Time independent perturbation theory - $\mathbb{H} = H + \lambda V$

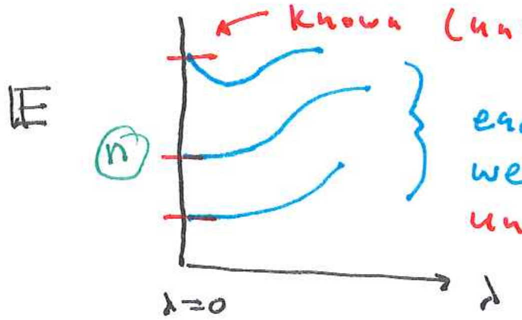
$\mathbb{H}$: full Hamiltonian we seek: $\mathbb{H}\Psi = \mathbb{E}_n \Psi$

H: a Hamiltonian we can solve $H\phi_n = E_n \phi_n$

V: perturbation

λ: adjustable parameter

Consider how the exact eigenenergies $\mathbb{E}$ depends on λ ... Taylor expand



known (unperturbed) eigenenergies

each exact solution will vary with λ

we seek (initially) how one particular unperturbed state (the n^{th}) depends on λ

$$\mathbb{H}\Psi = \mathbb{E}\Psi = (H + \lambda V)\Psi$$

$$\Psi = \Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \lambda^3 \Psi_3 + \cdots$$

$$\mathbb{E} = \mathbb{E}_0 + \lambda \mathbb{E}_1 + \lambda^2 \mathbb{E}_2 + \lambda^3 \mathbb{E}_3 + \cdots$$

Notation: for the 2-bar quantities subscript shows <u>order</u> in Taylor series expansion.

For the 1-bar (unperturbed) quantities subscript refers to which <u>state</u>

All quantities (2-bar) depend on which state (nth) we are following as a function of λ — the textbook displays this dependance I will not.

$\mathbb{E}_0 = E_n$

$\Psi_0 = \phi_n$

Critical note: WOLOG we assume there is no ϕ_n content in any Ψ_i $i \geq 1$. This is essentially a choice of normalization — but it is <u>NOT</u> the choice that yields $\langle \Psi | \Psi \rangle = 1$

In fact $\langle \Psi | \Psi \rangle = 1$ + terms order λ^2 & up

$$\underbrace{(H+\lambda V)}_{\mathbb{H}}\underbrace{(\Psi_0+\lambda\Psi_1+\lambda^2\Psi_2+\cdots)}_{\Psi}$$

$$=\underbrace{(\mathbb{E}_0+\lambda\mathbb{E}_1+\lambda^2\mathbb{E}_2+\cdots)}_{\mathbb{E}}\underbrace{(\Psi_0+\lambda\Psi_1+\lambda^2\Psi_2+\cdots)}_{\Psi}$$

Put together terms with same power of λ

0: $H\Psi_0=\mathbb{E}_0\Psi_0 \quad\longrightarrow\quad \Psi_0=\phi_n \quad \mathbb{E}_0=E_n$

1: $H\Psi_1+V\Psi_0=\mathbb{E}_0\Psi_1+\mathbb{E}_1\Psi_0$

$\boxed{\text{or}}$: $(H-\mathbb{E}_0)\Psi_1=(\mathbb{E}_1-V)\Psi_0$

2: $H\Psi_2+V\Psi_1=\mathbb{E}_0\Psi_2+\mathbb{E}_1\Psi_1+\mathbb{E}_2\Psi_0$

$\boxed{\text{or}}$ $(H-\mathbb{E}_0)\Psi_2=(\mathbb{E}_1-V)\Psi_1+\mathbb{E}_2\Psi_0$

3: $H\Psi_3+V\Psi_2=\mathbb{E}_0\Psi_3+\mathbb{E}_1\Psi_2+\mathbb{E}_2\Psi_1+\mathbb{E}_3\Psi_0$

$\boxed{\text{or}}$ $(H-\mathbb{E}_0)\Psi_3=(\mathbb{E}_1-V)\Psi_2+\mathbb{E}_2\Psi_1+\mathbb{E}_3\Psi_0$

The plan is to expand each of the Ψ_i in terms of a complete set of states: $\{\phi_i\}$ - but by our WULOG we exclude ϕ_n from this set

Note: since $\mathbb{E}_0=E_n$ the $(H-\mathbb{E}_0)$ term would kill any ϕ_n that happened to be in Ψ_i $i\geq 1$

If we take the lhs of any of the above $\boxed{\text{or}}$ statements and form: $\langle\phi_n(H-\mathbb{E}_0)\Psi_i\rangle$

the result is zero [cuz move $(H-E_n)$ to bra]

Further: terms like $\langle\phi_n\,\mathbb{E}_2\Psi_1\rangle$ are zero by WULOG

Result:

1: $$0 = \langle \phi_n (\overset{\text{constant}}{E_1} - V) \overset{\phi_n}{\Psi_0} \rangle = E_1 \langle \phi_n | \phi_n \rangle - \langle \phi_n | V | \phi_n \rangle$$

2: $$0 = \langle \phi_n (E_1 - V) \Psi_1 \rangle + E_2 \overbrace{\langle \phi_n | \Psi_0 \rangle}^{1}$$

$$= -\langle \phi_n V \Psi_1 \rangle + E_2$$

3: $$0 = \langle \phi_n (E_1 - V) \Psi_2 \rangle + E_2 \overbrace{\langle \phi_n | \Psi_1 \rangle}^{0} + E_3 \overbrace{\langle \phi_n | \Psi_0 \rangle}^{1}$$

$$= -\langle \phi_n | V | \Psi_2 \rangle + E_3$$

Result: $E_i = \langle \phi_n | V | \Psi_{i-1} \rangle$ so $E_1 = \langle \phi_n | V | \phi_n \rangle$

Find $\Psi_1 = \sum_{i \neq n} c_i \phi_i$ using the $\boxed{O^n}$ statement

$$(H - E_0)\Psi_1 = \sum (H - E_0) c_i \phi_i = \sum c_i (E_i - E_n) \phi_i$$

$$= (E_1 - V)\Psi_0 = (E_1 - V)\phi_n$$

Calculate $\langle \phi_j |$ above eqn$\rangle$ note $E_1 \overbrace{\langle \phi_j | \phi_n \rangle}^{0}$

$$c_j (E_j - E_n) = -\langle \phi_j | V | \phi_n \rangle$$

$$c_j = \frac{\langle \phi_j | V | \phi_n \rangle}{E_n - E_j} \equiv \frac{V_{jn}}{E_n - E_j}$$

Find $E_2 = \langle \phi_n | V | \sum c_j \phi_j \rangle$

$$= \sum_{j \neq n} \frac{\langle \phi_n | V | \phi_j \rangle V_{jn}}{E_n - E_j} = \sum \frac{V_{nj} V_{jn}}{E_n - E_j}$$

Note: if n is ground state, $E_2 < 0$

Note 2: big problems if $E_n - E_j = 0$ ie degenerate