time-independent non-degenerate perturbation theory

$$(\hat{H}_0 + \lambda \hat{V})\,|\psi_n(\lambda)\rangle = E_n(\lambda)\,|\psi_n(\lambda)\rangle$$

$$E_n(\lambda) = \boxed{E_n^{(0)}} + \lambda V_{nn} + \lambda^2 E_n^{(2)} + \dots$$

$$|\psi_n(\lambda)\rangle = \boxed{|\psi_n^{(0)}\rangle} + \lambda \sum_{l\neq n} \underbrace{\frac{V_{ln}}{E_n^{(0)} - E_l^{(0)}}}_{= C_{nl}^{(1)}} |\psi_l^{(0)}\rangle + \lambda^2 \underbrace{|\psi_n^{(2)}\rangle}_{= \sum_l C_{nl}^{(2)} |\psi_l^{(0)}\rangle} + \dots$$

$$\boxed{V_{mn} = \langle \psi_m^{(0)} | \hat{V} | \psi_n^{(0)} \rangle \quad \text{matrix element}}$$

- known
- unique due to assumed absence of degeneracy

Now: second order

- Schrödinger equation: $\hat{H}_0 |\psi_n^{(2)}\rangle + \hat{V} \underbrace{|\psi_n^{(1)}\rangle}_{= \sum_l C_{nl}^{(1)} |\psi_l^{(0)}\rangle} = E_n^{(2)} |\psi_n^{(0)}\rangle + E_n^{(1)} |\psi_n^{(1)}\rangle + E_n^{(0)} |\psi_n^{(2)}\rangle$ $\quad \langle \psi_m^{(0)}| \cdot$
- orthonormality: $\langle \psi_n^{(0)} | \psi_m^{(2)} \rangle + \langle \psi_n^{(1)} | \psi_m^{(1)} \rangle + \langle \psi_n^{(2)} | \psi_m^{(0)} \rangle = 0$

$$\sum_l C_{nl}^{(2)} E_l^{(0)} \delta_{ml} + \sum_l C_{nl}^{(1)} V_{ml} = E_n^{(2)} \delta_{mn} + E_n^{(1)} \sum_l C_{nl}^{(1)} \delta_{ml} + E_n^{(0)} \sum_l C_{nl}^{(2)} \delta_{lm}$$

$$E_m^{(0)} C_{nm}^{(2)} + \sum_l C_{nl}^{(1)} V_{ml} = E_n^{(2)} \underbrace{\delta_{mn}}_{=1} + E_n^{(1)} C_{nm}^{(1)} + E_n^{(0)} C_{nm}^{(2)}$$

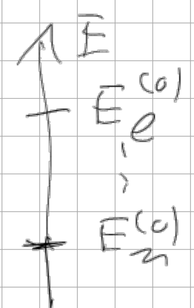
Index m is at our disposal:

$n = m$: $$E_n^{(2)} = \sum_{l\neq n} C_{nl}^{(1)} V_{nl} - E_n^{(1)} \underbrace{C_{nn}^{(1)}}_{=0} = \sum_{l \neq n} \frac{V_{nl} V_{ln}}{E_n^{(0)} - E_l^{(0)}}$$

$$V_{nl} V_{nl}^* = |V_{nl}|^2$$

$n_0 \mathrel{\hat{=}}$ ground state

$$E_{n_0}^{(2)} = \sum_{l \neq n_0} \frac{|V_{nl}|^2}{\underbrace{E_{n_0}^{(0)} - E_l^{(0)}}_{<0}} < 0$$



$n \neq m$: $\left[E_n^{(0)} - E_m^{(0)}\right] C_{nm}^{(2)} = \sum_{l\neq n} C_{nl}^{(1)} V_{ml} - E_n^{(1)} C_{nm}^{(1)}$

$$\Rightarrow C_{nm}^{(2)} = \sum_{l\neq n} \frac{V_{ln}}{E_n^{(0)} - E_l^{(0)}} \frac{V_{ml}}{E_m^{(0)} - E_l^{(0)}} - V_{nn} \sum_{m\neq n} \frac{V_{nm}}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} \quad n \neq m$$

intermediate result:

$$|\psi_n(\lambda)\rangle = \Big(1 + \underbrace{C_{nn}^{(2)}}_{\text{not yet known!}} \lambda^2 \Big) |\psi_n^{(0)}\rangle$$

$$+ \lambda^2 \sum_{m\neq n} \left[\sum_{l\neq n} \frac{V_{ml} V_{ln}}{\left(E_n^{(0)} - E_l^{(0)}\right)\left(E_m^{(0)} - E_l^{(0)}\right)} - V_{nn} \frac{V_{nm}}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} \right] |\psi_m^{(0)}\rangle + \ldots$$

back to orthonormality:

$$C_{nm}^{(2)} + \sum_{l\neq n} C_{nl}^{(1)*} C_{ml}^{(1)} + C_{mn}^{(2)*} = 0$$

$m \neq n$: all coefficients are known, can be inverted

no new information due to algebraic identity:

$$\frac{1}{x-y}\,\frac{1}{x-z} + \frac{1}{y-x}\,\frac{1}{y-z} + \frac{1}{z-x}\,\frac{1}{z-y} = 0; \quad x \neq y \neq z \neq x$$

$\hat{=}$ orthogonality

$m = n \,\hat{=}$ normalization

$$\rightarrow C_{nn}^{(2)} + C_{nn}^{(2)*} = - \sum_{l\neq n} C_{nl}^{(1)*} C_{nl}^{(1)}$$

$$c_{nn}^{(2)} = \underbrace{i\,\gamma_n^{(2)}}_{\substack{\text{unknown} \\ =0 \text{ without loss} \\ \text{of generality}}} - \underbrace{\frac{1}{2}\sum_{\ell\neq n}\frac{|V_{n\ell}|^2}{(E_n^{(0)}-E_\ell^{(0)})^2}}_{\text{will affect } E_n^{(3)}}$$

Summary:

$$E_n(\lambda=1) = E_n^{(0)} + V_{nn} + \sum_{m\neq n}\frac{|V_{nm}|^2}{E_n^{(0)}-E_m^{(0)}} + \dots$$

$$|\psi_n(\lambda=1)\rangle = \left[1 - \frac{1}{2}\sum_{\ell\neq n}\frac{|V_{\ell n}|^2}{(E_n^{(0)}-E_\ell^{(0)})^2} + \dots\right]|\psi_n^{(0)}\rangle$$

$$+ \sum_{m\neq n}\left[\frac{V_{mn}}{E_n^{(0)}-E_m^{(0)}} + \sum_{\ell\neq n}\frac{V_{m\ell}V_{\ell n}}{(E_n^{(0)}-E_m^{(0)})(E_n^{(0)}-E_\ell^{(0)})} - \frac{V_{nn}V_{nm}}{(E_n^{(0)}-E_m^{(0)})^2} + \dots\right]|\psi_m^{(0)}\rangle$$

$$V_{nm} = \langle\psi_n^{(0)}|\hat V|\psi_m^{(0)}\rangle = \int d^3x\, \psi_n^{(0)}(\vec x)^*\, V(\vec x)\, \psi_m^{(0)}(\vec x)$$

A posterio criterion: perturbative expansion makes sense provided $\boxed{\left|\frac{V_{nm}}{E_n^{(0)}-E_m^{(0)}}\right| \ll 1}$, $n\neq m$

Reminder: basic assumption $\Rightarrow$ $E_n^{(0)}$ due non-degenerate

Anharmonic Oscillator: $\hat H = \underbrace{\frac{\hat p^2}{2m} + \frac{m}{2}\omega^2\hat x^2}_{=\hat H_0} + \underbrace{g\,\hat x^4}_{=\hat V}$

$$E_n^{(1)} = \langle n|\hat V|n\rangle = g\int dx\, x^4\, |\psi_n^{(0)}(x)|^2$$

$$\psi_n^{(0)}(x) = \frac{1}{\sqrt{\sqrt{\pi}\, 2^n n!}}\, H_n\!\left(\frac{x}{\ell}\right) e^{-\frac{x^2}{2\ell^2}}, \qquad \ell = \sqrt{\frac{\hbar}{m\omega}}$$

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}$$

$$H_0(x) = 1, \quad H_1(x) = 2x, \quad H_2(x) = 4x^2 - 2, \quad \ldots$$

$$E_n^{(1)} \underset{\substack{\uparrow \\ x = \ell\xi}}{=} \frac{g}{\sqrt{\pi}\, 2^n n!} \left(\frac{\hbar}{m\omega}\right)^2 \underbrace{\int_{-\infty}^{+\infty} d\xi\, \boxed{\xi^4 H_n(\xi)}\, H_n(\xi)\, e^{-\xi^2}}_{\text{how to calculate this number?}}$$

recursion formula: $\xi H_n(\xi) = \frac{1}{2} H_{n+1}(\xi) + n H_{n-1}(\xi)$

iterate this: $\xi^2 H_n(\xi) = \ldots$, $\xi^3 H_n(\xi) = \ldots$

$$\xi^4 H_n(\xi) = \frac{1}{16} H_{n+4}(\xi) + \frac{2n+3}{4} H_{n+2}(\xi) + \boxed{\frac{3(2n^2+2n+1)}{4}} H_n(\xi) + (*)\, H_{n-2}(\xi) + (*)\, H_{n-4}(\xi)$$

orthonormality relation

$$\int_{-\infty}^{+\infty} dx\, \psi_n^{(0)*}(x)\, \psi_m^{(0)}(x) = \delta_{nm}$$

$$\Rightarrow E_n^{(1)} = g \underbrace{\left(\frac{\hbar}{m\omega}\right)^2}_{= \ell^4} \frac{3(2n^2+2n+1)}{4}$$

general remarks: quantity $f_N(g) = \sum_{n=0}^{N} g^n f_n$ based on perturbation theory expectation: perturbative result gets better for increasing N

at a first glance: yes, this is true

Landé factor: anomalous magnetic moment of electron

$$\underbrace{g_e}_{=f} \overset{N=3}{=\!=} \underbrace{2}_{\text{Dirac}}.\underbrace{\underbrace{0023}_{\text{Schwinger}}\;193\;043(74)}_{\text{electron interacting with vacuum}} = \sum_{n=0}^{N} (g_e)_n \underbrace{\alpha}_{=g}^{n}$$

↑ Taylor expanded in Sommerfeld finestructure constant α

α is the dimensionless quantity measuring interaction strength between light and matter

$$\alpha = \frac{e^2}{4\pi\hbar\varepsilon_0 c} \approx 0.0073 \approx \frac{1}{137}$$

$$\alpha = \frac{\text{ratio of}}{\text{two length scales}} = \frac{\lambda_C}{2\pi a_B}$$

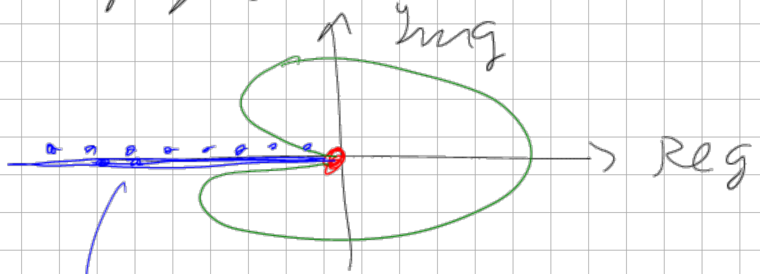
λ_C → compton wave length $\lambda_C = \frac{\hbar}{mc}$

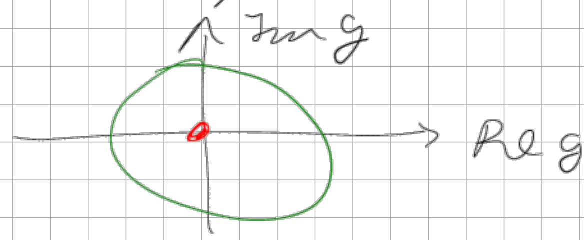
a_B → Bohr radius: $a_B = \frac{4\pi\varepsilon_0 \hbar^2}{m e^2}$

BUT: Freeman Dyson (1952)

- excellent agreement discussed above is due to the smallness of α
- discovery: Taylor series has convergence radius zero

asymptotic series $\longleftrightarrow$ convergent series





negative real axis has to be ex-
cluded from convergence region

convergence radius is zero

$$f_n \overset{n \text{ large}}{\sim} n!$$

large-order behaviour

finite convergence radius

f_n decreases with n

What can be done?

- Padé method cut approximation by poles
- Borel method
- variational perturbation theory

Hydrogen Atom:

$$\hat{H} = -\frac{\hbar^2}{2M}\Delta - \frac{e^2}{4\pi\varepsilon_0|\vec{x}|}, \quad \hat{H}\,\psi_E(\vec{x}) = E\,\psi_E(\vec{x})$$

energy eigenvalues:

$$E_n = -\underbrace{Ry}_{\text{Rydberg energy}}\frac{1}{n^2}; \quad n = 1, 2, 3 \dots \text{ principal quantum number}$$

$$= \frac{m e^4}{32 \pi^2 \epsilon_0^2 \hbar^2} = 13.6\,eV = \frac{1}{2} \underbrace{Mc^2}_{\text{rest energy of electron } 0.511\,MeV} \alpha^2$$

l angular quantum number $(0, \ldots, n-1)$

m magnetic " " $(-l, \ldots, +l)$

degeneracy with respect to l, m: $\sum_{l=0}^{n-1} \underbrace{(2l+1)}_{= \sum_{m=-l}^{+l} 1} = n^2 = d_n$

$d_1 = 1$ non-degenerate

$d_2 = 4$ degeneracy

$$\psi_{nlm}(\vec{x}) = \psi_{nlm}\underbrace{(r, \vartheta, \varphi)}_{\text{spherical coordinates}} = \underbrace{Y_{lm}(\vartheta, \varphi)}_{\text{spherical harmonics}} \underbrace{R_{nl}(r)}_{\text{radial wave function}}$$