

Perturbation Theory

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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 diagrams 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 1st 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 .

$$\text{full eigenstates } |\psi_n\rangle = |\psi_n^0\rangle + |\psi_n^1\rangle + |\psi_n^2\rangle + \dots$$

$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ \text{0th order} & \text{1st order} & \text{2nd order} \\ \text{eigenstate of } H_0 & \text{1 power of } \epsilon & \end{array}$

$$\text{full energy eigenvalues } E_n = E_n^0 + E_n^1 + E_n^2 + \dots$$

$\begin{array}{c} \uparrow \\ \text{0th order} \\ \text{energy eigenvalue of } H_0 \end{array}$

- 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

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

- At 0th 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 "

$$H_1 |4_n^0\rangle + H_0 |4_n^1\rangle = E_n^1 |4_n^0\rangle + E_n^0 |4_n^1\rangle$$

To find 1st order energy correction, take inner product with $\langle 4_n^0 |$
2nd terms on each side cancel since H_0 is Hermitian

$$E_n^1 = \langle 4_n^0 | H_1 | 4_n^0 \rangle$$

(*) like what we did for He ground state

You'll practice this a lot.

• Example 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

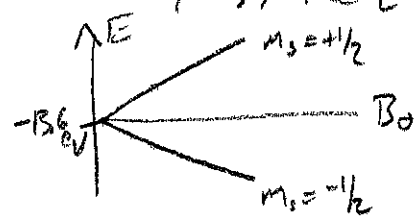
$$H_1 = -\vec{B} \cdot \vec{\mu} = \frac{e}{2m} B_0 (L_z + 2S_z)$$

\uparrow $\equiv \mu_B =$ Bohr magneton from orbiting current intrinsic magnetic moment

The 1st order energy shifts are

$$E_{nlmms}^1 = \langle nlmms | \mu_B B_0 (L_z + 2S_z) | nlmms \rangle = \mu_B B_0 (m_l + 2m_s)$$

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 $|4_m^0\rangle$ make complete basis

$$\Rightarrow |4_n^1\rangle = \sum_m C_{nm} |4_m^0\rangle$$

We can set $C_{nn} = 0$ (nonzero C_{nn} just changes norm of 0th order state)

Then 1st order Schr. eqn is

$$\sum_m C_{nm} (E_m^0 - E_n^0) |4_m^0\rangle = (E_n^1 - H_1) |4_n^0\rangle$$

Now take inner product with $\langle \psi_k^0 |$ + use orthonormality (59)

$$(k \neq n) \quad C_k (E_k^0 - E_n^0) = \langle \psi_k^0 | H_1 | \psi_n^0 \rangle$$

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

This works if $E_n^0 \neq E_m^0$ i.e., the state $|\psi_n^0\rangle$ is not degenerate.

- 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 $|\psi_n^0\rangle$ & state we study

Example 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 $|\psi_{n_i}^0\rangle, (i=1, \dots, j)$

$$\text{Then } W_{m'n'} = \langle \psi_{m'}^0 | H_1 | \psi_{n'}^0 \rangle = \lambda_{n'} \delta_{m'n'} \quad (\lambda_{n'} = \text{eigenvalue})$$

Notes: 1) W is not the matrix representation of H_1 . It is the matrix of H_1 truncated 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 non zero

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

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

$$U = \frac{eB_0 \hbar}{m} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \leftarrow \text{need to diagonalize spin states}$$

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

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

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

- 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 $KE = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \approx \frac{1}{2} \frac{p^2}{m} - \frac{p^4}{8m^3 c^2} + \dots$

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

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

3) Then

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

Use Hermiticity of H_0

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

$$= -\frac{\left(E_{nlmms}^0\right)^2}{2mc^2} \left[\frac{4n}{l+1/2} - 3 \right] \text{ after algebra}$$

• 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 $2\mu_B \vec{S}$.

$\Rightarrow H_1 = \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{1}{m^2 c^2 r^3} \vec{L} \cdot \vec{S}$ (Getting all factors requires annoying relativity calculations. See text for some details)

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

$$\vec{L} \cdot \vec{S} = \frac{1}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2) = \frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)] \leftarrow \text{eigenvalues}$$

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

$s = 1/2$

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

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

• 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 $E^0 + E'$ for $|n, j, m_j, l\rangle$ including fine structure is

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

3) $\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx 1/137$ is fine-structure constant ----- Bohr energy

- Hyperfine Structure of Hydrogen

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

This creates a magnetic field centered at origin of Coulomb potential

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

• The spin/magnetic moment of e^- feels this field and has perturbed Hamiltonian

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

• Let's look at the energy change in $n=1$ ground state.

Only δ -function contributes

$$E'_{n=1,m} = \frac{\mu_0 g_p e^2}{3m_p m} \langle \vec{S}_p \cdot \vec{S}_e \rangle |4_{100}(0)|^2 = \frac{\mu_0 g_p e^2}{6m_p m a^3} \langle S_{tot}^2 - S_e^2 - S_p^2 \rangle$$

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

Therefore

$$S_{tot}^2 - S_e^2 - S_p^2 = \begin{cases} \hbar^2/2 & \text{(triplet)} \\ -3\hbar^2/2 & \text{(singlet)} \end{cases} \text{ for eigenvalues}$$

• The splitting between triplet and singlet states is

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

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 2nd 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 2nd order energy correction, take inner product with $\langle \psi_n^0 |$.

1) 1st terms on LHS + RHS cancel b/c H_0 is Hermitian (see 1st order)

2) 2nd term on RHS = 0 b/c $\langle \psi_n^0 | \psi_n^1 \rangle = 0$ (see 1st 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.