Second-Order Result:

$$\hat{H}(\lambda) = \hat{H}_0 + \underbrace{\lambda}_{\text{smallness parameter}} \hat{V}$$

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

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

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

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

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

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

2.6 Anharmonic Oscillator:

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} + \frac{m}{2}\omega^2 \hat{x}^2}_{=\hat{H}_0} + \underbrace{g\,\hat{x}^4}_{=\hat{V}}$$

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

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

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

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

$$E_n^{(1)} \underset{\uparrow}{=} \frac{g}{\sqrt{\pi}\,2^n n!} \left(\frac{\hbar}{m\omega}\right)^2 \int_{-\infty}^{+\infty} d\xi\ \xi^4 \left[H_n(\xi)\right]^2 e^{-\xi^2}$$

$x = \ell z$

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

$$\xi^2 H_n(\xi) = - \dots, \quad \xi^3 H_n(\xi) = - \dots$$

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

orthonormality relations:

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

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

2.7 General remarks:

quantity $f_N(g) = \sum_{n=0}^{N} f_n g^n$ approximation

$\uparrow$ $g_0 = 0$

based on perturbation theory

expectation: perturbative result gets better for increasing N at first glance: yes, this is true

Landé factor, anomalous magnetic moment of electron

$$\underbrace{g_e}_{g} = \underbrace{2.}_{\text{Dirac}}\underbrace{00\,23}_{\text{Schwinger}}\underbrace{193043(74)}_{\text{electron is interacting with vacuum}} \overset{(N=3)}{=} \sum_{n=0}^{N} (g_e)_n \, \alpha^n$$

excellent agreement between theory and experiment

Taylor expanded in Sommerfeld fine-structure constant α

dimensionless quantity measuring interaction strength between light and matter

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

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

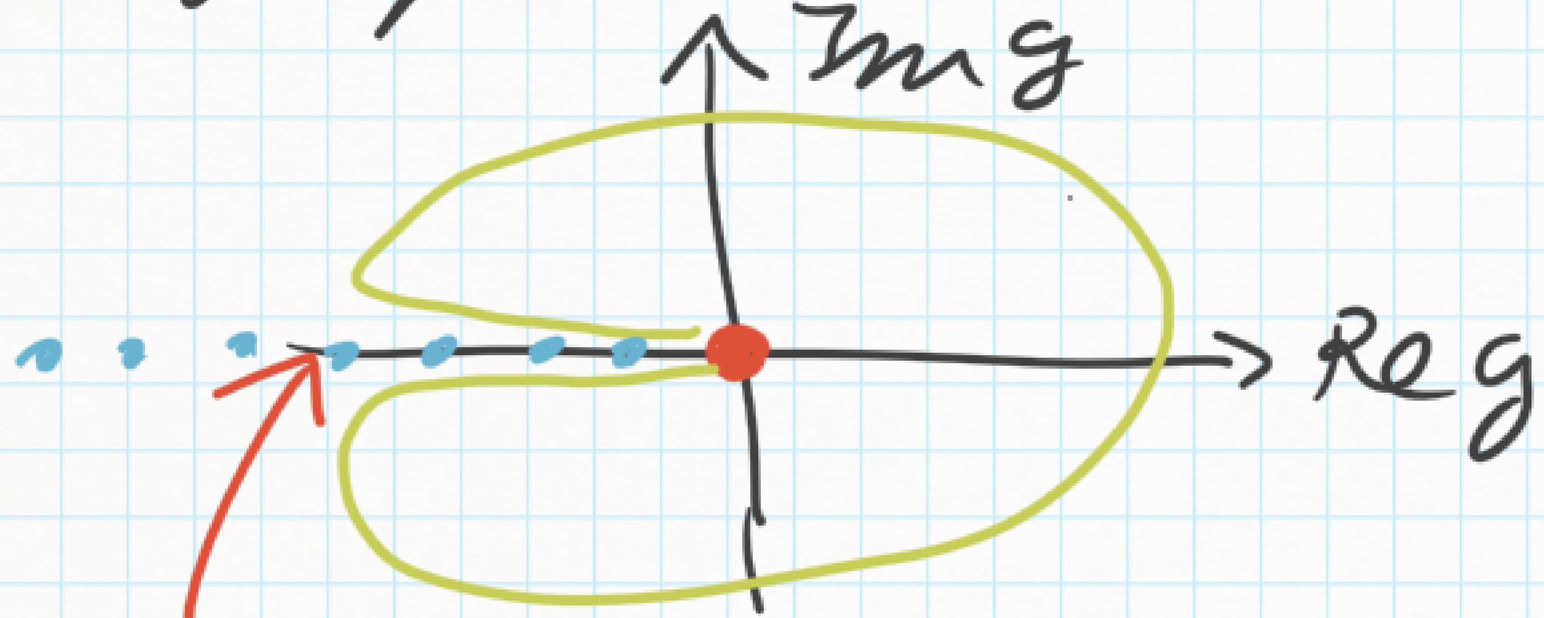
$\lambda_c \rightarrow$ Compton wave length of electron $\quad \lambda_c = \frac{\hbar}{mc}$

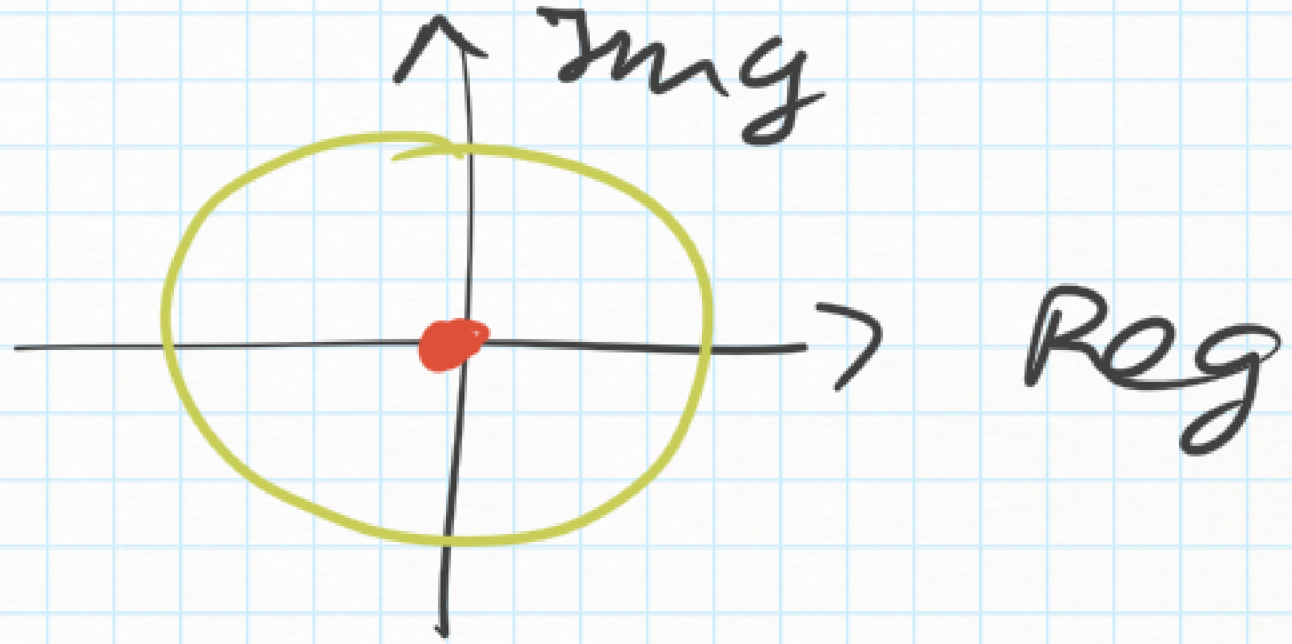
$a_B \rightarrow$ Bohr radius $\quad a_B = \frac{4\pi \varepsilon_0 \hbar^2}{me^2}$

BUT: Freeman Dyson (1952)

- excellent agreement discussed above is due to the smallness of Sommerfeld fine-structure constant
- discovery: Taylor series has convergence radius zero

→ asymptotic series <=> convergent series





negative real axis has to excluded from convergence region

$f_n \underset{\text{large } n}{\sim} n!$ large-order behaviour f_n decrease with n

What can be done? Resummation techniques

1) Padé method: cut approximation by simple poles
2) Borel
3) variational perturbation theory

1.4 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:

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

Rydberg energy $= \dfrac{me^4}{32\pi^2\varepsilon_0^2\hbar^2} = \dfrac{1}{2}\underbrace{mc^2}\alpha^2$

13.6 eV $\longleftarrow$ rest energy of electron $= 0.511\,\text{MeV}$

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

m magnetic $(-l, \dots 0, \dots, +l)$

$\Rightarrow$ degeneracy: $\sum_{l=0}^{n-1} \underbrace{2l+1} = n^2 = d_n$

degeneracy for l fixed

energy eigenfunctions: $\psi_{n\ell m}(r,\vartheta,\varphi) = \underbrace{R_{n\ell}(r)}_{\text{radial wave functions}} \underbrace{Y_{\ell m}(\vartheta,\varphi)}_{\text{spherical harmonics}}$

Chapter 3: Time-Independent degenerate Perturbation Theory

prime example: Stark effect, i.e. how the first excited state ($n=2$) with degeneracy $d_2 = 4$ reacts upon switching on an electric field

3.1 Motivation:

concentrate on subspace of spectrum, which has degeneracy d_n

$$\hat{H}_0 \, |\Psi^{(0)}_{n\alpha_n}\rangle = \underbrace{E^{(0)}_n}_{\text{does not depend on } \alpha_n} |\Psi^{(0)}_{n\alpha_n}\rangle$$

α_n: degeneracy index, running 1 to d_n

different eigenenergies: energy eigenfunctions orthonormal

degenerate eigenstates: rely on Schmidt orthonormalization procedure

$$\Rightarrow \langle \Psi^{(0)}_{n\alpha_n} | \Psi^{(0)}_{m\beta_m} \rangle = \delta_{nm} \, \delta_{\alpha_n \alpha_m}$$

also have: family of Hamilton operators

$$\underbrace{\hat{H}(\lambda)}_{= \hat{H}_0 + \lambda \hat{V}} |\tilde{\Psi}_{n\alpha_n}(\lambda)\rangle = \underbrace{E_{n\alpha_n}(\lambda)}_{} |\tilde{\Psi}_{n\alpha_n}(\lambda)\rangle$$

at least partially degeneracy is lifted due to impact of perturbation $\hat{V}$

$\lambda \to 0$: $\quad E_{n\alpha_n}(\lambda) = E^{(0)}_n + E^{(1)}_{n\alpha_n} \lambda + \ldots$

$|\tilde{\Psi}_{n\alpha_n}(\lambda)\rangle \neq |\Psi^{(0)}_{n\alpha_n}\rangle + |\Psi^{(1)}_{n\alpha_n}\rangle \lambda + \ldots$

in general this is violated

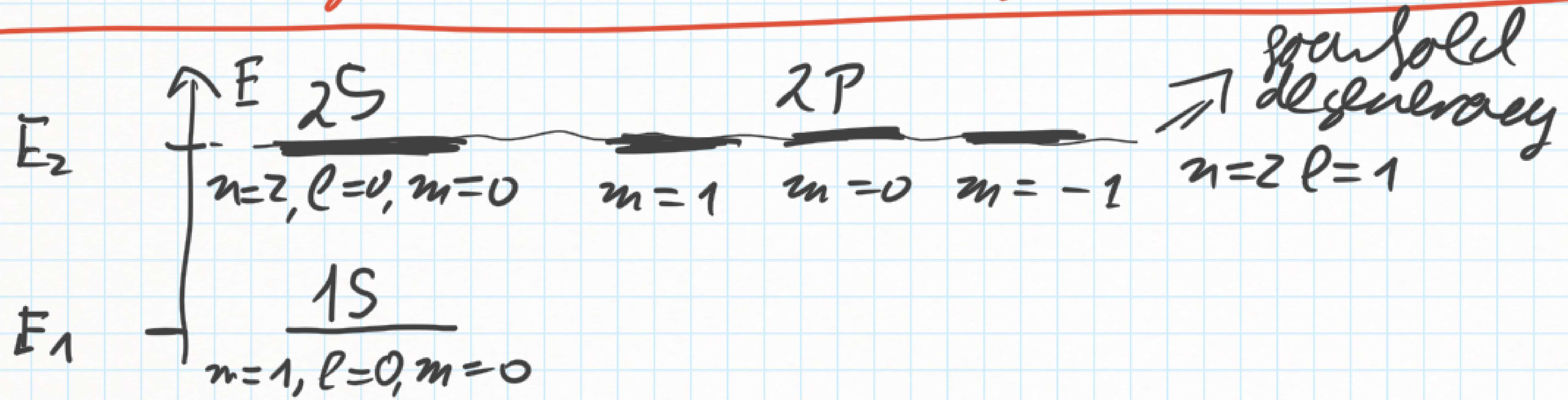
Be careful: basis in case of $\lambda = 0$ is not uniquely fixed

instead of $|\Psi^{(0)}_{n\alpha_n}\rangle$ also $\sum_{\beta_n=1}^{d_n} C^{(0)}_{n\alpha_n\beta_n} |\Psi^{(0)}_{n\beta_n}\rangle$ with suitably chosen coefficients $C^{(0)}_{n\alpha_n\beta_n}$ would be possible

Therefore:

$$\boxed{|\tilde{\Psi}_{n\alpha_n}(\lambda \to 0)\rangle = |\tilde{\Psi}^{(0)}_{n\alpha_n}\rangle = \sum_{\beta=1}^{d_n} C^{(0)}_{n\alpha_n\beta_n} |\Psi^{(0)}_{n\beta_n}\rangle}$$

$$|\tilde{\Psi}_{n\alpha_n}(\lambda)\rangle = \underbrace{|\tilde{\Psi}^{(0)}_{n\alpha_n}\rangle}_{\text{focus: how to get}} + |\tilde{\Psi}^{(1)}_{n\alpha_n}\rangle \lambda + \dots$$



$\ell = 0 \ \hat{=}$ s orbital
$\ell = 1 \ \hat{=}$ p "
$\ell = 2 \ \hat{=}$ d "
$\ell = 3 \ \hat{=}$ f "