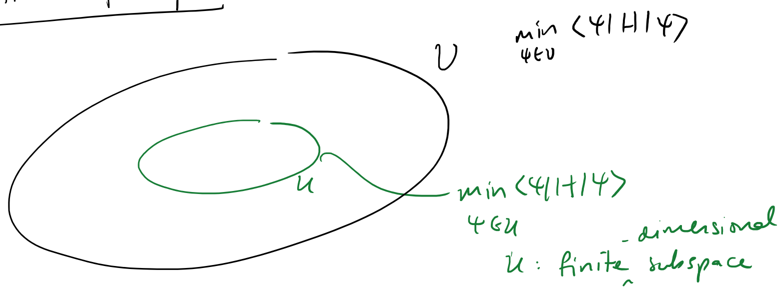
Variational principle :

(B)



$$\min_{\psi\in U}\langle\psi|H|\psi\rangle \geq \min_{\psi\in V}\langle\psi|H|\psi\rangle$$

Choose U then find $\min_{\psi\in U}\langle\psi|H|\psi\rangle$

Equivalent to choosing trial wavefunction.

method (A) – needed a functional form for the trial wavefunction that can be parametrized. Eg. gaussians in Harmonic Oscillator example.

method (B) – do not need such a functional form.

– Instead, choose a basis $\{|i\rangle\}$ for U

– Find $\min_{\psi\in U}\langle\psi|H|\psi\rangle$ by finding the lowest eigenvalue for the matrix $\langle i|H|j\rangle$

Eg. In practice,

can choose a plane wave basis set for U.

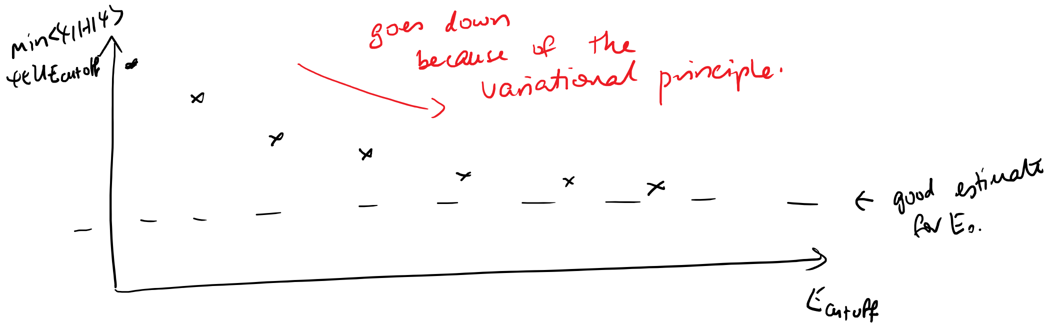
Eg. $\psi(x) = \sum_k c_k e^{ikx}$

Choose discrete values of k,

choose k such that $|k|$ satisfies

$$\frac{\hbar^2|k|^2}{2m} \leq E_{cutoff}.$$

(This means we ignore components that are highly oscillatory in real space.)



Expanding the basis for U to include larger $|k|$.

(C) Application of variational principle.
(not tested)

$\min_{\psi \in \mathcal{H}} \langle \psi | H | \psi \rangle$ to estimate E_0.

Calculus of variations.; Euler-Lagrange approaches.

Vary $|\psi\rangle$ itself.

$-\lambda \underbrace{(\qquad\qquad)}_{|\psi\rangle \text{ normalized.}}$

Time-independent Perturbation theory

Time-independent Hamiltonian H_0.
able to find the eigenstates and eigenvalues of H_0.

$$H = H_0 + V'$$

"small" — a perturbation (time-independent)

Goal : Find the eigenvalues (and eigenstates) of H.

time-independent.
$\Downarrow$
can define the stationary states, & eigenstates.

to $\mathcal{O}(V')$

to $\mathcal{O}(V'^2)$.

Recap Taylor series expansions.

$$f(x) = f(x_0) + f'(x_0)(x-x_0) + \frac{f''(x_0)}{2}(x-x_0)^2 + \cdots$$

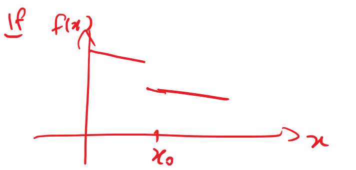
Know $f(x_0) \equiv f(x)\big|_{x=x_0}$.

Know $f'(x_0) \equiv \frac{df}{dx}\big|_{x=x_0}$

Know $f''(x_0)$

Using Taylor series, you can find $f(x)$ if $|x-x_0| \ll 1$

and if $f(x)$ depends on x smoothly for x close to x_0.



NOT suitable for Taylor series expansion near $x = x_0$.

We say $f(x) = f(x_0) + f'(x_0)(x-x_0)$ to $\mathcal{O}(|x-x_0|)$

$|x-x_0| \ll 1$

$$f(x) = f(x_0) + f'(x_0)(x-x_0) + \frac{f''(x_0)}{2}(x-x_0)^2 \text{ to } \mathcal{O}(|x-x_0|^2)$$

Zeroth order term

1st order correction

2nd order correction.

$|x-x_0| << 1$

$\Rightarrow \quad |(x-x_0)^2| << |x-x_0|$

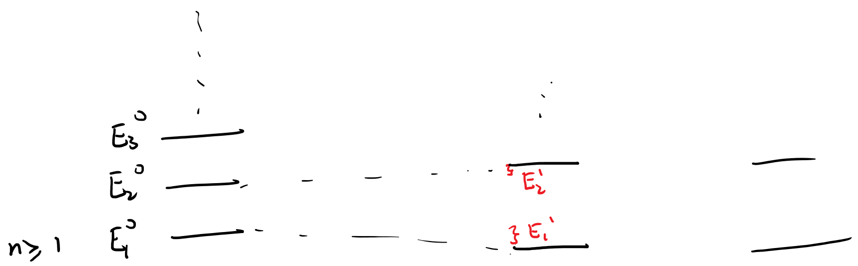
$|x-x_0|^3 << |x-x_0|^2$ etc.

Perturbation theory $\quad H = H_0 + V$ ← small

$$H_0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle$$

zeroth order eigenstates & eigenvalues.

Energy levels of H_0 $\qquad$ Energy levels of $H = H_0 + V$



$E_n = E_n^0 + E_n^1$ to $O(V)$ $\qquad$ $E_n = E_n^0 + E_n^1 + E_n^2$ to $O(V^2)$

★ Are there degeneracies?

$\Rightarrow$ Find E_n^1 $\rightarrow$ Need to check if E_n^0 is degenerate.

– Is there only 1 or more than 1 distinct state with $E = E_n^0$ for H_0?

(• Griffiths covers perturbation theory.

– non-degenerate

– degenerate

\# But you need to check for degeneracies & write it down.)

Final result

(I) Non-degenerate:

If E_n^0 is not degenerate,

1st order correction $\qquad E_n^1 = \langle\psi_n^0|V|\psi_n^0\rangle$

zeroth order eigenstate for n
$H_0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle$.

2nd order correction $$E_n^2 = \sum_{m\neq n} \frac{|\langle\psi_m^0|V|\psi_n^0\rangle|^2}{E_n^0 - E_m^0}$$

1st order correction to $|\psi_n^0\rangle$: $$|\psi_n^1\rangle = \sum_{m\neq n} \frac{\langle\psi_m^0|V|\psi_n^0\rangle}{E_n^0 - E_m^0}|\psi_m^0\rangle$$

(II) Degenerate

$|\psi_{p+1}^0\rangle$ ——— E_{p+1}^0 not degenerate.

$|\psi_1^0\rangle, \ldots, |\psi_p^0\rangle$ ——— $E_1^0 = E_2^0 = \ldots = E_p^0$

p-fold degeneracy

Degeneracies

We have a degenerate subspace.

Any $|\psi\rangle$ in this degenerate subspace is also an eigenstate, with the same eigenvalue of H_0.

Eg. $|\alpha\rangle, |\beta\rangle$. $\quad |\alpha\rangle \neq |\beta\rangle$

$H_0|\alpha\rangle = \varepsilon|\alpha\rangle$, $H_0|\beta\rangle = \varepsilon|\beta\rangle$

$H_0\left(\frac{1}{\sqrt{2}}(|\alpha\rangle + |\beta\rangle)\right) = \varepsilon\left(\frac{1}{\sqrt{2}}(|\alpha\rangle + |\beta\rangle)\right)$

To obtain the 1st corrections to $E_1^0, E_2^0, \ldots, E_p^0$, we should diagonalize V in the degenerate subspace, and the diagonal elements are the 1st order corrections.

Let $V_{ij} = \langle\psi_i^0|V|\psi_j^0\rangle$ matrix representation of V in the basis given by $\{|\psi_n^0\rangle_{N\geq n\geq 1}\}$

$N > p$.

In this basis

$$V = \overbrace{\begin{pmatrix} \underbrace{\overbrace{\tilde{V}}^{p}}_{p\times p \text{ matrix}} & \\ & \end{pmatrix}}^{N} \Bigg\} N$$

$\tilde{V}$ matrix of V in the degenerate subspace.

$\langle\psi_i^0|V|\psi_j^0\rangle$, $i,j = 1, 2, \ldots, p$.

Diagonalize the matrix $\tilde{V}$ $\rightarrow$ get eigenvalues, $\lambda_1, \lambda_2, \ldots, \lambda_p$.
$(p\times p)$

Then $E_1^1 = \lambda_1$
$\vdots$
$E_p^1 = \lambda_p$.

} 1st order corrections

(In the basis of eigenstates for $\tilde{V}$,

the matrix is $\begin{pmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ 0 & & \ddots \; \lambda_p \end{pmatrix}$

$\lambda_i = \langle \tilde{\psi}_i | V | \tilde{\psi}_i \rangle$

where $\{|\tilde{\psi}_i\rangle\}$ diagonalize V in the degenerate subspace.

$E_1^0 = \ldots = E_p^0$ p-fold degenerate

After perturbation

} typically, p distinct values. In that case the perturbation breaks the degeneracy.

Derivations for non-degenerate perturbation theory

Convenient to let the perturbation be λV, λ is a scalar, $\lambda \ll 1$.

$$H = H_0 + V', \qquad V' = \lambda V$$

(define V to be $\frac{1}{\lambda} V'$)

The introduction of λ here is for convenience.

Consider accuracy to $O(\lambda)$, to $O(\lambda^2)$.

Assume $|\psi_n\rangle$, E_n are eigenstates & eigenvalues of H, are smooth functions of λ.

As $\lambda \to 0$, $|\psi_n\rangle \longrightarrow |\psi_n^0\rangle$ the eigenstates of H_0

As $\lambda \to 0$, $E_n \longrightarrow E_n^0$, the eigenvalues of H_0.

We write

eigenstate of $H = H_0 + \lambda V$: $\quad |\psi_n\rangle = |\psi_n^0\rangle + \lambda |\psi_n^1\rangle + \lambda^2 |\psi_n^2\rangle + \ldots$

eigenvalue of $H = H_0 + \lambda V$: $\quad E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots \quad , \lambda \ll 1$

} (*)

We also require that all corrections to $|\psi_n^0\rangle$ are orthogonal to $|\psi_n^0\rangle$.
ie. $\langle \psi_n^0 | \psi_n^1 \rangle = 0$

Substitute (*) in

$$H|\psi_n\rangle = E_n |\psi_n\rangle$$

$$(H_0 + \lambda V)|\psi_n\rangle = E_n |\psi_n\rangle$$

$$(H_0 + \lambda V)\left(|\psi_n^0\rangle + \lambda|\psi_n^1\rangle + \lambda^2|\psi_n^2\rangle + \ldots\right) = \left(E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots\right)\left(|\psi_n^0\rangle + \lambda|\psi_n^1\rangle + \lambda^2|\psi_n^2\rangle + \ldots\right) \quad \text{--- (1)}$$

$$(H_0+\lambda V)\left(|\psi_n^0\rangle+\lambda|\psi_n^1\rangle+\lambda^2|\psi_n^2\rangle+\dots\right)=\left(E_n^0+\lambda E_n^1+\lambda^2 E_n^2+\dots\right)\left(|\psi_n^0\rangle+\lambda|\psi_n^1\rangle+\dots\right) \quad \text{--- (1)}$$

How to show that $E_n^1 = \langle\psi_n^0|V|\psi_n^0\rangle$?

Coeff of λ^0 in (1): $\quad H_0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle$.

Coeff of λ^1 in (1):

$$H_0|\psi_n^1\rangle + V|\psi_n^0\rangle = E_n^0|\psi_n^1\rangle + E_n^1|\psi_n^0\rangle. \quad \text{--- (2)}$$

Operate $\langle\psi_n^0|$ on both LHS and RHS of (2):

$$\underbrace{\langle\psi_n^0|H_0|\psi_n^1\rangle}_{E_n^0\underbrace{\langle\psi_n^0|\psi_n^1\rangle}_{0}} + \langle\psi_n^0|V|\psi_n^0\rangle = E_n^0\underbrace{\langle\psi_n^0|\psi_n^1\rangle}_{0} + E_n^1\underbrace{\langle\psi_n^0|\psi_n^0\rangle}_{1} \quad \text{--- (3)}$$

$$\boxed{E_n^1 = \langle\psi_n^0|V|\psi_n^0\rangle}$$

How to show that $|\psi_n^1\rangle = \sum_{m\neq n}\frac{\langle\psi_m^0|V|\psi_n^0\rangle}{\underbrace{E_m-E_n}_{}}|\psi_m^0\rangle$?

$$\langle\psi_m^0|\psi_n^1\rangle$$

There is a mistake here. In the denominator, we should have E_n - E_m.

$$\sum_m |\psi_m^0\rangle\langle\psi_m^0| = \mathbb{1}$$

$$|\psi_n^1\rangle = \sum_m |\psi_m^0\rangle\langle\psi_m^0|\psi_n^1\rangle$$

Since $\langle\psi_n^0|\psi_n^1\rangle = 0$,

$$|\psi_n^1\rangle = \sum_{m\neq n}|\psi_m^0\rangle\langle\psi_m^0|\psi_n^1\rangle$$