

III. INTRODUCTION TO APPROXIMATION SCHEMES

III.1 Variational Principles

* Recall: Let $L(q_i, \dot{q}_i, t)$ ($i=1, \dots, s$) be a function with $q_i = q_i(t)$
 $\dot{q}_i = \frac{dq_i}{dt}(t)$

The following two statements are equivalent:

(I) $q(t) = (q_i(t))_{i=1}^s$ is an extremum of the functional

$$S[q] = \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t) dt$$

i.e. $\delta S = 0$ for small variations $q_i \mapsto q_i + \delta q_i$ with $\delta q_i(t_1) = 0 = \delta q_i(t_2)$

(II) $q(t)$ satisfies the Euler-Lagrange eqs.

$$\frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} = 0 \quad \text{for } i=1, \dots, s$$

Example: In classical mechanics $q(t) = \text{motion}$, $L(q, \dot{q}, t) = \text{Lagrange fct.}$

$S = \text{action}$

* This can be generalized to fields $\psi_i(x_j) = \psi_i(t=x_0, x_1, \dots, x_N)$
 $i=1, \dots, s$. If $\mathcal{L}(\psi_i, \frac{\partial \psi_i}{\partial x_j}, x_k)$ is the Lagrange density for the ψ_i
then the following statements are equivalent:

(I) The $\psi_i(x_j)$, $i=1, \dots, s$ are an extremum of the functional

$$S[\psi] = \int_{\Gamma} \mathcal{L}(\psi_i, \frac{\partial \psi_i}{\partial x_j}, x_k) d^{N+1}x \quad \Gamma = \text{subvolume in } \mathbb{R}^{N+1}$$

i.e. $\delta S = 0$ for small variations $\psi_i \mapsto \psi_i + \delta \psi_i$ which vanish on the boundary $\partial \Gamma$ of Γ .

(ii) The $\psi_i(x_j)$ satisfy the Lagrange field equations

$$\frac{\partial \mathcal{L}}{\partial \psi_i} - \sum_{j=1}^{NH} \frac{\partial}{\partial x_j} \frac{\partial \mathcal{L}}{\partial (\frac{\partial \psi_i}{\partial x_j})} = 0 \quad i=1, \dots, S$$

Proof: HW

* $\mathcal{L} = i\hbar \psi^* \frac{\partial \psi}{\partial t} - \frac{\hbar^2}{2m} \nabla \psi^* \cdot \nabla \psi - V \psi^* \psi$

is the Lagrange density of the Schrödinger field $\psi(\vec{x}, t)$.

Why? Lagrange field equations for ψ and ψ^* :

$$0 \stackrel{!}{=} \frac{\partial \mathcal{L}}{\partial \psi^*} - \frac{\partial}{\partial t} \frac{\partial \mathcal{L}}{\partial (\frac{\partial \psi^*}{\partial t})} - \sum_{j=1}^3 \frac{\partial}{\partial x_j} \frac{\partial \mathcal{L}}{\partial (\frac{\partial \psi^*}{\partial x_j})} = i\hbar \frac{\partial \psi}{\partial t} - V\psi + \frac{\hbar^2}{2m} \Delta \psi$$

t-dep. Schrödinger equation! The equation with derivatives w.r.t ψ yields its complex conjugate. Note: ψ complex $\Rightarrow \text{Re } \psi, \text{Im } \psi$ (or ψ, ψ^*) are counted as two independent field degrees of freedom.

* $\mathcal{L}_{\text{stat}} = \frac{\hbar^2}{2m} \nabla \psi^* \cdot \nabla \psi + V \psi^* \psi - E \psi^* \psi$

is the Lagrange density which has the t-indep. S.E. as its Lagrange field equations.

Why? Check.

[i.e. $\delta(\text{functional}) = 0$]

* The most important statement of stationarity in terms of approximation schemes is that for the energy functional $\langle H \rangle$.

for (not necessarily normalized) wave fct. $\psi(\vec{r})$ the expectation value

of the Hamilton operator is

$$\langle H \rangle = \frac{\int \psi^* H \psi d^3r}{\int \psi^* \psi d^3r}$$

and can be interpreted as a functional depending on ψ .

Then:

$$\delta \langle H \rangle = 0 \quad \text{for } \sqrt{\text{small deviations from}} \psi(\vec{r}), \text{ i.e. } \langle H \rangle \text{ stationary at } \psi(\vec{r})$$

$$\iff$$

$\psi(\vec{r})$ is an eigenfct. of H and is normalized to 1 (w.r.t. L^2 norm)

$$\text{Why? } \delta \langle H \rangle = \langle H \rangle_{\psi+\delta\psi} - \langle H \rangle_{\psi} = \frac{\int \psi^* H \psi d^3r + \int \psi^* H \delta\psi d^3r + \int \delta\psi^* H \psi d^3r}{\int \psi^* \psi d^3r + \int \psi^* \delta\psi d^3r + \int \delta\psi^* \psi d^3r} - \frac{\int \psi^* H \psi d^3r}{\int \psi^* \psi d^3r} + O(\delta\psi)^2$$

$$\Rightarrow \left(\int \psi^* \psi d^3r \right) \delta \langle H \rangle = \left(\int \psi^* H \psi d^3r + \int \psi^* H \delta\psi d^3r + \int \delta\psi^* H \psi d^3r \right)$$

$$* \left(1 - \frac{\int \psi^* \delta\psi d^3r + \int \delta\psi^* \psi d^3r}{\int \psi^* \psi d^3r} \right) - \int \psi^* H \psi d^3r + O(\delta\psi)^2$$

$$\Rightarrow \left(\int \psi^* \psi d^3r \right)^2 \delta \langle H \rangle = \left(\int \psi^* \psi d^3r \right) \left(\int \psi^* H \delta\psi d^3r + \int \delta\psi^* H \psi d^3r \right)$$

$$- \int \psi^* H \psi d^3r \left(\int \psi^* \delta\psi d^3r + \int \delta\psi^* \psi d^3r \right) + O(\delta\psi)^2$$

Now ψ eigenfct. of H and $\int \psi^* \psi d^3r = 1 \Rightarrow \delta \langle H \rangle = 0$

Conversely: $\delta \langle H \rangle = 0$ for variation $\delta\psi = \epsilon \left[\left(\int \psi^* \psi d^3r \right) H \psi - \left(\int \psi^* H \psi d^3r \right) \psi \right]$

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$$\Rightarrow \langle H\psi | H\psi \rangle = \langle H\psi | \langle H \rangle \psi \rangle \Rightarrow H\psi = \langle H \rangle \psi$$

i.e. ψ is eigenfct. and $\langle H \rangle$ eigenvalue.

(check!)

* We can use this theorem to obtain the eigenstates or approximations thereof. Suppose you choose trial functions $\psi(\mathbb{R}, \lambda_i)$ as functions of parameters λ_i $i=1, \dots, k$

Then the extrema found by $\frac{\partial \langle H \rangle_\psi}{\partial \lambda_i}$, $i=1, \dots, k$

are approximations to the true extrema in (infinite-dimensional) function space.

But by choosing "good" trial functions one can obtain quite close approximations.

* Example 1: 1-parameter trial fct. which include the true stationary state. Here: harmonic oscillator with trial fct. $\psi_\lambda(x) = (\pi\sigma)^{-1/4} e^{-\frac{x^2}{2\lambda^2}}$

I.e. we suspect a Gaussian but don't know the width; the ψ_λ are already L^2 -normalized to 1.

$$\langle H \rangle_{\psi_\lambda} = \int_{\mathbb{R}} \psi_\lambda^*(x) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \right) \psi_\lambda(x) dx$$

$$= -\frac{\hbar^2}{2m} \int_{\mathbb{R}} \left(-\frac{1}{\lambda^2} + \frac{x^2}{\lambda^4} \right) \frac{1}{\sqrt{\pi\sigma}} e^{-\frac{x^2}{\lambda^2}} + \frac{1}{2} m \omega^2 \frac{1}{\sqrt{\pi\sigma}} \int_{\mathbb{R}} x^2 e^{-\frac{x^2}{\lambda^2}} dx$$

$$= \frac{\hbar^2}{4m} \frac{1}{\lambda^2} + \frac{1}{4} m \omega^2 \lambda^2$$

Extrema of functional: $\frac{d\langle H \rangle_{\psi_\lambda}}{d\lambda} = -\frac{\hbar^2}{2m} \frac{1}{\lambda^3} + \frac{1}{2} m \omega^2 \lambda \stackrel{!}{=} 0$

$\Rightarrow \lambda^2 = \frac{\hbar}{m\omega}$; exact solution for harm. osc. ground state.

* Example 2: 1-parameter trial fct. which does not include the true stationary state; $V(x) = c|x|$; see HW VIII

* Recall $\langle H \rangle > E_0$ (ground state energy) for any expectation value

\Rightarrow any approximation found for E_0 with this method is an upper bound for E_0 .

III.2 The Rayleigh - Ritz Method

* Assume we have a set of n linearly independent basis functions $X_i(\vec{r})$ $i=1, \dots, n$ in Hilbert space \mathcal{H} . Our trial functions for the functional

$\langle H \rangle$ will be
$$\psi(\vec{r}) = \sum_{i=1}^n c_i X_i(\vec{r})$$

with n parameters c_i .

Here: suppose the X_i are an orthonormal basis (linearly independent vectors can always be made orthonormal. For Rayleigh-Ritz without

this constraint see Herzberger, ch. 8.4

* Plugging into $\langle H \rangle$:
$$\langle H \rangle = \frac{\sum_{i=1}^n c_j^* c_i \langle j|H|i \rangle}{\sum_{i=1}^n c_j^* c_i \underbrace{\langle j|i \rangle}_{\delta_{ji}}}$$

where we defined the notation $\langle j|H|i \rangle = \langle X_j | H X_i \rangle = \int_{\mathbb{R}^3} X_j^* H X_i d^3r$

Since the c_i can be complex we have $2n$ conditions for the extrema:

$$\frac{\partial \langle H \rangle}{\partial c_i} = 0, \quad \frac{\partial \langle H \rangle}{\partial c_i^*} = 0, \quad i=1, \dots, n$$

However, since H is Hermitian we only get n independent equations. (check!)

$$\frac{\partial \langle H \rangle}{\partial c_k^*} = \frac{(\sum_i |c_i|^2) (\sum_i c_i \langle k|H|i \rangle) - c_j (\sum_i c_j^* c_i \langle j|H|i \rangle)}{(\sum_i |c_i|^2)^2} \stackrel{!}{=} 0$$

$$\Rightarrow \sum_{i=1}^n \langle j|H|i \rangle c_i - \langle H \rangle c_j = 0 \quad \text{for } j=1, \dots, n$$

For the optimal choice of c_i $\langle H \rangle$ will be an approximation for an energy eigenvalue E . Thus we need to solve the linear system

$$\sum_{i=1}^n (\langle j|H|i \rangle - E \delta_{ji}) c_i = 0 \quad j=1, \dots, n$$

* Hence finding the approximate solutions and eigenvalues is equivalent to solving the finite-dimensional eigenvalue problem for the matrix $\langle j|H|i \rangle$.

Non-trivial solutions for the c_i exist if

$$D_n(E) = \det (\langle j|H|i \rangle - E \delta_{ji}) = 0$$

The roots of the characteristic polynomial $D_n(E)$ give the eigenvalues of $\langle j|H|i \rangle$ which are the approximations of the energy eigenvalues of H .

For each eigenvalue E_i , $i=1, \dots, n$ we can determine the coefficients $c_j^{(i)}$ $j=1, \dots, n$ and the eigenfunction $\psi^{(i)} = \sum_{j=1}^n c_j^{(i)} \chi_j(\vec{r})$.
approximation to the real

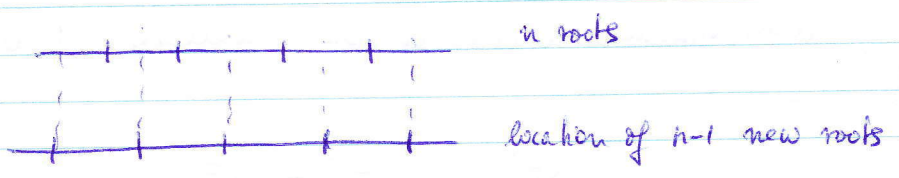
* Since H is Hermitian the matrix $\langle j|H|i \rangle$ is also Hermitian, i.e.

$$\langle j|H|i \rangle = \langle i|H|j \rangle^* \quad (\text{check!})$$

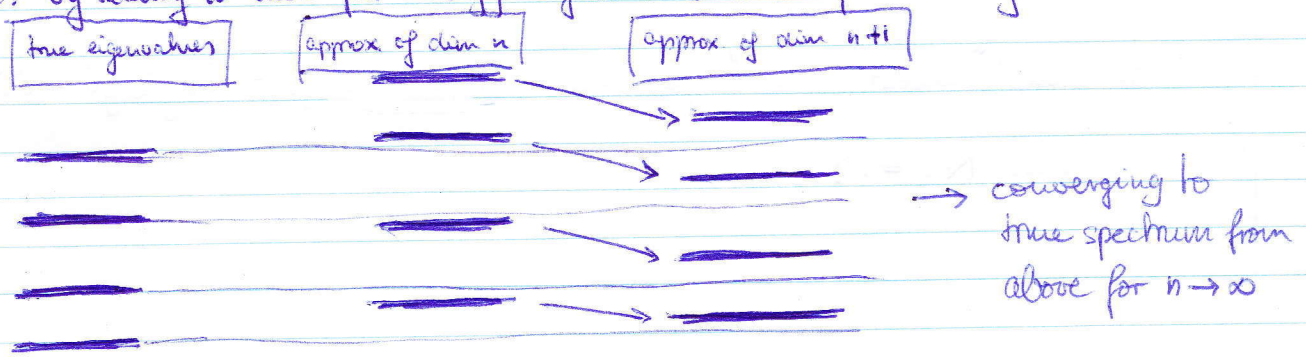
\Rightarrow Sets of coefficients $c^{(i)}$ and $c^{(j)}$ to different eigenvalues E_i, E_j are orthogonal as vectors \Rightarrow the functions $\psi^{(i)}$ and $\psi^{(j)}$ are orthogonal.

* Summary: For given n the $\psi^{(1)}, \dots, \psi^{(n)}$ are a finite-dimensional approximation to the true eigenfcts. with $E^{(i)}$ which are upper bounds for the true eigenvalues.

If one basis fct is added to the existing ones, $n \mapsto n+1$ one can show that the roots of the characteristic polynomial evolve in a simple way with n :



I.e. by adding a basis fct. energy eigenvalues move qualitatively like this:



III.3 Introduction to Perturbation Theory

* Suppose we would like to solve a quantum mechanical problem

with potential energy $V(\vec{r})$:
$$-\frac{\hbar^2}{2m}\Delta\psi + V\psi = E\psi$$

It is too difficult to solve analytically but we know the solutions for

a similar system with pot. energy $V_0(\vec{r})$:
$$-\frac{\hbar^2}{2m}\Delta\psi^{(0)} + V_0\psi^{(0)} = E^{(0)}\psi^{(0)}$$

and the difference between V and V_0 is small:

$$V(\vec{r}) = V_0(\vec{r}) + \delta V(\vec{r})$$

We call $E^{(0)}$, $\psi^{(0)}$ the eigenvalues and -functions of the "unperturbed" problem and δV the perturbation to V_0 .

* From III.1: $\langle H \rangle_{\psi^{(0)}} = \int \psi^{(0)*} H \psi^{(0)} d^3r$ with $H = -\frac{\hbar^2}{2m}\Delta + V$

is an approximation to the true eigenvalue of H . The quality of the approximation depends on the "smallness" of δV .⁽¹⁾

⁽¹⁾ quantified below

Thus

$$\langle H \rangle_{\psi^{(0)}} = E^{(0)} + \Delta E \quad \text{with} \quad \Delta E = \int \psi^{(0)*} \delta V \psi^{(0)} d^3r$$

* This "lowest order" perturbation theory is just Rayleigh-Ritz

with $n=1$!

* If $E^{(0)}$ is a degenerate eigenvalue of degeneracy d we have to go back to Rayleigh-Ritz with $n=d$ to determine the d perturbed eigenvalues. They might no longer be degenerate or only partially degenerate.

* Example for $d=2$ (will also serve to quantify the quality of perturbation theory)

Assume two eigenvalues $E_1^{(0)}, E_2^{(0)}$ of $H_0 = -\frac{\hbar^2}{2m}\Delta + V_0$ with $E_1^{(0)} \leq E_2^{(0)}$ (orthonormal eigenkets $\psi_1^{(0)}, \psi_2^{(0)}$)

Rayleigh-Ritz ($n=2$).

denote $\langle \psi_i^{(0)} | H | \psi_j^{(0)} \rangle$ as $\langle i | H | j \rangle$

$$\begin{pmatrix} \langle 1 | H | 1 \rangle - E & \langle 1 | H | 2 \rangle \\ \langle 2 | H | 1 \rangle & \langle 2 | H | 2 \rangle - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$$= \begin{pmatrix} \langle 1 | \delta V | 1 \rangle + E_1^{(0)} - E & \langle 1 | \delta V | 2 \rangle \\ \langle 2 | \delta V | 1 \rangle & \langle 2 | \delta V | 2 \rangle + E_2^{(0)} - E \end{pmatrix}$$

Determinant = 0 \Rightarrow

$$E_{1,2} = \frac{1}{2} \left[E_1^{(0)} + E_2^{(0)} + \langle 1 | \delta V | 1 \rangle + \langle 2 | \delta V | 2 \rangle \pm \sqrt{(E_2^{(0)} + \langle 2 | \delta V | 2 \rangle - E_1^{(0)} - \langle 1 | \delta V | 1 \rangle)^2 + 4 |\langle 1 | \delta V | 2 \rangle|^2} \right]$$

(check!)

- First assume non-degeneracy, $E_1^{(0)} < E_2^{(0)}$. Rayleigh-Ritz with $n=1$ would be sufficient if $|\langle 1 | \delta V | 2 \rangle| \ll E_2^{(0)} + \langle 2 | \delta V | 2 \rangle - E_1^{(0)} - \langle 1 | \delta V | 1 \rangle$ i.e. the "overlap" of $\psi_1^{(0)}$ and the next energy level through δV (i.e. the number $|\langle 1 | \delta V | 2 \rangle|$) should be small compared to the energy difference between $E_1^{(0)}$ and $E_2^{(0)}$. This is the "smallness"

constraint on δV that makes perturbation theory valid.

- Now $E_1^{(0)} = E_2^{(0)}$, i.e. degenerate unperturbed energy level.

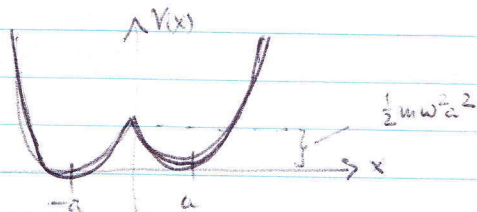
$$\Rightarrow E_{1,2} = E^{(0)} + \frac{1}{2} \left[\langle 1|\delta V|1\rangle + \langle 2|\delta V|2\rangle \pm \sqrt{(\langle 1|\delta V|1\rangle - \langle 2|\delta V|2\rangle)^2 + 4|\langle 1|\delta V|2\rangle|^2} \right]$$

Energy level remains degenerate under perturbation only if

$$\langle 1|\delta V|1\rangle = \langle 2|\delta V|2\rangle \text{ and } \langle 1|\delta V|2\rangle = 0.$$

III.4 Double Well Potentials

* Here double harmonic oscillator with $V(x) = \frac{1}{2}m\omega^2(|x|-a)^2$



Analytic solution possible: see Herzberger p. 156 ff

For most such potentials however be devise trial fets based on the underlying symmetry for approximating solutions.

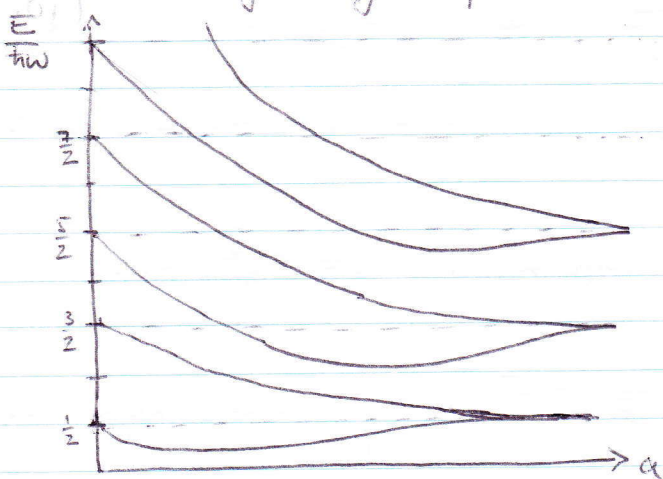
* Qualitative behavior clear:

- For $a = 0$ $V(x)$ becomes the usual harm. osc. with

energy eigenvalues $E_n = (n + \frac{1}{2})\hbar\omega$; degeneracy = 1 for each eigenvalue

- For $a \rightarrow \infty$ the potential resembles two independent harmonic osc. and the energy spectrum must again be $(n + \frac{1}{2})\hbar\omega$, $n \in \mathbb{N}$,

now with degeneracy 2 for each eigenvalue



* It commutes with the parity operator \Rightarrow stationary states (energy eigenfcts.)

can be chosen even or odd.

\Rightarrow probability density $|\psi_n|^2$ even and the same in both wells

\Rightarrow for $E_n < \frac{1}{2}m\omega^2 a^2 = V_0$ the particle must be tunnelling through the classically forbidden potential barrier.

* Symmetry and asymptotic limits for a large or vanishing suggest trial fcts.

$$\psi_{\pm}^n = N_{\pm}^n \left[\psi_n(x-a) \pm \psi_n(x+a) \right]$$

with $\psi_n(x) =$ harmonic osc. eigenfunctions

ψ_{\pm}^n is $\left\{ \begin{array}{l} \text{even} \\ \text{odd} \end{array} \right\}$ for n even and $\left\{ \begin{array}{l} \text{odd} \\ \text{even} \end{array} \right\}$ for n odd.

The estimated energy eigenvalues from these trial fets are obtained

from
$$\langle H \rangle_{n\pm} = \int_{\mathbb{R}} \psi_{\pm}^{n*} H \psi_{\pm}^n d^3r$$

Normalization:
$$N_{\pm}^n = \frac{1}{\sqrt{2(1 \pm C_n)}} \quad \text{where } C_n = \int \psi_n(x+a) \psi_n(x-a) dx$$

is the overlap integral of the two well fets.

* Example: for $n=0$ and large a (i.e. $\alpha = \sqrt{\frac{m\omega}{\hbar}} a \gg 1$)

$$\langle H \rangle_{0\pm} \approx \frac{1}{2} \hbar \omega \mp \frac{\hbar \omega}{\sqrt{\pi}} e^{-\alpha^2} \quad \text{Why? maybe HW IX}$$

Even trial fet \cong ground state, energy dips below $\frac{1}{2} \hbar \omega$.