Perturbation Theory

We have a problem we know how to solve.
This is the method of finding approximate solutions ~~of~~ a "perturbed" problem. In QM, this means starting w/ $H = H_0$ (solvable) $\rightarrow H = H_0 + H_1$ where H_1 is somehow "small" compared to H_0.
Techniques applicable in many fields: Newtonian gravity vs GR, Feynman diagram in particle physics, etc.

- Time-Independent Perturbation Theory

— Basic Idea:

- Hamiltonian $H = H_0 + H_1$ consists of part H_0 we know how to solve and perturbation H_1 which is 1^{st} order in some small quantity ε. ε may be a number in H_1 or a small expectation for an operator.
- Let's find eigenstates + eigenvalues of H as power series in ε.

full eigenstates
$$|\psi_n\rangle = \underbrace{|\psi_n^0\rangle}_{\substack{0^{th}\text{ order}\\ \text{eigenstate of } H_0}} + \underbrace{|\psi_n^1\rangle}_{\substack{1^{st}\text{ order}\\ 1 \text{ power of } \varepsilon}} + \underbrace{|\psi_n^2\rangle}_{2^{nd}\text{ order}} + \cdots$$

full energy eigenvalues
$$E_n = \underbrace{E_n^0}_{\substack{0^{th}\text{ order}\\ \text{energy eigenvalue of } H_0}} + E_n^1 + E_n^2 + \cdots$$

- We now want to solve the time-independent Schrödinger equation order by order in ε: $H|\psi_n\rangle = E_n|\psi_n\rangle$

— First Order: the Schrödinger equation 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 0^{th} order
$$H_0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle \leftarrow \text{solved already}$$

- The 1st order piece has "1 power of ε"

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

- To find 1st order energy correction, take inner product with $\langle\psi_n^0|$
2nd terms on each side cancel since H_0 is Hermitean

$$E_n^1 = \langle\psi_n^0|H_1|\psi_n^0\rangle \quad (\star)$$ like what we did for He ground state

You'll practice this a lot.

- <u>Example</u> Zeeman Effect for Hydrogen. (See text for details)

Consider hydrogen in magnetic field $B_0\hat{z}$ (B_0 bigger than internal B fields)
This B-field acts on e^- magnetic moment

$$H_1 = -\vec{B}\cdot\vec{\mu} = \underbrace{\frac{|e|}{2m}}_{\equiv \mu_B = \text{Bohr magneton}} B_0(L_z + 2S_z)$$

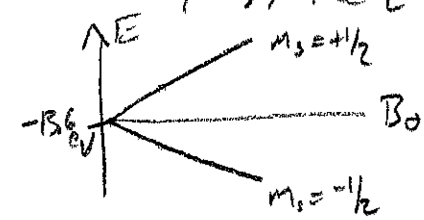
from orbiting current

intrinsic magnetic moment

The 1st order energy shifts are

$$E^1_{n\ell m m_s} = \langle n\ell m m_s|\mu_B B_0(L_z+2S_z)|n\ell m m_s\rangle = \mu_B B_0(m_\ell + 2m_s)$$

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



This is actually exact until we consider more details of hydrogen

- To get the 1st order state correction, note $|\psi_m^0\rangle$ make complete basis

$$\Rightarrow \quad |\psi_n^1\rangle = \sum_m c_{nm}|\psi_m^0\rangle$$

We can set $c_{nn}=0$ (nonzero c_{nn} just changes norm of 0th order state)
Then 1st order Schr. eqn is

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

Now take inner product with $\langle\psi_k^0|$ + use orthonormality

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

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

This works if $E_n^0 \neq E_m^0$ ie, the state $|\psi_n^0\rangle$ is <u>not degenerate</u>.

- Degenerate Perturbation Theory

• The idea is to get the matrix elements $\langle\psi_m^0|H_1|\psi_n^0\rangle = 0$ for all states $|\psi_m^0\rangle$ that are degenerate with $|\psi_n^0\rangle \leftarrow$ state we study

<u>Example</u> Suppose you are interested in some state in the H atom with principal # n=2. (Like n=2, l=0, m=0). Then you need to consider all the n=2 states, which are degenerate at 0th order

• Consider the truncated matrix $W_{mn} \equiv \langle\psi_m^0|H_1|\psi_n^0\rangle$. Then we can diagonalize it — changing to eigenbasis $|\psi_{n'}^0\rangle$,
Then $W_{m'n'} = \langle\psi_{m'}^0|H_1|\psi_{n'}^0\rangle = \lambda_{n'}\delta_{m'n'}$ ($\lambda_{n'}$ = eigenvalue)

Notes: 1) W is <u>not</u> the matrix representation of H_1. It is the matrix of H_1 <u>truncated</u> to a (0th order) degenerate set
In our previous example W_{mn} is only over the n=2 states but $\langle\psi_{n=3,lm}^0|H_1|\psi_{n=2,lm}^0\rangle$ might be nonzero

2) The new basis $|\psi_{n'}^0\rangle$ states are still eigenstates of H_0 b/c they are linear combinations of states with same E_n^0

3) <u>Example</u> Ground state of H in magnetic field $B_0\hat{x}$, $H_1 = \mu_B B_0(L_x + 2S_x)$

$$W = \frac{e}{m}B_0\hbar \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \leftarrow \text{need to diagonalize spin states}$$

• Now we apply 1st order perturbation theory on the diagonalized states (drop primes for now)

$$E_n^1 = \langle\psi_n^0|H_1|\psi_n^0\rangle \quad \text{still}$$

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

(Addendum on degenerate perturbation theory)

- Diagonalizing W may be easier if there is another hermitian operator $\mathcal{O}$ that commutes with both H_0 and H_1
  - \+ So we can write 0^{th} order stationary states as $\mathcal{O}$ eigenstates
  - \+ Also, $W_{mn} = 0$ unless $|\psi_m^0\rangle$ and $|\psi_n^0\rangle$ have same $\mathcal{O}$ eigenvalue

  Proof $\quad W_{mn} = \langle \psi_m^0 | H_1 | \psi_n^0 \rangle = \frac{1}{\lambda_n} \langle \psi_m^0 | H_1 \mathcal{O} | \psi_n^0 \rangle$

  where λ_n = eigenvalue of $|\psi_n^0\rangle$

  But then $\mathcal{O}$ commutes

  $$W_{mn} = \frac{1}{\lambda_n} \langle \psi_m^0 | \mathcal{O} H_1 | \psi_n^0 \rangle = \frac{1}{\lambda_n} \langle \psi_n^0 | H_1 \mathcal{O} | \psi_m^0 \rangle^*$$
  $$= (\lambda_m / \lambda_n) \langle \psi_m^0 | H_1 | \psi_n^0 \rangle = (\lambda_m / \lambda_n) W_{mn}$$

  This is zero unless $\lambda_m = \lambda_n$

  - \+ So look for some conserved hermitian operator.

  On HW, this is L_z

— Hydrogen Fine Structure

- Hydrogen is not just described by Coulomb potential (H_0). Let's look at 1st 2 corrections
- 1st relativistic correction to KE:

1) Relativistic $KE = \sqrt{p^2c^2 + m^2c^4} - mc^2 \simeq \frac{1}{2}\frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots$

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

2) We use $$H_1 = \frac{-1}{2mc^2}\left(\frac{p^2}{2m}\right)^2 = \frac{-1}{2mc^2}\left(H_0 + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\right)^2$$

3) Then
$$E^1_{n\ell m m_s} = \frac{-1}{2mc^2}\left\langle\left(H_0 + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\right)^2\right\rangle \text{ use Hermiticity of } H_0$$
$$= \frac{-1}{2mc^2}\left[\left(E^0_{n\ell m m_s}\right)^2 + 2E^0_{n\ell m m_s}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right]$$
$$= -\frac{\left(E^0_{n\ell m m_s}\right)^2}{2mc^2}\left[\frac{4n}{\ell + 1/2} - 3\right] \text{ after algebra}$$

- Spin-Orbit Coupling

1) Essentially, the e^- sees p moving, which means e^- sees a B field from p. This is $\propto$ to orbital ang momentum $\vec{L}$. But e^- has intrinsic magnetic moment $2\mu_B\vec{S}$.

$$\Rightarrow \quad H_1 = \frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{m^2c^2r^3}\vec{L}\cdot\vec{S}$$ (Getting all factors requires annoying relativity calculations. See text for some details)

2) We rewrite $\vec{L}\cdot\vec{S}$ using $\vec{J} = \vec{L} + \vec{S}$ = total angular momentum
$$\vec{L}\cdot\vec{S} = \frac{1}{2}\left(J^2 - L^2 - S^2\right) = \frac{\hbar^2}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right] \leftarrow \text{eigenvalues}$$
$s = 1/2$

3) Also $$\left\langle 1/r^3 \right\rangle = \frac{1}{\ell(\ell+1/2)(\ell+1)n^3a^3}$$

4) For this correction, we should write eigenstates in terms of total angular momentum: replace $l, m, s=1/2, m_s \to j, m_j, l, s=1/2$

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

- These two corrections together are "fine structure" – splits energy levels

1) $|n, j, m_j, l\rangle$ is eigenstate of H_0. So we can just use those

2) Total energy E^0+E^1 for $|n, j, m_j, l\rangle$ including fine structure is
$$E_{njm_jl} = -\underbrace{\frac{mc^2\alpha^2}{2n^2}}_{\text{Bohr energy}}\left[1+\frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2}-3/4\right)\right]$$

3) $\alpha = \dfrac{e^2}{4\pi\epsilon_0\hbar c} \simeq 1/137$ is <u>fine-structure constant</u>

- Hyperfine Structure of Hydrogen

- The spinning proton has a magnetic moment $\vec{\mu}_p = \dfrac{g_p e}{2m_p}\vec{S}_p$

This creates a magnetic field centered at origin of 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 spin/magnetic moment of e^- feels this field and has perturbed Hamiltonian
$$H_1 = \left(\frac{e}{m}\right)\vec{S}_e\cdot\vec{B} = \frac{g_p e^2}{2mm_p}\left[\frac{\mu_0}{4\pi r^3}\left[3(\vec{S}_p\cdot\hat{r})(\vec{S}_e\cdot\hat{r})-\vec{S}_p\cdot\vec{S}_e\right]+\frac{2\mu_0}{3}\vec{S}_p\cdot\vec{S}_e\,\delta^3(\vec{x})\right]$$

- Let's look at the energy change in $n=1$ ground state. Only δ-function contributes
$$E^1_{n=1,m} = \frac{\mu_0 g_p e^2}{3m_p m}\langle\vec{S}_p\cdot\vec{S}_e\rangle|\psi_{100}(0)|^2 = \frac{\mu_0 g_p e^2}{6mm_p\pi a^3}\langle S^2_{tot}-S_e^2-S_p^2\rangle$$

- By addition of angular momentum, $S_{tot} = 1$ or 0. $S_e = S_p = 1/2$

Therefore
$$S^2_{tot}-S_e^2-S_p^2 = \underset{(\text{triplet})}{\hbar^2/2} \text{ or } \underset{(\text{singlet})}{-3\hbar^2/2}$$ for eigenvalues

- The splitting between triplet and singlet states is

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

Radiation emitted from this transition in hydrogen is extremely important in astrophysics. Telescopes are now under construction to map the matter throughout the universe to a large distance using this signal.

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

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

  - To get the 2^{nd} order energy correction, take inner product with $\langle \psi_n^0|$.
    1) 1^{st} terms on LHS + RHS cancel b/c H_0 is Hermitian (see 1^{st} order)
    2) 2^{nd} term on RHS $=0$ b/c $\langle \psi_n^0 | \psi_n^1 \rangle = 0$ (see 1^{st} order)
    3) $\langle \psi_n^0 | \psi_n^0 \rangle = 1$ by normalization

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

  - Now we substitute back using the result for $|\psi_n^1\rangle$

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

We sandwich 2 powers of H_1 between $\langle \psi_n^0|$, $|\psi_n^0\rangle$ and insert the appropriate sum over "intermediate states"

  - We'll leave off here, but nothing stops you continuing in theory.