Professor (this week)

Dr. Andreas Shalchi
Office: 219 Allen Building
Email: Andreas.Shalchi@umanitoba.ca

Best way to reach me!

Classes:
Monday & Wednesday 9:30-10:20,
527 Buller

Office Hours:
Monday 10:30-11:30

Course Website:
www2.physics.umanitoba.ca/u/shalchi/PHYS3386

Time-Independent Perturbation Theory

➢ The Non-Degenerated Case

- Perturbation theory is a very powerful tool used to solve problems in theoretical physics. It is used to find approximative solutions in cases where an exact solution is not possible.

- Assume that we know the exact solution of the original problem

$$\hat{H}_0 \big| n \big\rangle = \epsilon_n \big| n \big\rangle .$$

- Let's assume the new Hamiltonian operator is given by

$$\hat{H} = \hat{H}_0 + \hat{V} .$$

perturbing potential!

- This means we are looking for the solution of

$$\hat{H} \big| \psi_n \big\rangle = E_n \big| \psi_n \big\rangle .$$

- We assume that the perturbing potential $\hat{V}$ is small.

Time-Independent Perturbation Theory

- The Non-Degenerated Case

  - It is convenient to write

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}.$$

  - Here λ is a small parameter.
  - We expand

$$E_n(\lambda) = \epsilon_n + \sum_{\nu=1}^{\infty} \lambda^\nu E_n^{(\nu)},$$

$$|\psi_n(\lambda)\rangle = |n\rangle + \sum_{\nu=1}^{\infty} \lambda^\nu |\psi_n^{(\nu)}\rangle.$$

  - For $\lambda=0$ we find the (exact) unperturbed case.
  - By setting $\lambda=1$ we find the solution to our problem.

Time-Independent Perturbation Theory

➢ The Non-Degenerated Case

- We can write

$$\hat{H}|\psi_n\rangle = (\hat{H}_0 + \lambda\hat{V})|\psi_n\rangle = E_n|\psi_n\rangle.$$

- With our two expansions this becomes

$$\left(\hat{H}_0 + \lambda\hat{V}\right)\left(|n\rangle + \sum_\nu \lambda^\nu |\psi_n^{(\nu)}\rangle\right)$$

$$= \left(\epsilon_n + \sum_\nu \lambda^\nu E_n^{(\nu)}\right)\left(|n\rangle + \sum_\nu \lambda^\nu |\psi_n^{(\nu)}\rangle\right).$$

- After factoring this out, we obtain

$$\hat{H}_0|n\rangle + \sum_\nu \lambda^\nu \hat{H}_0|\psi_n^{(\nu)}\rangle + \lambda\hat{V}|n\rangle + \sum_\nu \lambda^{\nu+1}\hat{V}|\psi_n^{(\nu)}\rangle$$

$$= \epsilon_n|n\rangle + \epsilon_n \sum_\nu \lambda^\nu |\psi_n^{(\nu)}\rangle + \sum_\nu \lambda^\nu E_n^{(\nu)}|n\rangle + \sum_{\nu,\mu} \lambda^{\nu+\mu} E_n^{(\nu)}|\psi_n^{(\mu)}\rangle.$$

Remember:

$$E_n = \epsilon_n + \sum_\nu \lambda^\nu E_n^{(\nu)}$$

$$|\psi_n\rangle = |n\rangle + \sum_\nu \lambda^\nu |\psi_n^{(\nu)}\rangle$$

Time-Independent Perturbation Theory

- The Non-Degenerated Case
  - We derived

$$\hat{H}_0|n\rangle + \sum_{\nu=1}^{\infty}\lambda^{\nu}\hat{H}_0|\psi_n^{(\nu)}\rangle + \lambda\hat{V}|n\rangle + \sum_{\nu=1}^{\infty}\lambda^{\nu+1}\hat{V}|\psi_n^{(\nu)}\rangle$$

$$= \quad \epsilon_n|n\rangle + \epsilon_n\sum_{\nu=1}^{\infty}\lambda^{\nu}|\psi_n^{(\nu)}\rangle + \sum_{\nu=1}^{\infty}\lambda^{\nu}E_n^{(\nu)}|n\rangle + \sum_{\nu,\mu=1}^{\infty}\lambda^{\nu+\mu}E_n^{(\nu)}|\psi_n^{(\mu)}\rangle.$$

  - From this we can read off the terms zeroth order in λ:

$$\hat{H}_0|n\rangle = \epsilon_n|n\rangle.$$

  - First order in λ we have:

$$\hat{H}_0|\psi_n^{(1)}\rangle + \hat{V}|n\rangle = \epsilon_n|\psi_n^{(1)}\rangle + E_n^{(1)}|n\rangle.$$

  - And second order in λ we obtain

$$\hat{H}_0|\psi_n^{(2)}\rangle + \hat{V}|\psi_n^{(1)}\rangle = \epsilon_n|\psi_n^{(2)}\rangle + E_n^{(2)}|n\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle.$$

Time-Independent Perturbation Theory

- <u>The Non-Degenerated Case</u>

  - In the same way we could obtain higher order terms but in this course we only do perturbation theory up to second order.
  - Note, the $|n\rangle$ form a <u>complete set</u>. Therefore, we can expand

$$|\psi_n^{(1)}\rangle = \sum_m a_{nm}^{(1)}|m\rangle.$$

  - On the previous slide we found in <u>first order</u>

$$\hat{H}_0|\psi_n^{(1)}\rangle + \hat{V}|n\rangle = \epsilon_n|\psi_n^{(1)}\rangle + E_n^{(1)}|n\rangle.$$

  - With our expansion this becomes

$$\hat{H}_0 \sum_m a_{nm}^{(1)}|m\rangle + \hat{V}|n\rangle = \epsilon_n \sum_m a_{nm}^{(1)}|m\rangle + E_n^{(1)}|n\rangle.$$

Time-Independent Perturbation Theory

- <u>The Non-Degenerated Case</u>
  - The unperturbed Hamiltonian acts on the unperturbed eigenket

$$\sum_m a_{nm}^{(1)} \underbrace{\hat{H}_0 \big| m \big\rangle} + \hat{V} \big| n \big\rangle = \epsilon_n \sum_m a_{nm}^{(1)} \big| m \big\rangle + E_n^{(1)} \big| n \big\rangle.$$

  - We can use the unperturbed eigenvalues therein to obtain

$$\sum_m a_{nm}^{(1)} \epsilon_m \big| m \big\rangle + \hat{V} \big| n \big\rangle = \epsilon_n \sum_m a_{nm}^{(1)} \big| m \big\rangle + E_n^{(1)} \big| n \big\rangle.$$

  - We can easily rearrange this to write

$$\sum_m \left(\epsilon_n - \epsilon_m \right) a_{nm}^{(1)} \big| m \big\rangle + E_n^{(1)} \big| n \big\rangle = \hat{V} \big| n \big\rangle.$$

  - Multiplying this from the left with the unperturbed eigenbra $\big\langle k \big|$ yields

$$\sum_m \left(\epsilon_n - \epsilon_m \right) a_{nm}^{(1)} \big\langle k \big| m \big\rangle + E_n^{(1)} \big\langle k \big| n \big\rangle = \big\langle k \big| \hat{V} \big| n \big\rangle.$$

Time-Independent Perturbation Theory

- The Non-Degenerated Case

  - In the latter equation we use the orthonormality relation

    $$\langle k | m \rangle = \delta_{km}.$$

  - We can easily derive

    $$\sum_m (\epsilon_n - \epsilon_m) a_{nm}^{(1)} \delta_{km} + E_n^{(1)} \delta_{kn} = \langle k | \hat{V} | n \rangle.$$

  - After evaluating the sum we find

    $$(\epsilon_n - \epsilon_k) a_{nk}^{(1)} + E_n^{(1)} \delta_{kn} = \langle k | \hat{V} | n \rangle.$$

  - For the case *k*=*n* this becomes

    $$E_n^{(1)} = \langle n | \hat{V} | n \rangle.$$

  - This is the first important result. These are (first-order) corrections to the energy eigenvalues!

Time-Independent Perturbation Theory

- The Non-Degenerated Case

  - For general k and n we have

$$(\epsilon_n - \epsilon_k) a_{nk}^{(1)} + E_n^{(1)} \delta_{kn} = \langle k | \hat{V} | n \rangle.$$

  - If $n \neq k$ this becomes

$$(\epsilon_n - \epsilon_k) a_{nk}^{(1)} = \langle k | \hat{V} | n \rangle.$$

  - This can easily be rewritten to obtain for the expansion coefficients

$$a_{nk}^{(1)} = \frac{\langle k | \hat{V} | n \rangle}{\epsilon_n - \epsilon_k} \qquad \text{if} \qquad n \neq k.$$

  - Problem: this does not work for

$$\epsilon_n = \epsilon_k \qquad \text{if} \qquad n \neq k.$$

  - This means that we need to discuss the degenerated case separately!

Time-Independent Perturbation Theory

- <u>The Non-Degenerated Case</u>
  - Furthermore, we cannot determine the coeffcients $a_{nn}^{(1)}$!
  - Remember, we have used the expansion

$$|\psi_n^{(1)}\rangle = \sum_m a_{nm}^{(1)} |m\rangle.$$

  - With the obtained coefficients this can be written as

$$|\psi_n^{(1)}\rangle = a_{nn}^{(1)} |n\rangle + \sum_{m \neq n} \frac{\langle m|\hat{V}|n\rangle}{\epsilon_n - \epsilon_m} |m\rangle.$$

  - Up to first order in λ we, therefore, find

$$|\psi_n(\lambda)\rangle = |n\rangle + \lambda a_{nn}^{(1)} |n\rangle + \lambda \sum_{m \neq n} \frac{\langle m|\hat{V}|n\rangle}{\epsilon_n - \epsilon_m} |m\rangle.$$

  - The only quantity therein which is not known is the coefficient $a_{nn}^{(1)}$!

Time-Independent Perturbation Theory

➢ <u>The Non-Degenerated Case</u>

- However, the new (corrected) states need to be normalized

$$\langle \psi_n | \psi_n \rangle = 1.$$

- Therein we use the expansion

$$|\psi_n\rangle = |n\rangle + \lambda a_{nn}^{(1)} |n\rangle + \lambda \sum_{m \neq n} \frac{\langle m|\hat{V}|n\rangle}{\epsilon_n - \epsilon_m} |m\rangle + \mathcal{O}(\lambda^2).$$

- For the needed *bra* we can simply use

$$\langle \psi_n | = \langle n| + \lambda a_{nn}^{(1)*} \langle n| + \lambda \sum_{m \neq n} \frac{\langle m|\hat{V}|n\rangle^*}{\epsilon_n - \epsilon_m} \langle m| + \mathcal{O}(\lambda^2).$$

- Those two formulas can be used in the normalization condition.

Time-Independent Perturbation Theory

- <u>The Non-Degenerated Case</u>

  - Up to first order in λ we find

$$\begin{aligned}\langle\psi_n|\psi_n\rangle &= \langle n|n\rangle + \lambda a_{nn}^{(1)}\langle n|n\rangle + \lambda a_{nn}^{(1)*}\langle n|n\rangle \\ &+ \lambda\sum_{m\neq n}\frac{\langle m|\hat{V}|n\rangle}{\epsilon_n-\epsilon_m}\underbrace{\langle n|m\rangle}_{=0} + \lambda\sum_{m\neq n}\frac{\langle m|\hat{V}|n\rangle^*}{\epsilon_n-\epsilon_m}\underbrace{\langle m|n\rangle}_{=0} + \mathcal{O}(\lambda^2).\end{aligned}$$

  - This can be simplified significantly by using that the unperturbed states are orthonormal

$$\langle n|m\rangle = \delta_{nm}.$$

  - Therewith, we obtain

$$1 + \lambda a_{nn}^{(1)} + \lambda a_{nn}^{(1)*} + \mathcal{O}(\lambda^2) = 1.$$

Time-Independent Perturbation Theory

- <u>The Non-Degenerated Case</u>
  - We derived

$$1 + \lambda a_{nn}^{(1)} + \lambda a_{nn}^{(1)*} + \mathcal{O}\left(\lambda^2\right) = 1.$$

  - This means that up to the considered order

$$a_{nn}^{(1)} + a_{nn}^{(1)*} = 0.$$

  - We conclude that the coefficients $a_{nn}^{(1)}$ are imaginary.
  - Therefore, we can write

$$a_{nn}^{(1)} = i\delta \qquad \text{where } \delta \text{ is real.}$$

  - We can use this result in our expansion

$$\left|\psi_n\right\rangle = \left|n\right\rangle + \lambda a_{nn}^{(1)}\left|n\right\rangle + \lambda \sum_{m \neq n} \frac{\left\langle m\middle|\hat{V}\middle|n\right\rangle}{\epsilon_n - \epsilon_m}\left|m\right\rangle + \mathcal{O}\left(\lambda^2\right).$$

Time-Independent Perturbation Theory

- The Non-Degenerated Case
  - We find

$$|\psi_n\rangle = \big(1 + i\lambda\delta\big)|n\rangle + \lambda \sum_{m\neq n} \frac{\langle m|\hat{V}|n\rangle}{\epsilon_n - \epsilon_m}|m\rangle + \mathcal{O}\big(\lambda^2\big).$$

  - Furthermore, we can write

$$1 + i\lambda\delta = e^{i\lambda\delta} + \mathcal{O}\big(\lambda^2\big).$$

  - We obtain

$$|\psi_n\rangle = e^{i\lambda\delta}|n\rangle + \lambda \sum_{m\neq n} \frac{\langle m|\hat{V}|n\rangle}{\epsilon_n - \epsilon_m}|m\rangle + \mathcal{O}\big(\lambda^2\big).$$

  - However, multiplying a state with a phase does not change the physics.

Time-Independent Perturbation Theory

- <u>The Non-Degenerated Case</u>
  - Therefore, we can set

    $$\delta = 0.$$

  - This corresponds to

    $$a_{nn}^{(1)} = 0.$$

  - Therewith our expansion becomes

    $$\left|\psi_n^{(1)}\right\rangle = \sum_{m \neq n} \frac{\langle m|\hat{V}|n\rangle}{\epsilon_n - \epsilon_m} |m\rangle.$$

  - The corrections to energy are

    $$E_n^{(1)} = \langle n|\hat{V}|n\rangle.$$

First-order perturbation theory!

Time-Independent Perturbation Theory

➢ The Non-Degenerated Case

- We now determine the second-order corrections to the energies.
- Previously we have derived the relation

$$\hat{H}_0 \big|\psi_n^{(2)}\big\rangle + \hat{V}\big|\psi_n^{(1)}\big\rangle = E_n^{(2)}\big|n\big\rangle + \epsilon_n\big|\psi_n^{(2)}\big\rangle + E_n^{(1)}\big|\psi_n^{(1)}\big\rangle.$$

- Therein we expand

$$\big|\psi_n^{(1)}\big\rangle = \sum_m a_{nm}^{(1)}\big|m\big\rangle \qquad \text{and} \qquad \big|\psi_n^{(2)}\big\rangle = \sum_m a_{nm}^{(2)}\big|m\big\rangle.$$

- Using this in our formula above yields

$$\begin{aligned} & \hat{H}_0 \sum_m a_{nm}^{(2)}\big|m\big\rangle + \hat{V}\sum_m a_{nm}^{(1)}\big|m\big\rangle \\ = \quad & E_n^{(2)}\big|n\big\rangle + \epsilon_n \sum_m a_{nm}^{(2)}\big|m\big\rangle + E_n^{(1)}\sum_m a_{nm}^{(1)}\big|m\big\rangle. \end{aligned}$$

Time-Independent Perturbation Theory

➢ <u>The Non-Degenerated Case</u>

- We derived

$$\hat{H}_0 \sum_m a_{nm}^{(2)} |m\rangle + \hat{V} \sum_m a_{nm}^{(1)} |m\rangle$$

$$= \quad E_n^{(2)} |n\rangle + \epsilon_n \sum_m a_{nm}^{(2)} |m\rangle + E_n^{(1)} \sum_m a_{nm}^{(1)} |m\rangle.$$

- First we can use the unperturbed eigenvalue equation.
- Thereafter we multiply this equation from the left with $\langle n|$ to obtain

$$\sum_m \epsilon_m a_{nm}^{(2)} \underbrace{\langle n|m\rangle} + \sum_m a_{nm}^{(1)} \langle n|\hat{V}|m\rangle$$

$$= \quad E_n^{(2)} \underbrace{\langle n|n\rangle} + \epsilon_n \sum_m a_{nm}^{(2)} \underbrace{\langle n|m\rangle} + E_n^{(1)} \sum_m a_{nm}^{(1)} \underbrace{\langle n|m\rangle}.$$

- Therein we use orthonormality of the unperturbed states.

Time-Independent Perturbation Theory

➢ <u>The Non-Degenerated Case</u>

- We find

$$\sum_m \epsilon_m a_{nm}^{(2)} \delta_{nm} + \sum_m a_{nm}^{(1)} \langle n|\hat{V}|m\rangle$$

$$= \quad E_n^{(2)} + \epsilon_n \sum_m a_{nm}^{(2)} \delta_{nm} + E_n^{(1)} \sum_m a_{nm}^{(1)} \delta_{nm}.$$

- The sums can easily be evaluated to get

$$\cancel{\epsilon_n a_{nn}^{(2)}} + \sum_m a_{nm}^{(1)} \langle n|\hat{V}|m\rangle = E_n^{(2)} + \cancel{\epsilon_n a_{nn}^{(2)}} + E_n^{(1)} a_{nn}^{(1)}.$$

- After rearranging this becomes

$$E_n^{(2)} = \sum_m a_{nm}^{(1)} \langle n|\hat{V}|m\rangle - a_{nn}^{(1)} E_n^{(1)}.$$

sum is over all m and contains the case $m=n$.

Time-Independent Perturbation Theory

- The Non-Degenerated Case
  - In the latter result we can use

$$E_n^{(1)} = \langle n|\hat{V}|n\rangle \quad \text{and} \quad a_{nm}^{(1)} = \frac{\langle m|\hat{V}|n\rangle}{\epsilon_n - \epsilon_m} \quad \text{if} \quad n \neq m.$$

  - Therewith, our formula turns into

$$\begin{aligned} E_n^{(2)} &= \sum_m a_{nm}^{(1)} \langle n|\hat{V}|m\rangle - \underbrace{a_{nn}^{(1)} E_n^{(1)}}_{=0} \\ &= \sum_{m\neq n} \frac{\langle m|\hat{V}|n\rangle}{\epsilon_n - \epsilon_m} \langle n|\hat{V}|m\rangle \\ &= \sum_{m\neq n} \frac{\left|\langle n|\hat{V}|m\rangle\right|^2}{\epsilon_n - \epsilon_m}. \end{aligned}$$

Time-Independent Perturbation Theory

➤ <u>The Non-Degenerated Case</u>

- We often approximate

$$E_n \approx \epsilon_n + \langle n|\hat{V}|n\rangle + \sum_{m\neq n} \frac{\left|\langle n|\hat{V}|m\rangle\right|^2}{\epsilon_n - \epsilon_m}$$

Second-order perturbation theory!

$$|\psi_n\rangle \approx |n\rangle + \sum_{m\neq n} \frac{\langle m|\hat{V}|n\rangle}{\epsilon_n - \epsilon_m}|m\rangle.$$

First-order perturbation theory!

- This means we go up to second-order in the energy and up to first order in the states.
- Note: everything we have done so far is only valid if

$$\epsilon_n \neq \epsilon_m \qquad \text{for} \qquad n \neq m.$$

Time-Independent Perturbation Theory

➢ Degenerate Perturbation Theory

- Assume that $N \geq 2$ states have the same (unperturbed) ϵ so that

$$\hat{H}_0|\alpha\rangle = \epsilon|\alpha\rangle, \qquad \alpha = 1, 2, \ldots, N.$$

- The $|\alpha\rangle$ are the degenerate states and ε the corresponding energies.
- In the following we are only interested in first-order corrections.
- What we have used before is

$$|\psi_n\rangle = |n\rangle + |\psi_n^{(1)}\rangle = |n\rangle + \lambda \sum_{m \neq n} a_{nm}^{(1)}|m\rangle$$

and

$$E_n = \epsilon_n + \lambda E_n^{(1)}.$$

- Furthermore

$$a_{nm}^{(1)} = \frac{\langle m|\hat{V}|n\rangle}{\epsilon_n - \epsilon_m} \quad \text{for} \quad n \neq m.$$

this does not work anymore!

Time-Independent Perturbation Theory

- <u>Degenerate Perturbation Theory</u>
  - Let's do the following

$$|\psi\rangle = \underbrace{\sum_{\alpha=1}^{N} c_\alpha |\alpha\rangle}_{\text{all states with same energy contribute}} + \underbrace{\lambda \sum_{\alpha=1}^{N} a_\alpha^{(1)} |\alpha\rangle + \lambda \sum_{m\neq\alpha} a_m^{(1)} |m\rangle}_{\text{as before, but we split the sum}}.$$

This notation means sum over all non-degenerate states ($m\neq\alpha$)

  - For energy we use

$$E = \epsilon + \lambda E^{(1)}.$$

  - Schrödinger's equation is

$$\left(\hat{H}_0 + \lambda \hat{V}\right)|\psi\rangle = E|\psi\rangle.$$

  - Therein we now use our two expansions and keep terms in lowest and first order in λ.

Time-Independent Perturbation Theory

- <u>Degenerate Perturbation Theory</u>
  - We find

$$
\begin{aligned}
&(\hat{H}_0 + \lambda \hat{V}) \left[\sum_{\alpha=1}^{N} c_\alpha |\alpha\rangle + \lambda \sum_{\alpha=1}^{N} a_\alpha^{(1)} |\alpha\rangle + \lambda \sum_{m \neq \alpha} a_m^{(1)} |m\rangle \right] \\
= \quad &(\epsilon + \lambda E^{(1)}) \left[\sum_{\alpha=1}^{N} c_\alpha |\alpha\rangle + \lambda \sum_{\alpha=1}^{N} a_\alpha^{(1)} |\alpha\rangle + \lambda \sum_{m \neq \alpha} a_m^{(1)} |m\rangle \right].
\end{aligned}
$$

  - Up to first order this becomes

use eigenvalue equation

$$
\begin{aligned}
&\sum_{\alpha=1}^{N} c_\alpha \hat{H}_0 |\alpha\rangle + \lambda \sum_{\alpha=1}^{N} c_\alpha \hat{V} |\alpha\rangle + \lambda \sum_{\alpha=1}^{N} a_\alpha^{(1)} \hat{H}_0 |\alpha\rangle + \lambda \sum_{m \neq \alpha} a_m^{(1)} \hat{H}_0 |m\rangle \\
= \quad &\epsilon \sum_{\alpha=1}^{N} c_\alpha |\alpha\rangle + \lambda\epsilon \sum_{m \neq \alpha} a_m^{(1)} |m\rangle + \lambda\epsilon \sum_{\alpha=1}^{N} a_\alpha^{(1)} |\alpha\rangle + \lambda E^{(1)} \sum_{\alpha=1}^{N} c_\alpha |\alpha\rangle.
\end{aligned}
$$

Time-Independent Perturbation Theory

➢ Degenerate Perturbation Theory

- After using the eigenvalue equation and cancelling the λ, we find

$$\sum_{\alpha=1}^{N} c_\alpha \hat{V}\big|\alpha\big\rangle + \sum_{m\neq\alpha} a_m^{(1)}\epsilon_m\big|m\big\rangle = \epsilon\sum_{m\neq\alpha} a_m^{(1)}\big|m\big\rangle + E^{(1)}\sum_{\alpha=1}^{N} c_\alpha\big|\alpha\big\rangle.$$

- We now multiply this from the left with one of the degenerate states, namely $\big\langle\beta\big|$.
- Note, we have

$$\big\langle\beta\big|m\big\rangle = 0 \qquad \text{if} \qquad m \neq \beta.$$

- We get

$$\sum_{\alpha=1}^{N} c_\alpha\big\langle\beta\big|\hat{V}\big|\alpha\big\rangle = E^{(1)}\sum_{\alpha=1}^{N} c_\alpha\big\langle\beta\big|\alpha\big\rangle = E^{(1)}c_\beta.$$

Time-Independent Perturbation Theory

- Degenerate Perturbation Theory

  - We found

$$\sum_{\alpha=1}^{N} c_\alpha \langle \beta | \hat{V} | \alpha \rangle = E^{(1)} \sum_{\alpha=1}^{N} c_\alpha \langle \beta | \alpha \rangle = E^{(1)} c_\beta .$$

  - We can write this as the a matrix equation of the form

$$V c = E^{(1)} c.$$

matrix of the potential operator

  - From this we obtain the eigenvectors c and eigenvalues $E^{(1)}$.

  - We find the corrections

$$E_\gamma \approx \epsilon + E_\gamma^{(1)} \qquad \text{and} \qquad |\psi_\gamma\rangle \approx \sum_{\alpha=1}^{N} c_\alpha^{(\gamma)} |\alpha\rangle .$$

eigenvalue with number γ

α-component of eigenvector with number γ

Time-Independent Perturbation Theory

➢ A Simple Example

- We consider a case where the quantum system has only two unperturbed states so that

$$\hat{H}_0|1\rangle = \epsilon_1|1\rangle \qquad \text{and} \qquad \hat{H}_0|2\rangle = \epsilon_2|2\rangle.$$

- We now add a perturbing potential so that the new Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{V}.$$

- The corresponding Schrödinger equation is

$$(\hat{H}_0 + \hat{V})|\psi_n\rangle = E_n|\psi_n\rangle.$$

- In the following we only determine the (perturbed) energy eigenvalues E_n and don't care about the states.

- The perturbed states can be expanded via

$$|\psi_n\rangle = \alpha|1\rangle + \beta|2\rangle.$$

Time-Independent Perturbation Theory

- A Simple Example
  - Therewith, Schrödinger's equation can be written as

$$\big(\hat{H}_0 + \hat{V}\big)\big(\alpha|1\rangle + \beta|2\rangle\big) = E_n\big(\alpha|1\rangle + \beta|2\rangle\big).$$

  - Multiplying this from the left by $\langle 1|$ yields

$$\alpha\epsilon_1 + \alpha\langle 1|\hat{V}|1\rangle + \beta\langle 1|\hat{V}|2\rangle = E\alpha.$$

  - Furthermore, we can multiply the equation above from the left with $\langle 2|$ to obtain

$$\beta\epsilon_2 + \alpha\langle 2|\hat{V}|1\rangle + \beta\langle 2|\hat{V}|2\rangle = E\beta.$$

  - To continue we use the notation

$$V_{nm} = \langle n|\hat{V}|m\rangle.$$

Time-Independent Perturbation Theory

- A Simple Example

  - Furthermore, our two equations can be written as the following matrix equation

$$\begin{pmatrix} \epsilon_1 - E + V_{11} & V_{12} \\ V_{12}^* & \epsilon_2 - E + V_{22} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0.$$

  - Furthermore, we consider a potential so that $V_{11}=V_{22}=0$.
  - Non-trivial solutions are obtained if the determinant of the above matrix is zero. Therefore, we find

$$(\epsilon_1 - E)(\epsilon_2 - E) - |V_{12}|^2 = 0.$$

  - This can easily be written as

$$E^2 - E(\epsilon_1 + \epsilon_2) + \epsilon_1\epsilon_2 - |V_{12}|^2 = 0.$$

Time-Independent Perturbation Theory

- A Simple Example

  - This quadratic equation has the solutions

$$
\begin{aligned}
E &= \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \frac{1}{2}\sqrt{(\epsilon_1 + \epsilon_2)^2 + 4|V_{12}|^2 - 4\epsilon_1\epsilon_2} \\
&= \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \frac{1}{2}\sqrt{(\epsilon_1 - \epsilon_2)^2 + 4|V_{12}|^2}.
\end{aligned}
$$

  - Note, we looked at a very special case but our result for the energy is exact.

  - In the following we look at the non-degenerated case meaning that $\varepsilon_1 \neq \varepsilon_2$.

  - In this case we can write

$$
E = \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \frac{1}{2}(\epsilon_1 - \epsilon_2)\sqrt{1+\lambda} \quad \text{with} \quad \lambda = \frac{4|V_{12}|^2}{(\epsilon_1 - \epsilon_2)^2}.
$$

Time-Independent Perturbation Theory

- A Simple Example

  - To continue we assume that λ is small and we Taylor-expand our result to find

$$
\begin{aligned}
E &= \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \frac{1}{2}(\epsilon_1 - \epsilon_2)\sqrt{1+\lambda} \\
&\approx \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \frac{1}{2}(\epsilon_1 - \epsilon_2)\left(1 + \frac{1}{2}\lambda\right) \\
&= \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \frac{1}{2}(\epsilon_1 - \epsilon_2)\left(1 + \frac{2|V_{12}|^2}{(\epsilon_1 - \epsilon_2)^2}\right).
\end{aligned}
$$

  - From this we can easily read off

$$
E_1 = \epsilon_1 + \frac{|V_{12}|^2}{\epsilon_1 - \epsilon_2} \qquad \text{and} \qquad E_2 = \epsilon_2 - \frac{|V_{12}|^2}{\epsilon_1 - \epsilon_2}.
$$

Time-Independent Perturbation Theory

➢ A Simple Example

- We found

$$E_1 = \epsilon_1 + \frac{|V_{12}|^2}{\epsilon_1 - \epsilon_2} \qquad \text{and} \qquad E_2 = \epsilon_2 - \frac{|V_{12}|^2}{\epsilon_1 - \epsilon_2}.$$

- Compare this with non-degenerated perturbation theory

$$E_n \approx \epsilon_n + \langle n|\hat{V}|n\rangle + \sum_{m\neq n} \frac{\left|\langle n|\hat{V}|m\rangle\right|^2}{\epsilon_n - \epsilon_m}.$$

- We can easily see that the two results are the same.
- What about the degenerated case where we have $\varepsilon_1 = \varepsilon_2$?
- We derived the exact result

$$E = \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \frac{1}{2}\sqrt{(\epsilon_1 - \epsilon_2)^2 + 4|V_{12}|^2}.$$

Time-Independent Perturbation Theory

- A Simple Example
  - For $\varepsilon_1 = \varepsilon_2$ our formula

$$E = \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \frac{1}{2}\sqrt{(\epsilon_1 - \epsilon_2)^2 + 4|V_{12}|^2}$$

simplifies to

$$E = \epsilon \pm |V_{12}|.$$

  - For the degenerated case we derived

$$Vc = E^{(1)}c.$$

  - Note, here we have used the matrix V of the perturbing potential with respect to the unperturbed states.
  - $E^{(1)}$ corresponds to the first order energy corrections.

Time-Independent Perturbation Theory

➢ <u>A Simple Example</u>

- We can write the matrix equation out and make the same assumption concerning *V* as above.
- We find

$$\begin{pmatrix} -E^{(1)} & V_{12} \\ V_{12}^{*} & -E^{(1)} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0.$$

- Setting the determinant equal to zero gives us

$$E^{(1)} = \pm \left| V_{12} \right|.$$

- Therefore, the corresponding (corrected) energy eigenvalues are

$$E = \epsilon \pm \left| V_{12} \right|$$

in agreement with the exact result derived above.