Quantenmechanik II

Vorlesungs-Skript

Mr. Adrian Signer

Mitschrift

Marc Maetz

FS 2013

Contents

Contents **1**

1 Approximation methods for stationary problems **3**
1.1 Time-independent perturbation theory, non-degenerate case 4
1.2 Time-independent perturbation theory: degenerate case 8
1.2.1 easy way out (sometimes) 11

Chapter 1

Approximation methods for stationary problems

- standard QM problem:
  - given $|\psi(t_0)\rangle$
  - wanted
    $$|\psi(t)\rangle = U\,(t, t_0)\,|\psi(t_0)\rangle$$
    $$U = e^{-\frac{i}{\hbar}H(t-t_0)}$$
- for time independent H
  $$U = e^{-\frac{i}{\hbar}H(t-t_0)} \tag{1.1}$$
  find eigenvalue and eigenstates (diagonalize H)

but: most problems cannot be solved exactly → find approximate solution.

1.1 Time-independent perturbation theory, non-degenerate case

Assume:

$$H = H_0 + \lambda V \tag{1.2}$$

with H_0 the Hamiltonian that I can solve ("free" Hamiltonian) and the perturbation V "small" and λ a dimensionless bookkeeping par.

$$\begin{aligned} \lambda &\to 0, \quad H \to H_0 \\ \lambda &\to 1, \quad \text{full } H \end{aligned}$$

We know

$$\left|\psi_n^{(0)}\right\rangle, E_n^{(0)}$$

with

$$H_0 \left|\psi_n^{(0)}\right\rangle = E_n^{(0)} \left|\psi_n^{(0)}\right\rangle$$

with

$$\left\langle\psi_n^{(0)}\middle|\psi_m^{(0)}\right\rangle = \delta_{mn}$$

(continuous spectrum also understood.)
We want $|\psi_n\rangle$ and E_n with

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

let

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

$$|\psi_n\rangle = \left|\psi_n^{(0)}\right\rangle + \lambda \left|\psi_n^{(1)}\right\rangle + \lambda^2 \left|\psi_n^{(2)}\right\rangle + \dots$$

seems obvious, but assumption. (convergence?)

$$\begin{aligned}
&\left(H_0 - E_n^{(0)}\right)\left|\psi_n^{(0)}\right\rangle + \lambda\left(\left(H_0 - E_n^{(0)}\right)\left|\psi_n^{(1)}\right\rangle\right) \\
&\quad + \lambda^2\left(\left(H_0 - E_n^{(0)}\right)\left|\psi_n^{(2)}\right\rangle + \left(V - E_n^{(1)}\right)\left|\psi_n^{(1)}\right\rangle - E_n^{(2)}\right) \\
&\quad + \mathcal{O}\left(\lambda^3\right) = 0
\end{aligned}$$

with $\mathcal{O}(1)$ "step 0", $\mathcal{O}(\lambda)$ "step 1", $\mathcal{O}(\lambda^2)$ "step 2".

Step 0: nothing to do

Step 1 multiply by $\left\langle\psi_m^{(0)}\right|$

$$\begin{aligned}
&\left\langle\psi_m^{(0)}\right| H_0 - E_n^{(0)} \left|\psi_n^{(1)}\right\rangle + \left\langle\psi_m^{(0)}\right| V - E_n^{(1)} \left|\psi_n^{(0)}\right\rangle = 0 \\
&= \left(E_m^{(0)} - E_n^{(0)}\right)\left\langle\psi_m^{(0)}\middle|\psi_n^{(1)}\right\rangle + \left\langle\psi_m^{(0)}\right| V \left|\psi_n^{(0)}\right\rangle - E_n^{(1)}\delta_{mn} = 0
\end{aligned}$$

to get $\left|\psi_n^{(1)}\right\rangle$

$$\begin{aligned}
\left|\psi_n^{(1)}\right\rangle &= \sum_m \underbrace{\left\langle\psi_m^{(0)}\middle|\psi_n^{(1)}\right\rangle}\left|\psi_m^{(0)}\right\rangle \\
&= \sum_m \frac{\left\langle\psi_m^{(0)}\right| V \left|\psi_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}}\left|\psi_m^{(0)}\right\rangle + \left|\psi_n^{(0)}\right\rangle\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle
\end{aligned}$$

from normalization

$$\begin{aligned}\langle \psi_n | \psi_n \rangle &\stackrel{!}{=} 1 \\ &= \underbrace{\left\langle \psi_n^{(0)} \middle| \psi_n^{(0)} \right\rangle}_{1} + \lambda \underbrace{\left\langle \psi_n^{(0)} \middle| \psi_n^{(1)} \right\rangle}_{0} + \lambda \left\langle \psi_n^{(1)} \middle| \psi_n^{(0)} \right\rangle + \mathcal{O}\left(\lambda^2\right)\end{aligned} \tag{1.3}$$

has to be small. If $E_n^{(0)} = E_m^{(0)}$?? degeneracy! $\rightarrow$ sec 1.2 if $E_n^{(0)} \simeq E_m^{(0)}$ quasi degenerate

step 2 take $\mathcal{O}(\lambda^2)$ terms $\left\langle \psi_k^{(0)} \right|$

$$\begin{aligned}&\left(E_k^{(0)} - E_n^{(0)}\right) \left\langle \psi_k^{(0)} \middle| \psi_n^{(2)} \right\rangle + \left\langle \psi_k^{(0)} \middle| V \middle| \psi_n^{(1)} \right\rangle \\ &\quad - E_n^{(1)} \left\langle \psi_k^{(0)} \middle| \psi_n^{(1)} \right\rangle = E_n^{(2)} \delta_{kn}\end{aligned} \tag{1.4}$$

for $k = n$

$$\begin{aligned}E_n^{(2)} &= \left\langle \psi_n^{(0)} \middle| V \middle| \psi_n^{(1)} \right\rangle \\ &= \sum_{m \neq n} \frac{\left\langle \psi_n^{(0)} \middle| V \middle| \psi_m^{(0)} \right\rangle \left\langle \psi_m^{(0)} \middle| V \middle| \psi_n^{(0)} \right\rangle}{E_n^{(0)} - E_m^{(0)}} \\ &= \sum_{m \neq n} \frac{\left| V_{nm}^2 \right|}{E_n^{(0)} - E_m^{(0)}}\end{aligned} \tag{1.5}$$

Note $E_n^{(2)} < 0$ for ground state.

Next compute $\left|\psi_n^{(2)}\right\rangle$: initially fix normalization such that

$$\left\langle\psi_n^{(0)}\middle|\psi_n^{(i)}\right\rangle = \delta_{i0} \tag{1.6}$$

this is in conflict

$$\left\langle\psi_n\middle|\psi_n\right\rangle = 1 \tag{1.7}$$

$\rightarrow$ sort out at the end.

$$\begin{aligned}\left|\psi_n^{(2)}\right\rangle &= \sum_{k\neq n}\left|\psi_k^{(0)}\right\rangle\left\langle\psi_k^{(0)}\middle|\psi_n^{(2)}\right\rangle + 0\\ &= \sum_{k\neq n}\left|\psi_k^{(0)}\right\rangle\left(\frac{\left\langle\psi_k^{(0)}\right|V\left|\psi_n^{(1)}\right\rangle}{E_n^{(0)}-E_k^{(0)}} - \frac{E_n^{(1)}\left\langle\psi_k^{(0)}\middle|\psi_n^{(1)}\right\rangle}{E_n^{(0)}-E_k^{(0)}}\right)\end{aligned} \tag{1.8}$$

plug in $\left|\psi_n^{(1)}\right\rangle$ and sort out normalization

$$\left|\psi_n\right\rangle_N = \mathbb{Z}^{1/2}\left|\psi_n\right\rangle \tag{1.9}$$

fix such that

$${}_N\left\langle\psi_n\middle|\psi_n\right\rangle_M = 1 \tag{1.10}$$

$$\begin{aligned}{}_N\left\langle\psi_n\middle|\psi_n\right\rangle_N &= 1\\ &= Z_n\left\langle\psi_n\middle|\psi_n\right\rangle\\ &= Z_n\left(\left\langle\psi_n^{(0)}\right| + \lambda\left\langle\psi_n^{(1)}\right| + \lambda^2\left\langle\psi_n^{(2)}\right|\right)\\ &\quad\times\left(\left|\psi_n^{(0)}\right\rangle + \lambda\left|\psi_n^{(1)}\right\rangle + \dots\right)\\ &= E_n^{(2)}\delta_{kn}\\ &= Z_n\left(1 + \lambda^2\left\langle\psi_n^{(1)}\middle|\psi_n^{(1)}\right\rangle + \mathcal{O}\left(\lambda^3\right)\right)\end{aligned} \tag{1.11}$$

$$Z_n^{1/2} = 1 - \frac{\lambda^2}{2} \left\langle \psi_n^{(1)} \middle| \psi_n^{(1)} \right\rangle \mathcal{O}\left(\lambda^3\right) \tag{1.12}$$

$$\Rightarrow \left|\psi_n^{(2)}\right\rangle$$

$$= \sum_{k\neq n} \sum_{m\neq n} \left|\psi_k^{(0)}\right\rangle \left[\frac{V_{km} - V_{mn}}{\left(E_n^{(0)} - E_k^{(0)}\right)\left(E_m^{(0)} - E_n^{(0)}\right)} \right. \tag{1.13}$$

$$\left. - \frac{V_{kn}V_{nn}}{\left(E_n^{(0)} - E_n^{(0)}\right)} \right] - \frac{1}{2} \sum_{k\neq n} \left|\psi_n^{(0)}\right\rangle \frac{\left|V_{kn}^2\right|}{\left(E_n^{(0)} - E_k^{(0)}\right)}$$

1.2 Time-independent perturbation theory: degenerate case

Assume $E_n^{(0)}$ is α-fold degenerate i.e.

$$H_0 \left|\psi_{n_i}^{(0)}\right\rangle = E_n^{(0)} \left|\psi_n^{(0)}\right\rangle, \quad 1 \leq i \leq \alpha \tag{1.14}$$

fix

$$\left\langle \psi_{n_i}^{(0)} \middle| \psi_{n_j}^{(0)} \right\rangle = \delta_{ij} \tag{1.15}$$

Any linear combination

$$\left|\chi_n^{(0)}\right\rangle = \sum_{i=1}^{\alpha} c_{n_i} \left|\psi_{n_i}^{(0)}\right\rangle \tag{1.16}$$

is an eigenstate of H_0 with evaluation $E_n^{(0)}$ Typically V “lifts”

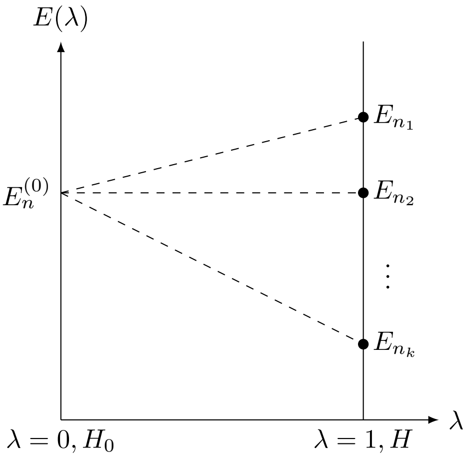

Figure 1.1

degeneracy at least partially since often

$$[H_0, V] \neq 0 \tag{1.17}$$

Pick one of the evals E_{n_k} with

$$H \left|\psi_{n_k}\right\rangle = E_{n_k} \left|\psi_{n_k}\right\rangle \tag{1.18}$$

for $\lambda \to 0$: $E_{n_k} \to E_n^{(0)}$ and

$$\begin{aligned} |\psi_{n_k}\rangle &\to |\chi_{n_k}(0)\rangle \\ &= \sum_{i=1}^{\alpha} \underbrace{c_{n_k i} \left|\psi_{n_i}^{(0)}\right\rangle}_{\substack{\text{some lin} \\ \text{comb}}} \end{aligned} \tag{1.19}$$

have to find "good" linear combination, i.e. coeff $c_{n_k i}$. Main idea as before:

$$|\psi_{n_k}\rangle = \left|\chi_{n_k}^{(0)}\right\rangle + \lambda \left|\psi_{n_k}^{(1)}\right\rangle \tag{1.20}$$

$$0 = \left(H_0 - E_n^{(0)}\right) \left|\psi_{n_k}^{(1)}\right\rangle + \left(V - E_{n_k}^{(1)}\right) \left|\chi_{n_k}^{(1)}\right\rangle \tag{1.21}$$

with

$$\left|\psi_{n_k}^{(1)}\right\rangle = \sum_{\ell=1}^{\dim(H_0)} a_{n_\ell} \left|\psi_\ell^{(0)}\right\rangle \tag{1.22}$$

and

$$\sum_{i\,=1}^{\alpha} c_{n_k i} \left|\psi_{n_i}^{(0)}\right\rangle \tag{1.23}$$

multiply by $\left\langle \psi_{n_j}^{(0)} \right|$.

$$\sum_{\ell=1}^{\dim H_0} \underbrace{\left(E_\ell^{(0)} - E_n^{(0)}\right)}_{=0 \text{ for } n=\ell} a_{n\ell} \underbrace{\left\langle \psi_{n_j}^{(0)} \middle| \psi_\ell^{(0)} \right\rangle}_{=0 \text{ for } n\neq\ell} + \sum_{i=1}^{\alpha} c_{n_k i} \left(\left\langle \psi_{n_j}^{(0)} \middle| V \middle| \psi_{n_i}^{(0)} \right\rangle \right.$$
$$\left. - E_{n_k}^{(1)} \underbrace{\left\langle \psi_{n_j}^{(0)} \middle| \psi_{n_i}^{(0)} \right\rangle}_{V_{ji}} - E_{n_k}^{(1)} \underbrace{\left\langle \psi_{n_j}^{(0)} \middle| \psi_{n_i}^{(0)} \right\rangle}_{\delta_{ij}} \right) \tag{1.24}$$

→ solve

$$\det \begin{pmatrix} V_{11} - E_{n_k}^{(1)} & V_{12} & \dots & V_{1\alpha} \\ V_{21} & V_{22} - E_{n_k}^{(1)} & \dots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ V_{\alpha 1} & \dots & \dots & V_{\alpha\alpha} - E_{n_k}^{(1)} \end{pmatrix} = 0 \tag{1.25}$$

→ eq. of order $\propto$ in $E_{n_k}^{(1)}$
→ α solutions

1.2.1 easy way out (sometimes)

if $V_{ij} = 0$ for $i \neq j$ problem already solved
→ α solutions are

$$E_{n_i}^{(1)} = \left\langle \psi_i^{(0)} \middle| V \middle| \psi_i^{(0)} \right\rangle \tag{1.26}$$

Note: if $\exists$ operator A with

$$[A, V] = 0 \tag{1.27a}$$

and

$$A \left|\psi_{n_i}^{(0)}\right\rangle = a_{n_i} \left|\psi_{n_i}^{(0)}\right\rangle , \tag{1.27b}$$

with

$$a_{n_i} \neq a_{n_k}, \quad \text{for } k \neq i \tag{1.27c}$$

then these $\left|\psi_{n_i}^{(0)}\right\rangle$ are "good" eigenstates

Proof:

$$\begin{aligned} \left\langle\psi_{n_i}^{(0)}\right| [A, V] \left|\psi_{n_k}^{(0)}\right\rangle &= 0 \\ &= \underbrace{(a_{n_i} - a_{n_k})}_{\neq 0} \underbrace{\left\langle\psi_{n_i}^{(0)}\right| V \left|\psi_{n_k}^{(0)}\right\rangle}_{V_{ik}} \end{aligned} \tag{1.28a}$$

$$\begin{aligned} &\Rightarrow V_{ik} \\ &= 0 \end{aligned} \tag{1.28b}$$