Time-independent perturbation theory

- We want to solve the time-independent Schrödinger equation $\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$ by separating the Hamiltonian $\hat{H}$ into a so-called "unperturbed" Hamiltonian $\hat{H}_0$ (for which we know all the orthonormal eigenvectors $\{|u_i\rangle\}_i$ and the associated eigenvalues $\{\mathcal{E}_i\}_i$) and a perturbation $\hat{W}$:

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

- For that purpose we introduce a so-called "perturbation strength" α that is a real number such that $0 \leq \alpha \leq 1$, and we consider the α-dependent Schrödinger equation

(1) $\hat{H}(\alpha)|\psi_i(\alpha)\rangle = E_i(\alpha)|\psi_i(\alpha)\rangle$ where $\hat{H}(\alpha) = \hat{H}_0 + \alpha\hat{W}$

- Note that when $\alpha = 0$, equation (1) reduces to

$$\hat{H}_0|\psi_i(0)\rangle = E_i(0)|\psi_i(0)\rangle$$

$$\rightarrow \boxed{\begin{cases} |\psi_i(0)\rangle = |u_i\rangle \\ E_i(0) = \mathcal{E}_i \end{cases}} \quad (2)$$

⚠ We will assume that none of the unperturbed energies $\mathcal{E}_i$ are degenerate (for simplicity...)

- Note also that $\boxed{\begin{aligned} |\psi_i(1)\rangle &= |\psi_i\rangle \\ E_i(1) &= E_i \end{aligned}}$ (3)

These are what we are looking for!

- $\forall\, 0 \leq \alpha \leq 1$, $|\psi_i(\alpha)\rangle$ can be expanded in the orthonormal basis $\{|u_i\rangle\}_i$ thus leading to

$$\boxed{|\psi_i(\alpha)\rangle = \sum_j C_{ji}(\alpha)|u_j\rangle} \quad (3)\text{ bis}$$

- <u>Approximation:</u> we consider the Taylor expansions

$$\forall i,j \quad C_{ji}(\alpha) = C_{ji}(0) + \left.\frac{dC_{ji}(\alpha)}{d\alpha}\right|_{\alpha=0}\alpha + \frac{1}{2}\left.\frac{d^2C_{ji}(\alpha)}{d\alpha^2}\right|_{\alpha=0}\alpha^2 + \dots$$

$$E_i(\alpha) = E_i(0) + \left.\frac{dE_i(\alpha)}{d\alpha}\right|_{\alpha=0}\alpha + \frac{1}{2}\left.\frac{d^2E_i(\alpha)}{d\alpha^2}\right|_{\alpha=0}\alpha^2 + \dots,$$

that we simply rewrite as

$$C_{ji}(\alpha) = C_{ji}(0) + C_{ji}^{(1)}\alpha + C_{ji}^{(2)}\alpha^2 + \dots \quad (4)$$

$$E_i(\alpha) = E_i(0) + E_i^{(1)}\alpha + E_i^{(2)}\alpha^2 + \dots, \quad (5)$$

and we assume that these expansions are valid up to $\alpha = 1$. This approach is referred to as <u>perturbation theory</u>.

Consequently the eigenvectors and associated energies of the full Hamiltonian $\hat{H}$ can be expanded as follows

$$|\Psi_i\rangle = |\Psi_i(0)\rangle + \sum_j \left(C_{ji}^{(1)} + C_{ji}^{(2)} + \dots \right) |u_j\rangle$$

$$E_i = E_i(0) + E_i^{(1)} + E_i^{(2)} + \dots$$

- <u>Finding wavefunction and energy contributions order by order:</u>

Equation (1) is fulfilled for any α in $[0,1]$. Using equations (3) bis, (4) and (5) we obtain

$$\left(\hat{H}_0 + \alpha \hat{W}\right)\left(|\Psi_i(0)\rangle + \sum_j \left(C_{ji}^{(1)}\alpha + C_{ji}^{(2)}\alpha^2 + \dots \right)|u_j\rangle \right)$$

$$= \left(E_i(0) + E_i^{(1)}\alpha + E_i^{(2)}\alpha^2 + \dots \right)\left(|\Psi_i(0)\rangle + \sum_j \left(C_{ji}^{(1)}\alpha + C_{ji}^{(2)}\alpha^2 + \dots \right)|u_j\rangle \right).$$

thus leading to, $\forall \alpha$,

$$\underbrace{\left(\hat{H}_0 |\Psi_i(0)\rangle - E_i(0)|\Psi_i(0)\rangle \right)} + \alpha \left[\sum_j C_{ji}^{(1)} \hat{H}_0 |u_j\rangle + \hat{W}|\Psi_i(0)\rangle - \sum_j C_{ji}^{(1)} E_i(0)|u_j\rangle - E_i^{(1)}|\Psi_i(0)\rangle \right]$$

$$+ \alpha^2 \left[\sum_j C_{ji}^{(2)} \hat{H}_0 |u_j\rangle + \sum_j C_{ji}^{(1)} \hat{W}|u_j\rangle - E_i(0) \sum_j C_{ji}^{(2)}|u_j\rangle - \sum_j E_i^{(1)} C_{ji}^{(1)}|u_j\rangle - E_i^{(2)}|\Psi_i(0)\rangle \right] + \alpha^3 [\dots] + \dots$$

- <u>Additional condition:</u> the intermediate normalization $\longrightarrow \forall i, \forall \alpha$ $\quad \boxed{\langle \Psi_i(0)|\Psi_i(\alpha)\rangle = 1 = \langle u_i|\Psi_i(\alpha)\rangle}$ (4) bis

that is equivalent to $|\Psi_i(\alpha)\rangle = |u_i\rangle + \sum_{j \neq i} C_{ji}(\alpha)|u_j\rangle$

Zeroth order: $\hat{H}_0 |\Psi_i(0)\rangle = E_i(0)|\Psi_i(0)\rangle \Rightarrow \hat{H}_0 |u_i\rangle = \varepsilon_i |u_i\rangle$ (ok!)

according to Eq. (2)

1st order:

$$\sum_j C_{ji}^{(1)} \overbrace{\hat{H}_0 |u_j\rangle}^{\varepsilon_j |u_j\rangle} + \hat{W}|u_i\rangle - \sum_j C_{ji}^{(1)} \varepsilon_i |u_j\rangle - E_i^{(1)}|u_i\rangle = 0 \quad (6)$$

$\forall k$ $\langle u_k|(6)\rangle$ leads to

$$\sum_j C_{ji}^{(1)} \varepsilon_j \underbrace{\langle u_k|u_j\rangle}_{\delta_{kj}} + \langle u_k|\hat{W}|u_i\rangle - \sum_j C_{ji}^{(1)} \varepsilon_i \underbrace{\langle u_k|u_j\rangle}_{\delta_{kj}} - E_i^{(1)} \underbrace{\langle u_k|u_i\rangle}_{\delta_{ki}} = 0$$

$$\Rightarrow C_{ki}^{(1)} \varepsilon_k + \langle u_k|\hat{W}|u_i\rangle - C_{ki}^{(1)} \varepsilon_i - E_i^{(1)} \delta_{ki} = 0 \quad (7)$$

Eq. (7) bis

- if $k = i$ then $C_{ii}^{(1)} \varepsilon_i + \langle u_i|\hat{W}|u_i\rangle - C_{ii}^{(1)} \varepsilon_i = E_i^{(1)}$

According to the intermediate normalization condition (see equation (4) bis) $C_{ii}(\alpha) = 1 \ \forall \alpha \Rightarrow \boxed{C_{ii}^{(1)} = 0,\ C_{ii}^{(2)} = 0, \dots}$

Consequently $\boxed{E_i^{(1)} = \langle u_i|\hat{W}|u_i\rangle}$

- if $k \neq i$ then Eq. (7) leads to $C_{ki}^{(1)}(\varepsilon_k - \varepsilon_i) + \langle u_k|\hat{W}|u_i\rangle = 0 \Rightarrow \boxed{C_{ki}^{(1)} = \frac{\langle u_k|\hat{W}|u_i\rangle}{\varepsilon_i - \varepsilon_k}}$ (7) ter

2nd order:

$$\sum_j C_{ji}^{(2)} \varepsilon_j |u_j\rangle + \sum_j C_{ji}^{(1)} \hat{W}|u_j\rangle - \varepsilon_i \sum_j C_{ji}^{(2)}|u_j\rangle - \sum_j E_i^{(1)} C_{ji}^{(1)}|u_j\rangle - E_i^{(2)}|u_i\rangle = 0 \quad (8)$$

$$\langle u_i|(8)\rangle \Rightarrow \varepsilon_i \underbrace{C_{ii}^{(2)}}_{=0} + \sum_{j \neq i} C_{ji}^{(1)} \langle u_i|\hat{W}|u_j\rangle - \varepsilon_i \underbrace{C_{ii}^{(2)}}_{=0} - E_i^{(1)} \underbrace{C_{ii}^{(1)}}_{=0} - E_i^{(2)} = 0$$

according to (7) bis

Therefore
$$\boxed{E_i^{(2)} = \sum_{j\neq i} \frac{\langle u_i|\hat{W}|u_j\rangle\langle u_j|\hat{W}|u_i\rangle}{\mathcal{E}_i - \mathcal{E}_j}}$$
according to Eq. (7) ter

<u>Summary</u>: The wavefunction is expanded through first order as follows

$$\boxed{|\psi_i\rangle = |u_i\rangle + \sum_{j\neq i} \frac{|u_j\rangle\langle u_j|\hat{W}|u_i\rangle}{\mathcal{E}_i - \mathcal{E}_j} + \cdots}$$

and the energy equals through second order

$$\boxed{E_i = \mathcal{E}_i + \langle u_i|\hat{W}|u_i\rangle + \sum_{j\neq i} \frac{\langle u_i|\hat{W}|u_j\rangle\langle u_j|\hat{W}|u_i\rangle}{\mathcal{E}_i - \mathcal{E}_j} + \cdots}$$

- <u>Application</u>: The one-dimensional harmonic oscillator perturbed by a static and uniform electric field $\vec{\mathcal{E}} = \mathcal{E}\vec{e}_x$

$$\boxed{\hat{H}_0 = \hbar\omega\left(\hat{N} + \frac{1}{2}\right)} \qquad \hat{N} = \hat{a}^\dagger\hat{a} \quad \text{and} \quad [\hat{a}, \hat{a}^\dagger] = 1$$

$\hat{W} = -q\mathcal{E}\hat{x}$ ⟵ interaction of the charged oscillating particle (with charge q) with the electric field.

where $\hat{a} = \frac{1}{\sqrt{2}}\left(\left(\frac{m\omega}{\hbar}\right)^{1/2}\hat{x} + i\frac{1}{(m\hbar\omega)^{1/2}}\hat{p}_x\right)$ and $\hat{a}^\dagger = \frac{1}{\sqrt{2}}\left[\left(\frac{m\omega}{\hbar}\right)^{1/2}\hat{x} - i\frac{1}{(m\hbar\omega)^{1/2}}\hat{p}_x\right]$

$$\Rightarrow \quad \hat{a} + \hat{a}^\dagger = \left(\frac{2m\omega}{\hbar}\right)^{1/2}\hat{x} \quad \Rightarrow \quad \hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a} + \hat{a}^\dagger\right),$$

thus leading to
$$\boxed{\hat{W} = -q\mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a} + \hat{a}^\dagger\right)}$$

• unperturbed eigenvectors:

$$[\hat{N}, \hat{a}^+] = \hat{N}\hat{a}^+ - \hat{a}^+\hat{N} = \hat{a}^+\underbrace{\hat{a}\,\hat{a}^+}_{(1+\hat{a}^+\hat{a})} - \hat{a}^+\hat{a}^+\hat{a}$$

$$\Rightarrow \quad [\hat{N}, \hat{a}^+] = \hat{a}^+$$

this means $\hat{N}|u_n\rangle = n|u_n\rangle$ and $\langle u_n|u_n\rangle = 1$!

if $|u_n\rangle$ is a normalized eigenvector of $\hat{N}$ associated with n ($n \in \mathbb{N}$)

then $[\hat{N}, \hat{a}^+]|u_n\rangle = \hat{a}^+|u_n\rangle \Rightarrow \hat{N}\hat{a}^+|u_n\rangle - \hat{a}^+\hat{N}|u_n\rangle = \hat{a}^+|u_n\rangle$

thus leading to $\hat{N}\hat{a}^+|u_n\rangle = (n+1)\,\hat{a}^+|u_n\rangle$.

Since $\langle \hat{a}^+u_n|\hat{a}^+u_n\rangle = \langle u_n|\hat{a}\,\hat{a}^+|u_n\rangle = \langle u_n|\hat{N}+1|u_n\rangle = n+1 \leftarrow$ not zero!

$\hat{a}^+|u_n\rangle$ is eigenvector of $\hat{N}$ associated with $(n+1)$. The normalized eigenvector $|u_{n+1}\rangle$ therefore equals

$$|u_{n+1}\rangle = \frac{\hat{a}^+|u_n\rangle}{\sqrt{\langle \hat{a}^+u_n|\hat{a}^+u_n\rangle}} = \frac{\hat{a}^+|u_n\rangle}{\sqrt{n+1}}.$$

(normalization procedure: $|\psi\rangle \longrightarrow \dfrac{|\psi\rangle}{\sqrt{\langle\psi|\psi\rangle}}$)

Conclusion: $$|u_n\rangle = \frac{\hat{a}^+|u_{n-1}\rangle}{\sqrt{n}} = \frac{1}{\sqrt{n}}\frac{1}{\sqrt{n-1}}(\hat{a}^+)^2|u_{n-2}\rangle = \frac{1}{\sqrt{n}}\frac{1}{\sqrt{n-1}}\frac{1}{\sqrt{n-2}}\cdot\frac{1}{\sqrt{1}}(\hat{a}^+)^n|u_0\rangle$$

$$\Rightarrow \boxed{|u_n\rangle = \frac{(\hat{a}^+)^n}{\sqrt{n!}}|u_0\rangle}$$

where $\hat{N}|u_0\rangle = 0 \Rightarrow \langle u_0|\hat{N}|u_0\rangle = 0 \Rightarrow \langle \hat{a}u_0|\hat{a}u_0\rangle = 0$

$$\Rightarrow \boxed{\hat{a}|u_0\rangle = 0}$$

$$\hat{H}_0 |u_n\rangle = \hbar\omega\big(\underbrace{\hat{N}|u_n\rangle}_{n|u_n\rangle} + \tfrac{1}{2}|u_n\rangle\big) = (n\hbar\omega + \tfrac{\hbar\omega}{2})|u_n\rangle$$

$$\rightarrow \boxed{\mathcal{E}_n = n\hbar\omega + \frac{\hbar\omega}{2}}$$

• Let $\{|\psi_n(\mathcal{E})\rangle\}_n$ denote the eigenvectors of $\hat{H}_0 + \hat{W}$ and $E_n(\mathcal{E})$ their associated energies. We obtain from perturbation theory the following expansions

$$|\psi_n(\mathcal{E})\rangle = |u_n\rangle + \sum_{k\neq n} \frac{|u_k\rangle\langle u_k|\hat{W}|u_n\rangle}{\mathcal{E}_n - \mathcal{E}_k} + \dots$$

where $\langle u_k|\hat{W}|u_n\rangle = -q\mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\,\underbrace{\langle u_k|\hat{a}+\hat{a}^\dagger|u_n\rangle}_{\langle\hat{a}^\dagger u_k|u_n\rangle + \langle u_k|\hat{a}^\dagger|u_n\rangle}$

with $\hat{a}^\dagger|u_n\rangle = \sqrt{n+1}\,|u_{n+1}\rangle$ and $\hat{a}^\dagger|u_k\rangle = \sqrt{k+1}\,|u_{k+1}\rangle$.

Therefore $\boxed{\langle u_k|\hat{W}|u_n\rangle = -q\mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{k+1}\,\delta_{k+1,n} + \sqrt{n+1}\,\delta_{k,n+1}\right)}$ (9) $\Leftrightarrow$ $\boxed{\langle u_k|\hat{W}|u_n\rangle = -q\mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n}\,\delta_{k,n-1} + \sqrt{n+1}\,\delta_{k,n+1}\right)}$

Simplified expression! used in the following

$$\Rightarrow |\psi_n(\mathcal{E})\rangle = |u_n\rangle + \sum_{k\neq n}\frac{1}{(n-k)\hbar\omega}\left(-q\mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\right)\left[\sqrt{n}\,\delta_{k,n-1} + \sqrt{n+1}\,\delta_{k,n+1}\right]|u_k\rangle$$

thus leading to the final expression:

$$\boxed{|\psi_n(\mathcal{E})\rangle = |u_n\rangle - \frac{q\mathcal{E}}{\hbar\omega}\sqrt{\frac{\hbar n}{2m\omega}}\,|u_{n-1}\rangle + \frac{q\mathcal{E}}{\hbar\omega}\sqrt{\frac{\hbar(n+1)}{2m\omega}}\,|u_{n+1}\rangle + O(\mathcal{E}^2)}$$

- Expectation value for the position

$$\langle x\rangle_{\psi_n(\mathcal{E})} = \frac{\langle\psi_n(\mathcal{E})|\hat{x}|\psi_n(\mathcal{E})\rangle}{\langle\psi_n(\mathcal{E})|\psi_n(\mathcal{E})\rangle} = \langle u_n|\hat{x}|u_n\rangle + 2\langle u_n|\hat{x}|\psi_n^{(1)}(\mathcal{E})\rangle + \mathcal{O}(\mathcal{E}^2)$$

Since $\langle\psi_n(\mathcal{E})|\psi_n(\mathcal{E})\rangle = 1 + \mathcal{O}(\mathcal{E}^2)$ (no first-order terms in $\mathcal{E}$)

and where $|\psi_n^{(1)}(\mathcal{E})\rangle = \frac{q\mathcal{E}}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n+1}\,|u_{n+1}\rangle - \sqrt{n}\,|u_{n-1}\rangle\right)$.

$$\langle u_n|\hat{x}|u_n\rangle = -\frac{1}{q\mathcal{E}}\langle u_n|\hat{W}|u_n\rangle \underset{\text{according to Eq. (9)}}{=} 0$$

and $$2\langle u_n|\hat{x}|\psi_n^{(1)}(\mathcal{E})\rangle = \frac{2q\mathcal{E}}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n+1}\,\underbrace{\langle u_n|\hat{x}|u_{n+1}\rangle}_{-\frac{1}{q\mathcal{E}}\langle u_n|\hat{W}|u_{n+1}\rangle} - \sqrt{n}\,\underbrace{\langle u_n|\hat{x}|u_{n-1}\rangle}_{-\frac{1}{q\mathcal{E}}\langle u_n|\hat{W}|u_{n-1}\rangle}\right)$$

$$\rightarrow 2\langle u_n|\hat{x}|\psi_n^{(1)}(\mathcal{E})\rangle = -\frac{2}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}}\left[\underbrace{\sqrt{n+1}\times\left(-q\mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\right)\sqrt{n+1} - \sqrt{n}\left(-q\mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\right)\sqrt{n}}_{\text{according to Eq. (9)}}\right]$$

$$= +\frac{\cancel{2}q\mathcal{E}}{\cancel{\hbar}\omega}\cdot\frac{\cancel{\hbar}}{\cancel{2}m\omega}(n+1-n)$$

$$\rightarrow \boxed{\langle x\rangle_{\psi_n(\mathcal{E})} = \frac{q}{m\omega^2}\mathcal{E} + \mathcal{O}(\mathcal{E}^2)}$$

Comment: the exact value for $\langle x\rangle_{\psi_n(\mathcal{E})}$ is in fact $\frac{q\mathcal{E}}{m\omega^2}$.
Perturbation theory through first order is therefore exact for the position expectation value in this context.

- The energy is expanded through second order as follows:

$$E_n(\xi) = (n+\tfrac{1}{2})\hbar\omega + \underbrace{\langle u_n|\hat{W}|u_n\rangle}_{0} + \sum_{k\neq n} \frac{\langle u_n|\hat{W}|u_k\rangle\langle u_k|\hat{W}|u_n\rangle}{\mathcal{E}_n - \mathcal{E}_k} + \dots$$

Since $\langle u_n|\hat{W}|u_k\rangle = \langle u_k|\hat{W}|u_n\rangle^* \quad (\hat{W}^\dagger = \hat{W})$

it comes from Eq. (9)

$$E_n(\xi) = (n+\tfrac{1}{2})\hbar\omega + \underbrace{\sum_{k\neq n} \frac{\left(\sqrt{n}\,\delta_{k,n-1} + \sqrt{n+1}\,\delta_{k,n+1}\right)^2}{(n-k)\hbar\omega}}_{\frac{n}{\hbar\omega} + \frac{(n+1)}{-\hbar\omega} = -\frac{1}{\hbar\omega}} \cdot q^2\xi^2 \cdot \frac{\hbar}{2m\omega} + \dots$$

Therefore:

$$\boxed{E_n(\xi) = (n+\tfrac{1}{2})\hbar\omega - \frac{q^2\xi^2}{2m\omega^2} + O(\xi^3)}$$

<u>Comment</u>: the exact energies are in fact $(n+\frac{1}{2})\hbar\omega - \frac{1}{2}\frac{q^2\xi^2}{m\omega^2}$.

<u>Perturbation theory</u> through second order is therefore exact for the energy in this context.