

Perturbation Theory for Eigenvalue Problem

$$(A + \epsilon B) \vec{x}_i = \lambda_i \vec{x}_i :$$

Unperturbed problem: $A \vec{e}_i = a_i \vec{e}_i$

Assuming a_i is non-degenerate use expansion:

$$\vec{x}_i(\epsilon) = \vec{e}_i + \epsilon \vec{x}_i^{(1)} + \epsilon^2 \vec{x}_i^{(2)} + \dots$$

$$\lambda_i(\epsilon) = a_i + \epsilon \lambda_i^{(1)} + \epsilon^2 \lambda_i^{(2)} + \dots$$

$$(A + \epsilon B)(\vec{e}_i + \epsilon \vec{x}_i^{(1)} + \epsilon^2 \vec{x}_i^{(2)} + \dots) = (a_i + \epsilon \lambda_i^{(1)} + \epsilon^2 \lambda_i^{(2)} + \dots)(\vec{e}_i + \epsilon \vec{x}_i^{(1)} + \epsilon^2 \vec{x}_i^{(2)} + \dots)$$

at ϵ^0 : $A \vec{e}_i = a_i \vec{e}_i$ (correct choice of $\vec{x}_i^{(0)}, \lambda_i^{(0)}$)

ϵ^1 : $A \vec{x}_i^{(1)} + B \vec{e}_i = a_i \vec{x}_i^{(1)} + \lambda_i^{(1)} \vec{e}_i$

ϵ^2 : $A \vec{x}_i^{(2)} + B \vec{x}_i^{(1)} = a_i \vec{x}_i^{(2)} + \lambda_i^{(1)} \vec{x}_i^{(1)} + \lambda_i^{(2)} \vec{e}_i$

...

First order perturbations

Define left eigenvectors: $\vec{f}_i A = a_i \vec{f}_i$

Note: $\vec{f}_j \cdot \vec{e}_i = 0$, $\forall j \neq i \Rightarrow$ Normalize: $(\vec{f}_i \cdot \vec{e}_i) = 1$

Note: For A -Hermitian (symmetric) $\vec{f}_i = \vec{e}_i$

$$\vec{f}_j \cdot (A \vec{x}_i^{(1)} + B \vec{e}_i) = \vec{f}_j \cdot (a_i \vec{x}_i^{(1)} + \lambda_i^{(1)} \vec{e}_i)$$

$$\Rightarrow a_j (\vec{f}_j \cdot \vec{x}_i^{(1)}) + (\vec{f}_j \cdot B \vec{e}_i) = a_i (\vec{f}_j \cdot \vec{x}_i^{(1)}) + \lambda_i^{(1)} \delta_{ij}$$

Solve with respect to $\lambda_i^{(1)}$ for $j=i$: $\lambda_i^{(1)} = (\vec{f}_i \cdot B \vec{e}_i)$

Let $\vec{x}_i^{(1)} = \sum_j c_j^{(1)} \vec{e}_j \Rightarrow (\vec{f}_j \cdot \vec{x}_i^{(1)}) = c_j^{(1)}$

Solve with respect to $c_j^{(1)}$ for $j \neq i$: $c_j^{(1)} = \frac{(\vec{f}_j \cdot B \vec{e}_i)}{a_i - a_j}$

Finally obtain $\vec{x}_i^{(1)} = c_i^{(1)} \vec{e}_i + \sum_{j \neq i} \frac{(\vec{f}_j \cdot B \vec{e}_i)}{a_i - a_j} \vec{e}_j$

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Note: perturbation expansion does not fix the value of $c_i^{(1)}$!

To make the choice unique can require $(\vec{f}_i \cdot \vec{x}_i^{(1)}) = c_i^{(1)} = 0$

Second order perturbations

$$\vec{f}_j \cdot (A \vec{x}_i^{(2)} + B \vec{x}_i^{(1)}) = \vec{f}_j \cdot (a_i \vec{x}_i^{(2)} + \lambda_i^{(1)} \vec{x}_i^{(1)} + \lambda_i^{(2)} \vec{e}_i)$$

$$\Rightarrow (a_j - a_i) (\vec{f}_j \cdot \vec{x}_i^{(2)}) + (\vec{f}_j \cdot B \vec{x}_i^{(1)}) = \lambda_i^{(1)} (\vec{f}_j \cdot \vec{x}_i^{(1)}) + \lambda_i^{(2)} \delta_{ij}$$

For $j=i$ obtain

$$\lambda_i^{(2)} = (\vec{f}_i \cdot B \vec{x}_i^{(1)}) = \sum_{j \neq i} \frac{(\vec{f}_j \cdot B \vec{e}_i)(\vec{f}_i \cdot B \vec{e}_j)}{a_i - a_j}$$

For $j \neq i$ obtain $(\vec{x}_i^{(2)} = \sum_j c_j^{(2)} \vec{e}_j)$:

$$(a_i - a_j) c_j^{(2)} = -(\vec{f}_j \cdot B \vec{x}_i^{(1)}) + \lambda_i^{(1)} (\vec{f}_j \cdot \vec{x}_i^{(1)})$$

so that

$$\vec{x}_i^{(2)} = c_i^{(2)} \vec{e}_i - \sum_{\substack{j \neq i \\ k \neq i, j}} \frac{(\vec{f}_k \cdot B \vec{e}_i)(\vec{f}_j \cdot B \vec{e}_k)}{(a_i - a_k)(a_i - a_j)} \vec{e}_j$$

Note: $c_i^{(2)}$ is again undetermined (neither will be $c_i^{(3)}, c_i^{(4)}, \dots$)!

Example:

$$\begin{pmatrix} E_1 & \varepsilon \\ \varepsilon & E_2 \end{pmatrix} = \underbrace{\begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}}_A + \varepsilon \underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_B$$

A-symmetric $\Rightarrow \vec{e}_1 = \vec{f}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \vec{e}_2 = \vec{f}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix} : a_1 = E_1, a_2 = E_2.$

First order: $\lambda_1^{(1)} = \vec{e}_1 \cdot B \vec{e}_1 = (1 \ 0) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0$

$$x_1^{(1)} = \frac{\vec{e}_2 \cdot B \vec{e}_1}{E_1 - E_2} \vec{e}_2 = \frac{1}{\Delta E} \vec{e}_2 \quad (\text{can add a multiple of } \vec{e}_1)$$

Similarly $\lambda_2^{(1)}, \vec{x}_2^{(1)} : \text{swap } 1 \leftrightarrow 2$

Second order: $\lambda_1^{(2)} = \frac{(\vec{e}_2 \cdot B \vec{e}_1)(\vec{e}_1 \cdot B \vec{e}_2)}{E_1 - E_2} = \frac{1}{\Delta E}$

$\vec{X}_1^{(2)} = 0$ (there is no index $k \neq 1, 2$: Generic feature of 2×2 matrices - 2nd order correction $\vec{X}_i^{(2)} = 0$!)

similarly $\lambda_2^{(2)}, \vec{X}_2^{(2)}$: swap $1 \leftrightarrow 2$

Collecting everything together:

$$\lambda_1 = E_1 + \frac{\mathcal{E}^2}{\Delta E} + o(\mathcal{E}^3), \quad \vec{X}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \frac{\mathcal{E}}{\Delta E} \begin{pmatrix} 0 \\ 1 \end{pmatrix} + o(\mathcal{E}^3)$$

Exact result: $\det \begin{pmatrix} E_1 - \lambda & \mathcal{E} \\ \mathcal{E} & E_2 - \lambda \end{pmatrix} = (E_1 - \lambda)(E_2 - \lambda) - \mathcal{E}^2 = 0$

$$\lambda^2 - (E_1 + E_2)\lambda + E_1 E_2 - \mathcal{E}^2 = 0$$

$$\lambda_{1,2} = \frac{E_1 + E_2 \pm \sqrt{(E_1 + E_2)^2 - 4(E_1 E_2 - \mathcal{E}^2)}}{2} =$$

$$= \frac{E_1 + E_2 \pm \sqrt{(E_1 - E_2)^2 + 4\mathcal{E}^2}}{2} =$$

$$= \frac{E_1 + E_2 \pm |E_1 - E_2| \left(1 + 2 \frac{\mathcal{E}^2}{\Delta E} + \dots\right)}{2} = \begin{cases} E_1 + \frac{\mathcal{E}^2}{\Delta E} + \dots \\ E_2 - \frac{\mathcal{E}^2}{\Delta E} + \dots \end{cases}$$

Example: Hydrogen atom in "strong" electric field:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r} + e\mathcal{E}z + \alpha e\mathcal{E}^2 z^2 \right] \Psi = E \Psi$$

\nwarrow polarization coeff.

For instance, 2p level $\Psi_{2p} = C(x \pm iy)e^{-r/2a_0}$, $C^{-2} = 64\pi a_0^5$

has unperturbed energy $E_{2p} = -\frac{e^2}{8a_0}$, $a_0^{-1} = \frac{2me^2}{\hbar^2}$

$$\Delta E_{2p} = \langle \Psi_{2p} | e\mathcal{E}z + \alpha e\mathcal{E}^2 z^2 | \Psi_{2p} \rangle = \int \Psi_{2p}^*(\vec{r}) \Psi_{2p}(\vec{r}) (e\mathcal{E}z + \alpha e\mathcal{E}^2 z^2) d\vec{r}$$

$$= \int e^2 e^{-r/a_0} (x^2 + y^2) (e\mathcal{E}z + \alpha e\mathcal{E}^2 z^2) d\Omega r^2 dr$$

$\overset{0 \text{ (odd)}}{\nearrow}$

$$= \frac{\alpha e \mathcal{E}^2}{64\pi a_0^5} \int r^2 dr e^{-r/a_0} \int (r^2 - z^2) z^2 d\Omega = (6\alpha e a_0^2) \mathcal{E}^2$$

$$\Rightarrow E = -\frac{e^2}{8a_0} + 6\alpha e a_0^2 \mathcal{E}^2$$

\uparrow

1st order correction, which is quadratic in the field \mathcal{E}

Degenerate perturbation theory

If a_1 is degenerate $a_1 = a_2 = \dots = a_n$, we have to perturb around a general eigenvector:

$$\vec{x}_1 = \sum_{k=1}^n \alpha_k \vec{e}_k + \varepsilon \vec{x}_1^{(1)} + \dots$$

$$\lambda_1 = a_1 + \varepsilon \lambda_1^{(1)} + \dots$$

Substitution into $(A + \varepsilon B)\vec{x}_1 = \lambda_1 \vec{x}_1$ gives

at order ε : $(A - a)\vec{x}_1 = \lambda_1^{(1)} \sum_{k=1}^n \alpha_k \vec{e}_k - \sum_{k=1}^n \alpha_k B \vec{e}_k$

Multiplying on the left by left eigenvectors $\vec{f}_k, k=1, \dots, n$ obtain a system of n equations for λ_1 :

$$\alpha_k \lambda_1^{(1)} = \sum_{i=1}^n \alpha_i \underbrace{(\vec{f}_k \cdot B \vec{e}_i)}_{\tilde{B}_{ki}} \Rightarrow \tilde{B} \vec{\alpha} = \lambda_1^{(1)} \vec{\alpha}, \quad \vec{\alpha} = (\alpha_1, \dots, \alpha_n)$$

Nontrivial solutions $\vec{\alpha} \neq 0$ only exist if $\lambda_1^{(1)}$ is an eigenvalue of \tilde{B} .

Secular equation: $\det(\tilde{B} - \lambda_1^{(1)} \mathbb{I}) = 0$ gives 1st order perturbations

Non-diagonalizable matrices

If A cannot be diagonalized, find generalized eigenvectors:

$$A \vec{e}_1 = a \vec{e}_1$$

$$A \vec{e}_2 = a \vec{e}_2 + \vec{e}_1$$

...

$$A \vec{e}_n = a \vec{e}_n + \vec{e}_{n-1}$$

} A is in Jordan normal form in the basis of $\vec{e}_1, \vec{e}_2, \dots, \vec{e}_n$

In this case, perturbation expansion in powers of $\varepsilon^{1/k}$ is needed, for some integer $k \leq n$:

$$\vec{x}(\varepsilon) = \vec{e}_1 + \varepsilon^{1/k} \alpha_2 \vec{e}_2 + \varepsilon^{2/k} \alpha_3 \vec{e}_3 + \dots + \varepsilon^{(k-1)/k} \alpha_k \vec{e}_k$$

$$\lambda(\varepsilon) = a + \varepsilon^{1/k} \lambda_1 + \varepsilon^{2/k} \lambda_2 + \dots$$

Example: $y'' - \lambda y + \epsilon y^k = 0$, $y(0) = y(\pi)$

Find eigenvalues $\lambda(\epsilon)$ up to 1st order

Rewrite as $\underbrace{\frac{d^2}{dx^2} y}_{Ay} + \underbrace{\epsilon y^k}_{B(y)} = \lambda y$

Note: the formulas don't change if we replace

$$\sum_i \alpha_i B \vec{e}_i \rightarrow B(\sum_i \alpha_i \vec{e}_i)$$

0th order eigenvalues & eigenvectors $\left\{ \begin{array}{l} y'' = \lambda y \text{ \& B.C.} \Rightarrow y_n^{(0)} = \frac{1}{\sqrt{\pi}} e^{inx} \\ \lambda_n^{(0)} = -n^2 \end{array} \right.$

Degenerate problem: $\lambda_n = \lambda_{-n}$

$$y_n = \alpha_+ y_n^{(0)} + \alpha_- y_{-n}^{(0)} + \epsilon y_n^{(1)} + \dots$$

$$\lambda_n = \lambda_n^{(0)} + \epsilon \lambda_n^{(1)} + \dots$$

Note: left & right e-vec. are the same (you'll have to trust this)

$$\int y_{\pm n}^{(0)}(x)^* \cdot B(\alpha_- y_{-n}^{(0)}(x) + \alpha_+ y_n^{(0)}(x)) dx = \alpha_{\pm} \lambda_n^{(1)}$$

k=1: $B(y) = y \Rightarrow \int = \alpha_{\pm} = \alpha_{\pm} \lambda_n^{(1)} \Rightarrow \lambda_n^{(1)} = 1$

Exactly what we expect: $\lambda_n = -n^2 + \epsilon + \dots$, $y_n = \alpha_+ y_n^{(0)} + \alpha_- y_{-n}^{(0)} + \dots$

k=2: $B(\alpha_+ y_+ + \alpha_- y_-) = \underbrace{\alpha_+^2 y_+^2}_{e^{2inx}} + \underbrace{2\alpha_+ \alpha_- y_+ y_-}_{e^{i0}} + \underbrace{\alpha_-^2 y_-^2}_{e^{-2inx}}$

$\int = 0 \Rightarrow \lambda_n^{(1)} = 0$

$\lambda_n = -n^2 + 0 \cdot \epsilon + \dots$, $y_n = \alpha_+ y_n^{(0)} + \alpha_- y_{-n}^{(0)} + \dots$

k=3: $B(\alpha_+ y_+ + \alpha_- y_-) = \underbrace{\alpha_+^3 y_+^3}_{e^{3inx}} + \underbrace{3\alpha_+^2 \alpha_- y_+^2 y_-}_{e^{inx}} + \underbrace{3\alpha_+ \alpha_-^2 y_+ y_-^2}_{e^{-inx}} + \underbrace{\alpha_-^3 y_-^3}_{e^{-3inx}}$

$\int = 3\alpha_+^2 \alpha_- = \alpha_{\pm} \lambda_n^{(1)} \Rightarrow 3\alpha_+ \alpha_- = \lambda_n^{(1)}$

$y_n = \alpha_- y_{-n}^{(0)} + \alpha_+ y_n^{(0)} + \dots$, $\lambda_n = -n^2 + 3\epsilon \alpha_+ \alpha_- + \dots$

Perturbation Theory for Degenerate Matrices

$$(A + \varepsilon B) \vec{x} = \lambda \vec{x}$$

$$\lambda_i = \lambda_i^{(0)} + \varepsilon \lambda_i^{(1)} + \dots$$

$$\vec{x}_i = \vec{x}_i^{(0)} + \varepsilon \vec{x}_i^{(1)} + \dots$$

$$\left. \begin{array}{l} \lambda_i = \lambda_i^{(0)} + \varepsilon \lambda_i^{(1)} + \dots \\ \vec{x}_i = \vec{x}_i^{(0)} + \varepsilon \vec{x}_i^{(1)} + \dots \end{array} \right\} (A + \varepsilon B) (\vec{x}_i^{(0)} + \varepsilon \vec{x}_i^{(1)} + \dots) = (\lambda_i^{(0)} + \varepsilon \lambda_i^{(1)} + \dots) (\vec{x}_i^{(0)} + \varepsilon \vec{x}_i^{(1)} + \dots)$$

$$\underline{\Sigma^0}: A \vec{x}_i^{(0)} = \lambda_i^{(0)} \vec{x}_i^{(0)}$$

$\Rightarrow \lambda_i^{(0)} = a_i$ - eigenvalue of A , $\vec{x}_i^{(0)}$ - some eigenvector, which corresponds to a_i

We have not determined $\vec{x}_i^{(0)}$, if $\lambda_i^{(0)}$ is degenerate.

If $\lambda_i^{(0)}$ is n -times degenerate, $\vec{x}_i^{(0)} = \alpha_1^i \vec{e}_1 + \alpha_2^i \vec{e}_2 + \dots + \alpha_n^i \vec{e}_n$

Coefficients α_i are not determined by 0th order equations, they are determined by higher order equations!

$$\underline{\Sigma^1}: A \vec{x}_i^{(1)} + B \vec{x}_i^{(0)} = \lambda_i^{(0)} \vec{x}_i^{(1)} + \lambda_i^{(1)} \vec{x}_i^{(0)}$$

Multiply by \vec{f}_j on the left: $a_j (\vec{f}_j \cdot \vec{x}_i^{(1)}) + (\vec{f}_j \cdot B \vec{x}_i^{(0)}) = a_i (\vec{f}_j \cdot \vec{x}_i^{(1)}) + \lambda_i^{(1)} \vec{x}_i^{(0)}$

a) $j = 1, \dots, n \rightarrow n$ equations for eigenvalue correction $\lambda_i^{(1)}$

b) $j \neq 1, \dots, n \Rightarrow N - n$ equations for eigenvector correction $\vec{x}_i^{(1)}$

$$a) | (\vec{f}_j \cdot B \vec{x}_i^{(0)}) = \sum_{k=1}^n \alpha_k^i \underbrace{(\vec{f}_j \cdot B \vec{e}_k)}_{\tilde{B}_{jk}} = \lambda_i^{(1)} \sum_{k=1}^n \alpha_k^i \underbrace{(\vec{f}_j \cdot \vec{e}_k)}_{\delta_{jk}} \Rightarrow \tilde{B} \vec{\alpha}^i = \lambda_i^{(1)} \vec{\alpha}^i$$

If \tilde{B} is non-degenerate, this eigenproblem determines

both $\lambda_i^{(1)}$ (1st order term in eigenvalue expansion)

and $\vec{\alpha}^i = (\alpha_1^i, \dots, \alpha_n^i)$ (0th order term in eigenvector expansion)

If \tilde{B} is also degenerate, α_k^i might (or might not be)

determined by higher orders of pert. theory

Example 1

$$A = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad B = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\vec{f}_1 = \vec{e}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \vec{f}_2 = \vec{e}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \lambda_{1,2}^{(0)} = 1$$

$$\vec{x}_i^{(0)} = \alpha_1^i \vec{e}_1 + \alpha_2^i \vec{e}_2; \quad \tilde{B}_{jk} = \vec{f}_j \cdot B \vec{e}_k = \delta_{jk} = B \text{ -degenerate!}$$

$$\Rightarrow \lambda_i^{(1)} = 1, \quad \alpha_{1,2}^i \text{ - arbitrary } \star$$

$$(\text{Solve exactly: } \lambda_{1,2} = 1 + \varepsilon, \quad \vec{x}_i = \alpha_1^i \vec{e}_1 + \alpha_2^i \vec{e}_2, \quad \forall \alpha_{1,2}^i)$$

Example 2

$$A = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad B = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\tilde{B}_{jk} = \vec{f}_j \cdot B \vec{e}_k = B_{jk} \Rightarrow \lambda_i^{(0)2} - 1 = 0 \Rightarrow \lambda_i^{(0)} = \pm 1 \text{ -non-degen. !}$$

$$\lambda_i^{(0)} = +1: \quad \vec{\alpha} = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \Rightarrow \vec{x}_i^{(0)} = \vec{e}_1 + \vec{e}_2 = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$\lambda_i^{(0)} = -1: \quad \vec{\alpha} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \Rightarrow \vec{x}_i^{(0)} = \vec{e}_1 - \vec{e}_2 = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$