Appendix A: Time-Independent Perturbation Theory in Quantum Mechanics

Some problem

$$\underset{\substack{\text{don't know how}\\ \text{to solve}}}{\hat{H}} = \underbrace{\underset{\text{exact}}{\hat{H}_0}}_{\text{solutions are known}} + \hat{H}' \qquad \text{(A1)}$$

$\hat{H}'$ ← deviation of $\hat{H}$ from $\hat{H}_0$ (perturbation)

$$\hat{H}_0 \psi_i^{(0)} = E_i^{(0)} \psi_i^{(0)} \quad \text{(A2)} \quad \left(\psi_i^{(0)} \leftrightarrow E_i^{(0)} \text{ all known} \right)$$

Want to solve $\hat{H}\psi = E\psi$ (A3) [many $\psi \leftrightarrow E$ pairs (unknowns)]

Expand

$$\underset{\text{unknowns}}{\psi} = \sum_i \underset{\text{unknowns}}{c_i} \psi_i^{(0)} \qquad \text{(A4)}$$

Plug expansion to TISE ⇒ Huge Matrix Equation for E's and $\{c_i\}$'s

$$\begin{pmatrix} \\ \text{Matrix} \\ \\ \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} = 0 \qquad \boxed{\begin{matrix}\text{Matrix Elements are} \\ H_{ij} - ES_{ij}\end{matrix}} \quad \text{(A5)} \quad \text{(Exact)}$$

$$H_{ij} \equiv \int \psi_i^{*(0)} \hat{H} \psi_j^{(0)} d^3r \ ; \quad S_{ij} \equiv \int \psi_i^{*(0)} \psi_j^{(0)} d^3r \qquad (A6)$$

(both can be evaluated, in principal, as $\{\psi_i^{(0)}\}$ and $\hat{H}$ are knowns)

General up to here and Exact up to here.

* * *

$\hat{H}_0$ is solvable, can make $\{\psi_i^{(0)}\}$ orthonormal, i.e. $S_{ij} = \delta_{ij}$ (A7)

Exact Matrix Problem becomes:

$$\begin{pmatrix} H_{11}-E & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22}-E & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33}-E & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} = 0 \qquad (A8)$$

Still exact for problems with $S_{ij} = \delta_{ij}$

$$H_{ii} = \int \psi_i^{*(0)} \hat{H} \psi_i^{(0)} d^3r = \int \psi_i^{*(0)} \overbrace{\hat{H}_0 \psi_i^{(0)}}^{E_i^{(0)} \psi_i^{(0)}} d^3r + \int \psi_i^{*(0)} \hat{H}' \psi_i^{(0)} d^3r$$

$$= E_i^{(0)} + H'_{ii}$$

$$\underset{(i \neq j)}{H_{ij}} = \int \cancelto{0}{\psi_i^{*(0)} \hat{H}_0} \psi_j^{(0)} d^3r + \int \psi_i^{*(0)} \hat{H}' \psi_j^{(0)} d^3r = H'_{ij} \overset{\text{Hermitian}}{=} H'^{*}_{ji}$$

Matrix Problem becomes:

$$\underbrace{\begin{pmatrix} E_1^{(0)} + H'_{11} & H'_{12} & H'_{13} & \cdots \\ H'_{21} & E_2^{(0)} + H'_{22} & H'_{23} & \cdots \\ H'_{31} & H'_{32} & E_3^{(0)} + H'_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}}_{\text{eigenvalue problem of a huge matrix}} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ \vdots \end{pmatrix} = E \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ \vdots \end{pmatrix} \qquad (A9)$$

Exact

Our Eq. (45) is of this form, because it is a special case of using plane waves for the expansion

$$\begin{array}{c|ccccc}
 & e^{i\vec{k}\cdot\vec{r}} & e^{i(\vec{k}+\vec{G}_1)\cdot\vec{r}} & e^{i(\vec{k}+\vec{G}_2)\cdot\vec{r}} & e^{i(\vec{k}+\vec{G}_3)\cdot\vec{r}} & \cdots \leftarrow \text{help you think} \\
\hline
e^{i\vec{k}\cdot\vec{r}} & \varepsilon^0(\vec{k})+\bar{V} & V(-\vec{G}_1) & V(-\vec{G}_2) & V(-\vec{G}_3) & \cdots \\
e^{i(\vec{k}+\vec{G}_1)\cdot\vec{r}} & V(\vec{G}_1) & \varepsilon^0(\vec{k}+\vec{G}_1)+\bar{V} & V(\vec{G}_1-\vec{G}_2) & V(\vec{G}_1-\vec{G}_3) & \cdots \\
e^{i(\vec{k}+\vec{G}_2)\cdot\vec{r}} & V(\vec{G}_2) & V(\vec{G}_2-\vec{G}_1) & \varepsilon^0(\vec{k}+\vec{G}_2)+\bar{V} & V(\vec{G}_2-\vec{G}_3) & \cdots \\
e^{i(\vec{k}+\vec{G}_3)\cdot\vec{r}} & V(\vec{G}_3) & V(\vec{G}_3-\vec{G}_1) & V(\vec{G}_3-\vec{G}_2) & \varepsilon^0(\vec{k}+\vec{G}_3)+\bar{V} & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots \\
\uparrow & & & & & \\
\text{Basis functions} & & & & &
\end{array} \qquad (45)$$

Eigenvalues of this Matrix give $\underbrace{E(\vec{k})\ [\text{many values}]}_{E_n(\vec{k})}$

Band Index $\nearrow$ n $\uparrow$ counting from lowest energy up

All effects of $\hat{H}'$ are included in Eq. (A9), thus Exact!

What if we only want the effects of $\hat{H}'$ order-by-order (1^{st}, 2^{nd} order)?

Two ways: → Perturbation Theories

→ Playing (approximating) with the exact Matrix Problem

Formulas of Non-degenerate Pertubation Theory

$$\underset{\substack{n^{th}\text{ eigenvalue}\\ \text{of } \hat{H} \text{ problem}}}{E_n} \cong \underbrace{E_n^{(0)}}_{0^{th}\text{ order}} + \underbrace{H'_{nn}}_{1^{st}\text{ order}} + \underbrace{\sum_{i\,(i\neq n)} \frac{|H'_{in}|^2}{E_n^{(0)} - E_i^{(0)}}}_{2^{nd}\text{ order}} \qquad (A10)$$

$$\underset{\substack{n^{th}\text{ eigenstate}\\ \text{of } \hat{H} \text{ problem}}}{\psi_n} \approx \underbrace{\psi_n^{(0)}}_{0^{th}\text{ order}} + \underbrace{\sum_{i\,(i\neq n)} \underbrace{\frac{H'_{in}}{E_n^{(0)} - E_i^{(0)}}}_{\text{mixing in } \psi_i^{(0)}\,(i\neq n) \text{ due to } \hat{H}'} \psi_i^{(0)}}_{1^{st}\text{ order}} \qquad (A11)$$

More important to get a sense of what the formulas mean and to apply them!

- Validity: When we ask what $\hat{H}'$ will do to change the eigenvalue of n^{th} state, we don't want some other unperturbed states with

$$E_n^{(0)} = E_i^{(0)} \quad \underline{\text{OR}} \quad E_n^{(0)} \approx E_i^{(0)}$$

state you want to get the effect of $\hat{H}'$

other states' energies

(Bad, see Eqs. (A10), (A11))

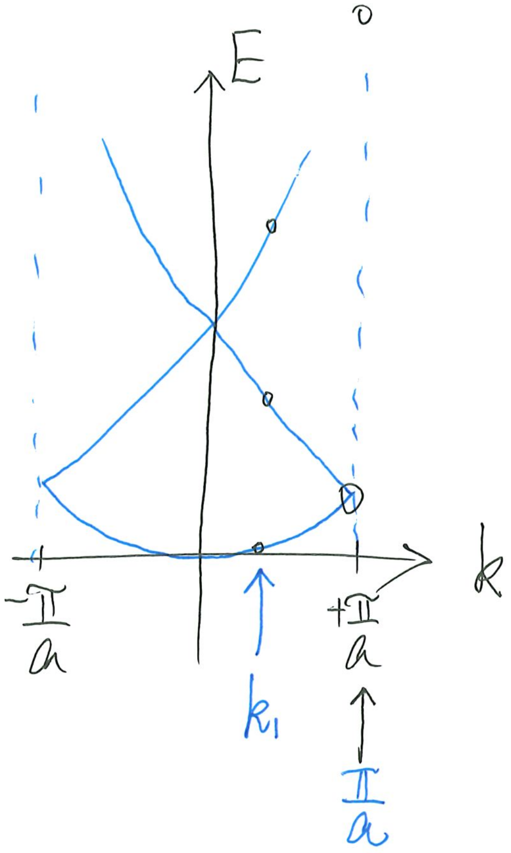
Want to have:

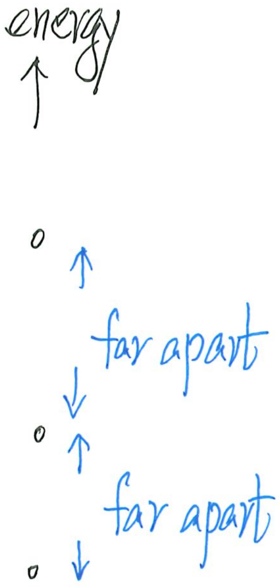
$$\underbrace{\left|E_n^{(0)} - E_i^{(0)}\right|}_{\text{energy difference to another state}} \gg \underbrace{\left|H'_{in}\right|}_{\left|\text{coupling between states due to } \hat{H}'\right|} \qquad (A12)$$

then Eqs. (A10), (A11) are valid

This is why it is called $\underbrace{\text{Non-Degenerate}}_{\text{state } n \text{ is non-degenerate}}$ Perturbation Theory

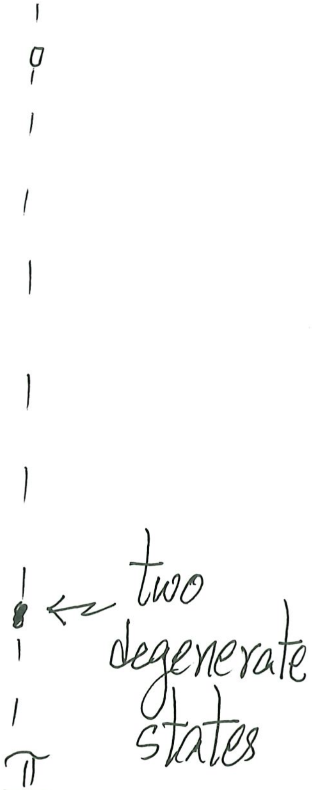
In our energy band context,





$k = k_1$

Can use Eqs.(A10), A(11) at $k = k_1$



$k = \frac{\pi}{a}$

Be careful! use something else.

"Professional" viewpoint of Perturbation Results

Matrix Problem becomes:

$$\underbrace{\begin{pmatrix} E_1^{(0)}+H'_{11} & H'_{12} & H'_{13} & \cdots \\ H'_{21} & E_2^{(0)}+H'_{22} & H'_{23} & \cdots \\ H'_{31} & H'_{32} & E_3^{(0)}+H'_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}}_{\text{eigenvalue problem of a huge matrix}} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} \qquad (A9)$$

Exact

Zeroth order

(ignore everything related to $\hat{H}'$)

$$\begin{pmatrix} E_1^{(0)} & 0 & 0 & \\ 0 & E_2^{(0)} & 0 & 0 \\ 0 & 0 & E_3^{(0)} & \\ & 0 & & \ddots \end{pmatrix}$$

$\therefore E_n \approx E_n^{(0)}$ 0th order

First Order

(ignore all off-diagonal terms)

$$\begin{pmatrix} E_1^{(0)}+H'_{11} & 0 & 0 & \\ 0 & E_2^{(0)}+H'_{22} & 0 & 0 \\ 0 & 0 & E_3^{(0)}+H'_{33} & \\ & 0 & & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix}$$

gives $E_n \approx \underbrace{E_n^{(0)}}_{0^{th}\text{ order}} + \underbrace{H'_{nn}}_{1^{st}\text{ order}}$

(c.f. Eq.(A10))

Second order

- Sit on "n" you want the perturbed energy E_n, ask how another state "i" could change your energy due to $\hat{H}'$

Two indices: n and i ($i \neq n$, another state)

$$\begin{pmatrix} E_n^{(0)} + H'_{nn} & H'_{ni} \\ H'_{in} & E_i^{(0)} + H'_{ii} \end{pmatrix} \rightarrow$$

Read out 2×2

(you sit here)

$$\begin{array}{c|cc} \text{"}n\text{"} & \overset{\text{(you sit here)}}{E_n^{(0)} + H'_{nn}} & H'_{ni} \\ \text{"}i\text{"} & H'_{in} & E_i^{(0)} + H'_{ii} \\ & \text{"}n\text{"} & \text{"}i\text{"} \end{array}$$

How state "i" affects me "n"?

$\boxed{H'_{ni} \text{ represents how states } n \text{ and } i \text{ are coupled through } \hat{H}'}$

Physical Sense

∴ "Solve" $\underbrace{\text{2×2 matrix}}_{\text{much chemistry and solid state physics/physics}}$ problems!

Street fighting Matrix Math : 2x2 matrices carry much physics

Eigenvalue Problem of $\begin{pmatrix} \varepsilon_A & \Delta \\ \Delta^* & \varepsilon_B \end{pmatrix}$

(i) Exact treatment $\begin{vmatrix} \varepsilon_A - E & \Delta \\ \Delta^* & \varepsilon_B - E \end{vmatrix} = 0$ (quadratic Eq. for E)

$$\boxed{E = \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{1}{2}\sqrt{(\varepsilon_A - \varepsilon_B)^2 + 4|\Delta|^2}}$$

exact!

(Matrix 1)

Applications in physics

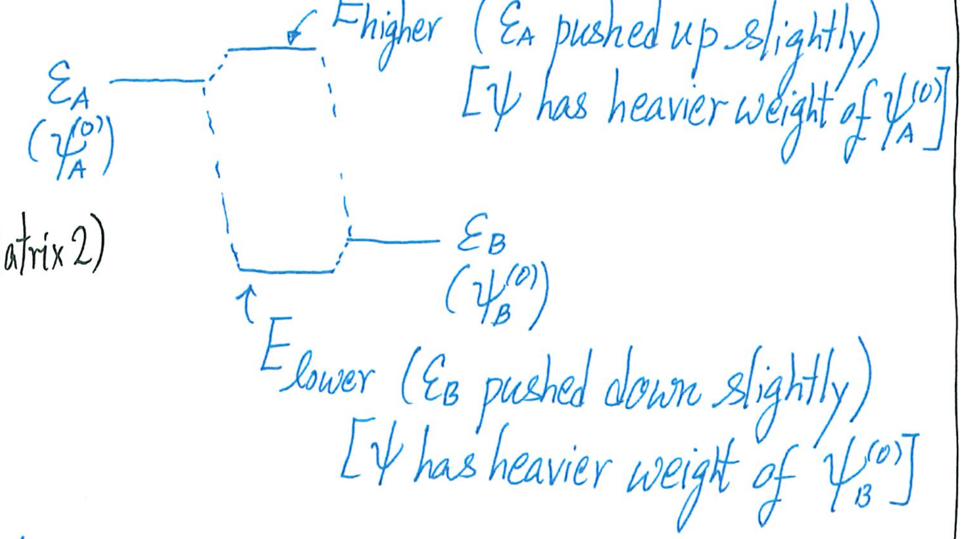
- Degenerate perturbation theory (see Sec. F)
- Bonding (general situation)

(ii) $\varepsilon_A - \varepsilon_B \gg |\Delta|$ (Using $\sqrt{1+x} \approx 1 + \frac{1}{2}x$)

$$E \approx \begin{cases} \varepsilon_A + \dfrac{|\Delta|^2}{\varepsilon_A - \varepsilon_B} \\ \varepsilon_B - \dfrac{|\Delta|^2}{\varepsilon_A - \varepsilon_B} \end{cases}$$

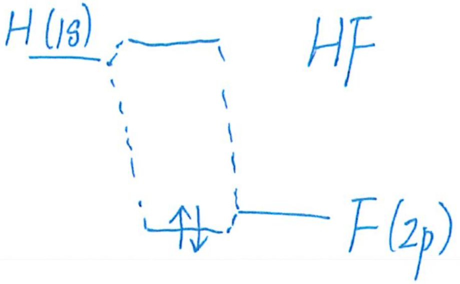
(Matrix 2)

(very useful approximation[†])



Applications in physics

- 2nd order non-degenerate perturbation theory
- Molecules formed by very different atoms
- 1st order correction in eigenstate

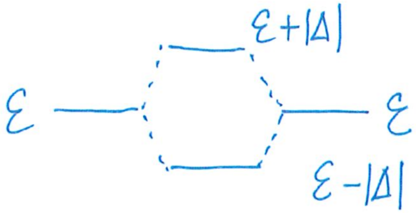


Notes of PHYS 3022

[†] This approximation is so important (and so simple) that it is called "folding a matrix", i.e. folding the off-diagonal effects into the diagonal (eigenvalue) term.

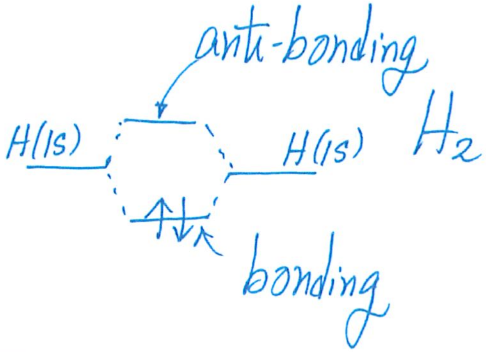
(iii) $\varepsilon_A = \varepsilon_B = \varepsilon$ (OR $\varepsilon_A \approx \varepsilon_B$)

$$E = \begin{cases} \varepsilon + |\Delta| \\ \varepsilon - |\Delta| \end{cases} \quad \text{(Matrix 3)}$$



Applications in physics

- Molecules formed by identical atoms
- Band Gap in Solids



Apply case (ii) to $\begin{pmatrix} E_n^{(0)} + H'_{nn} & H'_{ni} \\ H'_{in} & E_i^{(0)} + H'_{ii} \end{pmatrix}$, with $|E_n^{(0)} - E_i^{(0)}| >> |H'_{ni}|$

we have
$$E_n \approx E_n^{(0)} + H'_{nn} + \frac{|H'_{in}|^2}{(E_n^{(0)} - E_i^{(0)}) + (H'_{nn} + H'_{ii})}$$

$$\approx \underbrace{E_n^{(0)}}_{0^{th}\text{order}} + \underbrace{H'_{nn}}_{1^{st}\text{order}} + \underbrace{\frac{|H'_{in}|^2}{\underset{\substack{\uparrow \\ \text{my (unperturbed) energy}}}{E_n^{(0)}} - E_i^{(0)} \leftarrow \text{the other states energy}}}_{2^{nd}\text{ order}}$$

Repeat argument for all states $i (\neq n)$:

$$E_n \approx E_n^{(0)} + H'_{nn} + \sum_{\substack{i(i\neq n) \\ \uparrow \\ \text{Net effect}}} \underbrace{\frac{|H'_{in}|^2}{E_n^{(0)} - E_i^{(0)}}}_{\substack{+\text{ve if } E_n^{(0)} > E_i^{(0)} \text{ [lower states push energy up]} \\ -\text{ve if } E_n^{(0)} < E_i^{(0)} \text{ [higher states push energy down]}}}$$

Same as Eq. (A10)

This ends the discussion on Perturbation Theories in QM

- Non-degenerate Perturbation Theory

  (tiny changes) (many 2x2 matrices, pushing each other slightly)

- Degenerate Perturbation Theory

  (treat 2x2 (or 3x3, 4x4) exactly, big pushing; other effects are much smaller)