \quad |\psi_n^1\rangle = \sum_{m \neq n} |\psi_m^0\rangle \frac{\langle \psi_m^0 | H_1 | \psi_n^0 \rangle}{E_n^0 - E_m^0}$$

+ This breaks down if $E_n^0 = E_m^0$ for some $m \neq n$, ie, when $|\psi_n^0\rangle$ is degenerate

– Degenerate Perturbation Theory

- We want to set all matrix elements $\langle \psi_m^0 | H_1 | \psi_n^0 \rangle = 0$ whenever $|\psi_m^0\rangle$ + $|\psi_n^0\rangle$ are degenerate

  Ex We are interested in a state in H atom w/ $n=2$ (l.ke $n=2, l=0, m=0$). All the $n=2$ states are degenerate at 0th order, so we consider those

- We define the truncated matrix $W_{mn} = \langle \psi_m^0 | H_1 | \psi_n^0 \rangle$ where m, n run only over degenerate states. Then change to its diagonal basis $|\psi_{n'}^0\rangle$

  ie
  $$W_{m'n'} = \langle \psi_{m'}^0 | H_1 | \psi_{n'}^0 \rangle = \lambda_{n'} \delta_{m'n'}$$

  + W_{mn} is not the matrix form of H_1. It is the matrix of H_1 truncated to a (0th order) degenerate set of states

  In our example W runs only over $n=2$ states but $\langle \psi_{n=3,l,m}^0 | H_1 | \psi_{n=2,l',m'}^0 \rangle \neq 0$ maybe

  + The new basis states $|\psi_{n'}^0\rangle$ are still e'states of H_0 b/c they are superpositions of states with the same E_n^0.

  + Ex Ground state of H in field $\vec{B} = B_0 \hat{x}$,
  $$H_1 = \mu_B B_0 (L_x + 2S_x)/\hbar$$

  $$W = \frac{e\hbar}{2m} B_0 \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$ Diagonalize over spin states

- Now you can drop the prime + do 1st order perturbation theory as usual

$$E_n^1 = \langle \psi_n^0 | H_1 | \psi_n^0 \rangle \quad , \quad |\psi_n^1\rangle = \sum_{\substack{\text{nondegenerate} \\ \text{states}}} |\psi_m^0\rangle \frac{\langle \psi_m^0 | H_1 | \psi_n^0 \rangle}{E_n^0 - E_m^0}$$

- A trick for finding the "good" states

  + Look for another Hermitian operator A that commutes with both H_0 + H_1
  + Commuting w/ H_0 means we can write 0th order states $|\psi_n^0\rangle$ also as e'states of A.
  + Then $W_{mn} = 0$ unless $|\psi_m^0\rangle$ + $|\psi_n^0\rangle$ have same e'value for A.

  Proof

$$a_n W_{mn} = \langle \psi_m^0 | H_1 A | \psi_n^0 \rangle$$
$$= \langle \psi_m^0 | A H_1 | \psi_n^0 \rangle = a_m W_{mn}$$
$$\Rightarrow W_{mn} = 0 \quad \text{or} \quad a_m = a_n$$

  + The trick is to look for a conserved Hermitian operator. Some angular momentum is often helpful

– Hydrogen Fine Structure

- Hydrogen is not just the Coulomb Hamiltonian (H_0). Consider the 2 largest corrections

- Relativistic correction to KE
  + The relativistic kinetic energy is

$$\sqrt{p^2c^2 + m^2c^4} - mc^2 \approx \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots$$

so

$$H_1 = \frac{-p^4}{8m^3c^2} = -\frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2 \quad \text{w/ small } \epsilon = \frac{\langle p^2/2m \rangle}{mc^2}$$

  + We can re-write it as

$$H_1 = \frac{-1}{2mc^2}\left(H_0 + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right)^2$$

+ Because H_0 is Hermitian

$$E^1_{nlm_l m_s} = -\frac{1}{2mc^2}\left\langle\left(H_0 + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right)^2\right\rangle$$

$$= \frac{-1}{2mc^2}\left[\left(E^0_{nlm_l m_s}\right)^2 + 2E^0_{nlm_l m_s}\frac{e^2}{4\pi\epsilon_0}\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right]$$

$$= \ldots = \frac{-1}{2mc^2}\left(E^0_{nlm_l m_s}\right)^2\left[\frac{4n}{l+1/2} - 3\right]$$

- Spin-Orbit Coupling
  + The electron sees the proton as moving, so it experiences a magnetic field $\vec{B} \propto \vec{L}$. This couples to the intrinsic dipole moment.

$$H_1 = \frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\vec{L}\cdot\vec{S}$$

See text for details; this is really a relativistic effect also

  + We rewrite $\vec{L}\cdot\vec{S}$ using total angular momentum $\vec{J} = \vec{L} + \vec{S}$

$$\vec{L}\cdot\vec{S} = \frac{1}{2}\left(J^2 - L^2 - S^2\right) \rightarrow \hbar^2/2\left[j(j+1) - l(l+1) - s(s+1)\right]$$

for e'values with $s = 1/2$

  + It is possible to calculate

$$\langle 1/r^3 \rangle = 1/l(l+1/2)(l+1)n^3a^3$$

  + The "good states" for degenerate perturbation theory are states of total angular momentum $|\psi^0_{n,j,m_j,l,s=1/2}\rangle$

The energy correction is

$$E^1_{njm_jl} = \frac{\left(E^0_{njm_jl}\right)^2}{mc^2}\left[\frac{n\left(j(j+1) - l(l+1) - 3/4\right)}{l(l+1/2)(l+1)}\right]$$

- Together, these make the fine structure which splits energy levels
  + Note that $|n, j, m_j, l\rangle$ are e'states of H_0 and the relativistic KE term, so these are still good states.
  + The total energy is

$$E_{n,j,m_j,l} = E^0 + E^1 = \frac{-mc^2\alpha^2}{2n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right]$$

where

$mc^2\alpha^2/2n^2$ = Bohr energy and

$\alpha = e^2/4\pi\epsilon_0\hbar c \approx 1/137$ is the fine structure constant

— Hyperfine Structure of Hydrogen
? Much smaller than fine structure but the largest thing involving proton physics

- The spinning proton has magnetic moment $\vec{\mu}_p = \frac{g_p e}{2m_p} \vec{S}_p$
Creates a magnetic field w/ same center as Coulomb potential

$$\vec{B} = \frac{\mu_0}{4\pi r^3}\left[3(\vec{\mu}_p \cdot \hat{r})\hat{r} - \vec{\mu}_p\right] + \frac{2\mu_0}{3}\vec{\mu}_p \delta^3(\vec{x})$$

- The electron spin/magnetic moment interacts with $\vec{B}$ to give

$$H_1 = \frac{e}{m}\vec{S}_e \cdot \vec{B} = \frac{g_p e^2}{2m m_p}\left\{\frac{\mu_0}{4\pi r^3}\left[3(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r}) - \vec{S}_p \cdot \vec{S}_e\right] + \frac{2\mu_0}{3}\vec{S}_p \cdot \vec{S}_e \delta^3(\vec{x})\right\}$$

- Consider the energy change in the ground state only
Only the δ-function contributes

$$E^1_{n=1} = \frac{\mu_0 g_p e^2}{3m_p m}\langle \vec{S}_p \cdot \vec{S}_e \rangle |\psi_{100}(0)|^2 = \frac{\mu_0 g_p e^2}{6m m_p \pi a^3}\langle S_{tot}^2 - S_e^2 - S_p^2 \rangle$$

- We know $s_e = s_p = 1/2$. By addition of angular momentum, $s_{tot} = 1$ or 0, so the e'values are

$$S_{tot}^2 - S_e^2 - S_p^2 = \hbar^2/2 \text{ (triplet) or } -3\hbar^2/2 \text{ (singlet)}$$

- The splitting is (between singlet + triplet)

$$\Delta E = \frac{4 g_p m^2 c^2 \alpha^4}{3 m_p} = hc/\lambda \quad \text{for } \lambda = 21 \text{ cm}$$

This radiation is very important in astrophysics

— Second-Order Perturbation Theory
- The 2^{nd} order part of the Schr. eqn is

$$H_0|\psi_n^2\rangle + H_1|\psi_n^1\rangle = E_n^0|\psi_n^2\rangle + E_n^1|\psi_n^1\rangle + E_n^2|\psi_n^0\rangle$$

- For the 2^{nd} order energy correction, take inner product with $\langle\psi_n^0|$
  + 1^{st} terms on either side cancel
  + 2^{nd} term on RHS $= 0$ b/c $\langle\psi_n^0|\psi_n^1\rangle = 0$ by construction
  + $\langle\psi_n^0|\psi_n^0\rangle = 1$ by normalization

$$E_n^2 = \langle\psi_n^0|H_1|\psi_n^1\rangle$$

• Substituting back, $E_n^2 = \sum_{\text{nondegenerate}} \frac{|\langle \psi_m^0 | H_1 | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}$

This is schematically 2 powers of H_p between $\langle \psi_n^0 |$ and $| \psi_n^0 \rangle$ with a sum over "intermediate states."

This is how Feynman diagrams work in particle physics

• You can continue to higher orders, etc