Ch. 11 Time-independent Perturbation Theory

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \ ?$$

In general we cannot solve the energy eigenvalue problem in closed form. So we look for approximate techniques.

- Suppose

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

and we know how to solve

$$\hat{H}_0|\varphi_n^{(0)}\rangle = E_n^{(0)}|\varphi_n^{(0)}\rangle .$$

Can we find an approximation to $|\psi_n\rangle$ & E_n if, in some sense,

$$\text{“} \hat{H}_1 \ll \hat{H}_0 \text{”} \qquad ?$$

- There is no precise meaning to the above inequality between operators, but if the expectation value of $\hat{H}_1$ in the $\hat{H}_0$ basis are all small compared to the $\hat{H}_0$ eigenvalues:

$$|\langle \varphi_n^{(0)} | \hat{H}_1 | \varphi_n^{(0)} \rangle| \ll |\langle \varphi_n^{(0)} | \hat{H}_0 | \varphi_n^{(0)} \rangle| = |E_n^{(0)}|$$

then you might guess that $\hat{H}_1$ has a small effect.

- We formalize this by writing

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1$$

and consider λ to be an arbitrarily small parameter

$$|\lambda| \ll 1 .$$

- In real-life problems we often do <u>not</u> have such a parameter that can be adjusted to be arbitrarily small.

For example, in the hydrogen atom including relativistic corrections we have

$$\hat{H} = \hat{H}_0 + \alpha^2 \hat{H}_1$$

where $\hat{H}_0 = \frac{\hat{p}^2}{2\mu} - \frac{e^2}{\hat{r}}$ is the non-relativistic H-atom we have already solved, and

$$\alpha \approx \frac{1}{137}.$$

So α^2 is small, but <u>not</u> adjustable.

- So, $\boxed{\hat{H} = \hat{H}_0 + \lambda \hat{H}_1 \text{ w/ } |\lambda| \ll 1}$

& know $\hat{H}_0 |\varphi_n^{(0)}\rangle = E_n^{(0)} |\varphi_n^{(0)}\rangle$

with $\langle \varphi_n^{(0)} | \varphi_m^{(0)} \rangle = \delta_{n,m}$.

(Can also do for δ-function normalized scattering states, but more complicated...)

- Perturbation theory "ansatz"

("ansatz" is fancy for "guess")

$$(*)\quad \boxed{\begin{gathered}\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \quad \text{with} \\ |\psi_n\rangle = |\varphi_n^{(0)}\rangle + \lambda|\varphi_n^{(1)}\rangle + \lambda^2|\varphi_n^{(2)}\rangle + \cdots \\ E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\end{gathered}}$$

- Now solve for $|\varphi_n^{(1)}\rangle, |\varphi_n^{(2)}\rangle, \ldots$ and $E_n^{(1)}, E_n^{(2)}, \ldots$ simply by plugging power series into $(*)$ and solving order-by-order in λ:

$$(\hat{H}_0 + \lambda\hat{H}_1)\left(|\varphi_n^{(0)}\rangle + \lambda|\varphi_n^{(1)}\rangle + \lambda^2|\varphi_n^{(2)}\rangle + \cdots\right)$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\right)\left(|\varphi_n^{(0)}\rangle + \lambda|\varphi_n^{(1)}\rangle + \lambda^2|\varphi_n^{(2)}\rangle + \cdots\right)$$

Since this is true for <u>all</u> (small) λ, it must be true for each power separately:

$$\lambda^0: \quad \hat{H}_0|\varphi_n^{(0)}\rangle = E_n^{(0)}|\varphi_n^{(0)}\rangle \quad ✓$$

$$\lambda^1: \quad \hat{H}_0|\varphi_n^{(1)}\rangle + \hat{H}_1|\varphi_n^{(0)}\rangle = E_n^{(0)}|\varphi_n^{(1)}\rangle + E_n^{(1)}|\varphi_n^{(0)}\rangle$$

$$\lambda^2: \quad \hat{H}_0|\varphi_n^{(2)}\rangle + \hat{H}_1|\varphi_n^{(1)}\rangle = E_n^{(0)}|\varphi_n^{(2)}\rangle + E_n^{(1)}|\varphi_n^{(1)}\rangle + E_n^{(2)}|\varphi_n^{(0)}\rangle$$

$\vdots$

- Solve λ^1 for $|\varphi_n^{(1)}\rangle$ & $E_n^{(1)}$:

$\langle\varphi_k^{(0)}|\lambda^1 \Rightarrow$

$$\underbrace{\langle\varphi_k^{(0)}|\hat{H}_0}_{E_k^{(0)}\langle\varphi_k^{(0)}|}|\varphi_n^{(1)}\rangle + \langle\varphi_k^{(0)}|\hat{H}_1|\varphi_n^{(0)}\rangle =$$

$$= E_n^{(0)}\langle\varphi_k^{(0)}|\varphi_n^{(1)}\rangle + E_n^{(1)}\overbrace{\langle\varphi_k^{(0)}|\varphi_n^{(0)}\rangle}^{\delta_{k,n}}$$

$\Rightarrow$

$$\langle\varphi_k^{(0)}|\hat{H}_1|\varphi_n^{(0)}\rangle = (E_n^{(0)} - E_k^{(0)})\langle\varphi_k^{(0)}|\varphi_n^{(1)}\rangle + \delta_{k,n}E_n^{(1)}$$

$\therefore$ If $k=n$: $\boxed{E_n^{(1)} = \langle\varphi_n^{(0)}|\hat{H}_1|\varphi_n^{(0)}\rangle}$

& If $k\neq n$:

$$\langle\varphi_k^{(0)}|\varphi_n^{(1)}\rangle = \frac{\langle\varphi_k^{(0)}|\hat{H}_1|\varphi_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}$$

(Note: I have <u>assumed</u> $E_n^{(0)} \neq E_k^{(0)}$ if $k\neq n$!)

$$\Rightarrow |\varphi_n^{(1)}\rangle = \sum_k |\varphi_k^{(0)}\rangle\langle\varphi_k^{(0)}|\varphi_n^{(1)}\rangle \quad \text{so}$$

$$\boxed{|\varphi_n^{(1)}\rangle = \sum_{k\neq n} |\varphi_k^{(0)}\rangle \frac{\langle\varphi_k^{(0)}|\hat{H}_1|\varphi_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}} + |\varphi_n^{(0)}\rangle \cdot \underbrace{\langle\varphi_n^{(0)}|\varphi_n^{(1)}\rangle}_{?}}$$

- So, have "almost" solved for $|\varphi_n^{(1)}\rangle$.

But we haven't used the normalization condition

$$\langle\psi_n|\psi_m\rangle = \delta_{n,m}$$

yet. $\Rightarrow$

$$\delta_{n,m} = \left(\langle\varphi_n^{(0)}| + \lambda\langle\varphi_n^{(1)}| + \dots\right)\left(|\varphi_m^{(0)}\rangle + \lambda|\varphi_m^{(1)}\rangle + \dots\right)$$

$$= \delta_{n,m} + \lambda\left[\langle\varphi_n^{(1)}|\varphi_m^{(0)}\rangle + \langle\varphi_n^{(0)}|\varphi_m^{(1)}\rangle\right] + \dots$$

$$\Rightarrow \quad \langle\varphi_n^{(0)}|\varphi_m^{(1)}\rangle = -\langle\varphi_m^{(0)}|\varphi_n^{(1)}\rangle^*$$

$$\Rightarrow \text{if } m=n: \quad \langle\varphi_n^{(0)}|\varphi_n^{(1)}\rangle = i\,a \qquad a\in\mathbb{R}.$$

$$\therefore\ |\psi_n\rangle = |\varphi_n^{(0)}\rangle + \lambda|\varphi_n^{(1)}\rangle + \dots$$

$+ \dots$

$$= \underbrace{|\varphi_n^{(0)}\rangle + ia\lambda|\varphi_n^{(0)}\rangle}_{= \; e^{ia\lambda}|\varphi_n^{(0)}\rangle + \mathcal{O}(\lambda^2)} + \lambda \sum_{k\neq n} |\varphi_k^{(0)}\rangle \cdot \frac{\langle\varphi_k^{(0)}|\hat{H}_1|\varphi_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}$$

But, get to choose overall phase, so choose

$$e^{ia\lambda} = 1 \iff a = 0.$$

In other words, we can choose

$$\boxed{\langle\varphi_n^{(0)}|\varphi_n^{(1)}\rangle = 0}$$

- So, our final answer to first order in λ:

$$\boxed{\begin{aligned} E_n &= E_n^{(0)} + \lambda\langle\varphi_n^{(0)}|\hat{H}_1|\varphi_n^{(0)}\rangle + \mathcal{O}(\lambda^2) \\ |\psi_n\rangle &= |\varphi_n^{(0)}\rangle + \lambda\sum_{k\neq n}|\varphi_k^{(0)}\rangle \cdot \frac{\langle\varphi_k^{(0)}|\hat{H}_1|\varphi_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}} + \mathcal{O}(\lambda^2) \end{aligned}}$$

Next (2^{nd}) order: solve λ^2: e.g.

$\langle \varphi_n^{(0)} | \lambda^2 \Rightarrow$

$$\cancel{\langle \varphi_n^{(0)} | \hat{H}_0 | \varphi_n^{(2)} \rangle} + \langle \varphi_n^{(0)} | \hat{H}_1 | \varphi_n^{(1)} \rangle$$

$$= \cancel{E_n^{(0)} \langle \varphi_n^{(0)} | \varphi_n^{(2)} \rangle} + E_n^{(1)} \underbrace{\langle \varphi_n^{(0)} | \varphi_n^{(1)} \rangle}_{0} + E_n^{(2)} \underbrace{\langle \varphi_n^{(0)} | \varphi_n^{(0)} \rangle}_{1}$$

$$\therefore \quad E_n^{(2)} = \langle \varphi_n^{(0)} | \hat{H}_1 | \varphi_n^{(1)} \rangle$$

$$= \sum_{k \neq n} \langle \varphi_n^{(0)} | \hat{H}_1 | \varphi_k^{(0)} \rangle \frac{\langle \varphi_k^{(0)} | \hat{H}_1 | \varphi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}$$

$$\Rightarrow \boxed{E_n^{(2)} = \sum_{k \neq n} \frac{|\langle \varphi_k^{(0)} | \hat{H}_1 | \varphi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}}}$$

- Can solve for $|\varphi_n^{(2)}\rangle$ ... ad infinitum.

Example: 1d harmonic oscillator

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2}_{\hat{H}_0} + \lambda\left(\cancel{c_0} + \cancel{c_1 \hat{x}} + \cancel{c_2 \hat{x}^2} + c_3 \hat{x}^3 + c_4 \hat{x}^4 + \dots\right)$$

$$= \hat{H}_0 + \lambda \hat{H}_1 \quad \text{w/ } \hat{H}_1 = \hat{x}^3.$$

↙

$$|\varphi_n^{(0)}\rangle \equiv |n\rangle = \frac{(\hat{a}^+)^n}{\sqrt{n!}}|0\rangle \qquad E_n^{(0)} = \hbar\omega(n+\tfrac{1}{2}) \quad n=0,1,2,\ldots$$

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}+\hat{a}^+) \qquad \begin{cases} \hat{a}^+|n\rangle = \sqrt{n+1}\,|n+1\rangle \\ \hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle \end{cases}$$

F.N.O.: Set m so that $\sqrt{\frac{\hbar}{2m\omega}} = 1$

Then: $\hat{H} = \hat{H}_0 + \lambda\hat{H}_1 = \hat{H}_0 + \lambda(\hat{a}+\hat{a}^+)^3$

$$|\psi_n\rangle = |n\rangle + \lambda|\varphi_n^{(1)}\rangle + \ldots$$
$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$

$$E_n^{(1)} = \langle n|\hat{H}_1|n\rangle = \langle n|(\hat{a}+\hat{a}^+)^3|n\rangle$$

$$= \langle n|\Big[\hat{a}^3 + \hat{a}^2\hat{a}^+ + \hat{a}a^+\hat{a} + \hat{a}^+\hat{a}^2 + (\hat{a}^+)^2\hat{a} + \hat{a}^+\hat{a}a^+ + \hat{a}(\hat{a}^+)^2 + (\hat{a}^+)^3\Big]|n\rangle$$

$$= 0 \quad !$$

$$E_n^{(2)} = \sum_{k\neq n}\frac{|\langle k|\hat{H}_1|n\rangle|^2}{E_n^{(0)}-E_k^{(0)}} = \sum_{k\neq n}\frac{|\langle k|(\hat{a}+\hat{a}^+)^3|n\rangle|^2}{\hbar\omega(n-k)}$$

$\langle k|(\hat{a}+\hat{a}^+)^3|n\rangle \neq 0$ only if $k\in\{n+3, n+1, n-1, n-3\}$

E.g. $n=0 \Rightarrow k \in \{3,1\}$

$n=1 \Rightarrow k \in \{4,2,0\}$

$\vdots$

Compute $\underline{n=0}$:

$$\langle 3|\hat H_1|0\rangle = \langle 3|(\hat a^\dagger)^3|0\rangle = \sqrt{3!}\langle 3|3\rangle = \sqrt{6}.$$

$$\langle 1|\hat H_1|0\rangle = \langle 1|[\underbrace{\cancel{\hat a^{\dagger 2}\hat a}}_{0} + \hat a^\dagger \hat a \hat a^\dagger + \hat a \hat a^{\dagger 2}]|0\rangle$$

$$= \langle 1|\hat a^\dagger \hat a|1\rangle + \sqrt{2!}\langle 1|\hat a|2\rangle = \langle 1|\hat a^\dagger|0\rangle + 2\langle 1|1\rangle$$

$$= \langle 1|1\rangle + 2\langle 1|1\rangle = 3.$$

$$\therefore\ E_0^{(2)} = \frac{|\langle 3|\hat H_1|0\rangle|^2}{\hbar\omega(-3)} + \frac{|\langle 1|\hat H_1|0\rangle|^2}{\hbar\omega(-1)}$$

$$= \frac{1}{\hbar\omega}\left[-\frac{3!}{3} - \frac{3^2}{1}\right] = -\frac{11}{\hbar\omega}$$

$$\therefore\ E_0 = \frac{1}{2}\hbar\omega - \lambda^2\frac{11}{\hbar\omega} + O(\lambda^3)\ \ldots$$

- So, if $\left|-\lambda^2 \frac{11}{\hbar\omega}\right| \ll \left|\frac{1}{2}\hbar\omega\right|$

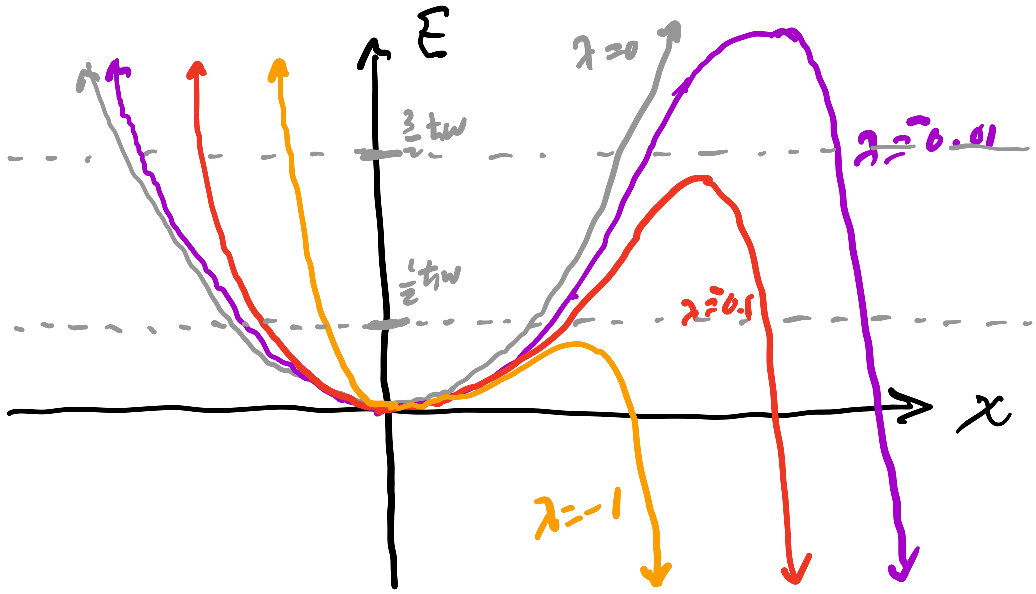
$$\Rightarrow\quad |\lambda| \ll \frac{\hbar\omega}{\sqrt{22}}$$

we expect to get a good approximation.

- The above answer is completely wrong!!

  Just look at potential:

$$V(x) = x^2 + \lambda x^3$$



<u>All</u> states are scattering states!

$\therefore$ No discrete eigenvalues no matter how small λ is, as long as $\lambda \neq 0$.

!!??

- What went wrong with our perturbation theory argument?

- The problem was our initial ansatz

$$E_n(\lambda) = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \cdots$$

This is <u>not</u> an innocuous assumption: it is actually a very strong assumption!

"Most" (almost all) functions do not have a convergent power series expansion.

If a function $f(x)$ has a power series expansion around $x = x_0$ with a non-zero radius of convergence

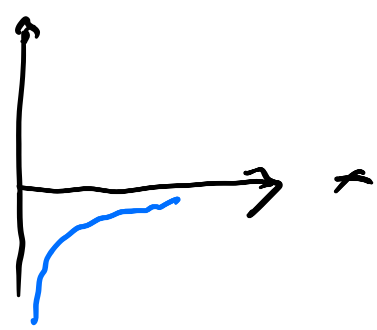
$$f(x) = f(x_0) + (x - x_0) f'(x_0) + \frac{1}{2}(x - x_0)^2 f''(x_0) + \cdots$$

for $|x - x_0| < r$

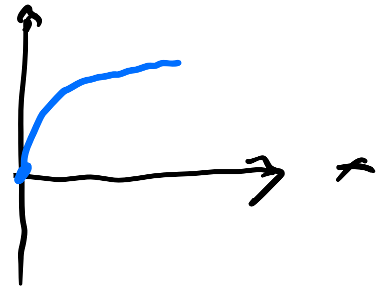
then we say "$f(x)$ is analytic at x_0".

- Examples of functions which are not analytic at $x = 0$:

$$f(x) = \frac{1}{x}$$



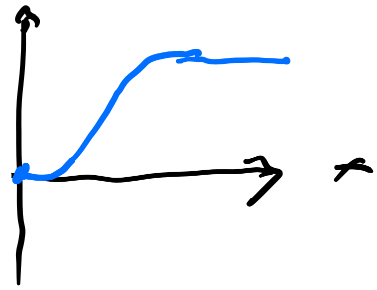
$f(x) = \sqrt{x}$



$f(x) = e^{-\frac{1}{x}}$

$\downarrow$

smooth as $x \to 0^+$



$\lim_{x\to 0^+} \frac{d^n f}{dx^n} = 0$, $\therefore$ Taylor series is

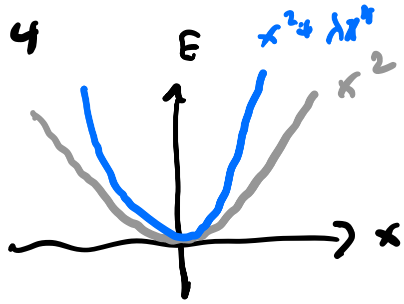
$$f(x) = f(0) + x f'(0) + \tfrac{1}{2} x^2 f''(0) + \cdots$$

$$= 0 + x\cdot 0 + \tfrac{1}{2} x^2 \cdot 0 + \tfrac{1}{3!} x^3 \cdot 0 + \cdots$$

$$\equiv 0$$ (∞ radius of convergence, but completely wrong!)

- Lesson: perturbation theory can be wrong! must always also ask about "non-perturbative physics" = non-analytic contributions

- Example: harm. oscill. $+ \lambda x^4$



  - Perturbation theory gives sensible results, and comparison to experiment/numerical sol^n seems to work for small enough λ.

  - But we know it is wrong:
    - $\rightarrow$ actually has 0 radius of convergence
    - $\rightarrow$ misses e^{-1/λ^2} non-analytic terms!

- Example: QED $\quad \lambda = \frac{\alpha^2}{4\pi} \approx 4 \times 10^{-6}$

  - Perturbation theory (computed to 5^{th} order) gives amazing agreement w/ experiment (accurate to 14 significant digits).

  - But we know is wrong:
    - $\rightarrow$ 0 radius of convergence
    - $\rightarrow$ misses $e^{-4\pi/\alpha} \approx 10^{-750}$ non-pert. terms

- Example: QCD : pert. theory is not reliable at energies $\lesssim 1\,\text{GeV}$.

Degenerate perturbation theory

- Say the n^{th} unperturbed eigenvalue is degenerate, i.e. there are $N > 1$ eigenstates $|\varphi_{n,i}^{(0)}\rangle$ $i = 1, \ldots, N$ all with the same eigenvalue $E_{n,i}^{(0)} = E_n^{(0)}$ $\forall i$

$$\hat{H}_0 |\varphi_{n,i}^{(0)}\rangle = E_n^{(0)} |\varphi_{n,i}^{(0)}\rangle \qquad i = 1, \ldots, N$$

$$\& \quad \langle \varphi_{n,i}^{(0)} | \varphi_{n,j}^{(0)} \rangle = \delta_{i,j}$$

- Then the earlier formula for the 1^{st}-order perturbative correction to $|\psi_{n,i}\rangle$ diverges:

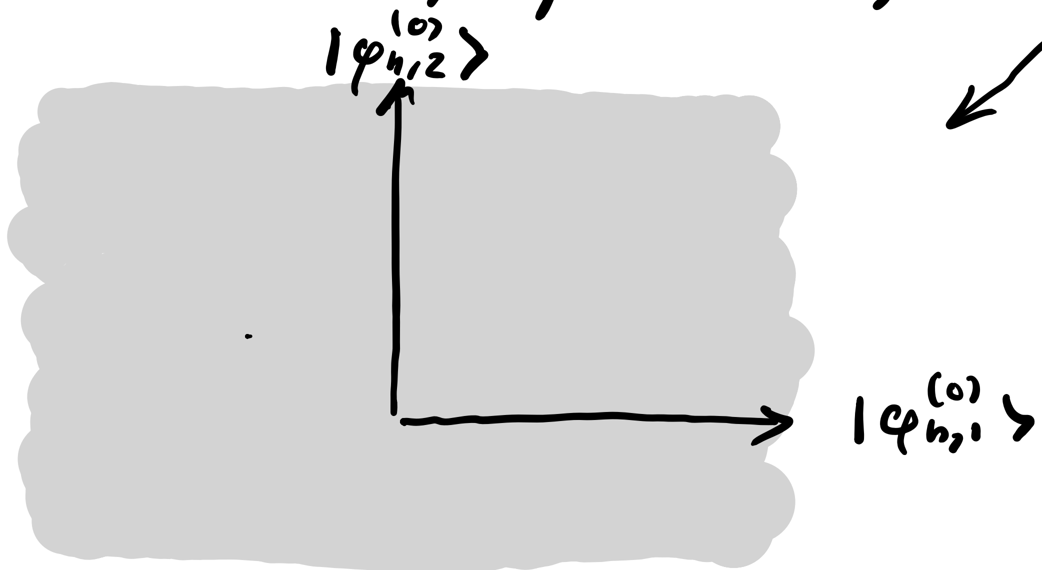
$$|\varphi_{n,i}^{(1)}\rangle = \sum_{k \neq (n,i)} |\varphi_k^{(0)}\rangle \frac{\langle \varphi_k^{(0)} | \hat{H}_1 | \varphi_{n,i}^{(0)} \rangle}{E_{n,i}^{(0)} - E_k^{(0)}}$$

$$\supset \sum_{j \neq i} |\varphi_{n,j}^{(0)}\rangle \frac{\langle \varphi_{n,j}^{(0)} | \hat{H}_1 | \varphi_{n,i}^{(0)} \rangle}{E_{n,i}^{(0)} - E_{n,j}^{(0)}}$$

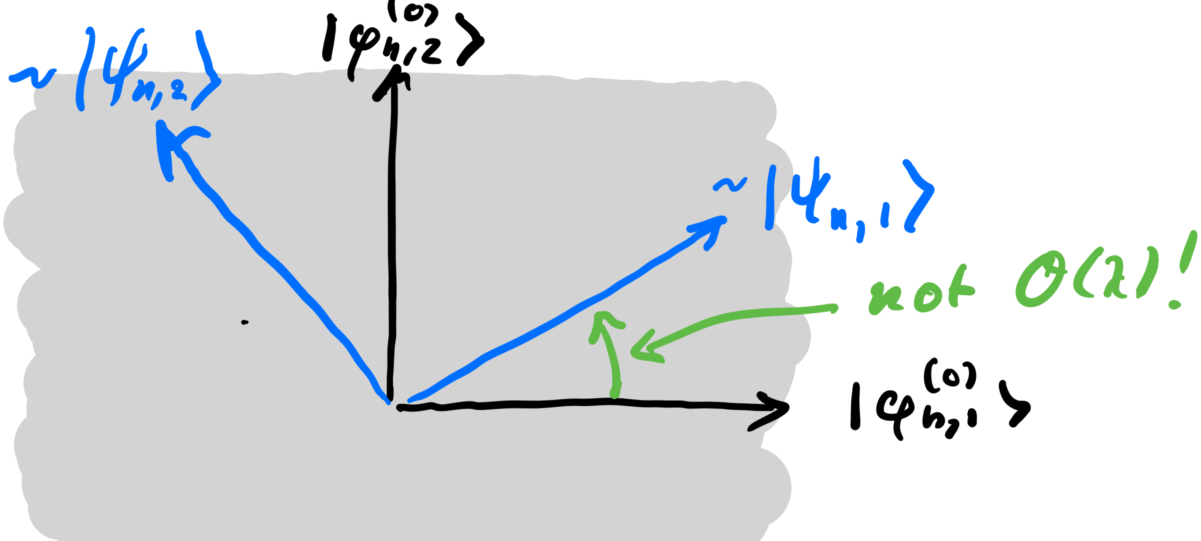
$$= \sum_{j \neq i} |\varphi_{n,j}^{(0)}\rangle \frac{\langle \varphi_{n,j}^{(0)} | \hat{H}_1 | \varphi_{n,i}^{(0)} \rangle}{\cancel{E_n^{(0)} - E_n^{(0)}} \to 0} \quad \#$$

- To understand what's going on, consider first the case $N=2$ (i.e., doubly degenerate)

Then $\{|\varphi_{n,1}^{(0)}\rangle, |\varphi_{n,2}^{(0)}\rangle\}$ = o-n basis of 2-dim'l eigenspace w/ eigenvalue $E_n^{(0)}$.



- After perturbation, the new (exact) eigenbasis $\{|\psi_{n,1}\rangle, |\psi_{n,2}\rangle\}$ need <u>not</u> be close to either $|\varphi_{n,1}^{(0)}\rangle$ or $|\varphi_{n,2}^{(0)}\rangle$:



- So our perturbative assumption:

$$\begin{cases} |\psi_{n,1}\rangle = |\varphi_{n,1}^{(0)}\rangle + \lambda |\varphi_{n,1}^{(1)}\rangle + \cdots \\ |\psi_{n,2}\rangle = |\varphi_{n,2}^{(0)}\rangle + \lambda |\varphi_{n,2}^{(1)}\rangle + \cdots \end{cases}$$

is simply wrong! We chose the wrong $\{ |\varphi_{n,1}^{(0)}\rangle, |\varphi_{n,2}^{(0)}\rangle \}$ basis of the degenerate eigenspace!

- Correct ansatz is

$$\boxed{|\psi_{n,i}\rangle = \sum_{j=1}^{N} c_{ji} |\varphi_{n,j}^{(0)}\rangle + \lambda |\varphi_{n,i}^{(1)}\rangle + \cdots}$$

where c_{ij} is some $N \times N$ $O(\lambda^0)$ unitary matrix.

(c_{ij} is unitary because it rotates o-n basis $\{ |\varphi_{n,j}^{(0)}\rangle \}$ to new o-n basis

$$|\tilde{\varphi}_{n,i}^{(0)}\rangle \doteq \sum_{j=1}^{N} c_{ji} |\varphi_{n,j}^{(0)}\rangle . \;)$$

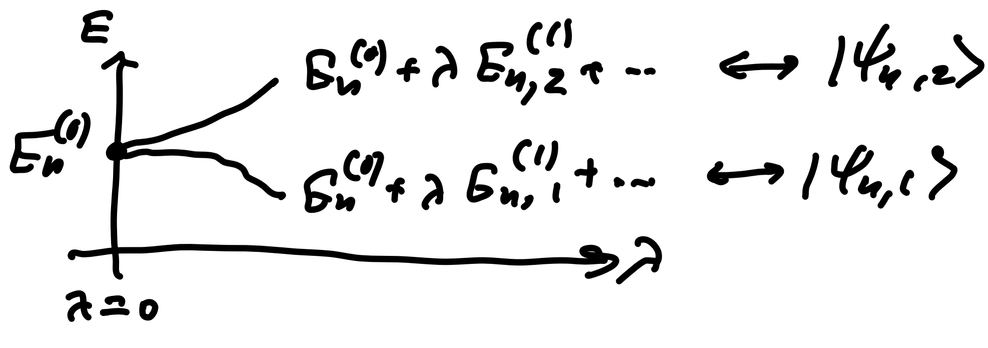
- So when we do perturbation theory for a degenerate level, the first step ($\mathcal{O}(\lambda^0)$) is to determine the c_{ij} matrix.

- Plug pert. ansatz into:

$$\hat{H}|\psi_{n,j}\rangle = \mathcal{E}_{n,j}|\psi_{n,j}\rangle$$

w/ $$\boxed{\mathcal{E}_{n,j} = E_n^{(0)} + \lambda E_{n,j}^{(1)} + \cdots}$$

Note that this allows for the possibility that the degenerate $E_n^{(0)}$ level can "split" to up to N non-degenerate levels, e.g.:



- $\mathcal{O}(\lambda^0)$:

$$\hat{H}_0\left(\sum_{i=1}^{N} c_{ij}|\varphi_{n,i}^{(0)}\rangle\right) = E_n^{(0)}\left(\sum_{i=1}^{N} c_{ij}|\varphi_{n,i}^{(0)}\rangle\right) \checkmark$$

This is satisfied for any c_{ij}.

• $O(\lambda^1)$:

$$\hat{H}_0 |\varphi_{n,j}^{(1)}\rangle + \hat{H}_1 \left(\sum_{i=1}^{N} c_{ij} |\varphi_{n,i}^{(0)}\rangle\right) =$$

$$= E_n^{(0)} |\varphi_{n,j}^{(1)}\rangle + E_{n,j}^{(1)} \left(\sum_{i=1}^{N} c_{ij} |\varphi_{n,i}^{(0)}\rangle\right)$$

$\langle\varphi_{n,k}^{(0)}| O(\lambda^1)$ & use $\langle\varphi_{n,k}|\varphi_{n,i}^{(0)}\rangle = \delta_{ki}$ $\Rightarrow$

$$\cancel{\langle\varphi_{n,k}^{(0)}|\underbrace{\hat{H}_0}_{E_n^{(0)}}|\varphi_{n,j}^{(1)}\rangle} + \sum_{i=1}^{N} c_{ij} \underbrace{\langle\varphi_{n,k}^{(0)}|\hat{H}_1|\varphi_{n,i}^{(0)}\rangle}_{\equiv (H_1)_{ki}}$$

$$= \cancel{E_n^{(0)}\langle\varphi_{n,k}^{(0)}|\varphi_{n,j}^{(1)}\rangle} + E_{n,j}^{(1)} \sum_{i=1}^{N} c_{ij}\, \delta_{ik}$$

$$\therefore \sum_{i=1}^{N} (H_1)_{ki}\, c_{ij} = E_{n,j}^{(1)}\, c_{kj}$$

for each value of j $\quad c_{ij} \equiv \left(\vec{v}^{(j)}\right)_i$ $\leftarrow$ j^{th} column of c_{ij}

$\Rightarrow \quad H_1 \vec{v}^{(j)} = E_{n,j}^{(1)} \vec{v}^{(j)}$ $\leftarrow$ Matrix eigenvalue problem!

$\therefore$ $E_{n,j}^{(1)}$ are the eigenvalues of the matrix

$$(H_1)_{ij} = \langle\varphi_{n,i}^{(0)}|\hat{H}_1|\varphi_{n,j}^{(0)}\rangle$$

& eigenvectors determine c_{ij} matrix.

(Note that H_1 is hermitian, so can choose the $\{\vec{v}^{(j)}\}$ eigenvectors to be o-n $\Rightarrow$ c_{ij} is unitary!)

Example: Hydrogen atom Stark effect

- Put an H-atom in a uniform electric field

$$\underbrace{\vec{E} = \underset{\text{constant}}{E}\,\underset{\text{unit vector in } z\text{-direction.}}{\hat{e}_z}}$$

- Then $\hat{H}_1 = -\underbrace{\hat{\mu}_e}_{\text{electric dipole moment of H-atom}} \cdot \vec{E} = -(-e\hat{\vec{r}})\cdot\vec{E} = eE\underbrace{\hat{z}}_{\hat{z}\text{ position operator}}$

- 1^{st}-order (in E) corrections to H-atom energy levels are given by

$$E^{(1)}_{n\ell m} = \langle n\ell m|\,\hat{H}_1\,|\underbrace{n\ell m}\rangle$$

by non-degenerate perturbation theory. (usual unperturbed H-atom eigenstate)

- E.g. $n=1 \Rightarrow \ell=m=0 \Rightarrow$ non-degenerate, so

$$E^{(1)}_{100} = \langle 100|\,\hat{H}_1\,|100\rangle = eE\langle 100|\hat{z}|100\rangle$$

$$\langle 100|\hat{z}|100\rangle = \int d^3\vec{r}\; \psi^*_{100}(\vec{r})\; z\; \psi_{100}(\vec{r})$$

$$= \int r^2 dr\, d\Omega\;\; R^*_{10}(r)\, \cancelto{1/\sqrt{4\pi}}{Y^*_{00}}(\theta,\varphi) \cdot r\cos\theta \cdot R_{10}(r) \cdot \cancelto{1/\sqrt{4\pi}}{Y_{00}}(\theta,\varphi)$$

$$= \left(\int dr \cdot r^3\, |R_{10}(r)|^2\right) \underbrace{\left(\frac{1}{4\pi}\int d\Omega \cdot \cos\theta\right)}_{=\,0}$$

$\therefore$ $E^{(1)}_{100} = 0$. Need to compute $E^{(2)}_{100}$ ...
... see text book ...

- Symmetry reason that $\langle 100|\hat{z}|100\rangle = 0$:

"$|n\,l\,m\rangle$ has parity $(-1)^l$ under $\vec{r} \to -\vec{r}$."

Call $P : (x,y,z) \mapsto (-x,-y,-z)$ "inversion"

P is a symmetry of the H-atom.

Quantumly $P \to \hat{\Pi}$, a unitary operator

satisfying: $\boxed{\hat{\Pi}^2 = 1,}$ $\quad (\Rightarrow \hat{\Pi} = \hat{\Pi}^\dagger)$

$$\boxed{\hat{\pi}\hat{x} = -\hat{x}\,\hat{\pi},\ \hat{\pi}\hat{y} = -\hat{y}\,\hat{\pi},\ \&\ \hat{\pi}\hat{z} = -\hat{z}\,\hat{\pi}.}$$

(Townsend uses $\hat{P}$ not $\hat{\pi}$, but don't confuse with momentum $\hat{p}$!)

$$\therefore\quad \hat{\pi}\,\hat{\vec{r}} = -\hat{\vec{r}}\,\hat{\pi} \Rightarrow \hat{\pi}\,\hat{r}^2 = \hat{r}^2\,\hat{\pi}$$

$$\hat{\pi}\,\hat{\vec{p}} = -\hat{\vec{p}}\,\hat{\pi} \Rightarrow \hat{\pi}\,\hat{p}^2 = \hat{p}^2\,\hat{\pi}$$

$$\Rightarrow \boxed{[\hat{\pi}, \hat{H}_0] = 0} \qquad \hat{H}_0 = \frac{1}{2\mu}\hat{p}^2 - \frac{e^2}{\hat{r}}$$

(definition of symmetry op. in QM)

- Since $\hat{\pi}^2 = 1$, its eigenvalues can only be ± 1.

Since $[\hat{\pi}, \hat{H}_0] = 0$, can find simultaneous eigenbasis, so eigenstates have definite parity

$$\hat{\pi}\,|n\ell m\rangle = \pm\,|n\ell m\rangle$$

- Compute: $\vec{r} \to -\vec{r}$: $(r, \theta, \varphi) \xrightarrow{\hat{\pi}} (r, \pi-\theta, \varphi+\pi)$

$$\langle \vec{r} | n \ell m \rangle = R_{n\ell}(r)\, Y_{\ell m}(\theta,\varphi) \xrightarrow{\hat{\pi}} R_{n\ell}(r)\, Y_{\ell m}(\pi-\theta, \varphi+\pi)$$

$$Y_{\ell m}(\theta,\varphi) = P_{\ell m}(\theta)\, e^{im\varphi}$$

$$Y_{\ell m}(\pi-\theta,\varphi+\pi) = P_{\ell m}(\pi-\theta)\, e^{im(\varphi+\pi)} = (-)^m P_{\ell m}(\pi-\theta) e^{im\varphi}$$

Recall (ch 9):

$$P_{\ell m}(\theta) \propto (\hat{L}_-)^{\ell-m} P_{\ell\ell} \propto \frac{1}{\sin^m\theta} \frac{d^{\ell-m} \sin^{2\ell}(\theta)}{(d\cos\theta)^{\ell-m}}$$

$$\therefore\ P_{\ell m}(\pi-\theta) \propto \frac{1}{\sin^m(\pi-\theta)} \frac{d^{\ell-m} \sin^{2\ell}(\pi-\theta)}{(d\cos(\pi-\theta))^{\ell-m}}$$

$$\sin(\pi-\theta) = \sin\theta \qquad \cos(\pi-\theta) = -\cos\theta \Rightarrow$$

$$P_{\ell m}(\pi-\theta) = (-)^{\ell-m} P_{\ell m}(\theta)$$

$$\therefore\ Y_{\ell m}(\pi-\theta,\varphi+\pi) = (-)^\ell Y_{\ell m}(\theta,\varphi)$$

$$\therefore\ \boxed{\hat{\Pi}\, |n \ell m\rangle = (-)^\ell\, |n \ell m\rangle}$$

Parity symm. of H-atom

- This symmetry implies the "selection rule"

$$\langle n', \ell', m' | \hat{z} | n, \ell, m \rangle = \langle n' \ell' m' | \hat{z}\, \hat{\Pi}^2 | n \ell m \rangle$$

$$= -\langle n'\ell'm'|\,\hat{\pi}\,\hat{z}\,\hat{\pi}\,|n\ell m\rangle$$

$$= -(-)^{\ell'+\ell}\langle n'\ell'm'|\,\hat{z}\,|n\ell m\rangle$$

$\therefore$

$$\boxed{\langle n'\ell'm'|\,\hat{z}\,|n\ell m\rangle = 0 \quad \text{unless} \quad \ell+\ell' = \text{odd}}$$

"Parity selection rule"

Back to Stark effect

- Compute $n=2$ energy level perturbations

But $|n=2,\ell,m\rangle \Rightarrow \left\{\begin{matrix} \ell=1, & m\in\{-1,0,1\} \\ \ell=0, & m=0 \end{matrix}\right\} \Rightarrow$ degeneracy 4

So have to use degenerate p.t.

$$E^{(1)}_{2,\ell,m} = \text{eigenvalues of } 4\times 4 \ H_1 \text{ matrix}$$

$$(H_1)_{\ell',m';\ell,m} \doteq \langle 2\ell'm'|\hat{H}_1|2\ell m\rangle = eE\langle 2\ell'm'|\hat{z}|2\ell m\rangle.$$

- So need to first compute H_1 matrix.

$$H_1 = \begin{array}{r} \ell'=m'=0 \\ \ell'=1 \quad m'=1 \\ 0 \\ -1 \end{array}\begin{pmatrix} * & * & * & * \\ * & * & * & * \\ * & * & * & * \\ * & * & * & * \end{pmatrix}$$

16 entries

- $H_1 = H_1^\dagger \Rightarrow$ only 10 indep't entries $\begin{pmatrix} \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix}$

- Use parity selection rule $\Rightarrow$

$$(H_1)_{l'm',lm} = 0 \quad \text{unless} \quad l+l' = \text{odd}$$

i.e. non-zero only $\text{for} \begin{cases} l=0 \ \& \ l'=1 \\ \text{or} \ l=1 \ \& \ l'=0 \end{cases}$.

$$\therefore \quad H_1 = \begin{pmatrix} 0 & \times & \times & \times \\ \times & 0 & 0 & 0 \\ \times & 0 & 0 & 0 \\ \times & 0 & 0 & 0 \end{pmatrix} \Rightarrow \text{only 3 indep't entries.}$$

- There is another selection rule, coming from rotational symmetry around z-axis:

$$[\hat{z}, \hat{L}_z] = 0 \qquad \Rightarrow$$

$$m'\hbar \langle n'l'm' | \hat{z} | nlm \rangle = \langle n'l'm' | \hat{L}_z \hat{z} | nlm \rangle$$

$$= \langle n'l'm' | \hat{z} \hat{L}_z | nlm \rangle = \hbar m \langle n'l'm' | \hat{z} | nlm \rangle$$

$$\therefore \quad \boxed{\langle n'l'm' | \hat{z} | nlm \rangle = 0 \quad \text{unless} \quad m = m'}$$

"L_z selection rule"

- $\therefore\ (H_1)_{l'm',lm} = 0$ unless $m = m'$

$$\therefore\ H_1 = \begin{pmatrix} 0 & 0 & * & 0 \\ 0 & 0 & 0 & 0 \\ * & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$\Rightarrow$ only 1 indep't entry!

$\langle 200|\hat{H}_1|210\rangle$

Compute:

$$\langle 200|\hat{H}_1|210\rangle = e\mathcal{E}\,\langle 200|\hat{z}|210\rangle$$

$$= e\mathcal{E}\int r^2 dr \int d\Omega\, R_{20}^* Y_{00}^*\, r\cos\theta\, R_{21} Y_{10}$$

$$= e\mathcal{E}\,\underbrace{\left(\int_0^\infty r^3 dr\, R_{20}^* R_{10}\right)}_{a_0\cdot\# = \dots = -3a_0}\,\underbrace{\left(\int d\Omega\, Y_{00}^* Y_{10}\cos\theta\right)}_{\text{dim'less no.} = \dots = 1}$$

$$= -3a_0 e\mathcal{E}.$$

Re-organize rows/colums so block diagonal:

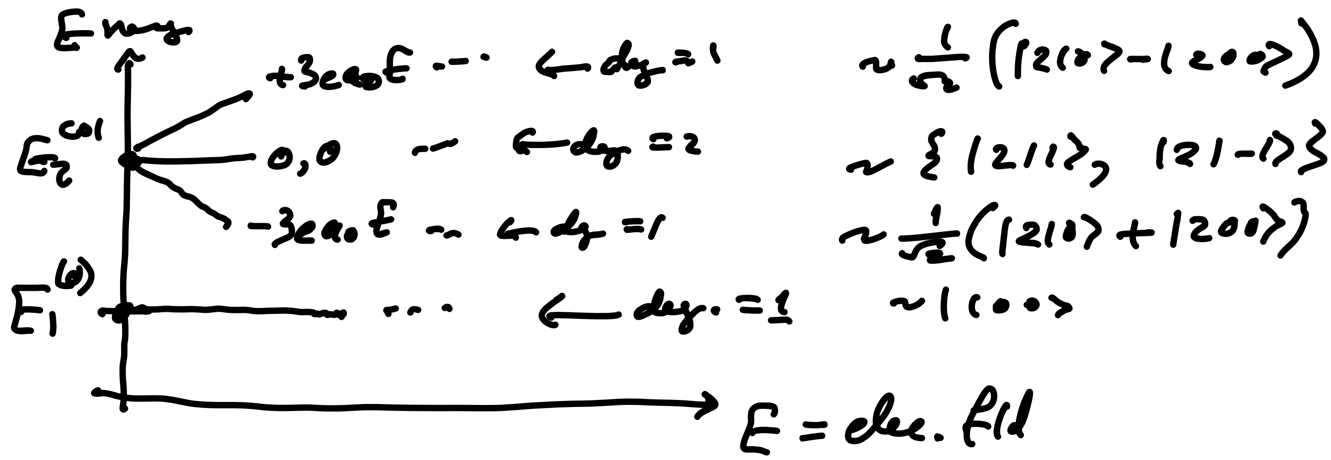
$$(H_1)_{l'm',lm} = \begin{array}{c} \\ (l,m) \rightarrow \end{array}\begin{array}{cc} \begin{array}{cccc} (00) & (10) & (11) & (1,-1) \end{array} & \\ \left(\begin{array}{cc|c} 0 & -3e\mathcal{E}a_0 & \\ -3e\mathcal{E}a_0 & 0 & 0 \\ \hline 0 & & 0 \end{array}\right) & \begin{array}{c} (00) \\ (10) \\ (11) \\ (1-1) \\ \uparrow \\ (l',m') \end{array} \end{array}$$

$\downarrow$ $\qquad\qquad\qquad\qquad$ $\downarrow$ 2 0-eigenvalues

$$0 = \det\begin{pmatrix} -\lambda & -3eEa_0 \\ -3eEa_0 & -\lambda \end{pmatrix} = \lambda^2 - 9e^2E^2a_0^2$$

$\Rightarrow$ eigenvalues $= \pm 3eEa_0$.

$\therefore$ $E_2^{(1)} = \{0, 0, +3eEa_0, -3eEa_0\}$



Other simple examples where you can practice p.t.

- Spin ½ or 1 systems w/ e.g. $\hat{H} = \hat{S}_z^2 + \lambda \hat{S}_x$
- 3d rigid rotor system
- 2d & 3d harmonic oscillator

"Fine structure" of the hydrogen atom

- Add relativistic corrections to H-atom Hamiltonian

$$\hat{H}_0 = \frac{\hat{P}^2}{2\mu} - \frac{e^2}{\hat{r}}$$

Relativistic corrections can be expanded in a power series in $\left(\frac{v}{c}\right)^2$ where v is the typical speed of the electron.

- Virial theorem (classical mechanics) says

$$2\langle \text{Kinetic energy} \rangle = -\langle \text{Pot'l energy} \rangle$$

(if the pot'l goes as $1/r$).

So for n^{th} energy level

$$E_n = \langle K.E. \rangle + \langle P.E. \rangle = -\langle K.E. \rangle$$

$$= -\frac{1}{2\mu}\langle p^2 \rangle = -\frac{\mu^2}{2\mu}\langle v^2 \rangle = \frac{-\mu c^2}{2}\left\langle \left(\frac{v}{c}\right)^2 \right\rangle$$

So $$\left\langle \left(\frac{v}{c}\right)^2 \right\rangle = \frac{-2E_n}{\mu c^2} = \frac{2}{\mu c^2} \cdot \frac{\mu c^2 \alpha^2}{2n^2} = \left(\frac{\alpha}{n}\right)^2.$$

- Thus $\left(\frac{v}{c}\right)^2 \sim \left(\frac{\alpha}{n}\right)^2$ in H-atom, so

$$\max\left(\frac{v}{c}\right)^2 \sim \alpha^2 \approx \frac{1}{(137)^2} \approx 5\times10^{-6} \ll 1.$$

$\therefore$ We expect perturbation theory expansion in $\left(\frac{v}{c}\right)^2$ should be pretty good!

- What are the leading relativistic corrections?

$$\hat{H} = \underset{\substack{\uparrow \\ \mathcal{O}\left(\frac{v}{c}\right)^0}}{\hat{H}_0} + \underset{\substack{\uparrow \\ \mathcal{O}\left(\frac{v}{c}\right)^2 \\ \uparrow \\ \text{"fine structure"}}}{\hat{H}_1} + \underset{\substack{\uparrow \\ \mathcal{O}\left(\frac{v}{c}\right)^4}}{\hat{H}_2} + \cdots$$

$$\hat{H}_1 = \underset{\substack{\uparrow \\ \text{Relativistic} \\ \text{Kinetic energy}}}{\hat{H}_T} + \underset{\substack{\uparrow \\ \text{Spin-orbit} \\ \text{coupling}}}{\hat{H}_{SO}} + \underset{\substack{\uparrow \\ \text{Darwin} \\ \text{term}}}{\hat{H}_{Dar}}$$

check:

$$\hat{H}_T = -\frac{1}{8\mu^3c^2}\hat{p}^4$$

$$H_T \sim \frac{p^2}{\mu}\cdot\frac{p^2}{\mu^2c^2} = KE\cdot\left(\frac{v}{c}\right)^2 \checkmark$$

$$\hat{H}_{SO} = + \frac{e^2}{2\mu^2 c^2} \frac{1}{\hat{r}^3} \hat{\vec{S}} \cdot \hat{\vec{L}}$$

(use $a_0 = \hbar/mc\alpha$)

$$H_{SO} \sim \frac{e^2\hbar^2}{\mu^2 c^2 a_0^3} \sim \frac{e^2}{a_0} \cdot \alpha^2 \approx PE \cdot \left(\frac{v}{c}\right)^2 \checkmark$$

$$\hat{H}_{Dar} = + \frac{\pi e^2 \hbar^2}{8\mu^2 c^2} \delta^3(\hat{\vec{r}})$$

$$H_{Dar} \sim \frac{e^2\hbar^2}{\mu^2 c^2} \cdot \frac{1}{a_0^3} \checkmark$$

- Somewhat amazingly, the $\hat{H}_0 + \hat{H}_1$ H-atom hamiltonian can be exactly diagonalized, giving the energy levels

$$E_{nj} = E_n \left(1 + \frac{\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right)$$

$$\left(E_n = -\frac{\mu c^2 \alpha^2}{2n^2}\right)$$

where j is $\hat{J}^2$ quantum number where

$$\hat{\vec{J}} = \hat{\vec{S}} + \hat{\vec{L}}$$ is <u>total</u> angular momentum.

spin of electron.

- Where do these terms come from?

non-relativistic kin. energy

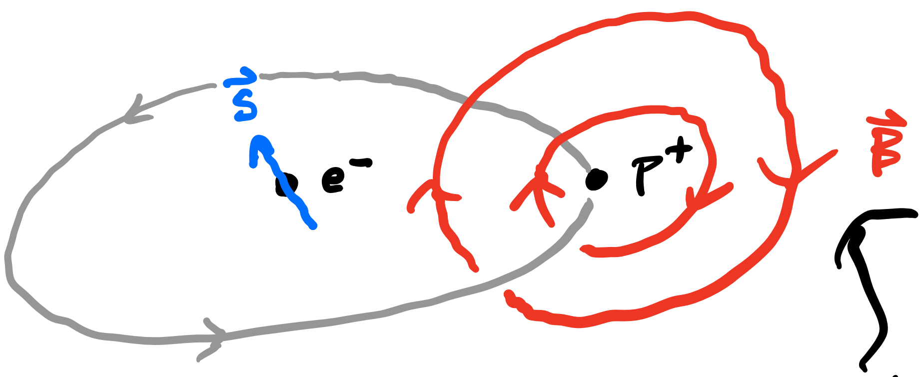
relativistic kin. energy

$$\hat{H}_T: \quad \frac{p^2}{2m} \longrightarrow \sqrt{m^2c^4 + p^2c^2} = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}}$$

$$= mc^2\left(1 + \frac{1}{2}\frac{p^2}{m^2c^2} - \frac{1}{8}\left(\frac{p^2}{m^2c^2}\right)^2 + \ldots\right)$$

$$= \underset{\substack{\uparrow \\ \text{constant}}}{mc^2} + \underset{\substack{\uparrow \\ \text{NR} \\ \text{KE}}}{\frac{p^2}{2m}} - \underset{\substack{\uparrow \\ \hat{H}_T \checkmark}}{\frac{1}{8}\frac{p^4}{m^3c^2}} + \underset{\ldots}{\ldots}$$

$\hat{H}_{SO}$: In rest frame of e^-, p^+ is orbiting:



Moving charge (current) creates magnetic field by Ampere's law

$$\vec{B} \sim \frac{e}{c}\frac{\vec{r}\times\vec{v}}{r^3} \sim \frac{e}{cm}\frac{\vec{L}}{r^3}$$

so $$\hat{H}_{SO} = \gamma\,\vec{S}\cdot\vec{B} = \frac{e}{mc}\cdot\frac{e}{cmr^3}\vec{S}\cdot\vec{L} \quad \checkmark$$

(Up to factor of $\frac{1}{2}$. Correct argument a bit more subtle bc rest frame of e^- is not an inertial frame.)

$\hat{H}_{Dar}$: This is more difficult to motivate intuitively. Relativity + QM implies the electron, e^-, must have an anti-particle, the positron, e^+. They are described together by the Dirac equation, a relativistic generalization of Schrödinger's eqn. Eliminating e^+ from this equation gives rise to $\hat{H}_{Dar}$. (Some people explain this in terms of "virtual particle-antiparticle pair production" near the proton...)

Note that since $\hat{H}_{Dar} \propto \delta^3(\vec{r})$, it will only perturb states that are non-zero at $\vec{r}=0$.
Recall that $\psi_{nlm}(r) \sim r^l$ as $r \to 0$ so $\hat{H}_{Dar}$ does not affect states with $l>0$.

Hyperfine structure of H-atom

Nuclei have spin, & therefore a magnetic dipole moment. So, by the same argument that gave $\hat{H}_{SO}$, we find another contribution

$$\hat{H}_D \sim \frac{e^2}{mMc^2r^3}\vec{S}_N\cdot\vec{L}$$

nucleus spin $\sim \hbar$

nucleus mass $\sim 10^3 \times m_e$

$$\therefore \quad \hat{H}_D \sim \frac{m}{M}\cdot\hat{H}_{SO} \sim 10^{-3}\cdot\hat{H}_{SO} \sim 10^{-3}\cdot \text{fine structure}$$

Nuclei have no electric dipole moments for symmetry reasons, but they can have a electric quadrupole moment giving

$$\hat{H}_Q \sim \ldots \sim 10^{-3}\cdot \text{fine structure.}$$