IV. III. INTRODUCTION TO APPROXIMATION SCHEMES

Sections in these notes are now renumbered. New numbers are indicated in Courier font to the left.

IV.1 III.1 Variational Principles

* Recall: Let $L(q_i, \dot{q}_i, t)$ $(i=1,..,s)$ 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.

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

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

S = action

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

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

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

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

$$\frac{\partial \mathcal{L}}{\partial \psi_i} - \sum_{j=1}^{N+1} \frac{\partial}{\partial x_j} \frac{\partial \mathcal{L}}{\partial\left(\frac{\partial \psi_i}{\partial x_j}\right)} = 0 \qquad i = 1, \dots, s$$

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^*:

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

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

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

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

Why? Check.

* The most important statement of stationarity [i.e. $\delta(\text{functional})=0$] in terms of approximation schemes is that for the energy functional $\langle H\rangle$.

For (not necessarily normalized) wave fcts. $\psi(\vec{r})$ 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:
$$\delta\langle H\rangle = 0 \quad \text{for small deviations from a } \psi(\vec{r}), \quad \text{i.e. } \langle H\rangle \text{ stationary at } \psi(\vec{r})$$
$$\Longleftrightarrow$$
$\psi(\vec{r})$ is an eigenfct. of H and is normalized to 1 (w.r.t. L^2 norm)

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 $\delta\psi = \varepsilon\left[\left(\int\psi^*\psi\, d^3r\right)H\psi - \left(\int\psi^* H\psi\, d^3r\right)\psi\right]$

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

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 $\psi(\vec{r}, \lambda_i)$ as functions of parameters λ_i, $i = 1, .., k$

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

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

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

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

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

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

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.

IV.2 ~~III~~.2 The Rayleigh – Ritz Method

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

$$\psi(\vec{r}) = \sum_{i=1}^{n} c_i\,\chi_i(\vec{r})$$

with n parameters c_i.

Here: suppose the χ_i are an orthonormal basis (linearly independent vectors can always be made orthonormal. For Rayleigh – Ritz without this constraint see Merzbacher, ch. 8.4

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

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

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

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

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

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

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

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

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

* 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

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

The roots of the ~~po~~ 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, $i=1,..,n$ we can determine the coefficients $c_j^{(i)}$ $j=1,..,n$ and the approximation to the real eigenfunction $\varphi^{(i)} = \sum_{j=1}^{n} c_j^{(i)} \chi_j(\vec{r})$.

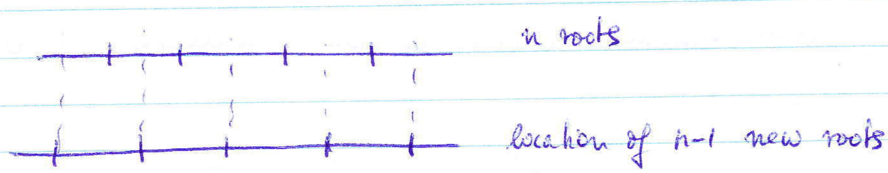
* Since H is Hermitian the matrix $\langle j|H|i\rangle$ is also Hermitian, i.e.

$\langle j|H|i\rangle = \langle i|H|j\rangle^*$ (check!)

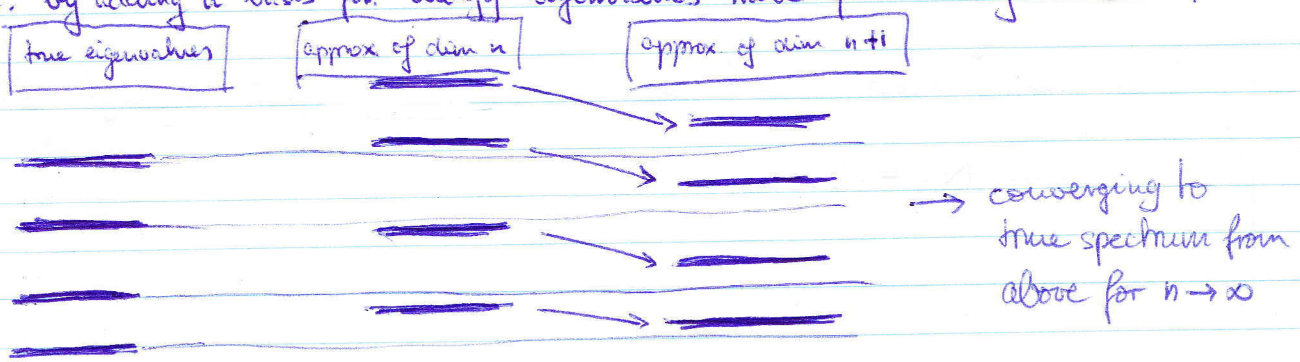
$\Rightarrow$ Sets of coefficients $c^{(i)}$ and $c^{(j)}$ to different eigenvalues E_i, E_j are orthogonal as vectors $\Rightarrow$ the functions $\varphi^{(i)}$ and $\varphi^{(j)}$ are orthogonal.

* Summary: For given n the $\varphi^{(1)}, .., \varphi^{(n)}$ are a finite-dimensional approximation to the true eigenfcts. with $E^{(i)}$ which are <u>upper bounds</u> 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:



IV.3 ~~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

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

* 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 eigenfcts. $\varphi_1^{(0)}, \varphi_2^{(0)}$)

Rayleigh-Ritz ($n=2$).

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

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

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

Determinante $= 0 \Rightarrow$

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

(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 $\varphi_1^{(0)}$ 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.

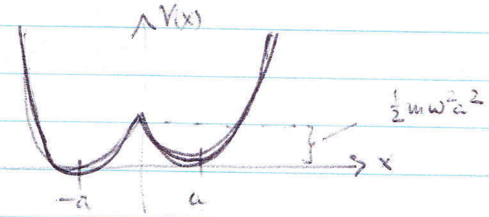
$$\Rightarrow E_{1,2} = E^{(0)} + \frac{1}{2}\left[\langle 1|\delta V|1\rangle + \langle 2|\delta V|2\rangle \pm \sqrt{(\langle 1|\delta V|1\rangle - \langle 2|\delta V|2\rangle)^2 - 4|\langle 1|\delta V|2\rangle|^2}\right]$$

Energy level remains degenerate under perturbation only if

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

IV.4 III.4 Double Well Potentials

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



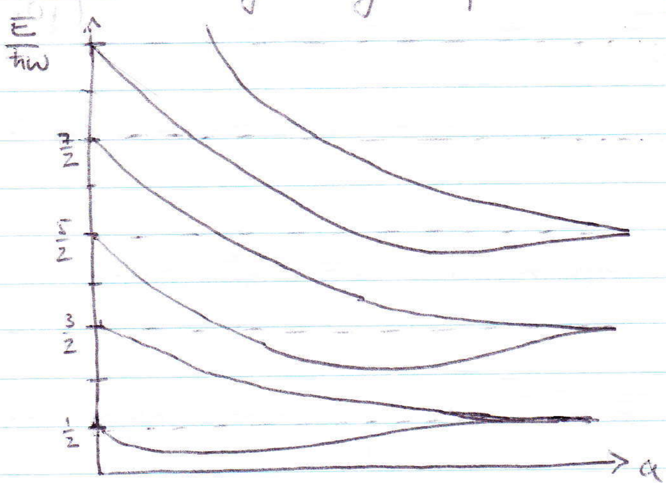
Analytic solution possible: see Merzbacher p. 156 ff

For most such potentials however we devise trial fcts 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 $a \to \infty$ 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



* H 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.

$$\psi^n_\pm = N^n_\pm \left[\varphi_n(x-a) \pm \varphi_n(x+a) \right]$$

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

$\psi^n_\pm$ is $\left\{ \begin{matrix} \text{even} \\ \text{odd} \end{matrix} \right\}$ for n even and $\left\{ \begin{matrix} \text{odd} \\ \text{even} \end{matrix} \right\}$ for n odd.

The estimated energy eigenvalues from these trial fcts are obtained

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

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

is the overlap integral of the two well fcts.

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

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

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