Perturbation theory

Quantum mechanics 2 - Lecture 2

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1. Time-independent nondegenerate perturbation theory
   - General formulation
   - First-order theory
   - Second-order theory
2. Time-independent degenerate perturbation theory
   - General formulation
   - Example: Two-dimensional harmonic oscilator
3. Time-dependent perturbation theory
4. Literature

Contents

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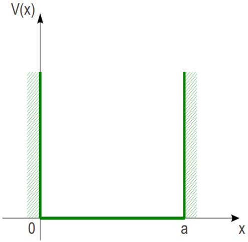
Do you remember this?



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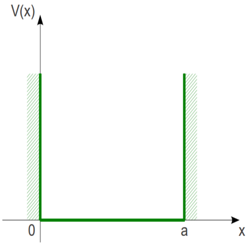
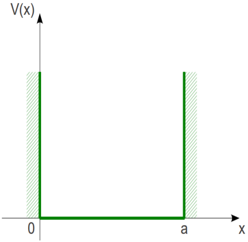


$$H^0\psi_n^0 = E_n^0\psi_n^0$$

$$\langle\psi_n^0|\psi_m^0\rangle = \delta_{nm} \quad \rightarrow \quad \text{complete set}$$

Now, let us kick the potential bottom a little...



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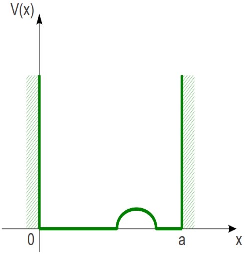
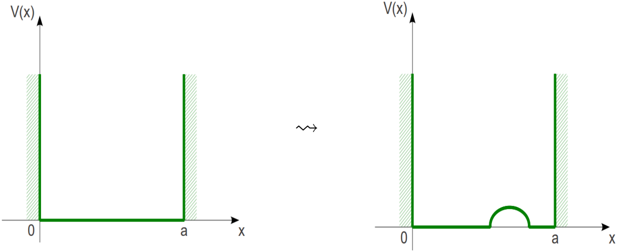


Now, let us kick the potential bottom a little...



What we'd like to solve now is...

$$H\psi_n = E_n\psi_n$$

A question

Does anyone have an idea how?

Assume

$$H = H^0 + \lambda H'$$

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- unperturbed Hamiltonian
- perturbation Hamiltonian
- small parameter

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Name	Description	Hamiltonian
L-S coupling	Coupling between orbital and spin angular momentum in a one-electron atom	$H = H_0 + f(r)\vec{L}\cdot\vec{S}$ $H' = f(r)\vec{L}\cdot\vec{S}$ $H_0 = p^2/2m - Ze^2/r$
Stark effect	One-electron atom in a constant uniform electric field $\vec{\mathbb{E}} = \vec{e_z}\mathbb{E}_0$	$H = H_0 + e\mathbb{E}_0 z$ $H' = e\mathbb{E}_0 z$ $H_0 = p^2/2m - Ze^2/r$
Zeeman effect	One-electron atom in a constant uniform magnetic field $\vec{\mathbb{B}}$	$H = H_0 + (e/2mc)\vec{J}\cdot\vec{\mathbb{B}}$ $H' = (e/2mc)\vec{J}\cdot\vec{\mathbb{B}}$ $H_0 = p^2/2m - Ze^2/r$
Anharmonic oscilator	Spring with nonlinear restoring force	$H = H_0 + K'x^4$ $H' = K'x^4$ $H_0 = p^2/2m + 1/2Kx^2$
Nearly free electron model	Electron in a periodic lattice	$H = H_0 + V(x)$ $V(x) = \sum_n V_n exp[i(2\pi nx/a)]$ $H_0 = p^2/2m$

Assume

- H' is small compared to H_0
- eigenstates and eigenvalues of H do not differ much from those of H_0
- eigenstates and eigenvalues of H_0 are known

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expand

$$\psi_n = \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots ,$$
$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots$$

Assume

- ♯ H' is small compared to H_0
- ♯ eigenstates and eigenvalues of H do not differ much from those of H_0
- ♯ eigenstates and eigenvalues of H_0 are known

expand

$$\begin{aligned} \psi_n &= \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots\,, \\ E_n &= E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \end{aligned}$$

and sort

$$\begin{aligned} (\lambda^0)\dots \quad & H^0\psi_n^0 &= E_n^0\psi_n^0\,, \\ (\lambda^1)\dots \quad & H^0\psi_n^1 + H'\psi_n^0 &= E_n^0\psi_n^1 + E_n^1\psi_n^0\,, \\ (\lambda^2)\dots \quad & H^0\psi_n^2 + H'\psi_n^1 &= E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0\,, \\ & & \vdots \end{aligned}$$

Making $\langle\psi_n^0| \Big/ (\lambda^1)$ and using the normalization property of ψ_n^0, we get

First-order correction to the energy

$$E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle$$

For calculation details, see Refs [2], [3] and [4].

First-order correction to the energy

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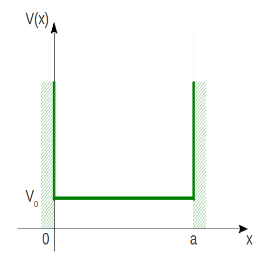
Example 1

Find the first-order corrections to the energy of a particle in a infinite square well if the "floor" of the well is raised by an constant value V_0.



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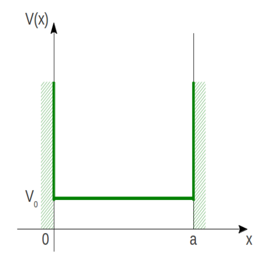

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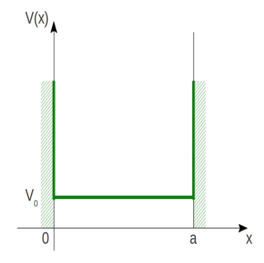

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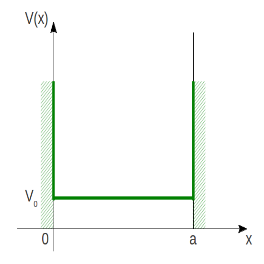

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  $E_n^1 = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \langle \psi_n^0 | \psi_n^0 \rangle = V_0$

  $\Rightarrow$ corrected energy levels: $E_n \approx E_n^0 + V_0$

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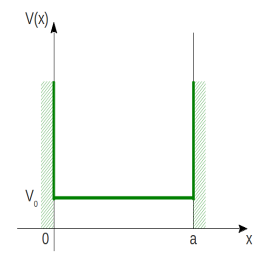
- Compare this result with an exact solution
  $\Rightarrow$ for a *constant* perturbation all the higher corrections vanish



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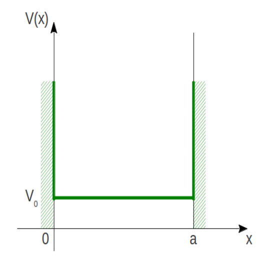

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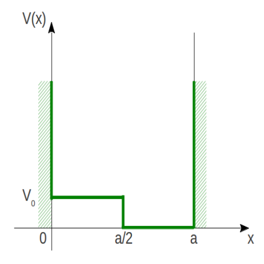
Example 1 (cont.)

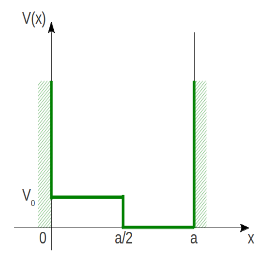
Now, cut the perturbation to only a half-way across the well



Example 1 (cont.)

Now, cut the perturbation to only a half-way across the well

$$\Rightarrow \quad E_n^1 = \frac{2V_0}{a}\int_0^{a/2} \sin^2\left(\frac{n\pi}{a}x\right)\mathrm{d}x = \frac{V_0}{2}$$



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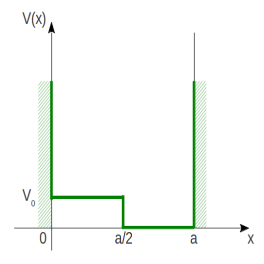
HW. Compare this result with an exact one.



Now we seek the first-order correction to the wave function. (λ^1) and $\psi_n^1 = \sum_{m \neq n} c_{mn} \psi_m^0$ give

First-order correction to the wave function

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0$$

For calculation details, see Refs [2], [3] and [4].

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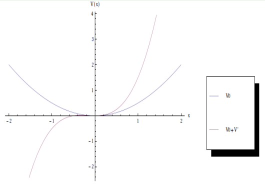
In conclusion

First-order perturbation theory gives:

- often accurate energies
- poor wave functions

Example 2

Compute the first-order corrections for a harmonic oscilator with applied small perturbation $W = ax^3$.



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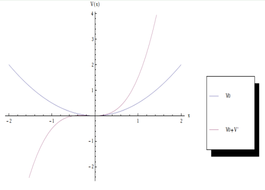
- Hamiltonian: $H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x} + \frac{1}{2}kx^2 + ax^3$



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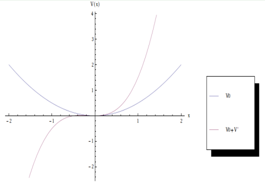

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- H^0 eigenfunctions:

$$\psi_n^0(x) = \sqrt{\frac{1}{2^n n!}\sqrt{\frac{\alpha}{\pi}}} e^{-\frac{\alpha x^2}{2}} H_n(x\sqrt{\alpha})$$

Don't forget...

n	$H_n(\xi)$
0	1
1	2ξ
2	$4\xi^2 - 2$
3	$8\xi^3 - 12\xi$
4	$16\xi^4 - 48\xi^2 + 12$
5	$32\xi^5 - 160\xi^3 + 120\xi$

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$\leftrightarrow$ for $m = n \pm 2k$, $k \in \mathbb{Z}$ these are zero

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$\leftrightarrow$ for $m = n \pm 2k\,,\, k \in \mathbb{Z}$ these are zero

$\Rightarrow$ so, we'll, for example, take only these: $m = n+3, n+1, n-1, n-3$

Don't forget...

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Compute the first-order corrections for a harmonic oscillator with applied small perturbation $W = ax^3$.

$$\langle n|ax^3|n+3\rangle = a\cdot\sqrt{\frac{(n+1)(n+2)(n+3)}{(2\alpha)^3}}$$

$$\langle n|ax^3|n+1\rangle = 3a\cdot\sqrt{\frac{(n+1)^3}{(2\alpha)^3}}$$

$$\langle n|ax^3|n-1\rangle = 3a\cdot\sqrt{\frac{n^3}{(2\alpha)^3}}$$

$$\langle n|ax^3|n-3\rangle = a\cdot\sqrt{\frac{n(n-1)(n-2)}{(2\alpha)^3}}$$

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Energy differences

m	$E_n - E_m$
n+3	$-3\hbar\omega$
n+1	$-\hbar\omega$
n-1	$\hbar\omega$
n-3	$3\hbar\omega$

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Compute the first-order corrections for a harmonic oscilator with applied small perturbation $W = ax^3$.

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n+3	$-3\hbar\omega$
n+1	$-\hbar\omega$
n-1	$\hbar\omega$
n-3	$3\hbar\omega$

$$\Rightarrow \psi_n^1 = \frac{a}{2\hbar\omega\alpha}\left[\frac{1}{3}\sqrt{\frac{n(n-1)(n-2)}{2\alpha}}\psi_{n-3}^0 + 3n\sqrt{\frac{n}{2\alpha}}\psi_{n-1}^0 - 3(n+1)\sqrt{\frac{n+1}{2\alpha}}\psi_{n+1}^0 - \frac{1}{3}\sqrt{\frac{(n+1)(n+2)(n+3)}{2\alpha}}\psi_{n+3}^0\right]$$

Making $\langle\psi_n^0|\Big/(\lambda^2)$, using the normalization property of ψ_n^0 and orthogonality between ψ_n^0 and ψ_n^1, we get

Second-order correction to the energy

$$E_n^2 = \sum_{m\neq n} \frac{|\langle\psi_m^0|H'|\psi_n^0\rangle|^2}{E_n^0 - E_m^0}$$

For calculation details, see Refs [2], [3] and [4].

Now we seek the second-order correction to the wave function.
(λ^2) and $\psi_n^1 = \sum_{m \neq n} c_{mn} \psi_m^0$ give

Second-order correction to the wave function

$$\psi_n^2 = \sum_{m\neq n} \left[-\frac{\langle \psi_n^0 | H' | \psi_n^0 \rangle \langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)^2} + \sum_{k\neq n} \frac{\langle \psi_m^0 | H' | \psi_k^0 \rangle \langle \psi_k^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)(E_n^0 - E_k^0)} \right] \psi_m^0$$

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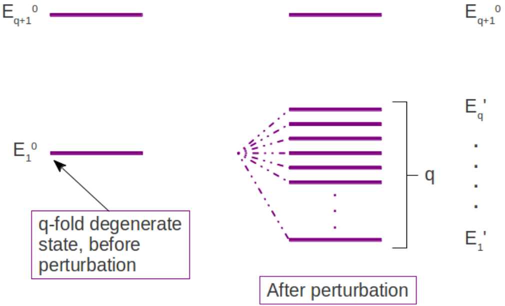
Symmetry

Degeneracy

Perturbation

Symmetry | Degeneracy | Perturbation



A question

What's wrong with

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}\,,\; m, n \leq q$$

if unperturbed eigenstates are degenerate $E_1^0 = E_2^0 = \cdots = E_q^0$?

$H = H_0 + H'$
$H_0 \psi_n^0 = E_n^0 \psi_n^0$
E_1^0 q-fold degenerate

(1) →

Construct
$$\varphi_n = \sum_{i=1}^{q} a_{nm} \psi_m^0$$
which diagonalizes submatrix of H':
$\langle \varphi_n | H' | \varphi_k \rangle = E' \delta_{nk}$

(2) →

$$\sum^{q} (H' - E'\delta) a = 0$$

(3) →

$\det \left| H' - E_n' I \right| = 0$

(4) →

$E_1', E_2', \ldots, E_q'$

(5) → back to $\sum^{q} (H' - E'\delta) a = 0$

(6) →

$\{a_{ni}\}$

(7) →

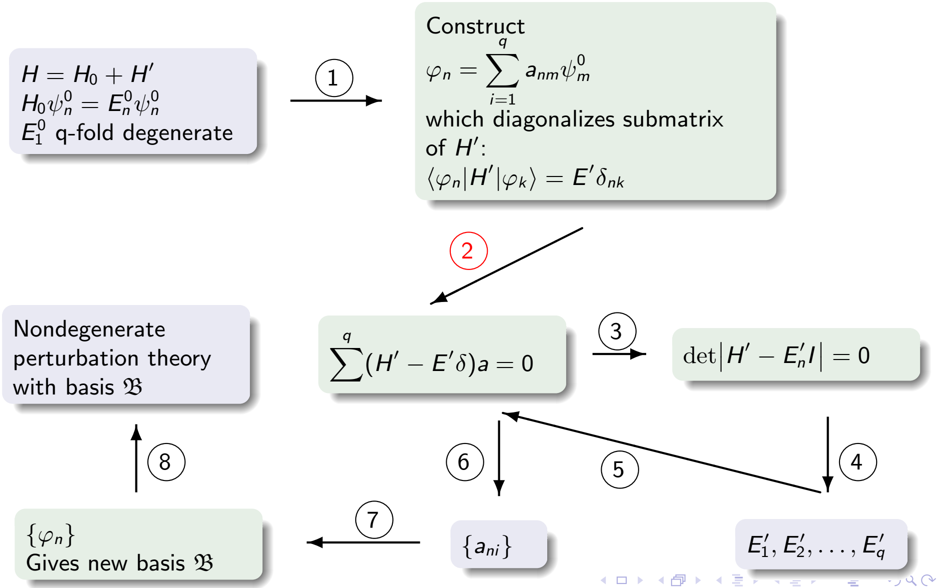
$\{\varphi_n\}$
Gives new basis $\mathfrak{B}$

(8) →

Nondegenerate perturbation theory with basis $\mathfrak{B}$

Matrix H' in basis $\mathfrak{B}$

$$H' = \left(\begin{array}{cccc|cc} H'_{11} & & & & H'_{1,q+1} & \cdots \\ & \ddots & & 0 & & \\ & & H'_{q/2,q/2} & & & \\ 0 & & & \ddots & & \\ & & & H'_{qq} & & \\ \hline H'_{q+1,1} & & & & & \\ \vdots & & & & & \end{array}\right)$$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$E_1', E_2', \ldots, E_q'$
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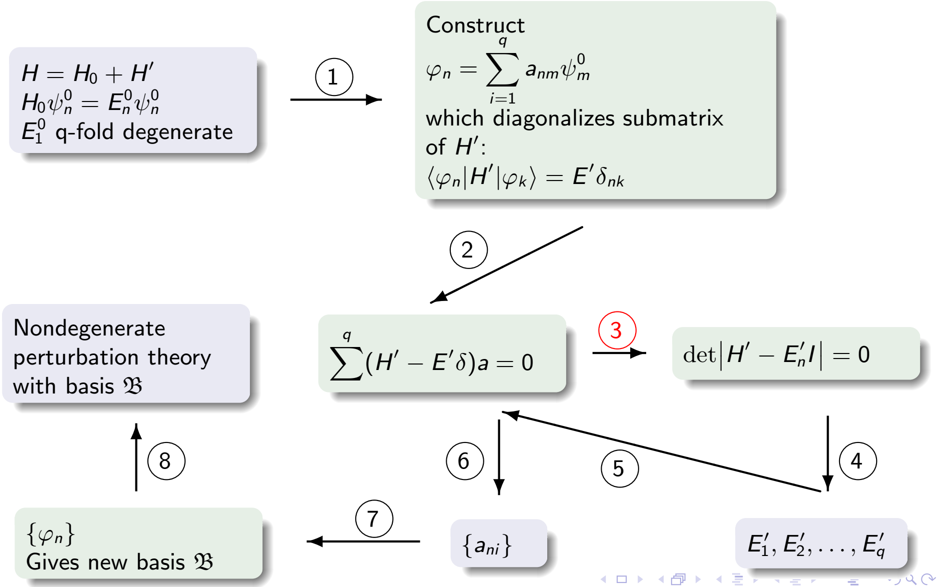
For $n = 1$, $\sum_{m=1}^{q}(H'_{pm} - E'_n\delta_{pm})a_{nm} = 0$ appear as

$$\begin{pmatrix} H'_{11} - E'_1 & H'_{12} & H'_{13} & \dots & H'_{1q} \\ H'_{21} & H'_{22} - E'_1 & H'_{23} & \dots & H'_{2q} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ H'_{q1} \end{pmatrix} \begin{pmatrix} a_{11} \\ a_{12} \\ \vdots \\ a_{1q} \end{pmatrix} = 0$$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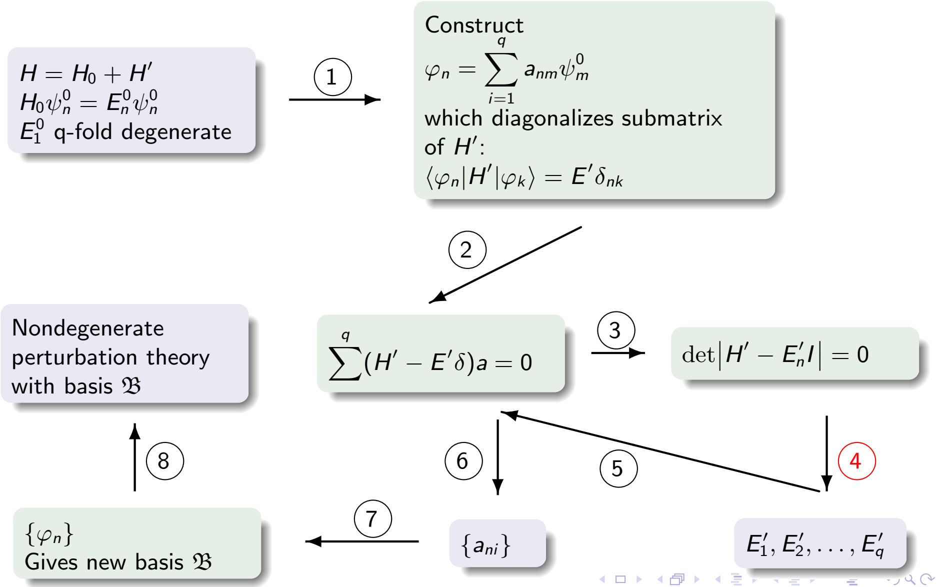
The q roots of *secular equation* $\det\left|H' - E_n' I\right| = 0$ are the diagonal elements of the submatrix of H'.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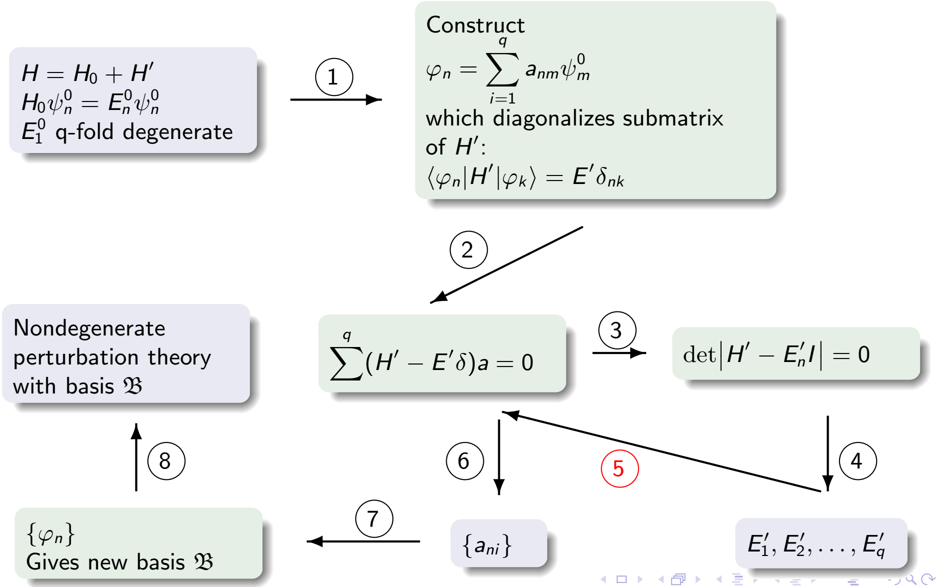
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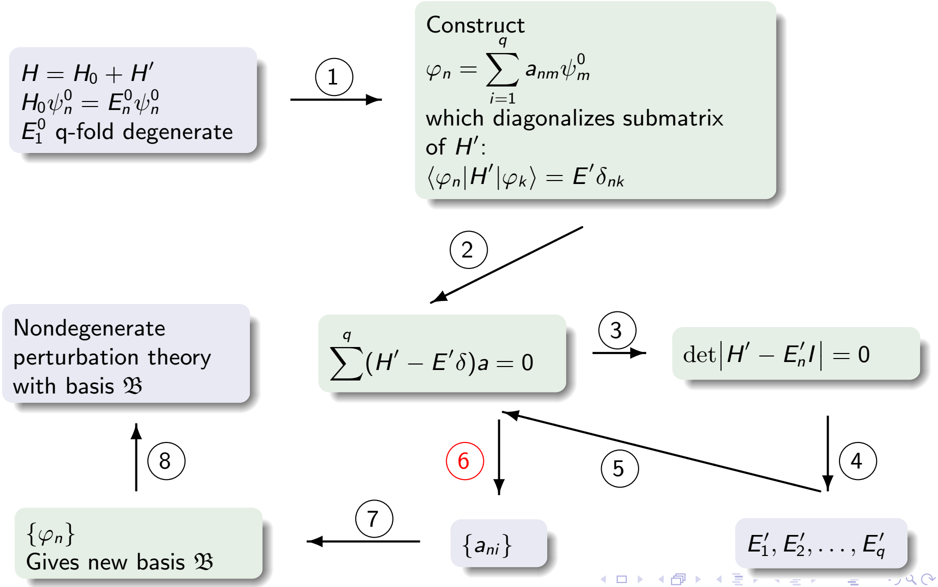
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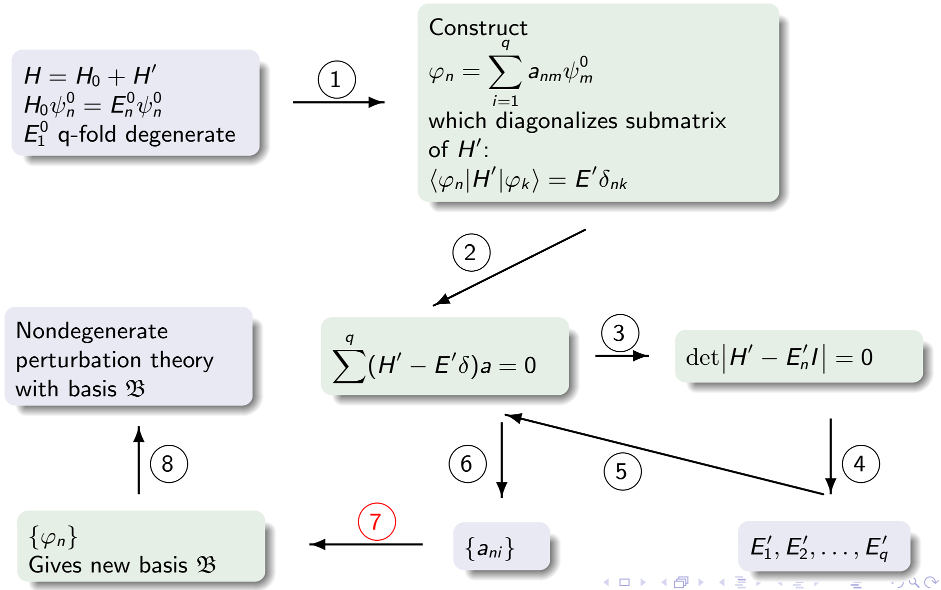
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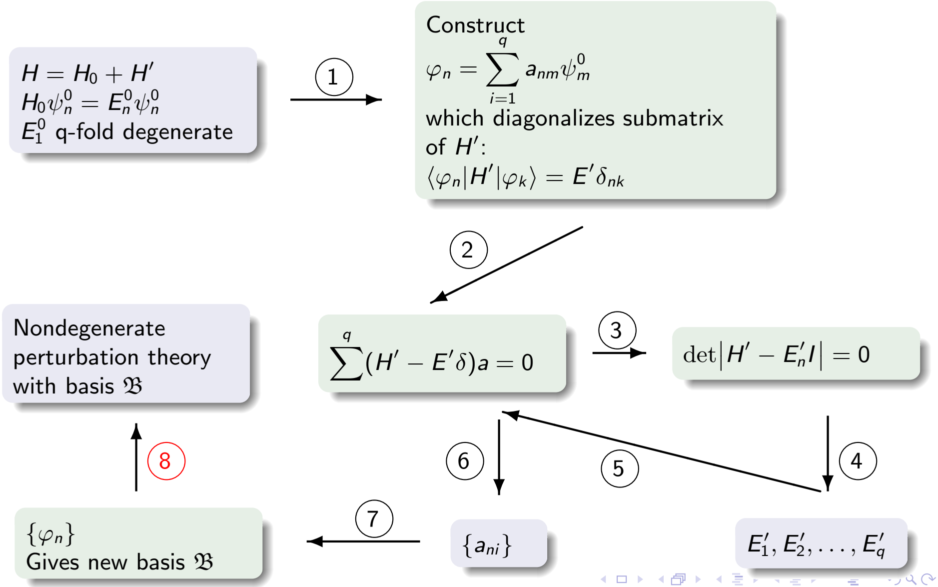
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$$
\begin{array}{llllll}
\psi_n = \varphi_n & +\lambda\varphi_n^1 & +\lambda^2\varphi_n^2 & +\dots & n \leq q & \\
\psi_n = \psi_n^0 & +\lambda\psi_n^1 & +\lambda^2\psi_n^2 & +\dots & n > q & \\
E_n = E_n^0 & +\lambda E_n'^1 & +\lambda^2 E_n'^2 & +\dots & n \leq q & (E_1^0 = \cdots = E_q^0)
\end{array}
$$

$$
\begin{aligned}
E_n &= E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots && n > q \\
E_n' &= \langle \varphi_n | H' | \varphi_n \rangle && n \leq q \\
E_n^1 &= \langle \psi_n^0 | H' | \psi_n^0 \rangle && n > q
\end{aligned}
$$

$$\begin{array}{lllll} \psi_n = \varphi_n & +\lambda\varphi_n^1 & +\lambda^2\varphi_n^2 & +\dots & n \leq q \\ \psi_n = \psi_n^0 & +\lambda\psi_n^1 & +\lambda^2\psi_n^2 & +\dots & n > q \\ E_n = E_n^0 & +\lambda E_n'^1 & +\lambda^2 E_n'^2 & +\dots & n \leq q \quad (E_1^0 = \cdots = E_q^0) \end{array}$$

$$\begin{array}{lll} E_n & = & E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \qquad n > q \\ E_n' & = & \langle\varphi_n|H'|\varphi_n\rangle \qquad n \leq q \\ E_n^1 & = & \langle\psi_n^0|H'|\psi_n^0\rangle \qquad n > q \end{array}$$

So, what do we get from degenerate perturbation theory:

- 1st-order energy corrections
- corrected w.f. (with nondegenerate states they serve as a basis for higher-order calculations)

- Two-dimensional harmonic oscilator Hamiltonian:

$$H_0 = \frac{p_x^2 + p_y^2}{2m} + \frac{K}{2}(x^2 + y^2)$$

$$\psi_{np} = \varphi_n(x)\varphi_p(y) \rightarrowtail |np\rangle$$

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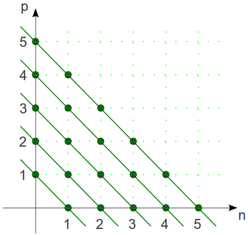
- $E_{np} = \hbar\omega(n + p + 1)$ is $(n + p + 1)$-fold degenerate. What's the degeneracy of $|01\rangle$ state?



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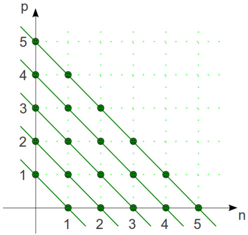
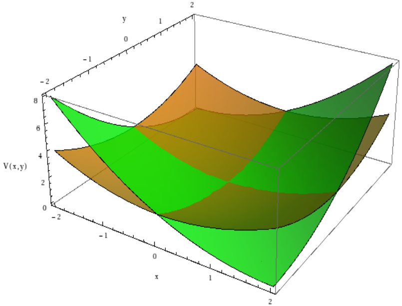


Now, turn on the perturbation: $H' = K'xy$



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$$\begin{aligned} \varphi_1 &= a\psi_{10} + b\psi_{01} \\ \varphi_2 &= a'\psi_{10} + b'\psi_{01} \end{aligned}$$

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- calculate the elements of submatrix of H' in the basis $\{\psi_{10}, \psi_{01}\}$

$$H' = K' \begin{pmatrix} \langle 10|xy|10\rangle & \langle 10|xy|01\rangle \\ \langle 01|xy|10\rangle & \langle 01|xy|01\rangle \end{pmatrix} = \mathbb{E} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\mathbb{E} = \frac{K'}{2\beta^2}\,,\ \beta^2 = \frac{m\omega_0}{\hbar}$$

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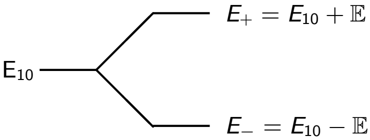
- solve the secular equation

$$\begin{vmatrix} -E' & \mathbb{E} \\ \mathbb{E} & -E' \end{vmatrix} = 0 \Rightarrow E' = \pm\mathbb{E}$$



- obtain the new w.f. from

$$\begin{pmatrix} -E' & \mathbb{E} \\ \mathbb{E} & -E' \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0$$

$$\Longrightarrow \quad \begin{array}{l} E' = +\mathbb{E} \rightsquigarrow \varphi_1 = \frac{1}{\sqrt{2}}(\psi_{10} + \psi_{01}) \\ E' = -\mathbb{E} \rightsquigarrow \varphi_2 = \frac{1}{\sqrt{2}}(\psi_{10} - \psi_{01}) \end{array}$$

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HW

How does the threefold-degenerate energy

$$E = 3\hbar\omega_0$$

of the two-dimensional harmonic oscilator separate due to the perturbation

$$H' = K'xy\,?$$

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1. Time-independent nondegenerate perturbation theory
   - General formulation
   - First-order theory
   - Second-order theory
2. Time-independent degenerate perturbation theory
   - General formulation
   - Example: Two-dimensional harmonic oscilator
3. Time-dependent perturbation theory
4. Literature

Problem

If the system is initially in H_0, what is the probability that, after time t, transition to another state (of H_0) occurs?

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Let us assume:

- $H(\vec{r}, t) = H_0(\vec{r}) + \lambda H'(\vec{r}, t)$
- $\psi_n(\vec{r}, t) = \varphi_n(\vec{r}) e^{-i\omega t}$
  $H_0 \varphi_n = E_n^0 \varphi_n$
- $\Psi(\vec{r}, t) = \sum_n c_n(t) \psi_n(\vec{r}, t)\,, \;\; t > 0$

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Can you remember the meaning of these coefficients?

Inserting $\Psi(\vec{r}, t)$ and $c_n(t) = c_n^0 + \lambda c_n^1(t) + \lambda^2 c_n^2(t) + \ldots$ into time-dependent S.E. and factorizing the perturbation Hamiltonian as $H'(\vec{r}, t) = \mathbb{H}'(\vec{r}) f(t)$ gives

Probability that the system has undergone a transition from state ψ_l to state ψ_k at time t

$$P_{l \to k} = P_{lk} = |c_n|^2 = \left| \frac{\mathbb{H}'_{kl}}{\hbar} \right|^2 \left| \int_{-\infty}^{t} e^{i\omega_{kl} t'} f(t') \mathrm{d}t' \right|^2$$

For calculation details, see Refs [2] and [3].

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