Overview of course

Part 1: 7 lectures in January (Piet Mulders)
- Basics of quantum mechanics
- Spin states
- Addition of angular momentum
- Identical particles
- Basic structure of atom

Part 2: 7 lectures in February and March (Florian Schreck)
- Structure of atoms & the periodic table
- Crystalline solids
- Time-independent perturbation theory
- Structure of hydrogen
- Variational principle
- Time-dependent perturbation theory, atom-light interaction

Lecture notes, problem sets and link to video recordings of C0.110 lectures available on Canvas

Questions: schreck@StrontiumBEC.com
Literature part 2

Griffiths (2nd edition)
Chapters 5, 6, 7, 9

Griffiths (3rd edition)
Chapters 5, 7, 8, 11
Other literature

Quantum Mechanics

Volume One

Claude Cohen-Tannoudji
Bernard Diu
Franck Laloe

Modern Quantum Mechanics

J. J. Sakurai

Revised Edition
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Questions: schreck@StrontiumBEC.com
Outline

• Reminder of Piet’s lecture on orbital and spin structure of atoms
  • Energy structure of He
    - „exchange energy“
    - shielding of nuclear charge by inner shell electrons

• Energy structure of atoms with many electrons
  • Hund’s rules
  • the periodic table
Orbital and spin structure of atoms

Atom with nuclear charge $Z$ and $Z$ electrons:

$$\hat{H} = \sum_{i=1}^{Z} \left( -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{j<i}^{Z} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} \right)$$

- Without ee repulsion separable
- First solve without ee repulsion
  then include ee repulsion as $Z(R)$ and/or in perturbation theory

Wavefunction and energy

for central potential and separable Hamiltonian

$$\Psi(...(\vec{r}_1, ..., \vec{r}_Z) = \mathcal{A} \left( \prod_{i=1}^{Z} \phi_{n_i l_i m_{l_i}} (\vec{r}_i) \cdot X s_i m_{s_i} \right)$$

Label: Term symbol

Antisymmetrize under electron exchange!

$$E = \sum_{i=1}^{Z} E_{n_i l_i} + ...$$

perturbation

energy without ee repulsion, i.e. single electron energy

shorthand:
$$|\uparrow\rangle, |\downarrow\rangle$$

2 states for each $e^-$
Example: Helium atom

2 electrons $\rightarrow$ $Z = 2$

assume separability $\rightarrow$ configurations: $(n_1 l_1)(n_2 l_2)$ + additional quantum numbers

Energies without ee repulsion

$$E = E_{n_1 l_1} + E_{n_2 l_2} = - \left( \frac{Z^2}{n_1^2} + \frac{Z^2}{n_2^2} \right) E_{\text{Rydberg}}$$

<table>
<thead>
<tr>
<th>configurations</th>
<th>$E/E_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1s)^2$</td>
<td>$-8 = 109 \text{ eV}$</td>
</tr>
<tr>
<td>$(1s)(2s)$</td>
<td>$-5$</td>
</tr>
<tr>
<td>$(1s)(2p)$</td>
<td>$-5$</td>
</tr>
<tr>
<td>$(2s)(2p)$</td>
<td>$-2$</td>
</tr>
<tr>
<td>$(2s)^2$</td>
<td>$-2$</td>
</tr>
<tr>
<td>$(2p)^2$</td>
<td>$-2$</td>
</tr>
<tr>
<td>$(1s)(3d)$</td>
<td>$\ldots$</td>
</tr>
</tbody>
</table>

Energies will change by ee repulsion
e.g. groundstate energy

$$E_{gs} \simeq -75 \text{ eV} \quad \text{, not} \quad -109 \text{ eV}$$

Explanation: Chapter „variational principle“
He wavefunctions

Wavefunction of the 2 He electrons

\[
\Psi(r_1, r_2) = \Phi_{n_1 l_1 m_{l_1}}(r_1) \Phi_{n_2 l_2 m_{l_2}}(r_2) \chi_{s_1 m_{s_1}} \chi_{s_2 m_{s_2}} \Phi(r_1, r_2) \chi
\]

must be antisymmetric!

Groundstate of He

\[
\Phi_0(r_1, r_2) = \Phi_{100}(r_1) \Phi_{100}(r_2)
\]

\(\Phi_0\) is symmetric \(\rightarrow\) \(\chi_0\) must be antisymmetric: singlet

\[
\chi_0 = (|\uparrow_1 \downarrow_2\rangle - |\downarrow_1 \uparrow_2\rangle) / \sqrt{2} \equiv |s\rangle
\]

Excited states of He

\[
\Phi_e(r_1, r_2) = (\Phi_{100}(r_1) \Phi_{n l m}(r_2) \pm \Phi_{100}(r_2) \Phi_{n l m}(r_1)) / \sqrt{2}
\]

(both e\(^-\) in excited states: He autoionizes)

\(\Phi_e\) can be both: symmetric or antisymmetric!

If \(\Phi_e\) symmetric \(\rightarrow\) \(\chi_e\) antisymmetric: singlet „parahelium“

If \(\Phi_e\) antisymmetric \(\rightarrow\) \(\chi_e\) symmetric: triplet „orthohelium“

\[
\chi_e = \begin{cases} 
|\uparrow_1 \uparrow_2\rangle & \equiv |t_{+1}\rangle \\
(|\uparrow_1 \downarrow_2\rangle + |\downarrow_1 \uparrow_2\rangle) / \sqrt{2} & \equiv |t_0\rangle \\
|\downarrow_1 \downarrow_2\rangle & \equiv |t_{-1}\rangle 
\end{cases}
\]
Examples of He states

**singlet**

S=0

„parahelium“

Hydrogen-like orbitals

Energy

Absolute ground state

$1^1S_0$

$n = 1$  $n = 2$  $n = 3$
Term symbols

\[ n^{2S+1} L_J \]
e.g. \( 2^3P_0 : \quad n = 2, \quad S = 1, \quad L = 1, \quad J = 0 \)

\( n \) : longform:

- orbital
- number of e\(^{-}\) in orbital
- next lighter noble gas

He: \((1s)^2\)
C: \((\text{He}) (2s)^2(2p)^2\)

shorthand: principal quantum number of highest occupied shell

\( S \) : total spin quantum number.

E.g. for two electrons \( S = 0 \) (singlet) or \( S = 1 \) (triplet)

\( L \) : total orbital angular momentum quantum number

E.g. for two electrons \( L = |l_1 - l_2|, |l_1 - l_2| + 1, \ldots, |l_1 + l_2| \)

\( L = 0, 1, 2, 3, \ldots \)
written as \( S,P,D,F,G,H,J,K \ldots \)

\( J \) : total angular momentum quantum number

\[ J = |L - S|, |L - S| + 1, \ldots, |L + S| \]

angular momentum = \( \hbar \) angular momentum quantum number
Examples of He states

**singlet**

$S=0$

„parahelium“

<table>
<thead>
<tr>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n=1$</td>
</tr>
<tr>
<td>$n=2$</td>
</tr>
<tr>
<td>$n=3$</td>
</tr>
</tbody>
</table>

2s 2p

**first excited singlet state**

$2^1S_0$

<table>
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<tr>
<th>Energy</th>
</tr>
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<tbody>
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<td>$n=1$</td>
</tr>
<tr>
<td>$n=2$</td>
</tr>
<tr>
<td>$n=3$</td>
</tr>
</tbody>
</table>

3s 3p 3d

**triplet**

$S=1$

„orthohelium“

<table>
<thead>
<tr>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n=1$</td>
</tr>
<tr>
<td>$n=2$</td>
</tr>
<tr>
<td>$n=3$</td>
</tr>
</tbody>
</table>

3s 3p 3d

**triplet ground state**

$2^3S_1$

(Stable by angular momentum conservation, as long as He atom doesn't touch anything)

Why different energy?

see later: „shielding of nucleus“

**absolute ground state**

$1^1S_0$

Energy

3s 3p 3d

**first excited triplet state**

$2^3P_0$

see later: 3rd Hund's rule
## Helium states

### Antisymmetrization and termsymbols

<table>
<thead>
<tr>
<th>config.</th>
<th>$E / E_R$</th>
<th>Parity</th>
<th>$L$ (sym)</th>
<th>$S$ (sym)</th>
<th>Term symbol</th>
<th>$J$</th>
<th># states</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1s)^2$</td>
<td>$-8$</td>
<td>+</td>
<td>0 ($S$)</td>
<td>0 ($A$)</td>
<td>(1$s)^2$ $^1S$</td>
<td>$^1S_0$</td>
<td>1</td>
</tr>
<tr>
<td>$(1s)(2p)$ &amp; $(2p)(1s)$</td>
<td>$-5$</td>
<td>-</td>
<td>1 ($A$)</td>
<td>0 ($A$)</td>
<td>(1$s)(2p)^1P$</td>
<td>$^1P_1$</td>
<td>3</td>
</tr>
<tr>
<td>&amp;</td>
<td></td>
<td></td>
<td>1 ($S$)</td>
<td>1 ($S$)</td>
<td>(1$s)(2p)^3P$</td>
<td>$^3P_{0,1,2}$</td>
<td>9</td>
</tr>
<tr>
<td>$(1s)(2s)$ &amp; $(2s)(1s)$</td>
<td>$-5$</td>
<td>+</td>
<td>0 ($A$)</td>
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<td>(1$s)(2s)^3S$</td>
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<td>3</td>
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<tr>
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</tr>
<tr>
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<td></td>
<td></td>
<td>0 ($A$)</td>
<td>1 ($S$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 ($S$)</td>
<td>0 ($A$)</td>
<td>(2$p)^2$ $^3P$</td>
<td>$^3P_{0,1,2}$</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2$p)^2$ $^1D$</td>
<td>$^3D_2$</td>
<td>5</td>
</tr>
</tbody>
</table>

So far:
Which states are allowed?

Now:
Energy shifts between states?

see Piet 6.2
He energy levels

Singlet \(S=0\) "parahelium"

Triplet \(S=1\) "orthohelium"

\[
\begin{align*}
E_{\text{relative to He}^+ \text{ion}} (\text{eV}) &
\quad 0 & 1 & 2 & 0 & 1 & 2 \\
\hline
n=1 & 1^1S & & & & \\
n=2 & 2^1S & 2^1P & & & & \\
n=3 & 3^1S & 3^1P & 3^1D & 3^3S & 3^3P & 3^3D \\
\end{align*}
\]

Orbital wavefunctions:

\[
\Phi_e(\vec{r}_1, \vec{r}_2) = \frac{(\Phi_{100}(\vec{r}_1)\Phi_{nln}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2)\Phi_{nln}(\vec{r}_1))}{\sqrt{2}}
\]

\[
\Phi_0(\vec{r}_1, \vec{r}_2) = \Phi_{100}(\vec{r}_1)\Phi_{100}(\vec{r}_2)
\]

Observations

\[
n^2S + 1 \ L
\]
He energy levels

<table>
<thead>
<tr>
<th>singlet</th>
<th>triplet</th>
</tr>
</thead>
<tbody>
<tr>
<td>S=0</td>
<td>S=1</td>
</tr>
<tr>
<td>„parahelium“</td>
<td>„orthohelium“</td>
</tr>
</tbody>
</table>

Energy levels relative to He$^+$ ion (eV):

<table>
<thead>
<tr>
<th>l=0</th>
<th>l=1</th>
<th>l=2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3^1S</td>
<td>3^3S</td>
<td>3^1P</td>
</tr>
<tr>
<td>2^1S</td>
<td>2^3S</td>
<td>2^1P</td>
</tr>
<tr>
<td>1^S</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Orbital wavefunctions:

$$\Phi_e(\vec{r}_1, \vec{r}_2) = \frac{(\Phi_{100}(\vec{r}_1)\Phi_{nlm}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2)\Phi_{nlm}(\vec{r}_1))}{\sqrt{2}}$$

$$\Phi_0(\vec{r}_1, \vec{r}_2) = \Phi_{100}(\vec{r}_1)\Phi_{100}(\vec{r}_2)$$

Observations

Ground state binding energy lower than predicted

See chapter „variational principle“

-75 eV total energy instead of -109 eV
He energy levels

singlet
S=0
„parahelium“

triplet
S=1
„orthohelium“

<table>
<thead>
<tr>
<th>l</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>l=0</td>
<td>3^1S</td>
<td>3^1P</td>
<td>3^1D</td>
</tr>
<tr>
<td>l=1</td>
<td>2^1S</td>
<td>2^1P</td>
<td></td>
</tr>
<tr>
<td>l=2</td>
<td></td>
<td>2^3S</td>
<td></td>
</tr>
<tr>
<td>l=3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Orbital wavefunctions:

$$\Phi_c(\vec{r}_1, \vec{r}_2) = \frac{(\Phi_{100}(\vec{r}_1)\Phi_{nlm}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2)\Phi_{nlm}(\vec{r}_1))}{\sqrt{2}}$$

$$\Phi_0(\vec{r}_1, \vec{r}_2) = \Phi_{100}(\vec{r}_1)\Phi_{100}(\vec{r}_2)$$

Observations

Ground state binding energy lower than predicted

See chapter „variational principle“

P levels always higher than S levels

Shielding of nuclear charge

term symbols

$$n^{2S+1}L$$
He energy levels

Singlet
S=0
"parahelium"

Triplet
S=1
"orthohelium"

<table>
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<tr>
<th>l</th>
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<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>4</td>
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<td>4</td>
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</tr>
<tr>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
</tbody>
</table>

Orbital wavefunctions:

$$\Phi_e(\vec{r}_1, \vec{r}_2) = \frac{(\Phi_{100}(\vec{r}_1)\Phi_{nlm}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2)\Phi_{nlm}(\vec{r}_1))}{\sqrt{2}}$$

$$\Phi_0(\vec{r}_1, \vec{r}_2) = \Phi_{100}(\vec{r}_1)\Phi_{100}(\vec{r}_2)$$

Observations

- Ground state binding energy lower than predicted
  - See chapter "variational principle"

- P levels always higher than S levels
  - Shielding of nuclear charge

- Singlet levels always higher than triplet levels
  - Reason: "exchange energy"
He energy levels

<table>
<thead>
<tr>
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<th>triplet</th>
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<tr>
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Orbital wavefunctions:
\[ \Phi_{\ell}(\vec{r}_1, \vec{r}_2) = \frac{\Phi_{100}(\vec{r}_1)\Phi_{nlm}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2)\Phi_{nlm}(\vec{r}_1)}{\sqrt{2}} \]
\[ \Phi_0(\vec{r}_1, \vec{r}_2) = \Phi_{100}(\vec{r}_1)\Phi_{100}(\vec{r}_2) \]

Observations

- Ground state binding energy lower than predicted
  - See chapter „variational principle“
- P levels always higher than S levels
  - Shielding of nuclear charge
- Singlet levels always higher than triplet levels
  - Reason: „exchange energy“

Term symbols:
\[ n^{2S+1}L \]

Energy relative to He+ ion (eV)

0       1        2      0       1        2

\[ l = \]

0       1        2

\[ n = 1 \]

\[ n = 2 \]

\[ n = 3 \]

\[ 0 \]

\[ -1 \]

\[ -2 \]

\[ -3 \]

\[ -4 \]

\[ -5 \]

\[ -24.5 \]

\[ 3^1S \quad 3^1P \quad 3^1D \]

\[ 3^3S \quad 3^3P \quad 3^3D \]

\[ n = 3 \]

\[ 2^1S \quad 2^1P \]

\[ 2^3S \quad 2^3P \]

\[ n = 2 \]

\[ 1^1S \]
Exchange energy

Energy shifts depend on spin state

(1) If spin state $\chi$: 
- singlet: antisymmetric
- triplet: symmetric

$\implies$ orbital wavefunc. $\Phi$: 
- symmetric
- antisymmetric

(2) $e^{-}$ distribution depends on symmetry of $\Phi$: 
$\implies$ Coulomb energy depends on symmetry of $\Phi$

(1) & (2) $\implies$ Energy depends on spin state $\chi$

Energy different for singlet and triplet

$\chi = |s\rangle \implies E = E_s$

$\chi = |t_{-1,0,+1}\rangle \implies E = E_t$

$E_s \neq E_t$

Energy shift $\Delta E = E_s - E_t$ is called "exchange energy"

It is as if spins would interact with each other, leading to different energies for $|s\rangle$ and $|t_{-1,0,+1}\rangle$.

This effective interaction is called "exchange interaction".

Can also lead to effective "exchange forces", pulling atoms together to form molecules.
Coulomb energy dependence on $\Phi$ sym.

First: handwaving argument

Coulomb energy strongest when e\textsuperscript{-} very close.

What is probability amplitude for e\textsuperscript{-} to be at same location for symmetric or antisymmetric wavefunction?

$$\Phi^\pm (\vec{r}_1, \vec{r}_2) = (\Phi_a(\vec{r}_1) \Phi_b(\vec{r}_2) \pm \Phi_a(\vec{r}_2) \Phi_b(\vec{r}_1)) / \sqrt{2}$$

$$\Phi^+ (\vec{r}_1, \vec{r}_2 = \vec{r}_1) = \sqrt{2} \Phi_a(\vec{r}_1) \Phi_b(\vec{r}_1) \implies \text{e}^\text{-} \text{can be close to each other}$$

$$\Phi^- (\vec{r}_1, \vec{r}_2 = \vec{r}_1) = 0 \implies \text{e}^\text{-} \text{never at same place}$$

Electrons closer to each other in symmetric than antisymmetric wavefunction.

$\implies$ Coulomb repulsion leads to different energy for singlet and triplet states: $E_s \neq E_t$

For He: $E_s > E_t$

Exchange energy between two electrons

$\chi = |s\rangle$ \hspace{1cm} $\implies$ \hspace{1cm} $\Phi^+$ \hspace{1cm} $\implies$ \hspace{1cm} $E = E_s$ \hspace{1cm} with \hspace{1cm} $E_s \neq E_t$

$\chi = |t_{-1,0,+1}\rangle$ \hspace{1cm} $\implies$ \hspace{1cm} $\Phi^-$ \hspace{1cm} $\implies$ \hspace{1cm} $E = E_t$
Coulomb energy dependence on $\Phi$ sym.

Now: calculation of average distance squared $\langle (\Delta x)^2 \rangle = (x_1 - x_2)^2$ of electrons, for simplicity in 1D system

$$|\Phi^{\pm}(x_1, x_2)\rangle = (|\Phi_a(x_1)\rangle |\Phi_b(x_2)\rangle \pm |\Phi_a(x_2)\rangle |\Phi_b(x_1)\rangle)/\sqrt{2} \quad \text{with} \quad |\Phi_a\rangle \text{ orthonormal} \quad |\Phi_b\rangle$$

$$\langle \Phi^{\pm}|(\Delta x)^2|\Phi^{\pm}\rangle = \langle (\Delta x)^2 \rangle_{\pm} = \langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x_1^2 \rangle_{\pm} + \langle x_2^2 \rangle_{\pm} - 2 \langle x_1 x_2 \rangle_{\pm}$$

$$\langle x_1^2 \rangle_{\pm} = \langle \Phi^{\pm}(x_1, x_2)|x_1^2|\Phi^{\pm}(x_1, x_2)\rangle$$

$$= \left[ \langle \Phi_a(x_1)|x_1^2|\Phi_a(x_1)\rangle \langle \Phi_b(x_2)|\Phi_b(x_2)\rangle \right] \equiv \langle x_1^2 \rangle_a = 1 \quad + \left[ \langle \Phi_b(x_1)|x_1^2|\Phi_b(x_1)\rangle \langle \Phi_a(x_2)|\Phi_a(x_2)\rangle \right] \equiv \langle x_1^2 \rangle_b = 1$$

$$\pm \langle \Phi_a(x_1)|x_1^2|\Phi_b(x_1)\rangle \langle \Phi_b(x_2)|\Phi_a(x_2)\rangle \quad \pm \langle \Phi_b(x_1)|x_1^2|\Phi_a(x_1)\rangle \langle \Phi_a(x_2)|\Phi_b(x_2)\rangle \right]/2$$

$$= [\langle x_1^2 \rangle_a + \langle x_1^2 \rangle_b]/2$$

Independent of symmetry:

$$\langle x_1^2 \rangle_{\pm} = \langle x_1^2 \rangle_{-}$$

Since electron 1 identical to electron 2:

$$\langle x_2^2 \rangle_{\pm} = \langle x_2^2 \rangle_{-}$$
Coulomb energy dependence on $\Phi_{\text{sym.}}$

Now: calculation of average distance squared $\langle (\Delta x)^2 \rangle = \langle x_1 - x_2 \rangle^2$ of electrons, for simplicity in 1D system

$$|\Phi^{\pm}(x_1, x_2)\rangle = (|\Phi_a(x_1)\rangle |\Phi_b(x_2)\rangle \pm |\Phi_a(x_2)\rangle |\Phi_b(x_1)\rangle) / \sqrt{2} \quad \text{with} \quad |\Phi_a\rangle \text{ orthonormal} \quad |\Phi_b\rangle$$

$$\langle \Phi^{\pm}|(\Delta x)^2|\Phi^{\pm}\rangle = \langle (\Delta x)^2 \rangle_{\pm} = \langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x_1^2 \rangle_{\pm} + \langle x_2^2 \rangle_{\pm} - 2 \langle x_1 x_2 \rangle_{\pm}$$

$$\langle x_1 x_2 \rangle_{\pm} = \langle \Phi^{\pm}(x_1, x_2)|x_1 x_2|\Phi^{\pm}(x_1, x_2)\rangle$$

$$= \left[ \langle \Phi_a(x_1)|x_1|\Phi_a(x_1)\rangle \langle \Phi_b(x_2)|x_2|\Phi_b(x_2)\rangle + \langle \Phi_b(x_1)|x_1|\Phi_b(x_1)\rangle \langle \Phi_a(x_2)|x_2|\Phi_a(x_2)\rangle \right]$$

$$= \langle x_1 \rangle_a = \langle x \rangle_a \quad \quad = \langle x \rangle_b \quad \quad = \langle x \rangle_b \quad \quad = \langle x \rangle_a$$

$$= \langle x \rangle_{ab} \quad \quad = \langle x \rangle_{ba} \quad \quad = \langle x \rangle_{ba} \quad \quad = \langle x \rangle_{ab}$$

$$= |\langle x \rangle_{ba}|^2 = |\langle x \rangle_{ba}|^2$$

$$= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2$$
Coulomb energy dependence on $\Phi$ sym.

Now: calculation of average distance squared $(\Delta x)^2 = (x_1 - x_2)^2$ of electrons, for simplicity in 1D system

$$|\Phi^\pm(x_1, x_2)\rangle = \left( |\Phi_a(x_1)\rangle |\Phi_b(x_2)\rangle \pm |\Phi_a(x_2)\rangle |\Phi_b(x_1)\rangle \right)/\sqrt{2} \quad \text{with} \quad |\Phi_a\rangle \text{ orthonormal} \quad |\Phi_b\rangle$$

$$\langle \Phi^\pm | (\Delta x)^2 | \Phi^\pm \rangle = \langle (\Delta x)^2 \rangle_\pm = \langle (x_1 - x_2)^2 \rangle_\pm = \langle x_1^2 \rangle_\pm + \langle x_2^2 \rangle_\pm - 2 \langle x_1 x_2 \rangle_\pm$$

with

$$\langle x_1^2 \rangle_+ = \langle x_1^2 \rangle_-$$

$$\langle x_2^2 \rangle_+ = \langle x_2^2 \rangle_-$$

$$\langle x_1 x_2 \rangle_\pm = \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2$$

Difference between symmetric and antisymmetric wavefunction:

$$\langle (\Delta x)^2 \rangle_+ - \langle (\Delta x)^2 \rangle_- = \langle x_1^2 \rangle_+ + \langle x_2^2 \rangle_+ - 2 \langle x_1 x_2 \rangle_+$$

$$- \langle x_1^2 \rangle_- - \langle x_2^2 \rangle_- + 2 \langle x_1 x_2 \rangle_-$$

$$= -2(\langle x \rangle_a \langle x \rangle_b + |\langle x \rangle_{ab}|^2)$$

$$+ 2(\langle x \rangle_a \langle x \rangle_b - |\langle x \rangle_{ab}|^2)$$

$$= -4 |\langle x \rangle_{ab}|^2$$

$$\langle x \rangle_{ab} = \int \Phi^*_a(x)x\Phi_b(x)dx$$

Effect plays only a role if wavefunctions overlap

Average electron distance smaller for symmetric than for antisymmetric wavefunction

$\rightarrow$ For He: leads to higher Coulomb energy for symmetric wavefunction
He energy levels

singlet
S=0
„parahelium“

triplet
S=1
„orthohelium“

Orbital wavefunctions:

\[ \Phi_e(\vec{r}_1, \vec{r}_2) = \frac{(\Phi_{100}(\vec{r}_1)\Phi_{nlm}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2)\Phi_{nlm}(\vec{r}_1))}{\sqrt{2}} \]

\[ \Phi_0(\vec{r}_1, \vec{r}_2) = \Phi_{100}(\vec{r}_1)\Phi_{100}(\vec{r}_2) \]

Observations

Ground state binding energy lower than predicted

See chapter „variational principle“

P levels always higher than S levels

Shielding of nuclear charge

Singlet levels always higher than triplet levels

Reason: „exchange energy“
He energy levels

Singlet
S=0
„parahelium“

Triplet
S=1
„orthohelium“

Energy relative to He$^+$ ion (eV)

Orbital wavefunctions:
\[ \Phi_e(\mathbf{r}_1, \mathbf{r}_2) = (\Phi_{100}(\mathbf{r}_1)\Phi_{nlm}(\mathbf{r}_2) \pm \Phi_{100}(\mathbf{r}_2)\Phi_{nlm}(\mathbf{r}_1)) / \sqrt{2} \]
\[ \Phi_0(\mathbf{r}_1, \mathbf{r}_2) = \Phi_{100}(\mathbf{r}_1)\Phi_{100}(\mathbf{r}_2) \]

Observations

Ground state binding energy lower than predicted
See chapter „variational principle“

P levels always higher than S levels
Shielding of nuclear charge

Singlet levels always higher than triplet levels
Reason: „exchange energy“

Term symbols
\[ n^{2S+1}L \]
Exchange energy

Exchange energy between two electrons

Spin

\[ \chi = |s\rangle \]

\[ \chi = |t_{-1,0,+1}\rangle \]

Orbital wavefunction

\[ \Phi^+ \]

\[ \Phi^- \]

Energy

\[ E = E_s \]

\[ E = E_t \]

with \[ E_s \neq E_t \]

Three examples

- Singlet – triplet shift in He

- Covalent bond in H₂

Bonus material

- Magnetic order
Example 2: covalent bonds

Example: \( H_2 \) molecule

For large \( R \gg a_0 \): no overlap \( \rightarrow \) no exchange energy shift

Hydrogen orbital wavefunction:

\[
\Phi^\pm(\vec{r}_1, \vec{r}_2) = \left( \Phi_a(\vec{r}_1) \Phi_b(\vec{r}_2) \pm \Phi_a(\vec{r}_2) \Phi_b(\vec{r}_1) \right)/\sqrt{2}
\]

Density distribution of electron 1:

\[
n^\pm(\vec{r}_1) = \int |\Phi^\pm(\vec{r}_1, \vec{r}_2)|^2 d\vec{r}_2 \propto |\Phi_a(\vec{r}_1)|^2 \int |\Phi_b(\vec{r}_2)|^2 d\vec{r}_2 + |\Phi_b(\vec{r}_1)|^2 \int |\Phi_a(\vec{r}_2)|^2 d\vec{r}_2
\]

\[
\pm \Phi_a^*(\vec{r}_1) \Phi_b(\vec{r}_1) \int \Phi_b^*(\vec{r}_2) \Phi_a(\vec{r}_2) d\vec{r}_2 \pm \Phi_b^*(\vec{r}_1) \Phi_a(\vec{r}_1) \int \Phi_a^*(\vec{r}_2) \Phi_b(\vec{r}_2) d\vec{r}_2
\]

\[
\propto |\Phi_a(\vec{r}_1)|^2 \pm |\Phi_b(\vec{r}_1)|^2 \pm \text{ (function that is positive in overlap region and approaches zero outside)}
\]

Same for electron 2.
Example 2: covalent bonds

Example: $H_2$ molecule

proton

H atom

e$^{-}$ wavefunc. $\Phi_a$

$\Phi_b$

nuclear distance $R$

For large $R \gg a_0$ : no overlap $\rightarrow$ no exchange energy shift

for $R \sim a_0$ : overlap $\rightarrow$ exchange energy shift by modified e$^{-}$ density distribution?

Density distribution of electron 1 and 2:

$$n^\pm(r) \propto |\Phi_a(r)|^2 + |\Phi_b(r)|^2$$

(function that is positive in overlap region and close to zero outside)

Singlet

symmetric orbital wavefunction

$\Psi^+$

Triplet

antisymmetric orbital wavefunction

$\Psi^-$

• in average e$^{-}$ closer together

• in average e$^{-}$ farther apart
**Example 2: covalent bonds**

**Example: H₂ molecule**

**Singlet**  
symmetric orbital wavefunction  
\[ \psi^+ \]

- high e⁻ density  
- attractive "exchange force" between protons for \( R \sim a_0 \)  
- lower energy

**Triplet**  
antisymmetric orbital wavefunction  
\[ \psi^- \]

- low e⁻ density  
- repulsive "exchange force" between protons

Protons in H₂ are bound by "covalent bond" established by electrons in singlet state.
Example 2: covalent bonds

Potential energy curves of H₂ molecule

\[ \chi = \begin{cases} 
|t_{+1}\rangle = |\uparrow_1\rangle |\uparrow_2\rangle \\
|t_0\rangle = (|\uparrow_1\rangle |\downarrow_2\rangle + |\downarrow_1\rangle |\uparrow_2\rangle) / \sqrt{2} \\
|t_{-1}\rangle = |\downarrow_1\rangle |\downarrow_2\rangle 
\end{cases} \]

\[ \chi = |s\rangle = (|\uparrow_1\rangle |\downarrow_2\rangle - |\downarrow_1\rangle |\uparrow_2\rangle) / \sqrt{2} \]
Example 2: covalent bonds

Fundamental bonding mechanism in many molecules, e.g.

- methane
- ammonia
- water

Other bonding mechanisms
- ionic bonds
- metallic bonds
- hydrogen bonds
- van der Waals attraction
Example 3: magnetism

Insulators of some materials have **lattice of localized electrons**

*Spin orientation* of electrons can **order** in many ways, e.g.

**Ferromagnetic order**

- on square lattice

**Antiferromagnetic order**

- on triangular lattice
Origin of magnetic order

Electrons are magnets with magnetic moment \( \mu = 1 \mu_B \).

- Is magnetic dipole-dipole interaction between e\(^-\) origin of magnetic order?
  distance of e\(^-\) \( \sim 2 \text{ Å} \)

\[
U_{dd} = \frac{\mu_0}{4\pi} \frac{\mu^2}{r^3} \approx 10^{-4} \text{ eV} \approx 1 \text{ K}
\]

\( \rightarrow \) magnetism would only occur below 1K, therefore it must have different origin

- typical Coulomb interaction between e\(^-\) :

\[
U_{el} \sim 1 \text{ eV} \sim 1000 \text{ K}
\]

Coulomb interaction strong enough, but not spin dependent

Is there a mechanism that renders Coulomb interaction spin dependent?

Yes, exchange interaction!
Exchange interaction

Each atom has one or more electrons that is not paired and can contribute to magnetism

Wavefunctions of these electrons on neighboring atoms overlap

Exchange energy shift between singlet and triplet spin configuration

If $E_t < E_s$ : ferromagnetic interaction

If $E_s < E_t$ : antiferromagnetic interaction
Effective interactions

Exchange energy between two electrons

spin
\[ \chi = |s\rangle \]

orbital wavefunction
\[ \Phi^+ \]

total wavefunction
antisymmetric

energy
\[ E = E_s \]

with
\[ E_s \neq E_t \]

Electronic wavefunction
\[ \chi = |t_{-1,0,+1}\rangle \]

Coulomb energy
different
\[ \Phi^- \]

Energy
\[ E = E_t \]

It is as if spins would interact with each other, leading to different energies for \(|s\rangle\) and \(|t_{-1,0,+1}\rangle\).

This effective interaction is called "exchange interaction".

Exchange interaction is not a real interaction. It is just a simplifying name for the reason behind the exchange energy.

Often only energy difference between singlet and triplet of interest, not microscopic origin

\[ \rightarrow \] simplified effective Hamiltonian
Effective spin Hamiltonian

\[ \hat{H}_{\text{spin}} = -J \mathbf{S}_1 \cdot \mathbf{S}_2 \quad \text{with} \quad J = \frac{1}{\hbar^2} (E_s - E_t) \]

has eigenvectors and -values as required for exchange interaction!

For simplicity, use \( \hat{H}_{\text{spin}} \) as effective Hamiltonian instead of true, microscopic Hamiltonian.

Check: eigenvectors and -values of \( \mathbf{S}_1 \cdot \mathbf{S}_2 \)

\[ \mathbf{S}^2 = \left( \mathbf{S}_1 + \mathbf{S}_2 \right)^2 = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2 \mathbf{S}_1 \cdot \mathbf{S}_2 \]

\[ \mathbf{S}_1 \cdot \mathbf{S}_2 = \frac{1}{2} \left( \mathbf{S}^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2 \right) = \begin{cases} -\frac{3}{4} \hbar^2 \hat{\mathbf{1}} & \text{for singlet} \\ \frac{1}{4} \hbar^2 \hat{\mathbf{1}} & \text{for triplet} \\ \text{difference of } \hbar^2 \hat{\mathbf{1}} \end{cases} \]

\[ S(S+1)\hbar^2 \hat{\mathbf{1}} \]

\[ \begin{cases} 0 & \text{for singlet} \\ 2\hbar^2 \hat{\mathbf{1}} & \text{for triplet} \end{cases} \]
Heisenberg Hamiltonian

Many spins with pairwise interactions:

$$\hat{H} = -\frac{1}{2} \sum_{i,j; i \neq j} J_{i,j} \hat{S}_i \cdot \hat{S}_j$$

\(i, j\) are indices enumerating the lattice sites

Examples:

Square lattice

Triangular lattice
### He energy levels

<table>
<thead>
<tr>
<th>Energy relative to He$^+$ ion (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-24.5$</td>
</tr>
<tr>
<td>$-5$</td>
</tr>
<tr>
<td>$-3$</td>
</tr>
<tr>
<td>$-1$</td>
</tr>
</tbody>
</table>

#### Term symbols

$nl^S_{L+1}$

#### Orbital wavefunctions:

$$
\Phi_e(r_1, r_2) = \\
(\Phi_{100}(r_1)\Phi_{nm}(r_2) \pm \Phi_{100}(r_2)\Phi_{nm}(r_1))/\sqrt{2}
$$

$$
\Phi_0(r_1, r_2) = \Phi_{100}(r_1)\Phi_{100}(r_2)
$$

### Observations

- Singlet levels always higher than triplet levels
- Ground state binding energy lower than predicted
- See chapter "variational principle"
- P levels always higher than S levels
- Shielding of nuclear charge
- Singlet levels always higher than triplet levels
  - Reason: "exchange energy"
He energy levels

Singlet
$S=0$
"parahelium"

Triplet
$S=1$
"orthohelium"

$\ell = 0 \quad 1 \quad 2$

Orbital wavefunctions:

$$\Phi_e(\vec{r}_1, \vec{r}_2) = (\Phi_{100}(\vec{r}_1)\Phi_{nlm}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2)\Phi_{nlm}(\vec{r}_1))/\sqrt{2}$$

$$\Phi_0(\vec{r}_1, \vec{r}_2) = \Phi_{100}(\vec{r}_1)\Phi_{100}(\vec{r}_2)$$

Observations

Ground state binding energy lower than predicted

See chapter "variational principle"

P levels always higher than S levels

Shielding of nuclear charge

Singlet levels always higher than triplet levels

Reason: "exchange energy"
Inner shell e$^-$ shield nuclear charge and reduce Coulomb potential experienced by far away e$^-$.

- e$^-$ with in higher orbitals farther away
- e$^-$ with higher angular momentum farther away
  (reason: classically: centrifugal force)

better shielding $\rightarrow$ less binding energy
He energy levels

<table>
<thead>
<tr>
<th>Singlet</th>
<th>Triplet</th>
<th>Orbital wavefunctions:</th>
</tr>
</thead>
<tbody>
<tr>
<td>S=0</td>
<td>S=1</td>
<td>( \Phi_e(\vec{r}_1, \vec{r}<em>2) = (\Phi</em>{100}(\vec{r}<em>1)\Phi</em>{nlm}(\vec{r}<em>2) \pm \Phi</em>{100}(\vec{r}<em>2)\Phi</em>{nlm}(\vec{r}_1))/\sqrt{2} )</td>
</tr>
<tr>
<td>&quot;parahelium&quot;</td>
<td>&quot;orthohelium&quot;</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy relative to He(^+) ion (eV)</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3^1\text{S})</td>
<td>(3^1\text{P})</td>
<td>(3^1\text{D})</td>
<td></td>
</tr>
<tr>
<td>(2^1\text{S})</td>
<td>dashed arrow to (2^3\text{S})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1^1\text{S})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Observations:
- Singlet levels always higher than triplet levels
- Ground state binding energy lower than predicted
- P levels always higher than S levels
- Reason: "exchange energy"
- Shielding of nuclear charge

Term symbols:
\(n^2S+1L\)
He energy levels

singlet  \( S=0 \)

"parahelium"

triplet  \( S=1 \)

"orthohelium"

\[
\begin{array}{c|ccc}
 l & 0 & 1 & 2 \\
 \hline
 S=0 & 3^1S & 3^1P & 3^1D \\
 S=1 & 3^3S & 3^3P & 3^3D \\
\end{array}
\]

Orbital wavefunctions:

\[
\Phi_e(r_1, r_2) = \frac{(\Phi_{100}(r_1)\Phi_{nlm}(r_2) \pm \Phi_{100}(r_2)\Phi_{nlm}(r_1))}{\sqrt{2}}
\]

\[
\Phi_0(r_1, r_2) = \Phi_{100}(r_1)\Phi_{100}(r_2)
\]

Observations

Ground state binding energy lower than predicted

See chapter "variational principle"

P levels always higher than S levels

Shielding of nuclear charge

Singlet levels always higher than triplet levels

Reason: "exchange energy"
Overview „Structure of atoms & the periodic table“

Outline

• Reminder of Piet‘s lecture on orbital and spin structure of atoms
• Energy structure of He
  - „exchange energy“
    examples: He, covalent bonds, magnetism
  - shielding of nuclear charge by inner shell electrons
• Energy structure of atoms with many electrons
  - Hund‘s rules
  - the periodic table

Griffiths 3rd 5.2.2
5.2.1
5.1.2
5.2.2
5.2.2
The periodic table

**Our goals**

- Understand structure of the periodic table
- Determine groundstate electron configuration
Starting point: hydrogen states

Hydrogen-like states for nucleus with charge \(+Ze\)

- maximally two e\(^{-}\) per state, spin ↑ and spin ↓
- in groundstate of multi-e\(^{-}\) atoms, e\(^{-}\) occupy lowest possible states
Energy shifts by shielding

Hydrogen-like states for nucleus with charge $+Ze$

Energy shifts for different principal quantum numbers $n$:

- $n = 1$:
  - 1s

- $n = 2$:
  - 2s
  - 2p

- $n = 3$:
  - 3s
  - 3p
  - 3d

- $n = 4$:
  - 4s
  - 4p
  - 4d
  - 4f
Filling in more electrons

Energy

\[ m_l = -1, 0, +1 \]

1s
2s
2p
3s
3p
3d
4s
4p
4d
4f

Where do the next e\(^-\) go?

\( n = 1 \)  \( n = 2 \)  \( n = 3 \)  \( n = 4 \)

K shell  L shell  M shell  N shell
Hund’s rules

1st Hund’s rule: maximize total e\(^{-}\) spin \(S\)

- \(m_l = \begin{pmatrix} -1 & 0 & +1 \end{pmatrix}\)
- Reason: \(\uparrow \downarrow \uparrow \) has higher energy than \(\uparrow \uparrow \uparrow \) or \(\downarrow \downarrow \downarrow \) because of increased shielding of nuclear charge (and increased repulsion between e\(^{-}\) in the same orbital)
- \(\uparrow \downarrow \uparrow \) has higher energy than \(\uparrow \uparrow \uparrow \) or \(\uparrow \downarrow \uparrow \) because of exchange interaction

2nd Hund’s rule: maximize total e\(^{-}\) orbital angular momentum \(L\) (and projection \(\sum_{i=1}^{Z} m_{l_i}\))

- Handwaving argument:
- \(m_l = \begin{pmatrix} -2 & -1 & 0 & +1 & +2 \end{pmatrix}\)
- \(\uparrow \downarrow \uparrow \uparrow \) has lower energy than e.g. \(\uparrow \uparrow \uparrow \uparrow \uparrow \)
- because e\(^{-}\) “rotate in same direction“ and encounter each other less often \(\longrightarrow\) less Coulomb repulsion

3rd Hund’s rule:

Total electronic angular momentul projection (spin + orbit) \(J\)

- \(J = |L - S|\) if last orbital no more than half filled
- \(J = |L + S|\) if last orbital more than half filled

Reason: spin-orbit coupling (see later)
Filling in more electrons

Energy

$m_l = -1 \ 0 \ +1$

Where do the next e⁻ go?

$n = 1 \quad n = 2 \quad n = 3 \quad n = 4$

K shell \quad L shell \quad M shell \quad N shell
Filling in more electrons

Energy

$m_l = -1 \quad 0 \quad +1$

1s  \quad 2s  \quad 2p  \quad 3s  \quad 3p  \quad 3d  \quad 4p  \quad 4d  \quad 4f

$n = 1 \quad n = 2 \quad n = 3 \quad n = 4$

K shell  \quad L shell  \quad M shell  \quad N shell

4s filled before M shell full
The periodic table

<table>
<thead>
<tr>
<th>Period</th>
<th>Group 1</th>
<th>Group 2</th>
<th>Group 3</th>
<th>Group 4</th>
<th>Group 5</th>
<th>Group 6</th>
<th>Group 7</th>
<th>Group 8</th>
<th>Group 9</th>
<th>Group 10</th>
<th>Group 11</th>
<th>Group 12</th>
<th>Group 13</th>
<th>Group 14</th>
<th>Group 15</th>
<th>Group 16</th>
<th>Group 17</th>
<th>Group 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H 1.008</td>
<td>Li 6.94</td>
<td>Be 4.805</td>
<td>B 1.80</td>
<td>C 1.29</td>
<td>N 1.59</td>
<td>O 1.6</td>
<td>F 1.87</td>
<td>Ne 20.18</td>
<td>Na 22.99</td>
<td>Mg 24.31</td>
<td>Al 13.4</td>
<td>Si 14.01</td>
<td>P 15.24</td>
<td>S 16.0</td>
<td>Cl 35.5</td>
<td>Ar 39.94</td>
<td>K 39.15</td>
</tr>
</tbody>
</table>

---

**Lanthanoids**

- La 138.9
- Ce 140.12
- Pr 140.91
- Nd 144.24
- Pm 145
- Sm 150.36
- Eu 151.96
- Gd 157.25
- Tb 158.93
- Dy 162.50
- Ho 164.93
- Er 167.26
- Tm 168.93
- Yb 173.05

**Actinoids**

- Ac 227.03
- Th 229.06
- Pa 231.04
- U 238.03
- Np 237.04
- Pu 243.04
- Am 243.04
- Cm 247.07
- Bk 247.07
- Cf 251.04
- Es 252.04
- Fm 257.07
- Md 258.1
- No 259.01

---

This plot shows the ground state configuration of neutral, gaseous atoms.

highest orbital with e⁻:

- s
- p
- d
- f
### The periodic table

#### Electronic configuration of chromium

- **Highest orbital with e⁻**: This plot shows the ground state configuration of neutral, gaseous atoms.

#### Period 1
- **Group 1**: 1H
  - Period 1
  - 1.008

#### Period 2
- **Group 2**: 2He
  - Period 2
  - 4.0026

#### Period 3
- **Group 3**: 3Li
  - Period 3
  - 6.94

#### Period 4
- **Group 4**: 4Be
  - Period 4
  - 9.0122

#### Period 5
- **Group 5**: 5B
  - Period 5
  - 10.81

#### Period 6
- **Group 6**: 6C
  - Period 6
  - 12.011

#### Period 7
- **Group 7**: 7N
  - Period 7
  - 14.017

#### Period 8
- **Group 8**: 8O
  - Period 8
  - 16.00

#### Period 9
- **Group 9**: 9F
  - Period 9
  - 19.00

#### Period 10
- **Group 10**: 10Ne
  - Period 10
  - 20.18

#### Period 11
- **Group 11**: 11Na
  - Period 11
  - 22.99

#### Period 12
- **Group 12**: 12Mg
  - Period 12
  - 24.305

#### Period 13
- **Group 13**: 13Al
  - Period 13
  - 26.982

#### Period 14
- **Group 14**: 14Si
  - Period 14
  - 28.085

#### Period 15
- **Group 15**: 15P
  - Period 15
  - 30.974

#### Period 16
- **Group 16**: 16S
  - Period 16
  - 32.06

#### Period 17
- **Group 17**: 17Cl
  - Period 17
  - 35.45

#### Period 18
- **Group 18**: 18Ar
  - Period 18
  - 39.948

---

**Lanthanoids**

<table>
<thead>
<tr>
<th>57 La</th>
<th>58 Ce</th>
<th>59 Pr</th>
<th>60 Nd</th>
<th>61 Pm</th>
<th>62 Sm</th>
<th>63 Eu</th>
<th>64 Gd</th>
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<tr>
<td>138.91</td>
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<td>142.24</td>
<td>144.24</td>
<td>150.36</td>
<td>151.96</td>
<td>157.25</td>
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<td>173.05</td>
<td>186.83</td>
<td>192.22</td>
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**Actinoids**

<table>
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<tr>
<th>89 Ac</th>
<th>90 Th</th>
<th>91 Pa</th>
<th>92 U</th>
<th>93 Np</th>
<th>94 Pu</th>
<th>95 Am</th>
<th>96 Cm</th>
<th>97 Bk</th>
<th>98 Cf</th>
<th>99 Es</th>
<th>100 Fm</th>
<th>101 Md</th>
<th>102 No</th>
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<tr>
<td>227.03</td>
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<td>231.96</td>
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<td>247.07</td>
<td>251.06</td>
<td>252.06</td>
<td>259.10</td>
<td></td>
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</tbody>
</table>
The periodic table

<table>
<thead>
<tr>
<th>Period</th>
<th>Group 1</th>
<th>Group 2</th>
<th>Group 3</th>
<th>Group 4</th>
<th>Group 5</th>
<th>Group 6</th>
<th>Group 7</th>
<th>Group 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H 1.008</td>
<td>Li 6.94</td>
<td>Na 22.99</td>
<td>K 39.10</td>
<td>Rb 85.46</td>
<td>Cs 132.91</td>
<td>Fr 223.02</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Be 9.022</td>
<td>Mg 12.01</td>
<td>Ca 40.08</td>
<td>Sr 38.08</td>
<td>Y 80.0</td>
<td>Ba 137.33</td>
<td>Ra 226.03</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>B 10.01</td>
<td>C 12.01</td>
<td>N 14.01</td>
<td>O 16.00</td>
<td>F 18.09</td>
<td>Ne 20.18</td>
<td><strong>Actinoids</strong></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Al 13.00</td>
<td>Si 14.01</td>
<td>P 15.00</td>
<td>S 16.00</td>
<td>Cl 35.45</td>
<td>Ar 39.94</td>
<td><strong>Actinoids</strong></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>P 15.00</td>
<td>S 16.00</td>
<td>Cl 35.45</td>
<td>Ar 39.94</td>
<td>K 40.08</td>
<td>Ca 40.08</td>
<td>Sr 87.62</td>
<td>Ba 137.33</td>
</tr>
<tr>
<td>6</td>
<td>Sc 44.96</td>
<td>Ti 47.87</td>
<td>V 50.94</td>
<td>Cr 52.93</td>
<td>Mn 55.85</td>
<td>Fe 56.94</td>
<td>Co 58.93</td>
<td>Ni 63.54</td>
</tr>
<tr>
<td>7</td>
<td>Y 88.91</td>
<td>Zr 91.22</td>
<td>Nb 92.91</td>
<td>Mo 95.96</td>
<td>Tc 98.96</td>
<td>Ru 101.07</td>
<td>Rh 102.91</td>
<td>Pd 106.42</td>
</tr>
<tr>
<td>8</td>
<td>Lu 174.97</td>
<td>Hf 178.49</td>
<td>Ta 180.95</td>
<td>W 183.84</td>
<td>Re 186.21</td>
<td>Os 189.23</td>
<td>Ir 192.22</td>
<td>Pt 195.08</td>
</tr>
<tr>
<td>9</td>
<td>Fr 223.02</td>
<td>Ra 226.03</td>
<td><strong>Lanthanoids</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This plot shows the ground state configuration of neutral, gaseous atoms.

The highest orbital with e− is indicated by the color coding:
- s: blue
- p: yellow
- d: red
- f: green

The periodic table includes the elements from hydrogen (H) to xenon (Xe), with periodic trends in atomic number, electron configuration, and chemical properties.
Outline

- Reminder of Piet’s lecture on orbital and spin structure of atoms
  Griffiths 3rd 5.2.2
- Energy structure of He
  - „exchange energy“
    examples: He, covalent bonds, magnetism
  - shielding of nuclear charge by inner shell electrons
- Energy structure of atoms with many electrons
  - Hund’s rules
  - the periodic table
Quantum mechanics 3
Structure of matter
Lecture 9

Piet Mulders
Florian Schreck
University of Amsterdam
Overview of course

Part 1: 7 lectures in January (Piet Mulders)
- Basics of quantum mechanics
- Spin states
- Addition of angular momentum
- Identical particles
- Basic structure of atom

Part 2: 7 lectures in February and March (Florian Schreck)
- Structure of atoms & the periodic table
- Crystalline solids
- Time-independent perturbation theory
- Structure of hydrogen
- Variational principle
- Time-dependent perturbation theory, atom-light interaction

Lecture notes, problem sets and link to video recordings of C0.110 lectures available on Canvas

Questions: schreck@StrontiumBEC.com
He energy levels

<table>
<thead>
<tr>
<th>Energy relative to He$^+$ ion (eV)</th>
<th>n</th>
<th>1S</th>
<th>1P</th>
<th>1D</th>
<th>2S</th>
<th>2P</th>
<th>2D</th>
<th>3S</th>
<th>3P</th>
<th>3D</th>
</tr>
</thead>
<tbody>
<tr>
<td>-24.5</td>
<td>n=1</td>
<td>1S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-5</td>
<td>n=2</td>
<td>2S</td>
<td>2P</td>
<td>2D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-2</td>
<td>n=3</td>
<td>3S</td>
<td>3P</td>
<td>3D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

singlet
S=0
„parahelium“

triplet
S=1
„orthohelium“

Orbital wavefunctions:

$$
\Phi_{\text{singlet}}(\vec{r}_1, \vec{r}_2) = \frac{(\Phi_{100}(\vec{r}_1)\Phi_{n0m}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2)\Phi_{n0m}(\vec{r}_1))}{\sqrt{2}}
$$

$$
\Phi_{\text{triplet}}(\vec{r}_1, \vec{r}_2) = \Phi_{100}(\vec{r}_1)\Phi_{100}(\vec{r}_2)
$$

Observations

$$
\eta^{2S+1} \ell
$$

term symbols
Example 2: covalent bonds

Potential energy curves of H$_2$ molecule

**Triplet**  
\[ \chi = \begin{cases}  
|t_{+1}\rangle = |\uparrow\rangle |\uparrow\rangle \\
|t_0\rangle = (|\uparrow\rangle |\downarrow\rangle + |\downarrow\rangle |\uparrow\rangle) / \sqrt{2} \\
|t_{-1}\rangle = |\downarrow\rangle |\downarrow\rangle 
\end{cases} \]

**Singlet**  
\[ \chi = |s\rangle = (|\uparrow\rangle |\downarrow\rangle - |\downarrow\rangle |\uparrow\rangle) / \sqrt{2} \]
Where do the next e\(^{-}\) go?
Overview of course

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today

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Questions: schreck@StrontiumBEC.com
Overview of topic „Solids“

1) The free electron gas (Bonus material)  
  Griffiths 5.3.1

   simple model describing metals
   explains why solid objects cannot easily be compressed
   essentially the same model describes shape of
      • white dwarfs
      • neutron stars
      • ultracold gases of fermionic atoms

2) Electrons in periodic potential  
  Griffiths 5.3.2

   simple model describing crystals
   explains under which conditions a solid is a
      • conductor
      • semiconductor
      • insulator
Crystalline solids

Selenite crystals, Naica mine, Mexico  © National Geographic
Overview „The free electron gas“

1) The free electron gas

simple model describing metals
explains why solid objects cannot easily be compressed
essentially the same model describes shape of

• white dwarfs
• neutron stars
• ultracold gases of fermionic atoms

Plan of section

• Electrons in a box: eigenstates and energies
• Zero temperature distribution of electrons over states
• Total energy of T=0 electron gas
• Pressure of T=0 electron gas
Solids

Structure

- nuclei
- tightly bound inner $e^-$
- loosely bound outer $e^-$ (valence $e^-$)

Valence $e^-$ determine many properties of solids
e.g. conductivity, magnetism, color,…

Here only interested in behavior of valence $e^-$

Potential seen by valence $e^-$:

Coulomb potential of "ionic core" = nucleus and inner $e^-$
The free electron gas

Potential seen by valence e⁻:

- Coulomb potential of "ionic core"
- Simplified description: e⁻ in box potential

Diagram:

- Edge of solid
- Coulomb potential
- Simplified description: e⁻ in box potential
Compare distinguishable particles and e\(^{-}\), both at zero temperature

Distinguishable particles:
- Number of particles times energy of lowest state
- Total energy: very small

Electrons:
- Sum of energies of all particles
- A significant fraction of the Fermi energy
- Increases with atom number and can be very large

Iron:
- \( E_F = 11 \text{eV} = k_B \times 10^5 \text{K} \)
- \( v_F = 2 \times 10^6 \text{m/s} \)
- Always the case if we have many identical fermions, not only for e\(^{-}\)
Compare same number of e\(^-\) in boxes of different size, always at zero temperature

identical fermions do not „like“ to be compressed
identical fermions will act against the compression by exerting a pressure against the box walls, the Fermi pressure

This pressure, e.g. stabilizes neutron stars against gravitational collapses. The box in that case is the gravitational well created by the star itself.
Preview of second essential result

Compare same number of distinguishable particles in boxes of different size, always at zero temperature

- total energy stays the same
- no energy needed to compress gas
- no pressure acts against compression
1) The free electron gas

In metals valence e\textsuperscript{-} move easily through lattice $\rightarrow$ neglect potential of ionic cores

Consider rectangular metal block with dimensions $l_i; \; i \in \{1, 2, 3\}$

e\textsuperscript{-} can’t leave solid

$\rightarrow$ potential $V(\vec{r}) = \begin{cases} 0 & \text{if } 0 < x_i < l_i \\ \infty & \text{else} \end{cases}$, $\vec{r} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$

Schrödinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) = E \psi(\vec{r})$$

; $\psi(\vec{r}) = 0$ outside solid

Ansatz $\psi(\vec{r}) = \prod_i \phi_i(x_i)$

$\rightarrow$ $-\frac{\hbar^2}{2m} \frac{d^2}{dx_i^2} \phi_i(x_i) = E_i \phi_i(x_i)$ and $E = \sum_i E_i$

Solution $\phi_i(x_i) = A_i \sin(k_i x_i) + B_i \cos(k_i x_i)$ with $k_i \equiv \sqrt{2mE_i/\hbar}$ $\rightarrow$ $E_i = \frac{\hbar^2 k_i^2}{2m}$

$\rightarrow$ $E = \sum_i \frac{\hbar^2 k_i^2}{2m}$
1) The free electron gas

In metals valence e\(^{-}\) move easily through lattice \(\rightarrow\) neglect potential of ionic cores

Consider rectangular metal block with dimensions \(l_{i}; \ i \in \{1, 2, 3\}\)
e\(^{-}\) can't leave solid

\[ V(\vec{r}) = \begin{cases} 0 & \text{if } 0 < x_{i} < l_{i} \\ \infty & \text{else} \end{cases} \]

\[ \vec{r} = \begin{pmatrix} x_{1} \\ x_{2} \\ x_{3} \end{pmatrix} \]

Solution \[ \phi_{i}(x_{i}) = A_{i} \sin(k_{i}x_{i}) + B_{i} \cos(k_{i}x_{i}) \]

with \[ k_{i} = \sqrt{2mE_{i}/\hbar} \]

\[ E = \sum_{i} \frac{\hbar^{2}k_{i}^{2}}{2m} \]

Boundary conditions: \( \phi_{i}(0) = 0 \) imposes \( B_{i} = 0 \)
\( \phi_{i}(l_{i}) = 0 \) imposes quantization \( k_{i} = n_{i}\pi/l_{i}, \ \text{with } n_{i} \in \{1, 2, \ldots\} \).

Energies:

\[ E_{\{n_{i}\}} = \frac{\hbar^{2}}{2m} \sum_{i} k_{i}^{2} = \frac{\hbar^{2}}{2m} |\vec{k}|^{2} \]

\[ \vec{k} = \begin{pmatrix} k_{1} \\ k_{2} \\ k_{3} \end{pmatrix} \]

“wavevector”

Sidenote: Why only positive \( k_{i} \)?

We used standing waves as ansatz.
For them \( -k_{i} \) leads after normalization to same wavefunction as \( k_{i} \).
\( \rightarrow \) No negative \( k_{i} \) to avoid double counting.
If we had used running waves, we would have found positive and negative \( k_{i} \), but half as densely spaced. Boils down to same result for total energy and pressure.
**k-space quantization**

Allowed points in $k$-space form a grid:

- One state per $k$-space volume: $V_k = \prod_i \frac{\pi}{l_i} = \frac{\pi^3}{V}$; $V$ is volume of solid.
- Each state can be occupied by one spin-up and one spin-down $e^-$.
- Each of the $N$ atoms in the metal contributes $q$ electrons to the free $e^-$ gas.
- $N_e = Nq$ valence $e^-$ exist in metal.

Griffiths Fig. 5.3
Zero temperature Fermi gas

Fill up lowest energy states with 2 e\(^{-}\) each until all \(N_q\) valence e\(^{-}\) are distributed

Since \(E = \frac{\hbar^2}{2m}k^2\), occupied states fill 1/8 of a sphere in \(k\)-space up to

\[k_F = \sqrt{\frac{2mE_F}{\hbar}},\] the Fermi wave vector.
Number of occupied states

k-space volume to be filled:

\[ k_1 \]

\[ k_F \]

Fermi surface

\[ k_2 \]

\[ k_3 \]

Conditions:

- one state per k-space volume
  \[ V_k = \prod_i \frac{\pi}{l_i} = \frac{\pi^3}{V} \]
- each state can be occupied by two e^-
- \[ N_e = N_q \] valence e^- exist in metal

# states to be filled:

\[ N_k = \frac{\text{Volume of 1/8 sphere in k space with radius } k_F}{\text{Volume of k-space per state}} \]

\[ = \frac{1}{8} \left( \frac{4}{3} \pi k_F^3 \right) / \left( \frac{\pi^3}{V} \right) \quad \text{(Valid since } l_i \ll k_F) \]

fill states with e^-:

\[ N_e = 2N_k = \frac{1}{3} k_F^3 V/\pi^2 \]

\[ \| \]

\[ N_q \]

\[ k_F^3 = 3\pi^2 \frac{N_q}{V} \rightarrow k_F = (3\pi^2 \rho)^{1/3} \quad \text{with e^- density } \rho = \frac{N_q}{V} \]
Energy of e\(^-\) gas

e\(^-\) on the shell of width \(dk\) have same \(|k|\) and same energy

\[
E(\vec{k}) = \frac{\hbar^2 k^2}{2m}
\]

Density in k-space of e\(^-\) with \(|k|\) is

\[
n(k) = \frac{\# e^- \text{ in shell as shown in figure}}{dk} = \frac{\text{Volume of shell as drawn}}{\text{Volume of } k^-\text{-space per state}} \cdot \frac{2(\text{for spin})}{dk}
\]

\[
= \frac{2}{8} (4\pi k^2) \frac{dk}{d\vec{k}} \frac{\pi^3}{V} = V \frac{k^2}{\pi^2}
\]

Energy density:

\[
\epsilon = \frac{E}{V} = \frac{1}{V} \int_0^{k_F} n(k)E(k)dk = \int_0^{k_F} \frac{k^2}{\pi^2} \frac{\hbar^2 k^2}{2m} \frac{d\vec{k}}{V} = \frac{\hbar^2}{2\pi^2 m} \frac{1}{5} k_F^5 = \frac{\hbar^2 (3\pi^2 \rho)^{5/3}}{10\pi^2 m}
\]

Energy:

\[
E = \epsilon V = \frac{\hbar^2 (3\pi^2 N q)^{5/3}}{10\pi^2 m} V^{-2/3} = CV^{-2/3}
\]

\(k_F = (3\pi^2 \rho)^{1/3}\)
Overview „The free electron gas“

1) The free electron gas

simple model describing metals
explains why solid objects cannot easily be compressed
essentially the same model describes shape of

• white dwarfs
• neutron stars
• ultracold gases of fermionic atoms

Plan of section

• Electrons in a box: eigenstates and energies
• Zero temperature distribution of electrons over states
• Total energy of T=0 electron gas
• Pressure of T=0 electron gas
Degeneracy pressure

Pressure $P$ of e$^-$ gas performs work on piston by moving it out a distance $dx$, thereby expanding the volume by $dV = Adx$

Energy change of e$^-$ gas:

$$\frac{dE}{dV} = -\frac{2}{3}CV^{-5/3} = -\frac{2}{3}E \frac{1}{V}$$

This energy was used to move piston outwards, doing work

$$dW = F \cdot dx = \frac{F}{A} \cdot Adx = P \cdot dV$$

$$dW = -dE$$

$$P = \frac{2}{3} \frac{E}{V} = \frac{(3\pi^2)^{2/3}}{5m} \frac{\hbar^2}{\rho^{5/3}}$$

"Pauli pressure" or "degeneracy pressure"

Origin of pressure is Pauli's exclusion principle!

It helps to stabilize objects, even without Coulomb repulsion and at zero temperature.
The Lifecycle of a Star

- Globule
- Dust Cloud
- Nebula
- Black Hole
- Protostar
- Brown Dwarf
- Main Sequence Star
- Red Giant
- White Dwarf
- Black Dwarf
- Neutron Star
- Supernova

Image: Christian Knigge
Indirect detection of gravitational waves

Nobel prize 1993

Russell A. Hulse
Prize share: 1/2

Joseph H. Taylor Jr.
Prize share: 1/2

The Nobel Prize in Physics 1993 was awarded jointly to Russell A. Hulse and Joseph H. Taylor Jr. “for the discovery of a new type of pulsar, a discovery that has opened up new possibilities for the study of gravitation”
Direct detection of gravitational waves

LIGO interferometer

Black hole merger, 14.9.2015
80 to 160 million years before 17 Aug 2017
Neutron star merger, 17 Aug 2017


Direct detection of gravitational waves

LIGO interferometer

The Nobel Prize in Physics 2017

Rainer Weiss
Prize share: 1/2

Barry C. Barish
Prize share: 1/4

Kip S. Thorne
Prize share: 1/4

The Nobel Prize in Physics 2017 was divided, one half awarded to Rainer Weiss, the other half jointly to Barry C. Barish and Kip S. Thorne "for decisive contributions to the LIGO detector and the observation of gravitational waves".
Overview of topic „Crystalline solids“

Electrons in periodic potential

simple model describing crystals

explains under which conditions a solid is a

• conductor
• semiconductor
• insulator

Applications

• LED
• solar cell
• transistor
Solids

Structure

- **Nuclei**
- **Tightly bound inner electrons**
- **Loosely bound outer electrons** (valence electrons)

Valence electrons determine many properties of solids:
- e.g. conductivity, magnetism, color, ...

Here only interested in behavior of valence electrons.

Potential seen by valence electrons:

- **Coulomb potential of “ionic core”** = nucleus and inner electrons
- **Edge of solid**
Goal of “Electrons in periodic potentials”

Goal of this section
   energy level structure of electron in periodic potential

\( e^{-} \) in free space

\( E(k) \)

\( E \)

\( k \)

allowed energies

all energies allowed

\( e^{-} \) in periodic potential
   (this chapter)

\( E(k) \)

\( E \)

\( k \)

allowed energies

forbidden energies!
Shooting an electron onto a solid

**Case 1: Energy within allowed band**

$t = t_0$

vaccum  solid

allowed energies

$t > t_0$

Electron continues to propagate in solid

**Case 2: Energy within band gap**

$t = t_0$

vaccum  solid

allowed energies

$t > t_0$

Electron unable to propagate through solid. (It is reflected.)
Band gaps in optics of visible light

Dichroic mirror
red reflected
green-blue transmitted

Dielectric dichroic mirror

red light
constructive interference
red reflected

Index of refraction
high
low

$\leftrightarrow d = \frac{\lambda_{\text{red}}}{2}$
(for small angle and wavelength in material)

green light
destructive interference
not reflected

Index of refraction
high
low

$\leftrightarrow d \neq \frac{\lambda_{\text{green}}}{2}$

transmitted

Wavelength dependent reflection and transmission

Lattice spacing: $\sim \lambda/2 \sim$ few 100 nm $\sim 100s$ of lattice spacings
X-ray diffraction

**X rays** $\lambda \sim \text{nm} \sim \text{order of lattice spacing}$

X rays are scattered by atoms

Emerald, a beryl crystal

Constructive interference when

$$n\lambda = 2d \sin\theta$$

Bragg's Law
X-ray diffraction

X rays

\[ \lambda \sim \text{nm} \sim \text{order of lattice spacing} \]

X rays are scattered by atoms

Constructive interference when

\[ n\lambda = 2d \sin \theta \]

Bragg’s Law

Beryllium crystal diffraction pattern

Maurice van Horn 1957
Shooting an electron onto a solid

Case 1: Energy within allowed band

\[ t = t_0 \]

<table>
<thead>
<tr>
<th>vacuum</th>
<th>solid</th>
</tr>
</thead>
</table>
| \( E \) allowed energies \( x \)

\[ t > t_0 \]

Electron continues to propagate in solid

Case 2: Energy within band gap

\[ t = t_0 \]

<table>
<thead>
<tr>
<th>vacuum</th>
<th>solid</th>
</tr>
</thead>
</table>
| \( E \) allowed energies \( x \)

\[ t > t_0 \]

Electron unable to propagate through solid. (It is reflected.)
Why bandgaps in electron energies?

Electrons are matter waves with \( \lambda_{\text{deBroglie}} = \frac{h}{p} \sim \text{nm} \sim \text{order of lattice spacing} \)

**Band gaps by Bragg reflection**

\[ d = \frac{\lambda_{\text{deBroglie}}}{2} \quad (\text{for small angle}) \]

If e\(^{-}\) with a wavelength that fulfills Bragg reflection condition tries to enter crystal it will be back reflected!

e\(^{-}\) with the corresponding momentum and energy can’t exist in crystal

\[ \rightarrow \text{forbidden energy} \]
Overview “Electrons in periodic potentials”

**Goal of this chapter**
energy level structure of electron in periodic potential

**Plan of this section**
1) Derive allowed and forbidden energies
   - Bloch’s theorem
   - solve Schrödinger equation of 1 particle in periodic potential
2) Discussion:
   - Placing many particles in that potential
   - Is a material an insulator or a conductor?
For a periodic potential the solution of Schrödinger equation satisfies (I) with \( x \)-independent \( K \). (\( K \) can depend on e.g. \( E \))

We assume ion cores form periodic structure

\[ V(x + a) = V(x) \]

**Bloch’s theorem**

For a periodic potential \( V(x + a) = V(x) \) the solution of Schrödinger equation

\[ \hat{H}\psi(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x) \]

satisfies

(I) \[ \psi(x + a) = e^{iKa}\psi(x) \] with \( x \)-independent \( K \). (\( K \) can depend on e.g. \( E \))

and

(II) \[ \psi(x) = e^{iKx}u(x) \] with periodic function \( u(x + a) = u(x) \)
Meaning of (II): Bloch wavefunction

\[ \psi(x) = e^{iKx} u(x) \]

- \( V(x) \) represents the potential energy function in the lattice.
- \( |u(x)|^2 \) describes the density of electron in the unit cell of the lattice.
- \( e^{iKx} \) describes transport through the lattice with momentum \( K \).
- \( \arg(\Psi) \) represents the phase of the wavefunction.
For a periodic potential the solution of Schrödinger equation satisfies (I) with \( x \)-independent \( K \). (\( K \) can depend on e.g. \( E \))

We assume ion cores form periodic structure

\[ V(x + a) = V(x) \]

### Bloch’s theorem

For a periodic potential \( V(x + a) = V(x) \) the solution of Schrödinger equation

\[ \hat{H}\psi(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x) \]

satisfies (I) \( \psi(x + a) = e^{iKa}\psi(x) \) with \( x \)-independent \( K \). (\( K \) can depend on e.g. \( E \))

and (II) \( \psi(x) = e^{iKx}u(x) \) with periodic function \( u(x + a) = u(x) \)
Equivalence of (I) and (II)

Show equivalence of (I) and (II)

(I) \[ \psi(x + a) = e^{iK_a} \psi(x) \] with x-independent \( K \). \( K \) can depend on e.g. \( E \)

(II) \[ \psi(x) = e^{iK_x} u(x) \] with periodic function \( u(x + a) = u(x) \)

Prove (II) \( \rightarrow \) (I):

\[ \Psi(x + a) = e^{iK(x+a)} u(x + a) = e^{iK_a} e^{iK_x} u(x) = e^{iK_a} \Psi(x) \rightarrow \] (I)
Equivalence of (I) and (II)

Show equivalence of (I) and (II)

(I) \( \psi(x + a) = e^{iKa} \psi(x) \) with \( x \)-independent \( K \). (\( K \) can depend on e.g. \( E \))

(II) \( \psi(x) = e^{iKx} u(x) \) with periodic function \( u(x + a) = u(x) \)

Prove (I) \( \rightarrow \) (II):

Ansatz: \( \psi(x) = e^{iKx} u(x) \), i.e. \( u(x) = e^{-iKx} \Psi(x) \)

Is \( u(x) \) periodic?

\[
\Psi(x + a) = e^{iK(x+a)} u(x + a)
\]

(\( I \)) \( \rightarrow \) \( || \) \( e^{iKx} \Psi(x) = e^{iKx} e^{iKa} u(x) \)

\[
\Psi(x + a) = e^{iK(x+a)} u(x + a)
\]

\( \Psi(x + a) = e^{iKx} \Psi(x) \)

\( u(x + a) = u(x) \)

\( e^{iKx} \Psi(x) = e^{iKx} e^{iKa} u(x) \)

\( \rightarrow \) (II) \( \psi(x) = e^{iKx} u(x) \) with periodic function \( u(x + a) = u(x) \)
For a periodic potential \( V(x + a) = V(x) \) the solution of Schrödinger equation satisfies (I) with \( \psi(x + a) = e^{iK_a} \psi(x) \) with \( x \)-independent \( K \). (\( K \) can depend on e.g. \( E \))

and (II) \( \psi(x) = e^{iKx} u(x) \) with periodic function \( u(x + a) = u(x) \)
Proof of Bloch’s theorem

We will show (I). In order to do this we need to first proof:

Let \( \hat{D} \) be displacement operator

\[
\hat{D} f(x) = f(x + a)
\]

then for periodic potential

\[
\left[ \hat{D}, \hat{H} \right] = 0
\]

Proof

\[
\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)
\]

\[
\hat{D} \frac{d^2}{dx^2} f(x) = \hat{D} f''(x) = f''(x + a) = \frac{d^2}{dx^2} f(x + a) = \frac{d^2}{dx^2} \hat{D} f(x)
\]

\[
\hat{D} V(x) f(x) = V(x + a) f(x + a) = V(x) f(x + a) = V(x) \hat{D} f(x)
\]

\( \hat{D} \) and \( \hat{H} \) commute and therefore have common basis.
Commuting observables have common basis

Wikipedia entry „Complete set of commuting observables“

When \( A \) has non-degenerate eigenvalues:

Let \( \{ |\psi_n\rangle \} \) be a complete set of eigenkets of \( A \) corresponding to the set of eigenvalues \( \{ a_n \} \). If the operators \( A \) and \( B \) commute, we can write

\[
A(B|\psi_n\rangle) = BA|\psi_n\rangle = a_n(B|\psi_n\rangle)
\]

So, we can say that \( B|\psi_n\rangle \) is an eigenket of \( A \) corresponding to the eigenvalue \( a_n \). The non-degeneracy of \( a_n \) implies that \( B|\psi_n\rangle \) and \( |\psi_n\rangle \) can differ at most by a multiplicative constant. We call this constant \( b_n \). So,

\[
B|\psi_n\rangle = b_n|\psi_n\rangle
\]

So, \( |\psi_n\rangle \) is eigenket of the operators \( A \) and \( B \) simultaneously.

Degenerate case also derived in this Wikipedia entry.
Proof of Bloch’s theorem

Want to show (I): \( \psi(x + a) = e^{iKa} \psi(x) \)

Let \( \psi \) be eigenvector of \( \hat{D} \) with eigenvalue \( \lambda \in \mathbb{C} \).

\[
\hat{D} \psi(x) = \lambda \psi(x) \quad \rightarrow \quad \psi(x + a) = \lambda \psi(x)
\]

Which values of \( \lambda \) are allowed?

\( \lambda \) can be written as

\[
\lambda = A e^{iKa}, \ A, K \in \mathbb{R}
\]

\( (\lambda = 0 \rightarrow \psi(x) = 0 \), not interesting \)

If crystal very large, boundaries don’t change physics in crystal.

We get rid of boundaries by bending huge crystal into a circle.

\[
\begin{align*}
\psi(x + Na) &= \psi(x) \\
\lambda^N \psi(x) &= \lambda^N \psi(x)
\end{align*}
\]

\[
\lambda^N = A^N e^{iNKa} = 1
\]

\( \Rightarrow A = 1 \quad \rightarrow \quad \text{(I)} \quad \square \)

\[
\Rightarrow NKa = 2\pi j; \ j \in \mathbb{Z}
\]

\[
K_j = \frac{2\pi}{aN} j
\]

Only \( j \in \{0, 1, \ldots, N - 1\} \) need to be considered. Beyond that interval \( \lambda = e^{iK_j a} \) values just repeat.
Goal of this chapter
energy level structure of electron in periodic potential

Plan of this section
1) Derive allowed and forbidden energies
   • Bloch’s theorem
   • solve Schrödinger equation of 1 particle in periodic potential
2) Discussion:
   • Placing many particles in that potential
   • Is a material an insulator or a conductor?
Solve Schr. eqn. for periodic potential

**Goal:** find allowed energies for electron in periodic potential

Model potential: Dirac comb with periodic boundaries

\[ V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - aj) \]

\( V(x) \) is the potential function, where \( \alpha \) is a constant, and \( \delta(x - aj) \) represents a \( \delta \)-function at points \( x = aj \), with \( j \) ranging from 0 to \( N-1 \). The potential is periodic with a period of \( a \), and the sum accounts for the repeated units of the potential across the space spanned by \( x \) from \(-a\) to \( 3a\).
Solve Schr. eqn. for periodic potential

Schrödinger equation for "right" interval $0 < x < a$

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi = E \psi$$

General solution of this differential equation:

$$\psi_{\text{right}}(x) = A \sin (kx) + B \cos (kx) \quad \text{with} \quad k = \frac{\sqrt{2mE}}{\hbar}$$

Our goal: find allowed values for $k$ and $E$. (Here not interested in $A$ and $B$)

Use Bloch's theorem to find solution in "left" interval $-a < x < 0$

$$\psi(x + a) = e^{iKa} \psi(x)$$

$$\psi(x) = e^{-iKa} \psi(x + a)$$

$$\psi_{\text{left}}(x) = e^{-iKa} \psi_{\text{right}}(x + a) = e^{-iKa} [A \sin (k(x + a)) + B \cos (k(x + a))]$$
Solve Schr. eqn. for periodic potential

\[ \psi_{\text{right}}(x) = A \sin(kx) + B \cos(kx) \]

\[ \psi_{\text{left}}(x) = e^{-ik_0^a} [A \sin(k(x + a)) + B \cos(k(x + a))] \]

Now stitch left and right solution together using continuity equations for \( \delta \)-function potential derived in Griffiths chapter 2.

\[ V(x) = \alpha \delta(x) \]

(a) \( \psi_{\text{right}}(x = 0) = \psi_{\text{left}}(x = 0) \)

(b) \[ \frac{d}{dx} \psi_{\text{right}} \bigg|_{x=0} - \frac{d}{dx} \psi_{\text{left}} \bigg|_{x=0} = \frac{2m\alpha}{\hbar^2} \psi(0) \]

(a) \[ B = e^{-ik_0^a} [A \sin(ka) + B \cos(ka)] \implies A \sin(ka) = B \left[e^{ik_0^a} - \cos(ka)\right] \quad (*) \]

(b) \[ ka - e^{-ik_0^a} k [A \cos(ka) - B \sin(ka)] = \frac{2m\alpha}{\hbar^2} B \]

Multiply by \( \sin(ka) \), insert (*)

\[ kB \left[e^{ik_0^a} - \cos(ka)\right] - e^{-ik_0^a} kB \left[\cos(ka) \left(e^{ik_0^a} - \cos(ka)\right) - \sin^2(ka)\right] = \frac{2m\alpha}{\hbar^2} B \sin(ka) \]
Solve Schr. eqn. for periodic potential

\[ kB \left[ e^{iKa} - \cos(ka) \right] - e^{-iKa}kB \left[ \cos(ka) \left( e^{iKa} - \cos(ka) \right) - \sin^2(ka) \right] = \frac{2m\alpha}{\hbar^2} B \sin(ka) \]

Divide by $kB$, sort terms

\[ e^{iKa} - \cos(ka) - \cos(ka) + e^{-iKa} \cos^2(ka) + e^{-iKa} \sin^2(ka) = \frac{2m\alpha}{\hbar^2 k} \sin(ka) \]

\[ 2 \cos(Ka) - 2 \cos(ka) = \frac{2m\alpha}{\hbar^2 k} \sin(ka) \]

\[ \cos(Ka) = \cos(ka) + \frac{m\alpha}{\hbar^2 k} \sin(ka) \quad (**) \]

Simplify notation

\[ z \equiv ka \; ; \quad \beta \equiv \frac{m\alpha a}{\hbar^2} \]

Right hand side of (**) becomes

\[ f(z) \equiv \cos(z) + \beta \frac{\sin(z)}{z} \]

Need to find solutions of

\[ (**) \quad \cos(Ka) = f(z) \]
Solve Schr. eqn. for periodic potential

For which values of $z$ do we have solutions of (**)?

\[
(**) \quad \cos(K_j a) = f(z) \quad ; \quad f(z) \equiv \cos(z) + \beta \frac{\sin(z)}{z} \quad ; \quad z \equiv ka \quad ; \quad \beta \equiv \frac{m \alpha a}{\hbar^2}
\]

\(\cos(K_j a)\) can take any value from +1 to -1 since \(K_j = \frac{2\pi}{aN} j \quad ; \quad j \in \{0, 1, \ldots, N-1\}\)

Find solutions of (**) graphically:

Solutions exist for these intervals of $z$ values.  

Griffiths Fig. 5.6
Let's zoom into one interval of allowed values:

\[ f(z) \]

\[ \cos(K_j a) \]

\[ K_j = \frac{2\pi}{aN} j \]

\[ j \in \{0, 1, \ldots, N-1\} \]

\[ N \text{ allowed values of } z = ka \]

N usually huge \((10^{20})\) → Virtually any value of \(z = ka\) within interval allowed, but non outside.

Since

\[ E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left( \frac{z}{a} \right)^2 \]

each interval of allowed \(z\) values corresponds to an interval of allowed energies, an "energy band".
Overview “Electrons in periodic potentials”

Goal of this chapter
energy level structure of electron in periodic potential

Plan of this section
1) Derive allowed and forbidden energies
   • Bloch’s theorem
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   • Placing many particles in that potential
   • Is a material an insulator or a conductor?
Band structure

- $N$ states per energy band
- $2$ $e^-$ per state (spin-up and spin-down)
- $N$ atoms in lattice, each providing $q$ valence $e^-$ to fill states

At zero temperature, assuming weakly-interacting $e^-$:

$q = 1$ : lowest band half filled

$E_F$ within lowest band

$q = 2$ : lowest band filled

$E_F$ at top of lowest band

$n = 1$ - band not filled

$q = 3$ : $n = 0$ - band filled

$n = 1$ - band half filled

$E_F$ in the middle of $n = 1$ - band

$n = 2$ - band not filled
Insulators, semiconductors, conductors

The solutions \( \psi(x) \) we found contain equal amounts of left & right moving waves, e.g. \( \sin(kx) = \frac{e^{ikx} - e^{-ikx}}{2i} \).

To obtain a current, we need an excess of occupied states moving in one direction. This can only be achieved by exciting electrons to higher states.

Cases:

- **\( q \) even**
  - \( E \)
  - Empty band
  - Filled band
  - \( \Delta E \gg k_B T \)
  - no excitations possible

- **\( q \) even**
  - \( E \)
  - Thermally excited \( e^- \)
  - Conduction band
  - Valence band
  - \( \Delta E < k_B T \)
  - \( e^- \) in conduction band and empty states ("holes") in valence band can easily move

- **\( q \) odd**
  - \( E \)
  - Partially filled band
  - Vanishingly small energy needed for excitation around Fermi energy.
  - Many \( e^- \) can easily move

**Insulator**

**Semiconductor**

**Conductor**

Conducts better for higher \( T \)
Doping

In a crystal with even $q$ (usually semiconductor) replace a few atoms with atoms that have more or less valence electrons than $q$.

**higher $q$**
- Si ($q = 2$)
- doped with P ($q = 3$)

**lower $q$**
- Si ($q = 2$)
- doped with Al ($q = 1$)

- Extra $e^-$ from P

$n$-doped
- $e^-$ in conduction band
- carry current

$p$-doped
- holes in valence band
- carry current

Interesting effects happen at interface between n-doped and p-doped semiconductors.

→ diodes, transistors,… Basis of semiconductor industry.
Light-emitting Diode (LED)

Placing n-doped and p-doped semiconductor next to each other leads to one-way conductor for current. Light can be emitted at interface.
Light-emitting Diode (LED)

Placing n-doped and p-doped semiconductor next to each other leads to one-way conductor for current. Light can be emitted at interface.

No current can flow if voltage connected as shown.
Light-emitting Diode (LED)

Placing n-doped and p-doped semiconductor next to each other leads to one-way conductor for current. Light can be emitted at interface.

Current flows if voltage connected as shown.

In LEDs energy of electron combining with hole liberated as photon.
Infrared light transmission through silicon

- **Partially absorbed**
- **Partially reflected**
- **Partially transmitted**

\[ E = h\nu_{\text{visible}} > E_{\text{gap}} \]
- Partially absorbed
- Partially reflected

\[ E = h\nu_{\text{infrared}} < E_{\text{gap}} \]
- Partially transmitted
- Partially reflected
n-p junction at rest: e\textsuperscript{-} combine with holes, creating charge distribution and E-field
Photodiode / solar cell

n-p junction at rest: e\(^{-}\) combine with holes, creating charge distribution and E-field
Photodiode / solar cell

n-p junction at rest: $e^-$ combine with holes, creating charge distribution and E-field

$n$ - doped  $p$ - doped

e$^-$ pulled to n-doped side by E-field

$\Delta E = \hbar \nu$

hole pulled to p-doped side by E-field

current flows
Photovoltaics learning curve

Swanson's law

Average module price (2015 USD/Wp)

Cumulative module shipments, MWp
Levelized cost of electricity

without storage

Levelized cost of electricity for Germany
in EuroCent/kWh, source: Fraunhofer ISE; March 2018

EuroCent/kWh

PV roof small  PV roof large  PV utility  Wind onshore  Wind offshore  Biogas  Coal lignite  Coal hard  CCGT natural gas

nuclear (OpenEL)
Energy storage

- Pumped hydro
- Compressed air
- Cranes lifting concrete blocks
- Flow battery
  - batteries
  - hydrogen
  - fly wheel
  - thermal storage
  - ...

energyinformative.org

University of British Columbia

Energy Vault
Solar increased by 30 million ton oil equivalent in 2018. All renewables increased by 71 million ton oil equivalent. Need 170 years to all renewable at this rate. Need to ramp up efforts by ~ factor 10.

1 million ton oil equivalent = 11.63 TWh
Bipolar transistor consists of three layers, doped n-p-n or p-n-p.

Small current inserted into base can control large flow of electrons from emitter to collector.

→ signal amplification
Overview “Electrons in periodic potentials”

Goal of this chapter
energy level structure of electron in periodic potential

Plan of this section
1) Derive allowed and forbidden energies
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Overview of topic „Crystalline solids“

Electrons in periodic potential

simple model describing crystals

explains under which conditions a solid is a

• conductor
• semiconductor
• insulator

Applications

• LED
• solar cell
• transistor
Quantum mechanics 3
Structure of matter

Bonus lecture

Piet Mulders
Florian Schreck
University of Amsterdam
Overview of course

Part 1: 7 lectures in January (P. Mulders)
Spin states, addition of angular momentum
Identical particles
Orbital and spin structure of atoms
Outline of quantum statistical mechanics

Part 2: 7 lectures in February and March (F. Schreck)
Energy level structure of atoms & the periodic table
Solids
Quantum statistics
Time-independent perturbation theory
Structure of hydrogen
Variational principle

Lecture notes, problem sets and link to video recordings of January lectures available on blackboard

Questions: schreck@StrontiumBEC.com
Overview of „Quantum stat. mech.“

Goal of this section

Distribution of particles over energy for finite temperature

Understand that the type of particle (bosons, fermions, distinguishable particles) changes physics dramatically

Application: spectrum of thermal electromagnetic radiation

Plan of this section

1) Introduction to the topic
2) Strategy to derive energy distributions
3) Step 1 of strategy
4) Step 2 of strategy
5) Derivation of energy distribution functions
6) Application: blackbody spectrum

Griffiths 5.4.1 5.4.2 5.4.3 5.4.4 5.4.5
**System:** $N$ weakly interacting particles with total energy $E$

**Question:** What is most likely number of particles in state with energy $\epsilon$?
Example 1: identical fermions in 1D

Pauli exclusion → at most 1 fermion per state

temperature $T = 0$

What are identical fermions?

Fermions have half-integer spin.

They always have two or more spin projections $m_J$.

„identical fermions“ means that all fermions have somehow been put into the same $m_J$ state and that they somehow can't leave that state.

Hard to do for e^-, but easy for fermionic atoms, use „optical pumping“.

Energy distribution $n(\varepsilon)$: Fermi-Dirac distribution

$n(\varepsilon)$

0 0.5 1

0 0.5 1 1.5

Fermi energy

Fermi energy
Example 1: identical fermions in 1D

Pauli exclusion → at most 1 fermion per state

temperature $T = 0$

Fermi energy

Fermi sea

Energy distribution $n(\varepsilon)$: Fermi-Dirac distribution

$T > 0$

$\varepsilon$

$\varepsilon$

$Fermi$ $energy$

$n(\varepsilon)$

$k_B T$
Example 2: distinguishable particles in 1D

Energy distribution $n(\varepsilon)$: Maxwell-Boltzmann distribution

$T = 0$

$T > 0$

$E_{\text{max}}$ $E_{\text{min}}$
Example 3: identical bosons in 1D

\[ T = 0 \]

\[ T > T_c \]

Energy distribution \( n(\varepsilon) \): Bose-Einstein distribution

\[ n(\varepsilon) \]

\[ 1 \]

\[ 0.5 \]

\[ 0 \]

\[ 0 \]

\[ k_B T \]
Example 3: identical bosons in 1D

$T = 0$

$0 < T < T_c$

$T > T_c$

BEC atom number over total atom number:

$N_0/N$

only limited number of bosons „fit“ in excited states

huge number of bosons $N_0$ „condense into“ ground state

They are Bose-Einstein condensate (BEC)
Goals of this lecture

- Fermi-Dirac distribution
- Maxwell-Boltzmann distribution
- Bose-Einstein distribution

Applications
- Blackbody radiation spectrum
- Bose-Einstein condensation (exercise)

Applications of quantum statistical mechanics beyond our scope
- microscopic principles underlying thermodynamics
- derivation of equations of state
  \( \epsilon \) = link between macroscopic thermodynamic observables of a system
Overview of „Quantum stat. mech.“

Goal of this section

Distribution of particles over energy for finite temperature
Understand that the type of particle (bosons, fermions, distinguishable particles) changes physics dramatically
Application: spectrum of thermal electromagnetic radiation

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Strategy to derive distribution functions

**Assumption 1:**

Fundamental assumption of statistical mechanics:
- all configurations of particles over energy states with same total energy are equally likely

Example:

Three distinguishable particles \( \{A, B, C\} \) in 1D square potential

Energy of one particle:

\[
E_n = \frac{\pi^2 \hbar^2}{2ma^2} n^2
\]

Energy of three particles:

\[
E = E_A + E_B + E_C = \frac{\pi^2 \hbar^2}{2ma^2} \left( n_A^2 + n_B^2 + n_C^2 \right)
\]

What are the possible configurations of particles over energy levels for \( E = \frac{\pi^2 \hbar^2}{2ma^2} \times 363 \)?
3 distinguishable particles in square well

\[(n_A, n_B, n_C)\]

example: \[n_A^2 + n_B^2 + n_C^2 = 363\]

(11, 11, 11)

(5, 13, 13)

(1, 1, 19)

each configuration of particles with same energy equally likely

We don't care about exact configuration

most likely state distribution

We care about state distributions = energy distributions
Strategy to derive distribution functions

Macroscopically we don’t care about the exact configuration

We only want to know the most likely number of particles with energy $\epsilon$, i.e. the energy distribution $n(\epsilon)$.

**Assumption 2:**

For large $N$, the average energy distribution is well approximated by the most likely energy distribution.

Strategy to find energy distribution

1. **Step 1)** Calculate number of configurations for given energy distribution
2. **Step 2)** Determine most probable energy distribution
Why does particle nature play a role?

Same example, but for **identical fermions**:

\[(n_A, n_B, n_C)\]

- **(11, 11, 11)**
  - Not allowed by Pauli exclusion

- **(5, 13, 13)**
  - Not allowed

- **(1, 1, 19)**
  - Not allowed

- **(5, 7, 17)**
  - Only one allowed configuration

„fermionic statistics“

(artefact of simple example: same energy distribution as for distinguishable particles)
Why does particle nature play a role?

Same example, but for **identical bosons**:

\((n_A, n_B, n_C)\)

\((11, 11, 11)\)  

\((5, 13, 13)\)  

\((1, 1, 19)\)  

\((5, 7, 17)\)

„bosonic statistics“

(artefact of simple example: can't decide which distribution is most likely)
Overview of „Quantum stat. mech.“

Goal of this section

Distribution of particles over energy for finite temperature
Understand that the type of particle (bosons, fermions, distinguishable particles) changes physics dramatically

Application: spectrum of thermal electromagnetic radiation

Plan of this section

1) Introduction to the topic
2) Strategy to derive energy distributions
3) Step 1 of strategy: calc. # of configurations for given energy distribution
4) Step 2 of strategy: determine most probable energy distribution
5) Derivation of energy distribution functions
6) Application: blackbody spectrum

Griffiths 5.4.1 5.4.2 5.4.3 5.4.4 5.4.5
Step 1)

Calculate number of configurations for given energy distribution

Only interested in \( n(\epsilon) \) with resolution \( d\epsilon \)

Treat states in interval \( d\epsilon \) around \( \epsilon \) as degenerate.

Alternative argument: think of system directly as having degenerate states with energy \( \epsilon_n \) with degeneracy \( d_n \)
Step 1 for identical fermions

Step 1) Calculate number of configurations for given energy distribution \( \{ N_n \} \)

Filling \( d_1 \) states with energy \( \epsilon_1 \) with \( N_1 \) of our \( N \) fermions:

\( \text{d}_1 \) degenerate states each may be occupied by 0 or 1 fermion

\( N-N_1 \) fermions in total \( N_1 \) particles in these \( d_1 \) states

How many ways are there to configure \( N_1 \) particles in these \( d_1 \) states?

Trick: arrange \( d_1 \) labelled boxes that are either empty or filled: \( d_1! \) configurations

However, we overcounted.

We don’t care which is where \( (\text{}/N_1!) \) or which is where \( (\text{}/(d_1 - N_1)!) \).

\[
\frac{d_1!}{N_1!(d_1 - N_1)!} \quad \text{configurations for level 1.}
\]

\#configurations for all levels:

\[
Q(N_n) = \prod_{n=1}^{\infty} \frac{d_n!}{N_n!(d_n - N_n)!}
\]
Step 1 for identical bosons

Step 1) Calculate number of configurations for given energy distribution \( \{N_n\} \)

Filling \( d_1 \) states with energy \( \epsilon_1 \) with \( N_1 \) of our \( N \) bosons:

\[ \text{\( N-N_1 \) bosons} \]

\[ \text{\( \text{in total} \ N_1 \text{ particles in these} \ d_1 \text{ states} \)} \]

How many ways are there to configure \( N_1 \) particles in these \( d_1 \) states?

Similar trick: arrange \( N_1 \) dots \( \bullet \) and \( (d_1 - 1) \) „separations between states“ \( \mid \) :

\[ \bullet \mid \bullet \bullet \mid \mid \bullet \bullet \bullet \mid \mid \bullet \]

For labeled \( \bullet \) and \( \mid \) we would have \( (N_1 + d_1 - 1)! \) arrangements.

We don’t care which \( \bullet \) is where \( (/N_1!) \) or which \( \mid \) is where \( (/ (d_1 - 1)!) \).

\[ \frac{(N_1 + d_1 - 1)!}{N_1! (d_1 - 1)!} \]

configurations for level 1.

#configurations for all levels: \( Q(N_n) = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n! (d_n - 1)!} \)
Step 1 for distinguishable particles

Step 1) Calculate number of configurations for given energy distribution \( \{ N_n \} \)

How many choices lead to the same distribution \( \{ N_n \} \)?

For indistinguishable particles only one choice, but for distinguishable particles many choices.

As before: there are \( N! \) ways to arrange \( N \) particles, but we don’t care how they arrange in bins (\( \prod_{n=1}^{\infty} \frac{N_n!}{N_n!} \)).

Filling \( d_1 \) states with energy \( \epsilon_1 \) with \( N_1 \) of our \( N \) particles:

How many ways are there to configure \( N_1 \) particles into \( d_1 \) states?

First particle can go into \( d_1 \) states. Second can go into \( d_1 \) states. Third can...

\[ d_1^{N_1} \text{ conf.} \]

#configurations for all levels:

\[
Q(N_n) = \frac{N!}{\prod_{n=1}^{\infty} N_n!} \prod_{n=1}^{\infty} d_n^{N_n} = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}
\]
Goal of this section

Distribution of particles over energy for finite temperature
Understand that the type of particle (bosons, fermions, distinguishable particles) changes physics dramatically

Application: spectrum of thermal electromagnetic radiation

Plan of this section

1) Introduction to the topic
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Griffiths 5.4.1
5.4.2
5.4.3
5.4.4
5.4.5
3 distinguishable particles in square well

\[(n_A, n_B, n_C)\]

example: \[n_A^2 + n_B^2 + n_C^2 = 363\]

(11, 11, 11)

(5, 13, 13)

(1, 1, 19)

We don't care about exact configuration

most likely state distribution

We care about state distributions = energy distributions
Step 2)

Determine most probable energy distribution $\{N_n\}$ with total energy $E$ and particle number $N$

\[
f_N(N_n) = N - \sum_{n=1}^{\infty} N_n \overset{!}{=} 0 \tag{(*)}
\]

\[
f_E(N_n) = E - \sum_{n=1}^{\infty} N_n E_n \overset{!}{=} 0 \tag{(**)}
\]

Most probable energy distribution: \( \frac{\partial Q}{\partial N_n} \overset{!}{=} 0 \) or, simpler, \( \frac{\partial}{\partial N_n} \ln Q \overset{!}{=} 0 \)

under constraints (\( \ast \)) and (\( \ast\ast \)).

Use Lagrange multipliers! (here: $\alpha$ and $\beta$)

Minimize

\[
G (N_n, \alpha, \beta) = \ln Q(N_n) + \alpha f_N(N_n) + \beta f_E(N_n)
\]

\[
\frac{\partial G}{\partial \alpha} \overset{!}{=} 0 \quad \text{imposes (\( \ast \))} \quad ; \quad \frac{\partial G}{\partial \beta} \overset{!}{=} 0 \quad \text{imposes (\( \ast\ast \))} \quad ;
\]

\[
\frac{\partial G}{\partial N_n} \overset{!}{=} 0 \quad \text{will find extremum of $\ln Q$ under constraints (\( \ast \)) and (\( \ast\ast \)).}
\]
**How do Lagrange multipliers work?**

**Example:**
Find extremum of
\[ f(x, y) = x + 2y \]
under constraint
\[ c(x, y) = x^2 + y^2 - 1 = 0 \]

Imagine moving along the curve \( c(x, y) = 0 \)
and compare gradient fields \( \nabla c \) and \( \nabla f \):

If \( \nabla f \parallel \nabla c \), the projection of \( \nabla f \) onto the tangent of the curve \( c(x, y) = 0 \) is not zero. Therefore we can move along the constraint and increase \( f \) in one direction and decrease \( f \) in the other.

If \( \nabla f \parallel \nabla c \), we have found an extremum.

\( \nabla f \parallel \nabla c \) is equivalent to \( \nabla (f - \lambda c) = 0 \) for some value of „Lagrange multiplier“ \( \lambda \).

\[ \Rightarrow \] Find extrema of \( f - \lambda c \).
Adjust \( \lambda \) such that constraint fulfilled.
Step 2

Determine most probable energy distribution \( \{N_n\} \) with total energy \( E \) and particle number \( N \)

\[
f_N(N_n) = N - \sum_{n=1}^{\infty} N_n = 0 \quad (\ast)
\]

\[
f_E(N_n) = E - \sum_{n=1}^{\infty} N_n E_n = 0 \quad (\ast\ast)
\]

Most probable energy distribution: \( \frac{\partial Q}{\partial N_n} = 0 \) or, simpler, \( \frac{\partial}{\partial N_n} \ln Q = 0 \)

under constraints \((\ast)\) and \((\ast\ast)\).

Use Lagrange multipliers! (here: \( \alpha \) and \( \beta \))

Minimize

\[
G(N_n, \alpha, \beta) = \ln Q(N_n) + \alpha f_N(N_n) + \beta f_E(N_n)
\]

\[
\frac{\partial G}{\partial \alpha} = 0 \quad \text{imposes} \quad (\ast) ; \quad \frac{\partial G}{\partial \beta} = 0 \quad \text{imposes} \quad (\ast\ast) ;
\]

\[
\frac{\partial G}{\partial N_n} = 0 \quad \text{will find extremum of} \quad \ln Q \quad \text{under constraints} \quad (\ast) \quad \text{and} \quad (\ast\ast).
\]
Step 2 for identical bosons

\[ G (N_n, \alpha, \beta) = \ln Q(N_n) + \alpha f_N(N_n) + \beta f_E(N_n) \]

\[ G = \sum_{n=1}^{\infty} \left[ \ln [(N_n + d_n - 1)!] - \ln (N_n!) - \ln [(d_n - 1)!] \right] \]

\[ + \alpha \left( N - \sum_{n=1}^{\infty} N_n \right) + \beta \left( E - \sum_{n=1}^{\infty} E_n N_n \right) \]

Use Stirling’s approximation:

\[ \ln(z!) \simeq z \ln(z) - z \quad \text{for} \quad z \gg 1 \]

\[ G \simeq \sum_{n=1}^{\infty} \left[ (N_n + d_n - 1) \ln [(N_n + d_n - 1)!] - (N_n + d_n - 1) \right. \]

\[ - N_n \ln(N_n) + N_n - \ln [(d_n - 1)!] - \alpha N_n - \beta E_n N_n \left. \right] + \alpha N + \beta E \]

\[ \frac{\partial G}{\partial N_{\tilde{n}}} = \ln (N_{\tilde{n}} + d_{\tilde{n}} - 1) - \ln (N_{\tilde{n}}) - \alpha - \beta E_{\tilde{n}} \overset{!}{=} 0 \]

Rename \( \tilde{n} \) to \( n \), solve for \( N_n \):

\[ N_n = \frac{d_n - 1}{e^{(\alpha+\beta E_n)} - 1} \sim \frac{d_n}{e^{(\alpha+\beta E_n)} - 1} \quad (1) \]
Step 2 for identical fermions

\[ G(N_n, \alpha, \beta) = \ln Q(N_n) + \alpha f_N(N_n) + \beta f_E(N_n) \]

Reminder

\[ Q(N_n) = \prod_{n=1}^{\infty} \frac{d_n!}{N_n! (d_n - N_n)!} \]

Exercise

\[ N_n = \frac{d_n}{e^{(\alpha + \beta E_n)} + 1} \quad \text{(II)} \]
Step 2 for distinguishable particles

\[ G(N_n, \alpha, \beta) = \ln Q(N_n) + \alpha f_N(N_n) + \beta f_E(N_n) \]

Reminder:

\[ Q(N_n) = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!} \]

Exercise

\[ \rightarrow N_n = d_ne^{-(\alpha + \beta E_n)} \]  \hspace{1cm} (III)
Overview of „Quantum stat. mech.‟

**Goal of this section**

Distribution of particles over energy for finite temperature

Understand that the type of particle (bosons, fermions, distinguishable particles) changes physics dramatically

Application: spectrum of thermal electromagnetic radiation

**Plan of this section**

1) Introduction to the topic
2) Strategy to derive energy distributions
3) Step 1 of strategy: calc. # of configurations for given energy distribution
4) Step 2 of strategy: determine most probable energy distribution
5) Derivation of energy distribution functions
6) Application: blackbody spectrum
Physical significance of $\alpha$ and $\beta$

Determining $\alpha$ and $\beta$: plug $N_n$ from (I), (II) or (III) into (*) and (***) and solve.
Step 2) Determine most probable energy distribution \( \{N_n\} \) with total energy \( E \) and particle number \( N \)

\[
f_N(N_n) = N - \sum_{n=1}^{\infty} N_n = 0 \quad (\ast)
\]

\[
f_E(N_n) = E - \sum_{n=1}^{\infty} N_n E_n = 0 \quad (\ast\ast)
\]

Most probable energy distribution: \( \frac{\partial Q}{\partial N_n} = 0 \) or, simpler, \( \frac{\partial}{\partial N_n} \ln Q = 0 \)

under constraints \((\ast)\) and \((\ast\ast)\).

Use Lagrange multipliers! (here: \( \alpha \) and \( \beta \))

Minimize

\[
G(N_n, \alpha, \beta) = \ln Q(N_n) + \alpha f_N(N_n) + \beta f_E(N_n)
\]

\[
\frac{\partial G}{\partial \alpha} = 0 \quad \text{imposes \((\ast)\)} \quad ; \quad \frac{\partial G}{\partial \beta} = 0 \quad \text{imposes \((\ast\ast)\)} \quad ;
\]

\[
\frac{\partial G}{\partial N_n} = 0 \quad \text{will find extremum of} \quad \ln Q \quad \text{under constraints \((\ast)\) and \((\ast\ast)\).} \]
Physical significance of $\alpha$ and $\beta$

Determining $\alpha$ and $\beta$: plug $N_n$ from (I), (II) or (III) into (**) and (***) and solve.

Need $E_n$ and $d_n$ to do this.

Example: distinguishable particles in 3D cube with edge length $l$.

From lecture on free electron gas:

$$E_k = \frac{\hbar^2 k^2}{2m} ; \quad \vec{k} = \frac{\pi}{l} \vec{n} ; \quad \vec{n} = (n_x, n_y, n_z)$$

$$n_i \in \{1, 2, \ldots\}$$

Number of states with energy $E_k$:

$$d_k = \frac{1}{8} \frac{4\pi k^2 \, dk}{\pi^3 / V} = \frac{V}{2\pi^2} k^2 \, dk$$
Physical significance of $\alpha$ and $\beta$

Plug (III) into $(*$):

$$N = \sum_{n=1}^{\infty} N_n = \sum_{n=1}^{\infty} d_n e^{-(\alpha+\beta E_n)} = \int dk \frac{V}{2\pi^2} k^2 e^{-(\alpha+\beta E_k)}$$

$$= Ve^{-\alpha} \left(\frac{m}{2\pi \beta \hbar^2}\right)^{3/2} \Rightarrow e^{-\alpha} = \frac{N}{V} \left(\frac{2\pi \beta \hbar^2}{m}\right)^{3/2}$$

Plug (III) into $(**$):

$$E = \frac{V}{2\pi^2} e^{-\alpha} \frac{\hbar^2}{2m} \int_0^{\infty} dke^{-\beta \hbar^2 k^2/2m} k^4 = \frac{3V}{2\beta} e^{-\alpha} \left(\frac{m}{2\pi \beta \hbar^2}\right)^{3/2}$$

Plug in $e^{-\alpha}$ from above:

$$E = \frac{3N}{2\beta}$$

Compare to energy of ideal gas at temperature $T$:

$$E = \frac{3}{2} N k_b T \Rightarrow \beta = \frac{1}{k_b T}$$

This holds in general (no proof here).
Energy distribution functions

Definition:

$$\mu \equiv -\alpha k_b T \quad \rightarrow \quad \alpha = -\frac{\mu}{k_b T}$$

$$\mu$$ is called „chemical potential”

Energy distribution functions

$$n(\varepsilon) = \text{most probable # of particles in a state with energy } \varepsilon$$

Divide (I), (II), (III) by \( d_n \), plug in \( \alpha \) and \( \beta \):

$$n(\varepsilon) = \begin{cases} \frac{1}{e^{(\varepsilon-\mu)/k_b T} - 1} & \text{Bose-Einstein} \\ \frac{1}{e^{(\varepsilon-\mu)/k_b T} + 1} & \text{Fermi-Dirac} \\ e^{-(\varepsilon-\mu)/k_b T} & \text{Maxwell-Boltzmann distribution} \end{cases}$$

ident. bosons

ident. fermions
distinguishable particles
Example 1: identical fermions in 1D

Pauli exclusion → at most 1 fermion per state

temperature $T = 0$

$T > 0$

Fermi energy

Fermi sea

Energy distribution $n(\varepsilon)$: Fermi-Dirac distribution

$$n(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1}$$
Example 2: distinguishable particles in 1D

Energy distribution $n(\varepsilon)$: Maxwell-Boltzmann distribution

$$n(\varepsilon) = e^{-(\varepsilon - \mu)/k_B T}$$
Example 3: identical bosons in 1D

\[ T = 0 \]

\[ n(\varepsilon) \]

Energy distribution \( n(\varepsilon) \): Bose-Einstein distribution

\[ n(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} - 1} \]

\[ T > T_c \]

\[ n(\varepsilon) \]

\[ k_B T \]
Example 3: identical bosons in 1D

- **$T = 0$**
  - Only limited number of bosons "fit" in excited states
  - Huge number of bosons $N_0$ "condense into" ground state
  - They are Bose-Einstein condensate (BEC)

- **$0 < T < T_c$**
  - Only limited number of bosons "fit" in excited states

- **$T > T_c$**

BEC atom number over total atom number:

$$\frac{N_0}{N}$$
Goals of this lecture

- Fermi-Dirac distribution
- Maxwell-Boltzmann distribution
- Bose-Einstein distribution

Applications
- Blackbody radiation spectrum
- Bose-Einstein condensation (exercise)

Applications of quantum statistical mechanics beyond our scope
- Microscopic principles underlying thermodynamics
- Derivation of equations of state
  ( = link between macroscopic thermodynamic observables of a system)
Overview of „Quantum stat. mech.“

Goal of this section

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Griffiths 5.4.1
Griffiths 5.4.2
Griffiths 5.4.3
Griffiths 5.4.4
Griffiths 5.4.5
The blackbody spectrum

Box at temperature $T$

What is the spectrum $\rho(\omega)$ of photons escaping from small hole in box?

Properties of photons

1. Photons are bosons

2. Energy of photons $E = \hbar \omega$; $\omega = 2\pi f$; $f$ : frequency

3. Momentum of photons $p = \hbar k$; $k = \frac{2\pi}{\lambda} = \frac{\omega}{c}$

4. Photons have two spin states ($m = \pm 1$; $m = 0$)

5. Photon number $N$ not conserved $\longrightarrow (\ast)$ doesn’t apply
Step 2

Step 2) Determine most probable energy distribution \( \{N_n\} \) with total energy \( E \) and particle number \( N \)

\[
f_N(N_n) = N - \sum_{n=1}^{\infty} N_n = 0 \quad (\ast)
\]

\[
f_E(N_n) = E - \sum_{n=1}^{\infty} N_n E_n = 0 \quad (**)
\]

Most probable energy distribution: \( \frac{\partial Q}{\partial N_n} = 0 \) or, simpler, \( \frac{\partial}{\partial N_n} \ln Q = 0 \)

under constraints \( (\ast) \) and \( (**). \)

Use Lagrange multipliers! (here: \( \alpha \) and \( \beta \))

Minimize

\[
G(N_n, \alpha, \beta) = \ln Q(N_n) + \alpha f_N(N_n) + \beta f_E(N_n)
\]

\( \frac{\partial G}{\partial \alpha} = 0 \) imposes \( (\ast) \); \( \frac{\partial G}{\partial \beta} = 0 \) imposes \( (**). \)

\( \frac{\partial G}{\partial N_n} = 0 \) will find extremum of \( \ln Q \) under constraints \( (\ast) \) and \( (**). \)
The blackbody spectrum

Box at temperature $T$

What is the spectrum $\rho(\omega)$ of photons escaping from small hole in box?

Properties of photons

(1) Photons are bosons

(2) Energy of photons $E = \hbar \omega = 2\pi f$; $\omega = 2\pi f$; $f$ : frequency

(3) Momentum of photons $k = \frac{2\pi}{\lambda} = \frac{\omega}{c}$

(4) Photons have two spin states $(m = \pm 1; \quad m = 0)$

(5) Photon number $N$ not conserved $\rightarrow$ $(\star)$ doesn’t apply $\rightarrow$ $\alpha = 0$

$\mu \equiv -\alpha k_b T = 0$
The blackbody spectrum

From (1) and (2):

\[ N_\omega = \frac{d_k}{e^{\frac{\hbar \omega}{k_b T}} - 1} \]

Photons in box of volume \( V \), taking into account (3) and (4):

\[ d_k = \frac{V}{\pi^2 c^3} \omega^2 d\omega \]

Energy density \( N_\omega \frac{\hbar \omega}{V} \) in \( d\omega \):

\[ \rho(\omega) = \frac{N_\omega \hbar \omega}{V d\omega} = \frac{\hbar \omega^3}{\pi^2 c^3 \left( e^{\frac{\hbar \omega}{k_b T}} - 1 \right)} \]

Planck's blackbody spectrum

reminder

\[ \frac{1}{e^{\frac{(\epsilon - \mu)}{k_b T}} - 1} \quad \text{Bose-Einstein} \]
Blackbody spectrum

Griffiths Fig. 5.9

T of sun surface
6000 K

Energy used for illumination
3000 K

Incandescent lightbulb

Energy wasted as heat

Frequency [10^{14} Hz]

\rho(\omega) [10^{-15} J/m^3 Hz]
Bose-Einstein condensate of strontium

Schreck group
University of Amsterdam
BEC and Fermi gas

BEC of $^7\text{Lithium}$

Fermi sea of $^6\text{Lithium}$

Salomon group
E.N.S, Paris
Overview of „Quantum stat. mech.„

**Goal of this section**

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Understand that the type of particle (bosons, fermions, distinguishable particles) changes physics dramatically

Application: spectrum of thermal electromagnetic radiation

**Plan of this section**

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Overview of course

Part 1: 7 lectures in January (Piet Mulders)
Basics of quantum mechanics
Spin states
Addition of angular momentum
Identical particles
Basic structure of atom

Part 2: 7 lectures in February and March (Florian Schreck)
Structure of atoms & the periodic table
Crystalline solids
Time-independent perturbation theory
Structure of hydrogen
Variational principle
Time-dependent perturbation theory, atom-light interaction

Lecture notes, problem sets and link to video recordings of C0.110 lectures available on Canvas

Questions: schreck@StrontiumBEC.com
Overview of „$t$-indep. pert. theory“

**Goal of this section**

Determine energies and eigenstates of system exposed to small perturbation.

Applications:

Absolutely everywhere. In quantum mechanics it is hard to calculate anything exactly, so we use perturbation theory nearly all the time.

Atoms, molecules, condensed-matter,…

**Plan of this section**

1) intro, examples
2) non-degenerate perturbation theory
3) 2-fold degenerate perturbation theory
4) $n$-fold degenerate perturbation theory
5) general perturbation theory

Griffiths 3rd 7.1.1

7.1.2 – 7.1.3

7.2.1 – 7.2.2

7.2.3
Starting point:

system with known eigenstates $\psi_n^0$ and energies $E_n^0$

Modification:

system is exposed to a small, time-independent perturbation

Question:

What are, approximately, the new eigenstates $\psi_n$ of the system and their energies $E_n$?
Example: Particle in nearly square box

Starting point
unperturbed system

Modification
perturbed system

We know \( E_0^0, \psi_0^0, E_1^0, \psi_1^0, \ldots \)

Small perturbation
potential slightly altered

Question
What are, approximately, \( E_0, \psi_0, E_1, \psi_1, \ldots \)?
Example: Atom in magnetic field

**Starting point**
unperturbed system

- e⁻
- proton

**Modification**
perturbed system

- Small perturbation
  weak magnetic field

---

**Question**

What are, approximately, perturbed eigenstates and energies?
Overview of „t-indep. pert. theory“

Goal of this section

Determine energies and eigenstates of system exposed to small perturbation.

Applications:

Absolutely everywhere. In quantum mechanics it is hard to calculate anything exactly, so we use perturbation theory nearly all the time.

Atoms, molecules, condensed-matter,…

Plan of this section

1) intro, examples  
2) non-degenerate perturbation theory  
3) 2-fold degenerate perturbation theory  
4) $n$-fold degenerate perturbation theory  
5) general perturbation theory

Griffiths 3rd 7.1.1

7.1.2 – 7.1.3

7.2.1 – 7.2.2

7.2.3
Non-degenerate perturbation theory

no two eigenstates of unperturbed system have same energy

Hamiltonian:

\[ H = H^0 + H' = H^0 + \lambda \tilde{H} \quad ; \quad \tilde{H} = \frac{H'}{\lambda} \quad ; \quad \lambda \ll 1 \]

small perturbation

(we define later what „small“ means)

Hamiltonian of unperturbed system

Unperturbed system has orthonormal eigenstates \( \{ \psi_n^0 \} \) with energies \( \{ E_n^0 \} \):

\[ H^0 |\psi_n^0\rangle = E_n^0 |\psi_n^0\rangle \quad ; \quad <\psi_n^0|\psi_m^0\rangle = \delta_{nm} \quad ; \quad E_n^0 \neq E_m^0 \quad \text{for} \quad n \neq m \]

Perturbed system has eigenstates \( |\psi_n^{\text{ex}}\rangle \) with energy \( E_n^{\text{ex}} \), i.e.

\[ H |\psi_n^{\text{ex}}\rangle = E_n^{\text{ex}} |\psi_n^{\text{ex}}\rangle \]

(„ex“ for „exact solution“)

These can be written as expansion in small parameter \( \lambda \):

\[ |\psi_n^{\text{ex}}\rangle = |\psi_n^0\rangle + \lambda |\tilde{\psi}_n^1\rangle + \lambda^2 |\tilde{\psi}_n^2\rangle + \cdots \]

\( \equiv |\psi_n^1\rangle \)

\( \equiv |\psi_n^2\rangle \)

\[ E_n^{\text{ex}} = E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \cdots \]

\( \equiv E_n^1 \)

\( \equiv E_n^2 \)
For comparison: Taylor expansion

\[
\sin(x + \pi/4) = \frac{1}{\sqrt{2}} + \frac{1}{\sqrt{2}}x - \frac{1}{\sqrt{8}}x^2 - \frac{1}{\sqrt{72}}x^3 + \mathcal{O}(x^4)
\]

In our case \( \lambda \) corresponds to \( x \) and the approximated function corresponds to e.g. the energy or the wavefunction at a certain location.

The higher the approximation order, the better the result.
Intuitive picture

**Eigenstates**
symbolize Hilbert space by 2D vector space

- $|\Psi_1^0\rangle$
- $|\Psi_1^{1st}\rangle$
- $|\Psi_2^0\rangle$
- $|\Psi_2^{1st}\rangle$
- $|\Psi_1^{ex}\rangle$
- $|\Psi_2^{ex}\rangle$

**Energies**

- $E_1^0$
- $E_1^{1st}$
- $E_2^0$
- $E_2^{1st}$

- $\lambda = 0$
- $\lambda > 0$

**Our goals**
- change in energy to 2\textsuperscript{nd} order
- eigenstates up to 1\textsuperscript{st} order

Notice: $|\Psi_1^1\rangle$ and $|\Psi_1^0\rangle$ nearly orthogonal because correction small
What is $|\psi^1_n\rangle$?

$|\psi^1_n\rangle$ is just a state in Hilbert space. It is not necessarily an eigenstate of a Hamiltonian and it does not have to be normalized, on the contrary, it’s norm is on the order of $\lambda^2$.

If you don’t like thinking of states in Hilbert space, think of the special case of a spatial wavefunction and apply $\langle x | \cdot$ to the equation to obtain a function of $x$. If you then think of a specific location, the equation is a Taylor expansion.

Phase choice

As usual, we are free to choose phases of eigenstates forming basis $\{|\psi^\text{ex}_n\rangle\}$. To simplify upcoming calculation, we will choose phase of $|\psi^\text{ex}_n\rangle$ such that $\langle \psi^0_n | \psi^\text{ex}_n \rangle$ is real. This implies that $\langle \psi^0_n | \tilde{\psi}^i_n \rangle$ is real for any order $i$, since orders can’t compensate each other.
Our goals

\[
\begin{array}{cccc}
\text{0th order} & \text{1st order} & \text{2nd order} & \text{3rd and higher orders in } \lambda \\
|\Psi_{n}^{\text{ex}}\rangle = |\Psi_{n}^{0}\rangle + \lambda |\tilde{\Psi}_{n}^{1}\rangle & + \lambda^2 |\tilde{\Psi}_{n}^{2}\rangle & + \ldots & \\
E_{n}^{\text{ex}} = E_{n}^{0} + \lambda \tilde{E}_{n}^{1} & + \lambda^2 \tilde{E}_{n}^{2} & + \ldots & \\
\end{array}
\]

Our goal is \textit{not} to find \( |\Psi_{n}^{\text{ex}}\rangle \) and \( E_{n}^{\text{ex}} \), solving \( H |\Psi_{n}^{\text{ex}}\rangle = E_{n} |\Psi_{n}^{\text{ex}}\rangle \), since this is (too) complicated.

We want to find \textit{approximations}, the energy to 2nd order in \( \lambda \) and the state to first order in \( \lambda \):

\[
|\Psi_{n}^{\text{1st}}\rangle = |\Psi_{n}^{0}\rangle + \lambda |\tilde{\Psi}_{n}^{1}\rangle = |\Psi_{n}^{\text{ex}}\rangle + \mathcal{O}(\lambda^2) \neq |\Psi_{n}^{\text{ex}}\rangle \\
E_{n}^{\text{2nd}} = E_{n}^{0} + \lambda \tilde{E}_{n}^{1} + \lambda^2 \tilde{E}_{n}^{2} = E_{n}^{\text{ex}} + \mathcal{O}(\lambda^3) \neq E_{n}^{\text{ex}}
\]

\( H |\Psi_{n}^{\text{1st}}\rangle \neq E_{n}^{\text{2nd}} |\Psi_{n}^{\text{1st}}\rangle \), but the error is of order \( \lambda^2 \) and therefore small

We need \( |\langle \Psi_{n}^{\text{1st}} |\Psi_{n}^{\text{1st}}\rangle|^2 = 1 \) to first order in \( \lambda \). If we wouldn’t, e.g. particle number not be conserved.

For simplicity we often write \( |\Psi_{n}^{\text{1st}}\rangle \) as \( |\Psi_{n}\rangle \) and \( E_{n}^{\text{2nd}} \) as \( E_{n} \).
Schrödinger equn. of perturbed system

\[ H |\Psi_n^{\text{ex}}\rangle = E_n |\Psi_n^{\text{ex}}\rangle \]

\[
\left( H^0 + \lambda \tilde{H} \right) \left[ |\psi_n^0 > + \lambda |\tilde{\psi}_n^1 > + \lambda^2 |\tilde{\psi}_n^2 > + \ldots \right] \\
= \left[ E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \ldots \right] \left[ |\psi_n^0 > + \lambda |\tilde{\psi}_n^1 > + \lambda^2 |\tilde{\psi}_n^2 > + \ldots \right]
\]

Collect like powers of \( \lambda \):

\[
H^0 |\psi_n^0 > + \lambda \left( H^0 |\tilde{\psi}_n^1 > + \tilde{H} |\psi_n^0 > \right) + \lambda^2 \left( H^0 |\tilde{\psi}_n^2 > + \tilde{H} |\tilde{\psi}_n^1 > \right) + \ldots \\
= E_n |\psi_n^0 > + \lambda \left( E_n^0 |\tilde{\psi}_n^1 > + \tilde{E}_n^1 |\psi_n^0 > \right) + \lambda^2 \left( E_n^0 |\tilde{\psi}_n^2 > + \tilde{E}_n^1 |\tilde{\psi}_n^1 > + \tilde{E}_n^2 |\psi_n^0 > \right) + \ldots
\]

0th order (\( \lambda^0 \)):
\[
H^0 |\psi_n^0 > = E_n |\psi_n^0 >
\]

1st order (\( \lambda^1 \)):
\[
H^0 |\tilde{\psi}_n^1 > + \tilde{H} |\psi_n^0 > = E_n^0 |\tilde{\psi}_n^1 > + \tilde{E}_n^1 |\psi_n^0 >
\]

2nd order (\( \lambda^2 \)):
\[
H^0 |\tilde{\psi}_n^2 > + \tilde{H} |\tilde{\psi}_n^1 > = E_n^0 |\tilde{\psi}_n^2 > + \tilde{E}_n^1 |\tilde{\psi}_n^1 > + \tilde{E}_n^2 |\psi_n^0 >
\]
First order correction to energy

To first order in the perturbation, energy is shifted by expectation value of perturbation of state under consideration.

\[ H^0 | \tilde{\psi}_n^1 > + \tilde{H} | \psi_n^0 >= E_n^0 | \tilde{\psi}_n^1 > + \tilde{E}_n^1 | \psi_n^0 > \]

\[ < \psi_n^0 | \cdot (I) : \]

\[ < \psi_n^0 | H^0 | \tilde{\psi}_n^1 > + < \psi_n^0 | \tilde{H} | \psi_n^0 >= E_n^0 < \psi_n^0 | \psi_n^1 > + \tilde{E}_n^1 < \psi_n^0 | \psi_n^0 > \]

\[ \tilde{E}_n^1 = < \psi_n^0 | \tilde{H} | \psi_n^0 > \]

\[ E_n^1 = < \psi_n^0 | H' | \psi_n^0 > \]

\[ E_n = E_n^0 + E_n^1 \]

Reminder:
\[ E_n^1 = \tilde{E}_n^1 / \lambda \]
\[ H' = \tilde{H} / \lambda \]
Example 1: shifted potential

$H = H^0 + H'$

$H^0 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$

$H' = V_0$

$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 < \psi_n^0 | \psi_n^0 > = V_0$

$E_n = E_n^0 + E_n^1$

All states simply shifted by potential shift.
Example 2: half-shifted symmetric potential

Perturbation: shift potential in energy for $x > 0$

All states shifted by half of potential shift.

$$H' = \begin{cases} 
V_0 & x > 0 \\
0 & \text{else} 
\end{cases}$$

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle = \int_0^\infty V_0 |\psi(x)|^2 \, dx = V_0 \int_0^\infty |\psi(x)|^2 \, dx = \frac{V_0}{2}$$

$$E_n = E_n^0 + E_n^1$$

All states shifted by half of potential shift.
Intuitive picture

**Eigenstates**

symbolize Hilbert space by 2D vector space

\[ |\Psi_1^0\rangle, \quad |\Psi_1^1\rangle, \quad |\Psi_2^0\rangle, \quad |\Psi_2^1\rangle, \quad |\Psi_2^{ex}\rangle \]

\[ |\Psi_1^{1st}\rangle, \quad |\Psi_2^{1st}\rangle \]

To do!

**Energies**

\[ E_1^0, \quad E_1^{1st}, \quad E_2^0, \quad E_2^{1st}, \quad E_2^{ex} \]

\[ \lambda = 0, \quad \lambda > 0 \]

**Our goals**

- change in energy to 2nd order
- eigenstates up to 1st order

**Notice:** \( |\Psi_1^1\rangle \) and \( |\Psi_0^1\rangle \) nearly orthogonal because correction small
First order correction to eigenstate

Perturbed eigenstates can be expressed in unperturbed basis
\[ |\Psi_n \rangle = |\Psi_n^0 \rangle + \lambda |\tilde{\Psi}_n^1 \rangle = |\Psi_n^0 \rangle + \lambda \sum_m c_m^{(n)} |\Psi_m^0 \rangle \]
with \[ c_m^{(n)} = \langle \Psi_m^0 | \tilde{\Psi}_n^1 \rangle \]

Our goal: determine \( c_m^{(n)} \)

Normalization:
\[ = \langle \Psi_n^0 | \Psi_n^0 \rangle + \lambda \left( \langle \Psi_n^0 | \tilde{\Psi}_n^1 \rangle + \text{c.c.} \right) + \lambda^2 (\ldots) \]
\[ = 1 \]
\[ \frac{1}{\lambda} = 0 \]
\[ \Rightarrow c_m^{(n)} = 0 \]

since \( \langle \Psi_n^0 | \tilde{\Psi}_n^1 \rangle \) is real

neglected in first order
Details of $|\Psi_n\rangle$

<table>
<thead>
<tr>
<th>0(^{th}) order</th>
<th>1(^{st}) order</th>
<th>2(^{nd}) order</th>
<th>3(^{rd}) and higher orders in $\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>\Psi_{n}^{ex}\rangle$</td>
<td>$</td>
<td>\Psi_{n}^{0}\rangle$</td>
</tr>
</tbody>
</table>

What is $|\Psi_{n}^{1}\rangle$?

$|\Psi_{n}^{1}\rangle$ is just a state in Hilbert space. It is not necessarily an eigenstate of a Hamiltonian and it does not have to be normalized, on the contrary, it’s norm is on the order of $\lambda$.

If you don’t like thinking of states in Hilbert space, think of the special case of a spatial wavefunction and apply $\langle x | \cdot \rangle$ to the equation to obtain a function of $x$. If you then think of a specific location, the equation is a Taylor expansion.

Phase choice

As usual, we are free to choose phases of eigenstates forming basis $\{ |\Psi_{n}^{ex}\rangle \}$.

To simplify upcoming calculation, we will choose phase of $|\Psi_{n}^{ex}\rangle$ such that $\langle \Psi_{n}^{0} | \Psi_{n}^{ex} \rangle$ is real.

This implies that $\langle \Psi_{n}^{0} | \tilde{\Psi}_{n}^{i} \rangle$ is real for any order $i$, since orders can’t compensate each other.
Intuitive picture

**Eigenstates**
symbolize Hilbert space by 2D vector space

- $|\Psi_1^0\rangle$
- $|\Psi_2^0\rangle$
- $|\Psi_1^{\text{ex}}\rangle$
- $|\Psi_2^{\text{ex}}\rangle$
- $|\Psi_1^{\text{1st}}\rangle$
- $|\Psi_2^{\text{1st}}\rangle$

**Energies**

- $E_2^0$
- $E_2^{\text{ex}}$
- $E_1^0$
- $E_1^{\text{ex}}$
- $E_2^{\text{1st}}$
- $E_1^{\text{1st}}$

**Our goals**
- change in energy to 2$^{\text{nd}}$ order
- eigenstates up to 1$^{\text{st}}$ order

- Notice: $|\Psi_1^0\rangle$ and $|\Psi_1^{\text{1st}}\rangle$ nearly orthogonal because correction small

- To do!
First order correction to eigenstate

Perturbed eigenstates can be expressed in unperturbed basis

\[ |\Psi_n \rangle = |\Psi_n^0 \rangle + \lambda |\tilde{\Psi}_n^1 \rangle = |\Psi_n^0 \rangle + \lambda \sum_m c_m^{(n)} |\Psi_m^0 \rangle \]

with \( c_m^{(n)} = \langle \Psi_m^0 | \tilde{\Psi}_n^1 \rangle \)

Our goal: determine \( c_m^{(n)} \)

Normalization:

\[ = \langle \Psi_n^0 | \Psi_n^0 \rangle + \lambda \left( \langle \Psi_n^0 | \tilde{\Psi}_n^1 \rangle + \text{c.c.} \right) + \lambda^2 (\ldots) \]

\[ = 1 \]

\[ \frac{1}{\lambda} = 0 \Rightarrow c_n^{(n)} = 0 \]

neglected in first order

reminder: eqn. (I)

\[ H^0 |\tilde{\Psi}_n^1 \rangle + \tilde{H} |\Psi_n^0 \rangle = E_n^0 |\tilde{\Psi}_n^1 \rangle + \tilde{E}_n^1 |\Psi_n^0 \rangle \]
Schrödinger equn. of perturbed system

\[ H^0 |\Psi_n^0\rangle = E_n |\Psi_n^0\rangle \]

\[ \left( H^0 + \lambda \tilde{H} \right) \left[ |\Psi_n^0\rangle > + \lambda |\tilde{\Psi}_n^1\rangle > + \lambda^2 |\tilde{\Psi}_n^2\rangle > + \ldots \right] \]

\[ = \left[ E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \ldots \right] \left[ |\psi_n^0\rangle > + \lambda |\tilde{\psi}_n^1\rangle > + \lambda^2 |\tilde{\psi}_n^2\rangle > + \ldots \right] \]

Collect like powers of \( \lambda \):

\[ H^0 |\psi_n^0\rangle > + \lambda \left( H^0 |\tilde{\psi}_n^1\rangle > + \tilde{H} |\psi_n^0\rangle > \right) + \lambda^2 \left( H^0 |\tilde{\psi}_n^2\rangle > + \tilde{H} |\tilde{\psi}_n^1\rangle > \right) + \ldots \]

\[ = E_n^0 |\psi_n^0\rangle > + \lambda \left( E_n^0 |\tilde{\psi}_n^1\rangle > + \tilde{E}_n^1 |\psi_n^0\rangle > \right) + \lambda^2 \left( E_n^0 |\tilde{\psi}_n^2\rangle > + \tilde{E}_n^1 |\tilde{\psi}_n^1\rangle > + \tilde{E}_n^2 |\psi_n^0\rangle > \right) + \ldots \]

0th order (\( \lambda^0 \)):

\[ H^0 |\psi_n^0\rangle >= E_n |\psi_n^0\rangle > \]

1st order (\( \lambda^1 \)):

\[ H^0 |\tilde{\psi}_n^1\rangle > + \tilde{H} |\psi_n^0\rangle >= E_n^0 |\tilde{\psi}_n^1\rangle > + \tilde{E}_n^1 |\psi_n^0\rangle > \] (I)

2nd order (\( \lambda^2 \)):

\[ H^0 |\tilde{\psi}_n^2\rangle > + \tilde{H} |\tilde{\psi}_n^1\rangle >= E_n^0 |\tilde{\psi}_n^2\rangle > + \tilde{E}_n^1 |\tilde{\psi}_n^1\rangle > + \tilde{E}_n^2 |\psi_n^0\rangle > \] (II)
First order correction to eigenstate

Perturbed eigenstates can be expressed in unperturbed basis

\[ |\psi_n\rangle = |\psi^0_n\rangle + \lambda |\tilde{\psi}^1_n\rangle = |\psi^0_n\rangle + \lambda \sum_m c^{(n)}_m |\psi^0_m\rangle \]

with \( c^{(n)}_m = \langle \psi^0_m | \tilde{\psi}^1_n \rangle \)

Our goal: determine \( c^{(n)}_m \)

Normalization:

\[ = \langle \psi^0_n | \psi^0_n \rangle + \lambda \left( \langle \psi^0_n | \tilde{\psi}^1_n \rangle + \text{c.c.} \right) + \lambda^2 (\ldots) \]

\[ = 1 \quad \Rightarrow \quad c^{(n)}_n = 0 \]

neglected in first order

Reminder: eqn. (I)

\[ H^0 |\tilde{\psi}^1_n\rangle + \tilde{\psi}^1_n |\psi^0_n\rangle = E^0_n |\tilde{\psi}^1_n\rangle + \tilde{E}^1_n |\psi^0_n\rangle \]

Insert (*):

\[ \sum_{m \neq n} (E^0_m - E^0_n) c^{(n)}_m |\psi^0_m\rangle = -(\tilde{H} - \tilde{E}^1_n) |\psi^0_n\rangle \]

\[ \langle \psi^0_l | \cdot : \]

\[ \sum_{m \neq n} (E^0_m - E^0_n) c^{(n)}_m \delta_{lm} \langle \psi^0_l | \psi^0_m \rangle = - \langle \psi^0_l | \tilde{H} | \psi^0_n \rangle + \tilde{E}^1_n \delta_{ln} \langle \psi^0_l | \psi^0_n \rangle \]

For \( l = n \) left-hand side (LHS) is zero \( \Rightarrow \) again we find \( E^1_n = \langle \psi^0_n | H' | \psi^0_n \rangle \)
First order correction to eigenstate

\[ l \neq n : \]
\[ (E_l^0 - E_n^0)c_l^{(n)} = - \langle \Psi_l^0 | \tilde{H} | \Psi_n^0 \rangle \]

Rename \( l = m \), solve for \( c_m^{(n)} \):

\[ c_m^{(n)} = \frac{\langle \Psi_m^0 | \tilde{H} | \Psi_n^0 \rangle}{E_n^0 - E_m^0} \] \((*)\)

Remember \( c_n^{(n)} = 0 \) and \( |\tilde{\Psi}_n^1 \rangle = \sum_m c_m^{(n)} |\Psi_n^1 \rangle \)

Insert \((*)\):

\[ |\Psi_n^1 \rangle = \lambda |\tilde{\Psi}_n^1 \rangle = \lambda \sum_{m \neq n} \frac{\langle \Psi_m^0 | \tilde{H} | \Psi_n^0 \rangle}{E_n^0 - E_m^0} |\Psi_m^0 \rangle \]

\[ |\Psi_n^1 \rangle = \sum_{m \neq n} \frac{\langle \Psi_m^0 | H' | \Psi_n^0 \rangle}{E_n^0 - E_m^0} |\Psi_m^0 \rangle \]

Perturbation contaminates state \( |\Psi_n \rangle \) with state \( |\Psi_m \rangle \) proportional to \( \langle \Psi_m^0 | H' | \Psi_n^0 \rangle \)

and the more, the closer the two unperturbed states are in energy \( \left( \propto \frac{1}{E_n^0 - E_m^0} \right) \).

Trouble if \( E_n^0 = E_m^0 \). That’s why we required non-degenerate spectrum.
Intuitive picture

**Eigenstates**

symbolize Hilbert space by 2D vector space

\[ |\Psi_1^0\rangle \quad |\Psi_1^{1st}\rangle \quad |\Psi_1^1\rangle \quad |\Psi_1^{ex}\rangle \quad |\Psi_2^0\rangle \quad |\Psi_2^{1st}\rangle \quad |\Psi_2^1\rangle \quad |\Psi_2^{ex}\rangle \]

- eigenstates of unperturbed system: \( \lambda = 0 \)
- exact eigenstates of perturbed system (very hard to determine)
- correction to first order
- approximate eigenstates to first order (would be happy if we could determine that)

Notice: \( |\Psi_1^1\rangle \) and \( |\Psi_1^0\rangle \) nearly orthogonal because correction small

**Energies**

\[ E_1^0 \quad E_1^{1st} \quad E_2^0 \quad E_2^{1st} \quad E_2^{ex} \]

- \( \lambda = 0 \)
- \( \lambda > 0 \)

Our goals

- change in energy to 2\(^{nd}\) order
- eigenstates up to 1\(^{st}\) order

Done.
Schrödinger equn. of perturbed system

\[ H |\Psi_n^{\text{ex}}\rangle = E_n |\Psi_n^{\text{ex}}\rangle \]

\[
(H^0 + \lambda \tilde{H}) \left[ |\psi_n^0 > + \lambda |\tilde{\psi}_n^1 > + \lambda^2 |\tilde{\psi}_n^2 > + \ldots \right] \\
= \left[ E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \ldots \right] \left[ |\psi_n^0 > + \lambda |\tilde{\psi}_n^1 > + \lambda^2 |\tilde{\psi}_n^2 > + \ldots \right]
\]

Collect like powers of \( \lambda \):

\[
H^0 |\psi_n^0 > + \lambda \left( H^0 |\tilde{\psi}_n^1 > + \tilde{H} |\psi_n^0 > \right) + \lambda^2 \left( H^0 |\tilde{\psi}_n^2 > + \tilde{H} |\tilde{\psi}_n^1 > \right) + \ldots
\]

\[
= E_0^0 |\psi_n^0 > + \lambda \left( E_n^0 |\tilde{\psi}_n^1 > + \tilde{E}_n^1 |\psi_n^0 > \right) + \lambda^2 \left( E_n^0 |\tilde{\psi}_n^2 > + \tilde{E}_n^1 |\tilde{\psi}_n^1 > + \tilde{E}_n^2 |\psi_n^0 > \right) + \ldots
\]

0th order (\( \lambda^0 \)): \( H^0 |\psi_n^0 > = E_n^0 |\psi_n^0 > \)

1st order (\( \lambda^1 \)): \( H^0 |\tilde{\psi}_n^1 > + \tilde{H} |\psi_n^0 > = E_n^0 |\tilde{\psi}_n^1 > + \tilde{E}_n^1 |\psi_n^0 > \) \( (\text{I}) \)

2nd order (\( \lambda^2 \)): \( H^0 |\tilde{\psi}_n^2 > + \tilde{H} |\tilde{\psi}_n^1 > = E_n^0 |\tilde{\psi}_n^2 > + \tilde{E}_n^1 |\tilde{\psi}_n^1 > + \tilde{E}_n^2 |\psi_n^0 > \) \( (\text{II}) \)

Reminder:

\[
H^0 + \lambda \tilde{H} \\
|\psi_n^{\text{ex}} > = |\psi_n^0 > + \lambda |\tilde{\psi}_n^1 > + \lambda^2 |\tilde{\psi}_n^2 > + \ldots \\
E_n^{\text{ex}} = E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \ldots
\]
Second order correction to energy

reminder: eqn. (II)

\[ H^0 |\tilde{\psi}_n^2 > + \tilde{\tilde{H}} |\tilde{\psi}_n^1 > = E_n^0 |\tilde{\psi}_n^2 > + \tilde{E}_n^1 |\tilde{\psi}_n^1 > + \tilde{E}_n^2 |\psi_n^0 > \]

\[ < \psi_n^0 | \cdot (\text{II}) : \]

\[ < \psi_n^0 | H^0 |\tilde{\psi}_n^2 > + < \psi_n^0 | \tilde{\tilde{H}} |\tilde{\psi}_n^1 > = E_n^0 < \psi_n^0 | \tilde{\psi}_n^2 > + \tilde{E}_n^1 < \psi_n^0 | \tilde{\psi}_n^1 > + \tilde{E}_n^2 < \psi_n^0 | \psi_n^0 > \]

\[ = < H^0 \psi_n^0 | \tilde{\psi}_n^2 > = E_n^0 < \psi_n^0 | \tilde{\psi}_n^2 > \]

reminder:

\[ |\psi_n^1 > = \sum_{m \neq n} \frac{< \psi_n^0 | H' | \psi_n^0 >}{E_n^0 - E_m^0} |\psi_m^0 > \]

\[ E_n^2 = \lambda^2 \tilde{E}_n^2 = < \psi_n^0 | \lambda \tilde{\tilde{H}} |\psi_n^1 > = \sum_{m \neq n} \frac{< \psi_n^0 | H' | \psi_n^0 >}{E_n^0 - E_m^0} < \psi_n^0 | H' | \psi_m^0 > \]
Second order correction to energy

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

Observations

\[ \left| \frac{\langle \psi_m^0 | H' | \psi_m^0 \rangle}{E_m^0 - E_n^0} \right|^2 > 0 \]

If \( E_m^0 > E_n^0 \), state \( m \) pushes state \( n \) down in energy.

If \( E_m^0 < E_n^0 \), state \( m \) pushes state \( n \) up in energy.

In second order, energy levels repel each other \((\propto \left| \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \right|^2)\)

The more repulsion the closer they are \((\frac{1}{E_n^0 - E_m^0})\)

If first order correction to energy is zero, ground state is shifted down.
Intuitive picture

**Eigenstates**

symbolize Hilbert space by 2D vector space

- $|\Psi_1^0\rangle$
- $|\Psi_1^{\text{ex}}\rangle$
- $|\Psi_1^{\text{1st}}\rangle$
- $|\Psi_2^0\rangle$
- $|\Psi_2^{\text{ex}}\rangle$
- $|\Psi_2^{\text{1st}}\rangle$

- eigenstates of unperturbed system
- exact eigenstates of perturbed system (very hard to determine)
- correction to first order
- approximate eigenstates to first order (would be happy if we could determine that)

Notice: $|\Psi_1^0\rangle$ and $|\Psi_1^{\text{ex}}\rangle$ nearly orthogonal because correction small

**Energies**

- $E_1^0$
- $E_1^{\text{ex}}$
- $E_2^0$
- $E_2^{\text{ex}}$
- $E_1^{\text{1st}}$
- $E_2^{\text{1st}}$

- $\lambda = 0$
- $\lambda > 0$

**Our goals**

- change in energy to 2nd order
- eigenstates up to 1st order

Done.
Summary

Compact notation: \[ W_{mn} \equiv \langle \Psi_m^0 | H' | \Psi_n^0 \rangle ; \quad \Delta_{mn} \equiv E_m^0 - E_n^0 \]

Energy

\[ E_n = E_n^0 + E_n^1 + E_n^2 + E_n^3 + \ldots \]

\[ \frac{W_{nm}^2}{\Delta_{nm}} \]

\[ E_n^3 = \sum_{l,m\neq n} \frac{W_{nl}W_{lm}W_{mn}}{\Delta_{nl}\Delta_{nm}} - W_{nn} \sum_{m\neq n} \frac{W_{nm}^2}{\Delta_{nm}^2} \]

State

\[ |\Psi_n^1> = |\Psi_n^0> + |\Psi_n^1> + \cdots \]

\[ |\Psi_n^1> = \sum_{m\neq n} \frac{W_{mn}}{\Delta_{nm}} |\Psi_m^0> \]

Validity

Consecutive orders need to deliver ever smaller correction \[ \Rightarrow |W_{nm}| \ll |\Delta_{nm}| \]

|Matrix elements| of perturbation have to be smaller than |energy level splittings|. 
Goal of this section

Determine energies and eigenstates of system exposed to small perturbation.

Applications:

Absolutely everywhere. In quantum mechanics it is hard to calculate anything exactly, so we use perturbation theory nearly all the time.

Atoms, molecules, condensed-matter,…

Plan of this section

1) intro, examples
2) non-degenerate perturbation theory
3) 2-fold degenerate perturbation theory
4) $n$-fold degenerate perturbation theory
5) general perturbation theory

Griffiths 3rd

7.1.1
7.1.2 – 7.1.3
7.2.1 – 7.2.2
7.2.3
Degenerate perturbation theory

Challenge

If \( E_n = E_m \) for \( n \neq m \), the correction obtained so far can become infinite \( \left( \frac{W_{nm}}{\Delta_{nm}} \rightarrow \infty \right) \) unless \( W_{nm} = 0 \). This hint towards solution of challenge

\[ W_{mn} \equiv \langle \psi_m | H' | \psi_n > \ ; \Delta_{mn} \equiv E_m^0 - E_n^0 \]

For simplicity consider system of only two degenerate states

\[ H^0 |\psi_a^0 > = E^0 |\psi_a^0 > \ ; \ H^0 |\psi_b^0 > = E^0 |\psi_b^0 > \]

Notice: all superpositions of these states still eigenstates of \( H^0 \)

\[ |\psi^0 > = \alpha^0 |\psi_a^0 > + \beta^0 |\psi_b^0 > \ ; \ |\alpha^0|^2 + |\beta^0|^2 = 1 \]

\[ H^0 |\psi^0 > = E^0 |\psi^0 > \]

This makes perturbative expansion more complicated

\[ |\psi_n^{ex} > = |\psi_n^0 > + \lambda |\tilde{\psi}_n^1 > + ... \]

\[ \uparrow \text{ We don’t know which superposition to use.} \]

Task: find good \( |\psi_n^0 > \)

For 2-fold degeneracy, there will be two good \( |\psi_n^0 > \), which we’ll label \( |\psi_+^0 > \) and \( |\psi_-^0 > \). (Often we will skip index \( n \) entirely.)
Intuitive picture

**Eigenstates**
symbolize Hilbert space by 3D vector space

Energies

Our goals
- change in energy to 1st order
- „good“ eigenstates (= „states to 0th order“)

„good choice“ of eigenstates: eigenstates that lead to first order correction orthogonal to degen. subspace
Degenerate perturbation theory

Often perturbation lifts degeneracy between states

Reminder: \[ H = H^0 + H' = H^0 + \lambda \tilde{H} \]

\( E_+^{\text{ex}} \) with eigenstate
\[ |\Psi_+^{\text{ex}}\rangle = \alpha(\lambda) |\Psi_a^{0}\rangle + \beta(\lambda) |\Psi_b^{0}\rangle + \gamma(\lambda) |\Psi_{\text{orth}}(\lambda)\rangle \]

in degenerate subspace

small vector orthogonal to degenerate subspace
\[ \lim_{\lambda \to 0} \gamma(\lambda) = 0 \]

We can guess that
\[ |\Psi_{\pm}^{0}\rangle = \lim_{\lambda \to 0} |\Psi_{\pm}^{\text{ex}}\rangle \]

\( \alpha^0 = \lim_{\lambda \to 0} \alpha(\lambda) ; \beta^0 = \lim_{\lambda \to 0} \beta(\lambda) \)
First order correction of energy

Solve \[ H|\psi> = E|\psi> \quad ; \quad H = H^0 + H' = H^0 + \lambda \tilde{H} \]

with \[ E^{ex} = E^0 + \lambda \tilde{E}^1 + \ldots \]
\[ |\psi^{ex}> = |\psi^0> + \lambda |\tilde{\psi}^1> + \ldots \]

Insert, expand, collect 1st order in \( \lambda \)

\[ \implies \text{eqn. (I) exactly as before:} \quad H^0|\tilde{\psi}^1> + \tilde{H}|\psi^0> = E^0|\tilde{\psi}^1> + \tilde{E}^1|\psi^0> \]

Here we skip index \( n = +/- \) for clarity.
Calculation applies for both states.
Schrödinger equation of perturbed system

\[ H |\Psi_n^{\text{ex}}\rangle = E_n |\Psi_n^{\text{ex}}\rangle \]

\[ (H^0 + \lambda \tilde{H}) \left[ |\psi_n^0 > + \lambda |\tilde{\psi}_n^1 > + \lambda^2 |\tilde{\psi}_n^2 > + \ldots \right] \]

\[ = \left[ E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \ldots \right] \left[ |\psi_n^0 > + \lambda |\tilde{\psi}_n^1 > + \lambda^2 |\tilde{\psi}_n^2 > + \ldots \right] \]

Collect like powers of \( \lambda \):

\[ H^0 |\psi_n^0 > + \lambda \left( H^0 |\tilde{\psi}_n^1 > + \tilde{H} |\psi_n^0 > \right) + \lambda^2 \left( H^0 |\tilde{\psi}_n^2 > + \tilde{H} |\tilde{\psi}_n^1 > \right) + \ldots \]

\[ = E_0 |\psi_n^0 > + \lambda \left( E_n^0 |\tilde{\psi}_n^1 > + \tilde{E}_n^1 |\psi_n^0 > \right) + \lambda^2 \left( E_n^0 |\tilde{\psi}_n^2 > + \tilde{E}_n^1 |\tilde{\psi}_n^1 > + \tilde{E}_n^2 |\psi_n^0 > \right) + \ldots \]

0th order (\( \lambda^0 \)):

\[ H^0 |\psi_n^0 > = E_n |\psi_n^0 > \]

1st order (\( \lambda^1 \)):

\[ H^0 |\tilde{\psi}_n^1 > + \tilde{H} |\psi_n^0 > = E_n^0 |\tilde{\psi}_n^1 > + \tilde{E}_n^1 |\psi_n^0 > \] (I)

2nd order (\( \lambda^2 \)):

\[ H^0 |\tilde{\psi}_n^2 > + \tilde{H} |\tilde{\psi}_n^1 > = E_n^0 |\tilde{\psi}_n^2 > + \tilde{E}_n^1 |\tilde{\psi}_n^1 > + \tilde{E}_n^2 |\psi_n^0 > \] (II)
First order correction of energy

Solve \( H|\psi \rangle = E|\psi \rangle \); \( H = H^0 + H' = H^0 + \lambda \tilde{H} \)

with \( E^{ex} = E^0 + \lambda \tilde{E}^1 + \ldots \)

\[ |\psi^{ex} \rangle = |\psi^0 \rangle + \lambda |\tilde{\psi}^1 \rangle + \ldots \]

Insert, expand, collect 1st order in \( \lambda \)

\[ \implies \text{eqn. (I) exactly as before: } H^0|\tilde{\psi}^1 \rangle + \tilde{H}|\psi^0 \rangle = E^0|\tilde{\psi}^1 \rangle + \tilde{E}^1|\psi^0 \rangle \]

\[ \langle \psi_0^0| \cdot (I): \]

\[ \frac{1}{\lambda} \left( \langle \psi_0^0| H^0|\tilde{\psi}^1 \rangle + \langle \psi_0^0| \tilde{H}|\psi^0 \rangle \right) = E^0 \langle \psi_0^0| \tilde{\psi}^1 \rangle \]

Insert \( |\psi^0 \rangle = \alpha^0 |\psi_a^0 \rangle + \beta^0 |\psi_b^0 \rangle \):

\[ \alpha^0 \langle \psi_a^0| \tilde{H}|\psi_a^0 \rangle + \beta^0 \langle \psi_b^0| \tilde{H}|\psi_b^0 \rangle = \alpha^0 \tilde{E}^1 \]

\( \lambda \) and compact notation:

\[ \alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1 \]

\( W_{ij} \equiv \langle \psi_i^0|H'|\psi_j^0 \rangle \); \( i, j \in \{a, b\} \)

Note: \( W_{ba} = W_{ab}^* \)

Similarly \( \langle \psi_b^0| \cdot (i) \) leads to:

\[ \alpha^0 W_{ba} + \beta^0 W_{bb} = \beta^0 E^1 \]
First order correction of energy

\[ \alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1 \]

\[ W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle \]

\[ \alpha^0 W_{ba} + \beta^0 W_{bb} = \beta^0 E^1 \]

Two equations to help determine \( \alpha^0, \beta^0, E^1 \)

Together with \( |\alpha^0|^2 + |\beta^0|^2 = 1 \), \( |\psi^0 > = \alpha^0 |\psi_a^0 > + \beta^0 |\psi_b^0 > \) and e.g. \( \alpha^0 \in \mathbb{R} \)

\[ \implies \text{good eigenstates and first order energy shifts } |\psi^0 >, E^1 \]

Matrix form

\[
\begin{pmatrix}
W_{aa} & W_{ab} \\
W_{ba} & W_{bb}
\end{pmatrix}
\begin{pmatrix}
\alpha^0 \\
\beta^0
\end{pmatrix}
= E^1
\begin{pmatrix}
\alpha^0 \\
\beta^0
\end{pmatrix}
\]

Find \( \alpha^0, \beta^0, E^1 \) by e.g. diagonalizing matrix.

Especially easy if \( W_{ab} = 0 \):

\[
\begin{pmatrix}
W_{aa} & 0 \\
0 & W_{bb}
\end{pmatrix}
\begin{pmatrix}
\alpha^0 \\
\beta^0
\end{pmatrix}
= E^1
\begin{pmatrix}
\alpha^0 \\
\beta^0
\end{pmatrix}
\]

Here \( |\psi_a^0 > \) and \( |\psi_b^0 > \) were already the desired zero order states \( |\psi_{\pm}^0 > \).

In that case energy correction expectation values of perturbation, as in non-degenerate case.
Intuitive picture

**Eigenstates**

symbolize Hilbert space by 3D vector space

- possible basisstates of degenerate manifold of unperturbed system
- state with different energy
- „good“ choice of basisstates of degenerate manifold of unperturbed system
- exact eigenstates of perturbed system
  (very hard to determine)
- correction to first order
- approximate eigenstates to first order
  (would be nice, but not our goal here)

Our goals

- change in energy to 1st order
- „good“ eigenstates
  (= „states to 0th order“)

„good choice“ of eigenstates: eigenstates that lead to first order correction orthogonal to degen. subspace
First order correction to eigenstate

(Assume degeneracy infinitessimally lifted)

\[ l \neq n : \]
\[ (E_l^0 - E_n^0)c_l^{(n)} = - \langle \psi_l^0 | \tilde{H} | \psi_n^0 \rangle \]

Rename \( l = m \), solve for \( c_m^{(n)} \):

\[ c_m^{(n)} = \frac{\langle \psi_m^0 | \tilde{H} | \psi_n^0 \rangle}{E_n^0 - E_m^0} \quad (\star) \]

Remember \( c_n^{(n)} = 0 \) and \( |\tilde{\psi}_n^1\rangle = \sum_m c_m^{(n)} |\psi_m^0\rangle \)

Insert (\( \star \)):

\[ |\psi_n^1\rangle = \lambda |\tilde{\psi}_n^1\rangle = \lambda \sum_{m \neq n} \frac{\langle \psi_m^0 | \tilde{H} | \psi_n^0 \rangle}{E_n^0 - E_m^0} |\psi_m^0\rangle \]

Here: \( W_{ab} = 0 \)  
\[ \text{No contamination} \]

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

Perturbation contaminates state \( |\psi_n\rangle \) with state \( |\psi_m\rangle \) proportional to \( \langle \psi_m^0 | H' | \psi_n^0 \rangle \)

and the more, the closer the two unperturbed states are in energy \( \left( \propto \frac{1}{E_n^0 - E_m^0} \right) \).

Trouble if \( E_n^0 = E_m^0 \). That’s why we required non-degenerate spectrum.
First order correction of energy

\[(\text{III}) \quad \alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1 \]

\[(\text{IV}) \quad \alpha^0 W_{ba} + \beta^0 W_{bb} = \beta^0 E^1 \]

Solve equation system by hand.

First solve for \( E^1 \):

\[(\text{III}) : \quad \beta^0 W_{ab} = \alpha^0 (E^1 - W_{aa}) \]

\( W_{ab} \cdot (\text{IV}) \), insert to get rid of \( \beta^0 W_{ab} \):

\[\alpha^0 W_{ab} W_{ba} + \alpha^0 (E^1 - W_{aa}) W_{bb} = \alpha^0 (E^1 - W_{aa}) E^1 \]

\[\alpha^0 [W_{ab} W_{ba} + (E^1 - W_{aa})(W_{bb} - E^1)] = 0 \]

If \( \alpha^0 \neq 0 \):

\[(E^1)^2 - E^1 (W_{bb} + W_{aa}) + (W_{aa} W_{bb} - \frac{|W_{ab}|^2}{q}) = 0 \]

Solution: \( E^1_{\pm} = \frac{1}{2} (-p \pm \sqrt{p^2 - 4q}) \)
First order correction of energy

If \( \alpha^0 \neq 0 \):

\[
E^1_{\pm} = \frac{1}{2} \left[ W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right]
\]

Energy of the two perturbed states to first order:

\[
E_{\pm} = E^0 + E^1_{\pm}
\]

Find good eigenstates (0 order eigenstates):

Inserting \( E^1_{\pm} \) into (III) \( \beta^0 W_{ab} = \alpha^0 (E^1 - W_{aa}) \) for \( W_{ab} \neq 0 \):

\[
\frac{\beta^0_{\pm}}{\alpha^0_{\pm}} = (E^1_{\pm} - W_{aa})/W_{ab}
\]

with \( |\alpha^0_{\pm}|^2 + |\beta^0_{\pm}|^2 = 1 \) and e.g. requiring \( \alpha^0_{\pm} \in \mathbb{R} \) gives \( |\Psi^0_{\pm}| > \)
**Intuitive picture**

**Eigenstates**

- Symbolize Hilbert space by 3D vector space.

Possible basis states of degenerate manifold of unperturbed system:

- State with different energy.
- "good" choice of basis states of degenerate manifold of unperturbed system.

**Energies**

- Exact eigenstates of perturbed system (very hard to determine).
- Correction to first order.
- Approximate eigenstates to first order (would be nice, but not our goal here).

Done for \( \alpha^0 \neq 0 \)

\[ \alpha^0 \neq 0 \]

\[ \lambda = 0 \]

\[ \lambda > 0 \]

**Our goals**

- Change in energy to 1\(^{\text{st}}\) order.
- "good" eigenstates (= "states to 0\(^{\text{th}}\) order").

"good choice" of eigenstates: eigenstates that lead to first order correction orthogonal to degenerate subspace.
First order correction of energy

If $\alpha^0 = 0$:
\[ |\alpha^0|^2 + |\beta^0|^2 = 1 \rightarrow \beta^0 = e^{i\Phi_b} \]

Using (III):
\[ \alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1 : \]
\[ \beta^0 W_{ab} = 0 \Rightarrow W_{ab} = 0 \]

Using (IV):
\[ \alpha^0 W_{ba} + \beta^0 W_{bb} = \beta^0 E^1 : \]
\[ E^1_b = W_{bb} = \langle \psi^0_b | H' | \psi^0_b \rangle \]

If $W_{ab} = 0$ second solution:
\[ \alpha^0 = e^{i\Phi_a} \rightarrow \beta^0 = 0 \]
\[ \rightarrow E^1_a = W_{aa} = \langle \psi^0_a | H' | \psi^0_a \rangle \]

Matrix form:
\[
\begin{pmatrix}
W_{aa} & 0 \\
0 & W_{bb}
\end{pmatrix}
\begin{pmatrix}
\alpha^0 \\
\beta^0
\end{pmatrix}
= E^1
\begin{pmatrix}
\alpha^0 \\
\beta^0
\end{pmatrix}
\]

Here $|\psi^0_a\rangle$ and $|\psi^0_b\rangle$ were already the desired zero order states $|\psi^0_{\pm}\rangle$.

In that case energy correction expectation values of perturbation, as in non-degenerate case.
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symbolize Hilbert space by 3D vector space

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- approximate eigenstates to first order (would be nice, but not our goal here)

**Energies**

- Energies
- Degenerate 2D subspace
- State with different energy
- „Good“ choice of eigenstates
- Exact eigenstates of perturbed system
- Correction to first order
- Approximate eigenstates to first order

**Our goals**

- change in energy to 1st order
- „good“ eigenstates (= „states to 0th order“)

„good choice“ of eigenstates: eigenstates that lead to first order correction orthogonal to degenerate subspace

Done. Done.
Overview of „t-indep. pert. theory“

**Goal of this section**

Determine energies and eigenstates of system exposed to small perturbation.

Applications:

Absolutely everywhere. In quantum mechanics it is hard to calculate anything exactly, so we use perturbation theory nearly all the time.

Atoms, molecules, condensed-matter,…

**Plan of this section**

1) intro, examples
2) non-degenerate perturbation theory
3) 2-fold degenerate perturbation theory
4) $n$-fold degenerate perturbation theory
5) general perturbation theory

Griffiths 3rd 7.1.1

7.1.2 – 7.1.3

7.2.1 – 7.2.2

7.2.3
Overview of course

Part 1: 7 lectures in January (Piet Mulders)
- Basics of quantum mechanics
- Spin states
- Addition of angular momentum
- Identical particles
- Basic structure of atom

Part 2: 7 lectures in February and March (Florian Schreck)
- Structure of atoms & the periodic table
- Crystalline solids
- Time-independent perturbation theory
- Structure of hydrogen
- Variational principle
- Time-dependent perturbation theory, atom-light interaction

Lecture notes, problem sets and link to video recordings of C0.110 lectures available on Canvas

Questions: schreck@StrontiumBEC.com
Overview of „t-indep. pert. theory“

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Griffiths 3rd 7.1.1
7.1.2 – 7.1.3
7.2.1 – 7.2.2
7.2.3
Example: Particle in nearly square box

Starting point
unperturbed system

Modification
perturbed system

We know $E_0^0, \psi_0^0, E_1^0, \psi_1^0,...$

Small perturbation
potential slightly altered

Question
What are, approximately, $E_0, \psi_0, E_1, \psi_1,...$?
Example: Atom in magnetic field

Starting point
unperturbed system

Modification
perturbed system

Small perturbation
weak magnetic field

Question
What are, approximately, perturbed eigenstates and energies?
Intuitive picture

Eigenstates
symbolize Hilbert space by 2D vector space

|\Psi_1^0\rangle \quad |\Psi_1^{1st}\rangle \quad |\Psi_1^{ex}\rangle

|\Psi_2^0\rangle \quad |\Psi_2^{1st}\rangle \quad |\Psi_2^{ex}\rangle

Energies

Energies of unperturbed system
\lambda = 0

Energies of perturbed system
\lambda > 0

Our goals
- change in energy to 2\textsuperscript{nd} order
- eigenstates up to 1\textsuperscript{st} order

Notice: \( |\Psi_1^{1}\rangle \) and \( |\Psi_1^{0}\rangle \) nearly orthogonal because correction small
Non-degenerate perturbation theory

Hamiltonian:

\[ H = H^0 + H' = H^0 + \lambda \tilde{H} \quad ; \quad \tilde{H} = \frac{H'}{\lambda} \quad ; \quad \lambda \ll 1 \]

(no two eigenstates of unperturbed system have same energy)

Unperturbed system has orthonormal eigenstates \{\psi_n^0\} with energies \{E_n^0\}:

\[ H^0 |\psi_n^0 \rangle = E_n^0 |\psi_n^0 \rangle \quad ; \quad \langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} \quad ; \quad E_n^0 \neq E_m^0 \quad \text{for} \quad n \neq m \]

Perturbed system has eigenstates \{|\psi_{n_{\text{ex}}}^\text{ex}\rangle\} with energy \{E_{n_{\text{ex}}}^\text{ex}\}, i.e.

\[ H |\psi_{n_{\text{ex}}}^\text{ex}\rangle = E_{n_{\text{ex}}}^\text{ex} |\psi_{n_{\text{ex}}}^\text{ex}\rangle \]

("ex" for "exact solution")

These can be written as expansion in small parameter \(\lambda\):

- \(0^{\text{th}}\) order:
  \[ |\psi_{n_{\text{ex}}}^\text{ex}\rangle = |\psi_n^0 \rangle \]

- \(1^{\text{st}}\) order:
  \[ |\psi_{n_{\text{ex}}}^\text{ex}\rangle = |\psi_n^0 \rangle + \lambda |\tilde{\psi}_n^1 \rangle \quad \equiv |\psi_n^1 \rangle \]

- \(2^{\text{nd}}\) order:
  \[ |\psi_{n_{\text{ex}}}^\text{ex}\rangle = |\psi_n^0 \rangle + \lambda |\tilde{\psi}_n^1 \rangle + \lambda^2 |\tilde{\psi}_n^2 \rangle \quad \equiv |\psi_n^2 \rangle \]

- \(3^{\text{rd}}\) and higher orders in \(\lambda\):
  \[ |\psi_{n_{\text{ex}}}^\text{ex}\rangle = |\psi_n^0 \rangle + \lambda |\tilde{\psi}_n^1 \rangle + \lambda^2 |\tilde{\psi}_n^2 \rangle + \ldots \]

\[ E_{n_{\text{ex}}}^\text{ex} = E_n^0 + \lambda \tilde{E}_n^1 \quad \equiv E_n^1 \quad \text{for} \quad n \neq m \]

\[ + \lambda^2 \tilde{E}_n^2 \quad \equiv E_n^2 \quad + \ldots \]
Schrödinger equation of perturbed system

\[ H \left| \Psi_n^{\text{ex}} \right\rangle = E_n \left| \Psi_n^{\text{ex}} \right\rangle \]

\[ \left( H^0 + \lambda \tilde{H} \right) \left[ \left| \Psi_n^0 \right\rangle + \lambda \left| \tilde{\Psi}_n^1 \right\rangle + \lambda^2 \left| \tilde{\tilde{\Psi}}_n^2 \right\rangle + \ldots \right] = \left[ E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \ldots \right] \left[ \left| \Psi_n^0 \right\rangle + \lambda \left| \tilde{\Psi}_n^1 \right\rangle + \lambda^2 \left| \tilde{\tilde{\Psi}}_n^2 \right\rangle + \ldots \right] \]

Collect like powers of \( \lambda \):

\[ H^0 \left| \Psi_n^0 \right\rangle + \lambda \left( H^0 \left| \tilde{\Psi}_n^1 \right\rangle + \tilde{H} \left| \Psi_n^0 \right\rangle \right) + \lambda^2 \left( H^0 \left| \tilde{\Psi}_n^2 \right\rangle + \tilde{H} \left| \tilde{\Psi}_n^1 \right\rangle \right) + \ldots = E_n^0 \left| \Psi_n^0 \right\rangle + \lambda \left( E_n^0 \left| \tilde{\Psi}_n^1 \right\rangle + \tilde{E}_n^1 \left| \Psi_n^0 \right\rangle \right) + \lambda^2 \left( E_n^0 \left| \tilde{\Psi}_n^2 \right\rangle + \tilde{E}_n^1 \left| \tilde{\Psi}_n^1 \right\rangle + \tilde{E}_n^2 \left| \Psi_n^0 \right\rangle \right) + \ldots \]

0th order (\( \lambda^0 \)):

\[ H^0 \left| \Psi_n^0 \right\rangle = E_n \left| \Psi_n^0 \right\rangle \]

1st order (\( \lambda^1 \)):

\[ H^0 \left| \tilde{\Psi}_n^1 \right\rangle + \tilde{H} \left| \Psi_n^0 \right\rangle = E_n^0 \left| \tilde{\Psi}_n^1 \right\rangle + \tilde{E}_n^1 \left| \Psi_n^0 \right\rangle \quad (I) \]

2nd order (\( \lambda^2 \)):

\[ H^0 \left| \tilde{\tilde{\Psi}}_n^2 \right\rangle + \tilde{H} \left| \tilde{\Psi}_n^1 \right\rangle = E_n^0 \left| \tilde{\tilde{\Psi}}_n^2 \right\rangle + \tilde{E}_n^1 \left| \tilde{\Psi}_n^1 \right\rangle + \tilde{E}_n^2 \left| \Psi_n^0 \right\rangle \quad (II) \]
First order correction to energy

\[(I)\quad H^0 |\tilde{\Psi}_n^1 > + \tilde{H} |\psi_n^0 >= E_n^0 |\tilde{\Psi}_n^1 > + \tilde{E}_n^1 |\psi_n^0 >\]

\[<\psi_n^0| \cdot (I) : \]

\[<\psi_n^0|H^0|\tilde{\Psi}_n^1 > + <\psi_n^0|\tilde{H}|\psi_n^0 >= E_n^0 <\psi_n^0|\tilde{\Psi}_n^1 > + \tilde{E}_n^1 <\psi_n^0|\psi_n^0 >\]

\[= <H^0 \psi_n^0|\tilde{\Psi}_n^1 > = E_n^0 <\psi_n^0|\tilde{\Psi}_n^1 > \]

\[\tilde{E}_n^1 = <\psi_n^0|\tilde{H}|\psi_n^0 >\]

\[E_n^1 = <\psi_n^0|H'|\psi_n^0 >\]

\[E_n = E_n^0 + E_n^1\]

To first order in the perturbation, energy is shifted by expectation value of perturbation of state under consideration.
First order correction to eigenstate

\( l \neq n \):

\[
(E_i^0 - E_n^0) c_l^{(n)} = - \langle \psi_i^0 | \tilde{H} | \psi_n^0 \rangle
\]

Rename \( l = m \), solve for \( c_m^{(n)} \):

\[
c_m^{(n)} = \frac{\langle \psi_m^0 | \tilde{H} | \psi_n^0 \rangle}{E_n^0 - E_m^0} \quad (*)
\]

Remember \( c_n^{(n)} = 0 \) and \( |\tilde{\psi}_n^1\rangle = \sum_m c_m^{(n)} |\psi_m^0\rangle \)

Insert (*):

\[
|\psi_n^1\rangle = \lambda |\tilde{\psi}_n^1\rangle = \lambda \sum_{m \neq n} \frac{\langle \psi_m^0 | \tilde{H} | \psi_n^0 \rangle}{E_n^0 - E_m^0} |\psi_m^0\rangle
\]

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

Perturbation contaminates state \( |\psi_n\rangle \) with state \( |\psi_m\rangle \) proportional to \( \langle \psi_m^0 | H' | \psi_n^0 \rangle \)

and the more, the closer the two unperturbed states are in energy \( \left( \propto \frac{1}{E_n^0 - E_m^0} \right) \).

Trouble if \( E_n^0 = E_m^0 \). That’s why we required non-degenerate spectrum.
Second order correction to energy

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

Observations

\[ | \langle \psi_m^0 | H' | \psi_m^0 \rangle |^2 > 0 \]

If \( E_m^0 > E_n^0 \), state \( m \) pushes state \( n \) down in energy.

If \( E_m^0 < E_n^0 \), state \( m \) pushes state \( n \) up in energy.

In second order, energy levels repel each other \( (\propto | \langle \psi_m^0 | H' | \psi_n^0 \rangle |^2) \)

The more repulsion the closer they are \( \left( \frac{1}{E_n^0 - E_m^0} \right) \)

If first order correction to energy is zero, ground state is shifted down.
Summary

Compact notation: \[ W_{mn} \equiv < \psi_m^0 | H' | \psi_n^0 > \; ; \; \Delta_{mn} \equiv E_m^0 - E_n^0 \]

Energy

\[ E_n = E_n^0 + E_n^1 + E_n^2 + E_n^3 + \ldots \]

\[ \frac{W_{nm}^2}{\Delta_{nm}} \]

\[ E_n^3 = \sum_{l,m \neq n} \frac{W_{nl} W_{lm} W_{mn}}{\Delta_{nl} \Delta_{nm}} - W_{nn} \sum_{m \neq n} \frac{W_{nm}^2}{\Delta_{nm}^2} \]

State

\[ |\psi_n> = |\psi_n^0> + |\psi_n^1> + \cdots \]

\[ |\psi_n^1> = \sum_{m \neq n} \frac{W_{mn}}{\Delta_{nm}} |\psi_m^0> \]

Validity

Consecutive orders need to deliver ever smaller correction \( \Rightarrow |W_{nm}| \ll |\Delta_{nm}| \)

|Matrix elements| of perturbation have to be smaller than |energy level splittings|. 
Overview of „t-indep. pert. theory“

Goal of this section
Determine energies and eigenstates of system exposed to small perturbation.

Applications:
Absolutely everywhere. In quantum mechanics it is hard to calculate anything exactly, so we use perturbation theory nearly all the time.
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Griffiths 3rd 7.1.1
7.1.2 – 7.1.3
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symbolize Hilbert space by 3D vector space

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- "good" choice of basis states of degenerate manifold of unperturbed system
- exact eigenstates of perturbed system (very hard to determine)
- correction to first order
- approximate eigenstates to first order (would be nice, but not our goal here)

Our goals

- change in energy to 1\textsuperscript{st} order
- "good" eigenstates (= "states to 0\textsuperscript{th} order")
Degenerate perturbation theory

Challenge

If $E_n = E_m$ for $n \neq m$, the correction obtained so far can become infinite $\left( \frac{W_{nm}}{\Delta_{nm}} \to \infty \right)$ unless $W_{nm} = 0$.

$W_{mn} \equiv \langle \psi_m | H' | \psi_n \rangle$; $\Delta_{mn} \equiv E_m^0 - E_n^0$

For simplicity consider system of only two degenerate states

$H^0 | \psi_a^0 > = E^0 | \psi_a^0 >$; $H^0 | \psi_b^0 > = E^0 | \psi_b^0 >$

Notice: all superpositions of these states still eigenstates of $H^0$

e.g. $| \psi^0 > = \alpha^0 | \psi_a^0 > + \beta^0 | \psi_b^0 >$; $| \alpha^0 |^2 + | \beta^0 |^2 = 1$

$H^0 | \psi^0 > = E^0 | \psi^0 >$

This makes perturbative expansion more complicated

$| \psi_{ex}^n > = | \psi_n^0 > + \lambda | \tilde{\psi}_1^0 > + \ldots$

We don't know which superposition to use.

Task: find good $| \psi_n^0 >$

For 2-fold degeneracy, there will be two good $| \psi_n^0 >$, which we'll label $| \psi_+^0 >$ and $| \psi_-^0 >$. (Often we will skip index $n$ entirely.)
First order correction of energy

Solve \[ H |\psi\rangle = E |\psi\rangle \quad ; \quad H = H^0 + H' = H^0 + \lambda \tilde{H} \]

with \[ E^\text{ex} = E^0 + \lambda \tilde{E}^1 + ... \]
\[ |\Psi^\text{ex}\rangle = |\Psi^0\rangle + \lambda |\tilde{\Psi}^1\rangle + ... \]

Insert, expand, collect 1st order in \( \lambda \)

\[ \rightarrow \text{ eqn. (I) exactly as before:} \quad H^0 |\tilde{\Psi}^1\rangle + \tilde{H} |\Psi^0\rangle = E^0 |\tilde{\Psi}^1\rangle + \tilde{E}^1 |\Psi^0\rangle \]

\( < \Psi^0_a | \cdot (I): \)

\[
\frac{< \Psi^0_a | H^0 | \tilde{\Psi}^1 > + < \Psi^0_a | \tilde{H} | \Psi^0 >}{=} E^0 < \Psi^0_a | \tilde{\Psi}^1 >
\]

use \( |\Psi^0\rangle = \alpha^0 |\Psi^0_a\rangle + \beta^0 |\Psi^0_b\rangle \):

\[ \alpha^0 < \Psi^0_\alpha | \tilde{H} | \Psi^0_a > + \beta^0 < \Psi^0_a | \tilde{H} | \Psi^0_b > = \alpha^0 \tilde{E}^1 \]

\( \lambda \) and compact notation:

\[ \alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1 \quad \text{and} \quad W_{ij} \equiv < \psi^0_i | H' | \psi^0_j > \quad ; \quad i, j \in \{a, b\} \]

note: \( W_{ba} = W_{ab}^* \)

Similarly \( < \Psi^0_b | \cdot (i) \) leads to:

\[ \alpha^0 W_{ba} + \beta^0 W_{bb} = \beta^0 E^1 \]
First order correction of energy

\[ \alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1 \]
\[ \alpha^0 W_{ba} + \beta^0 W_{bb} = \beta^0 E^1 \]

Two equations to help determine \( \alpha^0, \beta^0, E^1 \)

Together with \( | \alpha^0 |^2 + | \beta^0 |^2 = 1 \), \( | \psi^0 > = \alpha^0 | \psi^0_a > + \beta^0 | \psi^0_b > \) and e.g. \( \alpha^0 \in \mathbb{R} \)

\[ \Rightarrow \text{good eigenstates and first order energy shifts} \ | \psi^0 >, E^1 \]

Matrix form

\[
\begin{pmatrix}
W_{aa} & W_{ab} \\
W_{ba} & W_{bb}
\end{pmatrix}
\begin{pmatrix}
\alpha^0 \\
\beta^0
\end{pmatrix}
= E^1
\begin{pmatrix}
\alpha^0 \\
\beta^0
\end{pmatrix}
\]

Find \( \alpha^0, \beta^0, E^1 \) by e.g. diagonalizing matrix.

Especially easy if \( W_{ab} = 0 \):

\[
\begin{pmatrix}
W_{aa} & 0 \\
0 & W_{bb}
\end{pmatrix}
\begin{pmatrix}
\alpha^0 \\
\beta^0
\end{pmatrix}
= E^1
\begin{pmatrix}
\alpha^0 \\
\beta^0
\end{pmatrix}
\]

Here \( | \psi^0_a > \) and \( | \psi^0_b > \) were already the desired zero order states \( | \psi^0_{\pm} > \).

In that case energy correction expectation values of perturbation, as in non-degenerate case.
Overview of „t-indep. pert. theory“

**Goal of this section**

Determine energies and eigenstates of system exposed to small perturbation.

**Applications:**

Absolutely everywhere. In quantum mechanics it is hard to calculate anything exactly, so we use perturbation theory nearly all the time.

Atoms, molecules, condensed-matter,…

**Plan of this section**

1) intro, examples
2) non-degenerate perturbation theory
3) 2-fold degenerate perturbation theory
4) $n$-fold degenerate perturbation theory
5) general perturbation theory

Griffiths 3rd 7.1.1

7.1.2 – 7.1.3

7.2.1 – 7.2.2

7.2.3
Generalization to $n$-fold degeneracy

Manifold of eigenstates of unperturbed system with energy $E^0$:

$$H^0 |\psi_i^0 > = E^0 |\psi_i^0 > ; \quad i \in \{1, 2, \ldots, n\}$$
Intuitive picture

**Eigenstates**
symbolize Hilbert space by 3D vector space

degenerate 6D subspace

**Energies**

- state with different energy
- „good“ choice of basis states of degenerate manifold of unperturbed system

Our goals
- change in energy to 1st order
- „good“ eigenstates (= „states to 0th order“)
Generalization to $n$-fold degeneracy

Manifold of eigenstates of unperturbed system with energy $E^0$:

$$H^0 |\psi_i^0> = E^0 |\psi_i^0> ; \quad i \in \{1, 2, \ldots, n\}$$

General eigenstate with that energy:

$$|\psi^0> = \sum_{i=1}^{n} \alpha_i^0 |\psi_i^0>$$

As before, $<\psi_j^0| \cdot (I)$:
First order correction of energy

Solve \[ H |\psi\rangle = E |\psi\rangle \quad ; \quad H = H^0 + H' = H^0 + \lambda \tilde{H} \]
with \[ E^{\text{ex}} = E^0 + \lambda \tilde{E}^1 + ... \]
\[ |\Psi^{\text{ex}}\rangle = |\Psi^0\rangle + \lambda |\tilde{\Psi}^1\rangle + ... \]

Insert, expand, collect 1st order in \( \lambda \)

\[ \Rightarrow \quad \text{eqn. (I) exactly as before:} \quad H^0 |\tilde{\Psi}^1\rangle + \tilde{H} |\psi^0\rangle = E^0 |\tilde{\Psi}^1\rangle + \tilde{E}^1 |\psi^0\rangle \]
\[ < \psi^0_a | \cdot (I) : \]
\[ < \psi^0_a | H^0 |\tilde{\Psi}^1\rangle + < \psi^0_a | \tilde{H} |\psi^0\rangle = E^0 < \psi^0_a | \tilde{\Psi}^1\rangle + \tilde{E}^1 < \psi^0_a | \psi^0\rangle \]
\[ = < H^0 \psi^0_a | \tilde{\Psi}^1\rangle = E^0 < \psi^0_a | \tilde{\Psi}^1\rangle \]

use \[ |\psi^0\rangle = \alpha^0 |\psi^0_a\rangle + \beta^0 |\psi^0_b\rangle : \]
\[ \alpha^0 < \psi^0_\alpha | \tilde{H} |\psi^0_a\rangle + \beta^0 < \psi^0_\beta | \tilde{H} |\psi^0_b\rangle = \alpha^0 \tilde{E}^1 \]

\( \cdot \lambda \) and compact notation:
\[ \alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1 \]
\[ W_{ij} \equiv < \psi^0_i | H' | \psi^0_j \rangle \quad ; \quad i, j \in \{ a, b \} \]

note: \( W_{ba} = W_{ab}^* \)

Similarly \( < \psi^0_b | \cdot (i) \) leads to:
\[ \alpha^0 W_{ba} + \beta^0 W_{bb} = \beta^0 E^1 \]
First order correction of energy

\[ \alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1 \]

\[ W_{ij} \equiv < \psi_i^0 | H' | \psi_j^0 > \]

\[ \alpha^0 W_{ba} + \beta^0 W_{bb} = \beta^0 E^1 \]

Two equations to help determine \( \alpha^0, \beta^0, E^1 \)

Together with \( |\alpha^0|^2 + |\beta^0|^2 = 1 \), \( |\psi^0> = \alpha^0 |\psi_a^0> + \beta^0 |\psi_b^0> \) and e.g. \( \alpha^0 \in \mathbb{R} \)

\[ \implies \text{good eigenstates and first order energy shifts } |\psi^0>, E^1 \]

Remark

Equation system can be written in matrix form

\[
\begin{pmatrix}
W_{aa} & W_{ab} \\
W_{ba} & W_{bb}
\end{pmatrix}
\begin{pmatrix}
\alpha^0 \\
\beta^0
\end{pmatrix} = E^1
\begin{pmatrix}
\alpha^0 \\
\beta^0
\end{pmatrix}
\]

Find \( \alpha^0, \beta^0, E^1 \) by e.g. diagonalizing matrix.
Generalization to $n$-fold degeneracy

Manifold of eigenstates of unperturbed system with energy $E^0$:

$$H^0 |\psi_i^0\rangle = E^0 |\psi_i^0\rangle ; \quad i \in \{1, 2, \ldots, n\}$$

General eigenstate with that energy:

$$|\psi^0\rangle = \sum_{i=1}^{n} \alpha_i^0 |\psi_i^0\rangle$$

As before, $< \psi_j^0 | \cdot (I)$:

$$\begin{pmatrix} W_{11} & W_{12} & \cdots & W_{1n} \\ W_{21} & W_{22} & \cdots & W_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ W_{n1} & W_{n2} & \cdots & W_{nn} \end{pmatrix} \begin{pmatrix} \alpha_1^0 \\ \alpha_2^0 \\ \vdots \\ \alpha_n^0 \end{pmatrix} = E^1 \begin{pmatrix} \alpha_1^0 \\ \alpha_2^0 \\ \vdots \\ \alpha_n^0 \end{pmatrix}$$

or simply

$$W \overrightarrow{\alpha} = E^1 \overrightarrow{\alpha}$$

$$W_{ij} = < \psi_i^0 | H' | \psi_j^0 >$$

Energy shifts are eigenenergies of $W$.
Eigenvectors of $W$ are good basis states, left unchanged by perturbation.
Choice of basis determines calculation effort

Using "bad" basis states:

\[
\begin{pmatrix}
    W_{11} & W_{12} & \cdots & W_{1n} \\
    W_{21} & W_{22} & \cdots & W_{2n} \\
    \vdots & \vdots & \ddots & \vdots \\
    W_{n1} & W_{n2} & \cdots & W_{nn}
\end{pmatrix}
\begin{pmatrix}
    \alpha_1^0 \\
    \alpha_2^0 \\
    \vdots \\
    \alpha_n^0
\end{pmatrix}
= E^1
\begin{pmatrix}
    \alpha_1^0 \\
    \alpha_2^0 \\
    \vdots \\
    \alpha_n^0
\end{pmatrix}
\]

Perturbation mixes chosen basis states of degenerate manifold. Need to diagonalize perturbation matrix \( W \) in order to find good basis and \( E^1 \) for each basis vector.

Using "good" basis states:

\[
\begin{pmatrix}
    W_{11} & 0 & \cdots & 0 \\
    0 & W_{22} & \cdots & 0 \\
    \vdots & \vdots & \ddots & \vdots \\
    0 & 0 & \cdots & W_{nn}
\end{pmatrix}
\begin{pmatrix}
    \alpha_1^0 \\
    \alpha_2^0 \\
    \vdots \\
    \alpha_n^0
\end{pmatrix}
= E^1
\begin{pmatrix}
    \alpha_1^0 \\
    \alpha_2^0 \\
    \vdots \\
    \alpha_n^0
\end{pmatrix}
\]

Perturbation diagonal in chosen basis. Diagonal elements are the first order energy corrections \( E^1 \) for each state.
Trick to find good basis for perturbation

Task: determine eigenenergies and states of $W$.

Especially simple if $W$ is diagonal.

Trick to quickly find basis $\{|\Psi_i^0>\}$ in which $W$ is diagonal:

Theorem: Let $A$ be a hermitian operator with $[A, H^0] = [A, H'] = 0$

with $A|\Psi_i^0> = \mu_i|\Psi_i^0>$; $i, j \in \{1, \ldots, n\}$

If $\mu_i \neq \mu_j$ for all $i \neq j$, then $W_{ij} = 0$, i.e. $|\Psi_i^0>$ have been chosen such that $W$ is diagonal.

Proof: $[A, H'] = 0$

$<\Psi_i^0|[A, H']|\Psi_j^0> = 0$

$0 = <\Psi_i^0|AH'|\Psi_j^0> - <\Psi_i^0|H'A|\Psi_j^0>$

$= <A\Psi_i^0|H'\Psi_j^0> - <\Psi_i^0|H'\mu_j|\Psi_j^0>$

$= (\mu_i - \mu_j) <\Psi_i^0|H'|\Psi_j^0> = (\mu_i - \mu_j) W_{ij}$ $\neq 0 \implies W_{ij} = 0$ Q.E.D.

Strategy: find $A$ with $[A, H^0] = [A, H'] = 0$ (e.g. from symmetry considerations)

Use eigenstates of $A$ (which are also eigenstates of $H^0$ and $H'$) $\implies E_i^1 = W_{ii}$

(If degeneracy not completely lifted, find several commuting observables $A$ and their common eigenstates.)
Intuitive picture

Eigenstates
symbolize Hilbert space by 3D vector space

degenerate 6D subspace

Energies

Our goals
• change in energy to 1st order
• „good“ eigenstates (= „states to 0th order“)

state with different energy
„good“ choice of basis states of degenerate manifold of unperturbed system
Overview of „t-indep. pert. theory“

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Determine energies and eigenstates of system exposed to small perturbation.

Applications:

Absolutely everywhere. In quantum mechanics it is hard to calculate anything exactly, so we use perturbation theory nearly all the time.

Atoms, molecules, condensed-matter,…

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Griffiths 3rd 7.1.1
7.1.2 – 7.1.3
7.2.1 – 7.2.2
7.2.3
Generalization to $m$ manifolds

Starting point so far: $n$ states with same unperturbed energy (1 manifold of $n$ states)

Now: $m$ manifolds with $n_i$ states of energy $E_i$ each ; $i \in \{1, \ldots, m\}$

If mixing matrix elements between two manifolds are all much smaller than energy gap between manifolds ($|W_{mn}| \ll |\Delta_{nm}|$), different manifolds can be approximated as independent and treated as discussed.
Generalization to several perturbations

Two perturbations

\[ H' = H'_1 + H'_2 \]

If we can find basis in which they are both diagonal then

\[ E^1 = \langle H' \rangle = \langle H'_1 + H'_2 \rangle = \langle H'_1 \rangle + \langle H'_2 \rangle = E^1_1 + E^1_2 \]

\[ \rightarrow \] We can simply add up the first order energy shifts.
Overview of „t-indep. pert. theory“

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Griffiths 3rd 7.1.1
Griffiths 3rd 7.1.2 – 7.1.3
Griffiths 3rd 7.2.1 – 7.2.2
Griffiths 3rd 7.2.3
Overview of course

Part 1: 7 lectures in January (Piet Mulders)
- Basics of quantum mechanics
- Spin states
- Addition of angular momentum
- Identical particles
- Basic structure of atom

Part 2: 7 lectures in February and March (Florian Schreck)
- Structure of atoms & the periodic table
- Crystalline solids
- Time-independent perturbation theory
- Structure of hydrogen
- Variational principle
- Time-dependent perturbation theory, atom-light interaction

Lecture notes, problem sets and link to video recordings of C0.110 lectures available on Canvas

Questions: schreck@StrontiumBEC.com
Goal of this section

Discuss effects in atoms beyond Coulomb interaction between nucleus and electron(s), using hydrogen as simplest possible example

Crucial knowledge for anything involving atoms

Plan of this section

1) Intro
2) Fine structure
3) Lamb shift
4) Hyperfine structure
5) Zeeman effect

Griffiths 3rd 7.3
7.3
7.5
7.4
The energy spectrum of hydrogen

So far, we considered only kinetic and potential energy

\[ H^0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r} \]

\[ \rightarrow \text{Bohr energy levels.} \]

Only correction taken into account:

Finite mass of nucleus \[ \rightarrow \text{replace } m \text{ by effective mass.} \]

Lots of smaller terms exist in more realistic Hamiltonian e.g.

• coupling of magnetic moments of e\(^{-}\) and nuclear spin
• effect of static magnetic field on magnetic moment

Task: take these effects into account, e.g. by perturbation theory.
Hierarchy of corrections

Contributions to energies can be classified after their order of magnitude.

- **Bohr energies** of order $\alpha^2 mc^2$
- **Fine structure** of order $\alpha^4 mc^2$
- **Lamb shift** of order $\alpha^5 mc^2$
- **Hyperfine structure** of order $(\frac{m_e}{m_p})^4mc^2$

**Zeeman effect** typically in labs, same order as hyperfine, sometimes fine structure.

**DC Stark effect** effects intrinsic to atom

- **effect by static, external B- respective E-field**

where

$$\alpha \equiv \frac{e^2}{4\pi \varepsilon_0 \hbar c} \simeq \frac{1}{137.036}$$

“fine structure constant”

The only dimensionless quantity you can form from constants of electromagnetism ($e$), quantum theory ($\hbar$) and relativity ($c$).

Fundamental constant with no known derivation from first principles.
Overview of „Structure of hydrogen“

Goal of this section

Discuss effects in atoms beyond Coulomb interaction between nucleus and electron(s), using hydrogen as simplest possible example

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Griffiths 3rd 7.3

7.3
7.5
7.4
Overview of “Structure of hydrogen“

Goal of this section

Discuss effects in atoms beyond Coulomb interaction between nucleus and electron(s), using hydrogen as simplest possible example

Crucial knowledge for anything involving atoms

Plan of this section

1) Intro
2) Fine structure
   1) relativistic correction
      origin
      good basis for pert. theory
      Feynman-Hellman theorem and the determination of $<1/r>$ and $<1/r^2>$ result
   2) spin-orbit coupling
3) Lamb shift
4) Hyperfine structure
5) Zeeman effect
Fine structure: 1) relativistic correction

Relativistic expression for kinetic energy:

\[ E_{\text{kin}} = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \quad \text{with} \quad p = \frac{mv}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} \]

\[ E_{\text{kin}} = mc^2 \left[ \sqrt{\left(\frac{p}{mc}\right)^2 + 1} - 1 \right] = mc^2 \left[ 1 + \frac{1}{2} \left( \frac{p}{mc} \right)^2 - \frac{1}{8} \left( \frac{p}{mc} \right)^4 + \ldots \right] \]

\[ = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots \]

non-relativistic, included in \( H^0 \)

\[ = H'_r \quad \text{lowest order relativistic correction} \]

Use first order perturbation theory. For eigenstates in which perturbation is diagonal:

\[ E^1_r = \langle H'_r \rangle = -\frac{1}{8m^3c^2} \langle \psi^0 \mid p^4 \mid \psi^0 \rangle = -\frac{1}{8m^3c^2} \langle p^2 \psi^0 \mid p^2 \psi^0 \rangle \]
Good basis for perturbation theory?

Eigenstates of hydrogen Hamiltonian without perturbation highly degenerate, e.g. each level $n$ has $n^2$ states $|l, m_l\rangle$.

We need to identify a good basis to easily apply degenerate perturbation theory.

**Strategy:** find $A$ with $[A, H^0] = [A, H'] = 0$ (e.g. from symmetry considerations)

Use eigenstates of $A$ (which are also eigenstates of $H^0$ and $H'$) $\rightarrow$$E_i^1 = W_{ii}$

(If degeneracy not completely lifted, find several commuting observables $A$ and their common eigenstates.)

Suitable operators $A$:

$L^2$ and $L_z$

Both commute with $H$ and $H'$ and each other

(they correspond to conserved quantities in spherically symmetric system)

$\implies |l, m_l\rangle$ are the good eigenstates
Relativistic correction in 1\textsuperscript{st} order

\[ E_1^r = \langle H'_r \rangle = -\frac{1}{8m^3c^2} \langle p^2 \psi^0 \mid p^2 \psi^0 \rangle \]

To do: determine \( p^2 \mid \psi^0 \rangle \)

Schrödinger equation for \( \mid \psi^0 \rangle \)

\[ \frac{p^2}{2m} \mid \psi^0 \rangle + V \mid \psi^0 \rangle = E \mid \psi^0 \rangle \quad \rightarrow \quad p^2 \mid \psi^0 \rangle = 2m(E - V) \mid \psi^0 \rangle \]

\[ E_1^r = -\frac{1}{2mc^2} \langle (E - V)^2 \rangle = -\frac{1}{2mc^2} \left[ E^2 - 2E \langle V \rangle + \langle V^2 \rangle \right] \]

For hydrogen \( V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \)

\[ E_{r,n}^1 = -\frac{1}{2mc^2} \left[ E_n^2 + 2E_n \left( \frac{e^2}{4\pi\varepsilon_0} \right) \langle \frac{1}{r} \rangle + \left( \frac{e^2}{4\pi\varepsilon_0} \right)^2 \langle \frac{1}{r^2} \rangle \right] \]

To do: determine \( \langle \frac{1}{r} \rangle \) and \( \langle \frac{1}{r^2} \rangle \)

Trick: use Feynman-Hellman theorem
Feynman-Hellman theorem

Given: a hamiltonian that depends on a parameter $\gamma$

$$H(\gamma) = H(\gamma^0 + \Delta \gamma) \simeq H(\gamma^0) + \Delta \gamma \frac{\partial H}{\partial \gamma} = H^0 + H'$$

The eigenenergies will also depend on $\gamma$

$$E(\gamma) = E(\gamma^0 + \Delta \gamma) \simeq E(\gamma^0) + \Delta \gamma \frac{\partial E}{\partial \gamma} = E^0 + E^1$$

First order perturbation theory:

$$E^1 = \langle H' \rangle = \Delta \gamma \langle \frac{\partial H}{\partial \gamma} \rangle$$

Feynman-Hellman theorem
Determination of $\langle \frac{1}{r} \rangle$ and $\langle \frac{1}{r^2} \rangle$

**To do:** determine $\langle \frac{1}{r} \rangle$ and $\langle \frac{1}{r^2} \rangle$

**Trick:** use Feynman-Hellman theorem with

\[
H = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2}{2m} \frac{l(l + 1)}{r^2} - \frac{e^2}{4\pi \varepsilon_0} \frac{1}{r}
\]

We know (Griffiths 3rd ed., Ch. 4, eqn. 4.70)

\[
E_n = -\frac{m e^4}{32\pi^2 \varepsilon_0^2 \hbar^2 (j_{\text{max}} + l + 1)^2}
\]

some integer $n = n$

Use Feynman-Hellman theorem $\frac{\partial E}{\partial \gamma} = \langle \frac{\partial H}{\partial \gamma} \rangle$ with $\gamma = e$

exercise $\Rightarrow \langle \frac{1}{r} \rangle = \frac{1}{n^2 a}$

Use Feynman-Hellman theorem $\frac{\partial E}{\partial \gamma} = \langle \frac{\partial H}{\partial \gamma} \rangle$ with $\gamma = l$

exercise $\Rightarrow \langle \frac{1}{r^2} \rangle = \frac{1}{(l+\frac{1}{2})n^3 a^2}$

Bohr radius $a = \frac{4\pi \varepsilon_0 \hbar^2}{m e^2} = 0.5 \times 10^{-10} \text{ m}$
Relativistic correction in 1\textsuperscript{st} order

\[ E_{r,n}^1 = -\frac{1}{2mc^2} \left[ E_n^2 + 2E_n \left( \frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right] \]

Insert \( \left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2\alpha} \) and \( \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l + \frac{1}{2}) n^3 \alpha^2} \), simplify:

\[ E_r^1 = -\frac{E_n^2}{2mc^2} \left[ \frac{4n}{l + 1/2} - 3 \right] \]

Easily checked, that \( E_r^1 \) is on the order of \( \alpha^2 \) times smaller than \( E_n \).
Fine structure: 1) relativistic correction

Relativistic expression for kinetic energy:

\[ E_{\text{kin}} = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \]

with

\[ p = \frac{mv}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} \]

\[ E_{\text{kin}} = mc^2 \left[ \sqrt{\left(\frac{p}{mc}\right)^2 + 1} - 1 \right] \]

\[ \rightarrow \quad E_{\text{kin}} = mc^2 \left[ 1 + \frac{1}{2} \left( \frac{p}{mc} \right)^2 - \frac{1}{8} \left( \frac{p}{mc} \right)^4 + \ldots - \frac{1}{1} \right] \]

\[ \rightarrow \quad \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots = H'_r \]

non-relativistic, included in \( H^0 \)

\[ = H'_r \] lowest order relativistic correction

Use first order perturbation theory. For eigenstates in which perturbation is diagonal:

\[ E^1_r = \langle H'_r \rangle = -\frac{1}{8m^3c^2} \langle \psi^0 | p^4 | \psi^0 \rangle \]

\[ \rightarrow \quad E^1_r = -\frac{E^2_n}{2mc^2} \left[ \frac{4n}{l + 1/2} - 3 \right] \]
Overview of „Structure of hydrogen“

Goal of this section

Discuss effects in atoms beyond Coulomb interaction between nucleus and electron(s), using hydrogen as simplest possible example

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      origin
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Griffiths 3rd 7.3

7.3 7.3.1
7.3.2 7.4 7.5
Classical spin-orbit coupling

Spin-orbit coupling: interaction of the spin of an object with its trajectory (orbit)

Classical example of spin orbit coupling: tidal locking of moon to earth
We always see the same side of the moon!

Reason:

Moon deformed by gravitational field of earth. Adaptation of deformation to gravitational field takes time.
If rotation frequency not synchronized with orbital frequency, deformation lags behind and torque is exerted.
After some time, rotation and orbital frequencies the same.
Angular momentum conserved by also changing orbital angular momentum.
Fine structure: 2) Spin-orbit coupling

Correctly treated using relativistic quantum mechanics (Dirac equation).

Here: rough, classical calculation

Consider hydrogen atom:

![Diagram showing proton's and electron's points of view.](image)

- Proton circles around e\(^{-}\) with velocity \(v\) and period \(T = \frac{2\pi r}{v}\).
- Leading to current \(I = \frac{e}{T} = \frac{ev}{2\pi r}\).
- Creating B-field \(B = \frac{\mu_0 I}{2r} = \frac{\mu_0 ev}{2r 2\pi r}\).

Magnetic moment \(\mu\) of e\(^{-}\) experiences shift in that B-field

\[
H = -\vec{\mu} \cdot \vec{B}
\]

B-field of proton: Angular momentum of e\(^{-}\): \(L = rmv\)

\[
B = \frac{\mu_0}{2r} \frac{ev}{2\pi r} = \frac{1}{4\pi \varepsilon_0 mc^2 r^3} L
\]

\[
c = 1/\sqrt{\mu_0 \varepsilon_0}
\]
Magnetic moment of e⁻

Classical picture of spinning electron:
Imagine charge \( q \) and mass \( m \) of e⁻ concentrated in point, which is somehow rotating around the electron’s centre.

\[
\begin{align*}
\mu &= l \cdot A = \frac{q}{r^2} \\
S &= mvr = m\frac{2\pi r}{T} \\
\end{align*}
\]

Gyromagnetic ratio = ratio between magnetic moment and angular momentum

\[
\frac{\mu}{S} = \frac{q}{2m}
\]

notice: independent of \( r \)

Holds for any rotationally symmetric charge/mass distribution
(Think of object as made up of many rings of various \( r \))

Direction of \( \vec{\mu} \) and \( \vec{S} \) the same for \( q > 0 \), opposite for \( q < 0 \) (e⁻ case).

\[
\vec{\mu} = g \frac{q}{2m} \vec{S}
\]

\( g_{\text{classical}} = 1 \)
Quantum mechanical calculation

(Special) relativistic quantum mechanics (Dirac equation) delivers

\[ g_{el} = 2 \quad \text{where} \quad \vec{\mu} = g \frac{q}{2m} \vec{\Sigma} = -g \frac{|e|\hbar \vec{S}}{2m \hbar} \]

\[ = \mu_B \simeq 1.4 \frac{\text{MHz}}{\text{G} \cdot \hbar} \]

„Bohr magneton“

Vacuum fluctuations of electromagnetic field give rise to a \( \%_0 \)-level correction:

\[ g_{el}^{\text{QED}} = 2.002319304361... \]

One of the most precisely determined numbers from ab-initio calculations in physics. Experiments deliver precision test of quantum electrodynamics.

In the following we don‘t consider this correction and use \( g_{el} = 2 \).
Spin-orbit coupling

We know:

\[ H = -\vec{\mu} \cdot \vec{B} \]

\[ \vec{\mu} = -g \frac{|e| \hbar}{2m} \vec{S} \quad ; \quad \vec{B} = \frac{1}{4\pi\varepsilon_0} \frac{e}{mc^2r^3} \vec{L} \]

Putting it all together: \( g_{el} = 2 \) for simplicity

\[ H = \left( \frac{e^2}{4\pi\varepsilon_0} \right) \frac{1}{m^2c^2r^3} \vec{S} \cdot \vec{L} \]

This is not quite correct. Problem in our derivation:

going from lab frame to e- frame in derivation of B-field is not a change between two inertial systems. e\(^-\) is constantly accelerated.

Taking this continuous change of inertial system into account delivers correction, known as „Thomas precession“, reducing \( H \) by factor of 2:

\[ H'_{SO} = \left( \frac{e^2}{8\pi\varepsilon_0} \right) \frac{1}{m^2c^2r^3} \vec{S} \cdot \vec{L} = \text{constant} \quad \frac{1}{r^3} \vec{S} \cdot \vec{L} \]

To do: determine spin-orbit correction by first order perturbation theory
Basis for perturbation theory

We know solutions of unperturbed Hamiltonian $H^0$:

$$E_n = \frac{E_1}{n^2} \quad \quad E_1 = -\frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi \varepsilon_0} \right)^2 \simeq -13.6 \text{ eV}$$

$$|\psi^0_{nlm_ism_s}\rangle = |\psi^0_n(r)\rangle |\psi^0_{lm_ism_s}\rangle$$

angular momentum, i.e. orbital momentum wavefunction and spin wavefunction
radial wavefunction, only dependent on principal quantum number $n$

We perform perturbation in manifold of states belonging to same $n$, since perturbation much smaller than energy splitting between states of different $n$

$$H'_{SO} = \left( \frac{e^2}{8\pi \varepsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} = C_1 \frac{1}{r^3} \vec{S} \cdot \vec{L}$$

Perturbation matrix elements

$$\langle \psi^0_{nlm_ism_s} | H'_{SO} | \psi^0_{nl'm_is'm_s} \rangle = C_1 \langle \psi^0_n(r) | \frac{1}{r^3} | \psi^0_n(r) \rangle \langle \psi^0_{lm_ism_s} | \vec{S} \cdot \vec{L} | \psi^0_{l'm_is'm_s} \rangle$$

$$= C_2 \langle \psi^0_{lm_ism_s} | \vec{S} \cdot \vec{L} | \psi^0_{l'm_is'm_s} \rangle$$

for chosen $n$

Only need to consider perturbation proportional to $\vec{S} \cdot \vec{L}$
Quantum mechanics 3
Structure of matter

Lecture 12

Piet Mulders
Florian Schreck
University of Amsterdam
Overview of course

Part 1: 7 lectures in January  (Piet Mulders)
- Basics of quantum mechanics
- Spin states
- Addition of angular momentum
- Identical particles
- Basic structure of atom

Part 2: 7 lectures in February and March  (Florian Schreck)
- Structure of atoms & the periodic table
- Crystalline solids
- Time-independent perturbation theory
- Structure of hydrogen
- Variational principle
- Time-dependent perturbation theory, atom-light interaction

Today

Lecture notes, problem sets and link to video recordings of C0.110 lectures available on Canvas

Questions: schreck@StrontiumBEC.com
Goal of this section

Discuss effects in atoms beyond Coulomb interaction between nucleus and electron(s), using hydrogen as simplest possible example

Crucial knowledge for anything involving atoms

Plan of this section

1) Intro
2) Fine structure
   1) relativistic correction
   2) spin-orbit coupling
      origin
      good basis for pert. theory
      result
3) Lamb shift
4) Hyperfine structure
5) Zeeman effect
Fine structure: 1) relativistic correction

Relativistic expression for kinetic energy:

\[ E_{\text{kin}} = \sqrt{p^2c^2 + m^2c^4} - mc^2 \]

with

\[ p = \frac{mv}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} \]

\[ E_{\text{kin}} = mc^2 \left[ \sqrt{\left(\frac{p}{mc}\right)^2} + 1 - 1 \right] \]

\[ \downarrow \quad p \ll mc \]

\[ = mc^2 \left[ 1 + \frac{1}{2} \left(\frac{p}{mc}\right)^2 - \frac{1}{8} \left(\frac{p}{mc}\right)^4 + \ldots \right] \]

\[ \begin{array}{c}
= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots \\
\end{array} \]

non-relativistic, included in \( H^0 \)

\[ = H'_r \] lowest order relativistic correction

Use first order perturbation theory. For eigenstates in which perturbation is diagonal:

\[ E^1_r = \langle H'_r \rangle = - \frac{1}{8m^3c^2} \langle \psi^0 | p^4 | \psi^0 \rangle \]

\[ \Rightarrow \quad E^1_r = - \frac{E_n^2}{2mc^2} \left[ \frac{4n}{l + 1/2} - 3 \right] \]
Fine structure: 2) Spin-orbit coupling

Correctly treated using relativistic quantum mechanics (Dirac equation).
Here: rough, classical calculation
Consider hydrogen atom:

- **proton’s point of view**
  - Proton circles around e\(^-\) with velocity \(v\) and creating B-field leading to current \(I = \frac{e}{T} = \frac{ev}{2\pi r}\)
  - Angular momentum of e\(^-\): \(L = rmv\)

- **electron’s point of view**
  - Magnetic moment \(\mu\) of e\(^-\) experiences shift in that B-field
    \[
    H = -\vec{\mu} \cdot \vec{B}
    \]

B-field of proton:

\[
B = \frac{\mu_0 I}{2r} = \frac{\mu_0}{2r} \frac{ev}{2\pi r} = \frac{1}{4\pi\varepsilon_0} \frac{e}{mc^2 r^3} L
\]

\[
c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}}
\]
Magnetic moment of e⁻

Classical picture of spinning electron:

Imagine charge \( q \) and mass \( m \) of e⁻ concentrated in point, which is somehow rotating around the electron’s centre.

Gyromagnetic ratio = ratio between magnetic moment and angular momentum

\[
\frac{\mu}{S} = \frac{q}{2m}
\]

notice: independent of \( r \)

Holds for any rotationally symmetric charge/mass distribution
(Think of object as made up of many rings of various \( r \))

Direction of \( \vec{\mu} \) and \( \vec{S} \) the same for \( q > 0 \), opposite for \( q < 0 \) (e⁻ case).

\[
\vec{\mu} = g \frac{q}{2m} \vec{S}
\]

\( g_{\text{classical}} = 1 \)
Quantum mechanical calculation

(Special) relativistic quantum mechanics (Dirac equation) delivers

\[ g_{el} = 2 \quad \text{where} \quad \mu = g \frac{q}{2m} \hat{S} = -g \frac{|e| \hbar}{2m} \hat{S} \]

\[ = \mu_B \simeq 1.4 \frac{\text{MHz}}{G} \hbar \]

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Spin-orbit coupling

We know:

\[ H = -\vec{\mu} \cdot \vec{B} \]

\[ \vec{\mu} = -g \frac{|e| \hbar \vec{S}}{2m \hbar} ; \quad \vec{B} = \frac{1}{4\pi \varepsilon_0} \frac{e}{mc^2 r^3} \vec{L} \]

Putting it all together: \( (g_{el} = 2 \text{ for simplicity}) \)

\[ H = \left( \frac{e^2}{4\pi \varepsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} \]

This is not quite correct. Problem in our derivation:

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\[ H'_{SO} = \left( \frac{e^2}{8\pi \varepsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} = \text{constant} \quad \frac{1}{r^3} \vec{S} \cdot \vec{L} \]

To do: determine spin-orbit correction by first order perturbation theory
Overview of „Structure of hydrogen“

Goal of this section

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Griffiths 3rd 7.3
Griffiths 3rd 7.3.1
Griffiths 3rd 7.3.2
Griffiths 3rd 7.3
Griffiths 3rd 7.4
Griffiths 3rd 7.5
Good basis states for perturbation theory

In order for perturbation matrix to be diagonal, we need to use the basis states corresponding to a complete set of commuting operators including $H$ and $H'$. So far we used eigenstates of

$$H^0, L^2, L_z, S^2, S_z$$

**Problem:** $L_z$ and $S_z$ do not commute with $H'$

$$H' \propto \vec{S} \cdot \vec{L} = S_x L_x + S_y L_y + S_z L_z$$

e.g. $[L_y, L_z] = i\hbar L_x$

**Solution:** good basis formed by eigenstates of complete set of commuting operators

$$H^0, L^2, S^2, J^2, J_z$$

with $\vec{J} = \vec{S} + \vec{L}$

**Proof:** show that all commutators between these operators among each other and between these operators and $H'$ are zero.

\[
\begin{align*}
[L^2, J_z] &= [L^2, S_z] + [L^2, L_z] = 0 \\
[S^2, J_z] &= [S^2, S_z] + [S^2, L_z] = 0 \\
[J^2, J_z] &= 0
\end{align*}
\]
Good basis states for perturbation theory

Proof: (continued)

\[ [H'_{SO}, J_z] \propto [\vec{L} \cdot \vec{S}, J_z] \propto [J^2, J_z] - [L^2, J_z] - [S^2, J_z] = 0 \]

\[ J^2 = (\vec{L} + \vec{S}) \cdot (\vec{L} + \vec{S}) = L^2 + S^2 + 2\vec{L} \cdot \vec{S} \]

\[ \vec{L} \cdot \vec{S} = \frac{1}{2} \left( J^2 - L^2 - S^2 \right) \]

and similar for all combinations within set of operators and between those ops. and \( H'_{SO} \).

Q.E.D.

Eigenstates of \( H^0, L^2, S^2, J^2, J_z \) expressed in known eigenstates of \( H^0, L^2, L_z, S^2, S_z \):

\[ |\psi_{lsjm}\rangle = \sum_{m_j, m_s} c_{m_j, m_s} |\psi_{lmjsm_s}\rangle \]

Clebsch-Gordan coefficients (known, can e.g. be looked up in tables)

These are eigenstates of \( \vec{L} \cdot \vec{S} \):

\[ \vec{L} \cdot \vec{S} |\psi_{lsjm}\rangle = \frac{1}{2} \left( J^2 - L^2 - S^2 \right) |\psi_{lsjm}\rangle \]

\[ = \frac{\hbar^2}{2} [j(j + 1) - l(l + 1) - s(s + 1)] |\psi_{lsjm}\rangle \]
Spin-orbit coupling in first order

Spin-orbit coupling

\[ H'_{SO} = \left( \frac{e^2}{8\pi \epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} \]

Energy correction in first order perturbation theory

\[ E_{SO}^1 = \langle \psi_{lsjm}^0 \mid H'_{SO} \mid \psi_{lsjm}^0 \rangle = \left( \frac{e^2}{8\pi \epsilon_0} \right) \frac{1}{mc^2} \left\langle \frac{1}{r^3} \right\rangle \frac{\hbar^2}{2} \left[ j(j+1) - l(l+1) - s(s+1) \right] \]

\[ \left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l + 1/2)(l + 1)n^3 a^3} \]  

(Griffiths)

Energy shift of hydrogen from spin-orbit coupling

\[ E_{SO}^1 = \left( \frac{E_n}{mc^2} \right)^2 \left[ n \frac{j(j+1) - l(l+1) - 3/4}{l(l + 1/2)(l + 1)} \right] \]  

(for \( l \neq 0 \))
Hydrogen with fine-structure

Two contributions to fine structure:

- **relativistic**
  \[ E_r^1 = - \frac{E_n^2}{2mc^2} \left( \frac{4n}{l + 1/2} - 3 \right) \]

- **spin-orbit coupling**
  \[ E_{SO}^1 = \frac{(E_n)^2}{mc^2} \left[ \frac{n[j(j + 1) - l(l + 1) - 3/4]}{l(l + 1/2)(l + 1)} \right] \]
  (for \( l \neq 0 \))

Both have same order of magnitude \( \frac{(E_n)^2}{mc^2} \)

Add both fine-structure contributions: (use \( j = l + 1/2 \) or \( j = l - 1/2 \). Delivers same result.)

\[ E_{fs}^1 = \frac{(E_n)^2}{2mc^2} \left( 3 - \frac{4n}{j + 1/2} \right) \]

also valid for \( l = 0 \)
(no prove here)

Energy of hydrogen levels with fine structure

\[ E_{nj} = E_n + E_{fs}^1 = \frac{E_1}{n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j + 1/2} - \frac{3}{4} \right) \right] \]

\[ E_1 = -\frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\varepsilon_0} \right)^2 \approx -13.6 \text{ eV} \]

\[ j = l + s \quad ; \quad \alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \approx \frac{1}{137.036} \]
Hydrogen with fine-structure

Griffiths Ch. 6, Fig. 9

$E_{nj}$

$n = 4$

$n = 3$

$n = 2$

$n = 1$

$l = 0$ (S)

$l = 1$ (P)

$l = 2$ (D)

$l = 3$ (F)

Bohr energies

Dirac energies (relativistic + spin-orbit)

$j = 7/2$

$j = 5/2$

$j = 3/2$

$j = 1/2$

$j = 5/2$

$j = 3/2$

$j = 1/2$

$j = 3/2$

$j = 1/2$
Na vapour lamp

https://www.flickr.com/photos/14892851@N06/7115824707
https://nl.rs-online.com/web/p/son-lamps/7193711
https://www.tes.com/lessons/KovNVxjL_E1wwQ/flame-test
Fine structure in sodium spectrum

- $3^2P_{3/2}$
- $3^2P_{1/2}$
- $3^2S_{1/2}$

D1 line: 589.755 nm
D2 line: 589.158 nm

Emission spectroscopy

Absorption spectroscopy

Overview of „Structure of hydrogen“

Goal of this section

Discuss effects in atoms beyond Coulomb interaction between nucleus and electron(s), using hydrogen as simplest possible example

Crucial knowledge for anything involving atoms

Plan of this section

1) Intro
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3) Lamb shift
4) Hyperfine structure
5) Zeeman effect

Griffiths 3rd 7.3
7.3
7.5
7.4
Lamb shift

The electromagnetic vacuum performs quantum fluctuations. These fluctuating electromagnetic fields create forces on the $e^-$, changing its trajectory.

The $e^-$ samples different regions of the Coulomb potential compared with what it would have sampled on its original trajectory.

$\implies$ s states slightly shifted
Hydrogen with fine-structure

Griffiths Ch. 6, Fig. 9
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1) Intro
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   origin
   good basis for perturbation theory
   result and discussion
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Griffiths 3rd 7.3
7.3
7.5
7.4
Hyperfine structure

Hyperfine structure has several contributions. Here:

**e⁻ spin – nuclear spin coupling**

Energy shift from e⁻ magnetic moment immersed in B-field created by nuclear magnetic moment.

Nuclear magnetic moment

\[ \mu_n = g_n \frac{|e| \hbar}{2m_p} \hat{I} \]

for proton

\[ g_n = g_p = 5.59 \]

\[ \mu_n = \left( \frac{m_{el}}{m_p} \right) \mu_B \approx \hbar \cdot 0.762 \frac{\text{kHz}}{\text{G}} \]

\( \hat{I} \): nuclear spin (operator) with eigenstates \( |I, m_i\rangle \)

as usual

\[ I^2 |I, m_i\rangle = \hbar^2 I(I+1) |I, m_i\rangle \]

\[ I_z |I, m_i\rangle = \hbar m_i |I, m_i\rangle \]

\[ \mu_{el} = -g_{el} \frac{|e| \hbar}{2m_{el}} \hat{S} = -g_{el} \mu_B \frac{\hat{S}}{\hbar} \]

Attention:

confusing fonts:
lower case \( L \) and upper case \( I \) look similar: \( l, I \)

Clearer in „hand writing“:

\[ L^2 |l, m_L\rangle = \hbar^2 l(l+1) |l, m_L\rangle \]

\[ J^2 |J, m_J\rangle = \hbar^2 J(J+1) |J, m_J\rangle \]

No problem here since lower case „\( L \)“ not used
Hyperfine structure

Interaction energy:

\[ H'_{\text{hf}} = -\mu_{\text{el}} \cdot \vec{B}_n \]

with \[ \mu_{\text{el}} \approx -\frac{|e|}{m_{\text{el}}} \vec{S} \] (for \( g_{el} = 2 \))

Magnetic field created by nucleus (see e.g. Griffiths, Am. J. Phys. 50, 698 (1982))

\[ \vec{B}_n = \frac{\mu_0}{4\pi r^3} [3(\vec{\mu}_n \cdot \hat{r})\hat{r} - \vec{\mu}_n] + \frac{2\mu_0}{3} \vec{\mu}_n \delta^3(\vec{r}) \]

with \[ \vec{\mu}_n = g_p \frac{|e|}{2m_p} \vec{l} \]

\( \hat{r} \): unit vector (operator) of electron position

Perturbation term:

\[ H'_{\text{hf}} = \frac{\mu_0 g_p e^2}{8\pi m_p m_{\text{el}}} \frac{3(\vec{l} \cdot \hat{r})(\vec{S} \cdot \hat{r}) - \vec{l} \cdot \vec{S}}{r^3} + \frac{\mu_0 g_p e^2}{3m_p m_{\text{el}}} \vec{l} \cdot \vec{S} \delta^3(\vec{r}) \]

First order perturbation theory (using good basis):

\[ \langle H'_{\text{hf}} \rangle \]
Basis for perturbation theory

We know solutions of unperturbed Hamiltonian $H^0$:

$$E_n = \frac{E_1}{n^2}$$

$$E_1 = -\frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\varepsilon_0} \right)^2 \simeq -13.6 \text{ eV}$$

$$|\psi^0_{n|m;sm_i m_i}\rangle = |\psi^0_n(r)\rangle \psi^0_{im;sm_i m_i}$$

angular momentum, i.e. orbital momentum wavefunction and spin wavefunction

radial wavefunction, only dependent on principal quantum number $n$

We perform perturbation in manifold of states belonging to same $n$, since perturbation much smaller than energy splitting between states of different $n$.

We can ignore $l, m_l$ since we are only interested in ground state where $l = 0, m_l = 0$.

Perturbation matrix elements

$$\langle \psi^0_n(r) | H'_{\text{hf}} | \psi^0_n(r) \rangle \psi^0_{ns; m_s; m_s} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \frac{3(\hat{r} \cdot \vec{r})(\vec{S} \cdot \hat{r}) - \hat{r} \cdot \vec{S}}{r^3} +$$

$$= 0 \text{ for } l = 0 \quad (\text{exercise})$$

$$+ \frac{\mu_0 g_p e^2}{3m_p m_e} \langle \psi^0_{l|sm_i m_i} | \hat{l} \cdot \vec{S} | \psi^0_{l|m_i sm_i m_i} \rangle \langle \psi^0_n(r) | \delta^3(\vec{r}) | \psi^0_n(r) \rangle$$

$$= |\psi^0_n(0)|^2$$
Hyperfine structure in hydrogen ground state

To do: first order perturbation theory with perturbation

\[ H'_{\text{hf}} = \frac{\mu_0 g_p e^2}{3 m_p m_e} \vec{l} \cdot \vec{S} |\psi(0)|^2 \]

Again: find good basis states in which perturbation is diagonal

Complete set of commuting observables for uncoupled spins:

\[ H^0, L^2, L_z, S^2, S_z, I^2, I_z \]

We can ignore \( L^2, L_z \) since we are only interested in ground state with single \( I = 0 \) state.

\[ H^0, S^2, S_z, I^2, I_z \] as before do not lead to good basis, since \( [S_z, \vec{l} \cdot \vec{S}] \neq 0 \)

Suitable set of commuting observables for coupled \( S \) and \( I \):

\[ H^0, S^2, I^2, F^2, F_z \] with \( \vec{F} = \vec{I} + \vec{S} \)

Proof: as before, check commutators among those operators and among them and with coupling operator \( \vec{l} \cdot \vec{S} \)
Hyperfine structure in hydrogen ground state

As before:

Eigenstates of $H^0$, $S^2$, $I^2$, $F^2$, $F_z$ expressed in known eigenstates of $H^0$, $S^2$, $S_z$, $I^2$, $I_z$:

$$|\psi_{\text{sifm}_f}^0\rangle = \sum_{m_s, m_i} c_{m_s, m_i} |\psi_{s_m s_i}^0\rangle$$

Clebsch-Gordan coefficients (known, can e.g. be looked up in tables)

These are eigenstates of $\vec{I} \cdot \vec{S}$:

$$\vec{I} \cdot \vec{S} |\psi_{\text{sifm}_f}^0\rangle = \frac{1}{2} \left( F^2 - I^2 - S^2 \right) |\psi_{\text{sifm}_f}^0\rangle$$

$$= \frac{\hbar^2}{2} \left[ f(f + 1) - s(s + 1) - i(i + 1) \right] |\psi_{\text{sifm}_f}^0\rangle$$

$$= -2 \frac{3}{4} \quad \text{since } s \text{ and } i = 1/2$$

2 $S$ and $I$ parallel: $f=1$

0 $S$ and $I$ anti-parallel: $f=0$

$$\vec{I} \cdot \vec{S} |\psi_{\text{sifm}_f}^0\rangle = \begin{cases} 
+ \frac{1}{4} \hbar^2 |\psi_{\text{sifm}_f}^0\rangle & \text{for } F = 1 \\
- \frac{3}{4} \hbar^2 |\psi_{\text{sifm}_f}^0\rangle & \text{for } F = 0
\end{cases}$$

(capital "F" more common than "f")
Hyperfine structure in hydrogen ground state

To do: first order perturbation theory with perturbation

\[ \frac{\mu_0 g_p e^2}{3m_pm_e} \langle \vec{I} \cdot \vec{S} \rangle |\psi(0)|^2 \]

For hydrogen ground state \( |\psi_{100}(0)|^2 = \frac{1}{\pi a^3} \); \( a = \frac{4\pi\varepsilon_0 \hbar^2}{m_e c^2} \)

with

\[ \vec{I} \cdot \vec{S} |\psi_{sifm_F}^0 \rangle = \begin{cases} 
\frac{1}{4} \hbar^2 |\psi_{sifm_F}^0 \rangle & \text{for } F = 1 \\
\frac{3}{4} \hbar^2 |\psi_{sifm_F}^0 \rangle & \text{for } F = 0 
\end{cases} \]

Hyperfine energy shift

\[ E_{hf}^1 = \frac{4g_p \hbar^4}{3m_pm_e^2 c^2 a^4} \begin{cases} 
\frac{1}{4}, & \text{for } F = 1 \\
-\frac{3}{4}, & \text{for } F = 0 
\end{cases} \]

Hyperfine splitting: energy difference the two states

\[ \Delta E_{hf} = \frac{4g_p \hbar^4}{3m_pm_e^2 c^2 a^4} = \hbar \cdot 1420 \text{MHz} \]
Microwave radiation at \( \nu = \frac{\Delta E}{h} = 1420 \text{ MHz} \), corresponding to a wavelength of \( \lambda = \frac{c}{\nu} = 21 \text{ cm} \), is seen from everywhere in the universe where atomic hydrogen exists. Very important in astronomy to detect and investigate hydrogen clouds.
The HI Nearby Galaxy Survey (THINGS)

F. Walter, E. Brinks, E. de Blok, F. Bigiel, M. Thornley, R. Kennicutt
Radioastronomy of hydrogen

Messier 81

Radioastronomy of hydrogen

Hydrogen gas (blue) in image of the post-merger pair of galaxies UGC 813 and UGC 816

http://images.nrao.edu/?id=531
Other hyperfine contributions

Quadrupole interaction

Nuclear electric quadrupole moment experiences energy shift in gradient of electric field created by electrons

Finite size of nucleus

While electrons are inside nucleus, they see an electric potential that deviates from the Coulomb potential of a point charge, which we used so far. This leads to an energy shift compared to what we calculated so far.
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3) Lamb shift
4) Hyperfine structure
5) Zeeman effect
   - weak B-field
   - strong B-field
   - all B-fields

Griffiths 3rd 7.3
Griffiths 3rd 7.3
7.3
7.5
7.4
7.4.1
7.4.2
7.4.3
Example: Atom in magnetic field

Starting point
unperturbed system

Modification
perturbed system

Small perturbation
weak magnetic field

Question
What are, approximately, perturbed eigenstates and energies?
Atom in magnetic field: Zeeman effect

Here: neglect hyperfine interaction

**Exact** if no nuclear magnetic moment

**Good approximation** if we only want to calculate energy levels to a precision much less than the hyperfine splitting and if effect of external B-field much larger than that

B-field couples to 2 types of magnetic momenta in atom

1) spin magnetic moment

\[ \vec{\mu}_s = -g_{e1} \mu_B \frac{\vec{S}}{\hbar} \]

2) orbital magnetic moment

\[ \vec{\mu}_I = -\mu_B \frac{\vec{L}}{\hbar} \]

e\(^{-}\) rotates around nucleus, giving rise to magnetic moment

\[ p \]

\[ e^{-} \]

\[ \text{p} \]

\[ \text{e}^{-} \]
Atom in magnetic field: Zeeman effect

Total perturbation:

\[
H'_{z} = - \left( \vec{\mu}_l + \vec{\mu}_s \right) \cdot \vec{B}_{\text{ext}} = \frac{\mu_B}{\hbar} \left( \vec{L} + 2 \vec{S} \right) \cdot \vec{B}_{\text{ext}} \quad (g_{el} = 2 \text{ for simplicity})
\]

Chose quantization axis parallel to external magnetic field

\[
= - (\mu_L + \mu_S) B_{\text{ext}} = \frac{\mu_B}{\hbar} (L_z + 2 S_z) B_{\text{ext}}
\]

Total Hamiltonian:

\[
H^0 + H'_{\text{rel}} + H'_{\text{so}} + H'_{z}
\]

\[\nearrow \text{ good quantum numbers: } l, m_l, s, m_s\]

\[\propto \vec{L} \cdot \vec{S} \quad \rightarrow \quad \vec{L} \text{ and } \vec{S} \text{ coupled to } \vec{J}\]

\[\rightarrow \quad \text{good quantum numbers: } l, s, j, m_j\]

Two competing effects:

\[H'_{\text{so}}: \text{internal B-field created by nucleus circling around e}^{-} \text{acts on e}^{-} \text{magnetic moment and locks } \vec{L} \text{ and } \vec{S} \text{ to } \vec{J}.\]
Fine structure: 2) Spin-orbit coupling

Correctly treated using relativistic quantum mechanics (Dirac equation).
Here: rough, classical calculation
Consider hydrogen atom:

proton’s point of view

\[
\text{proton circles around } e^- \text{ with velocity } v \text{ and period } T = \frac{2\pi r}{v}
\]

leading to current \( I = \frac{e}{T} = \frac{ev}{2\pi r} \)
creating B-field \( B = \frac{\mu_0 I}{2r} \)

Magnetic moment \( \mu \) of e\(^-\) experiences shift in that B-field

\[
H = -\vec{\mu} \cdot \vec{B}
\]

B-field of proton: \( B = \frac{\mu_0 I}{2r} = \frac{\mu_0 ev}{2r 2\pi r} = \frac{1}{4\pi \varepsilon_0} \frac{e}{mc^2 r^3} L \)

Angular momentum of e\(^-\): \( L = rmv \)
\[
c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}}
\]
Atom in magnetic field: Zeeman effect

Total perturbation:

\[ H'_z = - (\mu_l + \mu_s) \cdot \vec{B}_{\text{ext}} = \frac{\mu_B}{\hbar} \left( \vec{L} + 2\vec{S} \right) \cdot \vec{B}_{\text{ext}} \quad (g_{el} = 2 \text{ for simplicity}) \]

Chose quantization axis parallel to external magnetic field

\[ = - (\mu_L + \mu_S) B_{\text{ext}} = \frac{\mu_B}{\hbar} (L_z + 2S_z) B_{\text{ext}} \]

Total Hamiltonian:

\[ H^0 + H'_{\text{rel}} + H'_{\text{so}} + H'_z \]

\[ \leftarrow \text{good quantum numbers: } l, m_l, s, m_s \]

\[ \propto \vec{L} \cdot \vec{S} \rightarrow \vec{L} \text{ and } \vec{S} \text{ coupled to } \vec{J} \]

\[ \rightarrow \text{good quantum numbers: } l, s, j, m_j \]

Two competing effects:

\[ H'_{\text{so}}: \text{internal B-field created by nucleus circling around } e^- \text{ acts on } e^- \text{ magnetic moment and locks } \vec{L} \text{ and } \vec{S} \text{ to } \vec{J}. \]

\[ H'_z: \text{external B-field acts on } e^- \text{ spin and orbital magnetic moment and locks } \vec{L} \text{ and } \vec{S} \text{ to } \vec{B}. \]
Atom in magnetic field: Zeeman effect

For $B_{\text{ext}} \ll B_{\text{int}}$ : $H'_{\text{so}}$ wins $\implies |\psi_{nlsjm}^0\rangle$ good states, perturbed by $H'_{z}$

$B_{\text{ext}} \gg B_{\text{int}}$ : $H'_{z}$ wins $\implies |\psi_{nls,m}^0\rangle$ good states, perturbed by $H'_{\text{so}}$

$B_{\text{ext}} \sim B_{\text{int}}$ : need to diagonalize $H'_{\text{so}} + H'_{z}$ to find eigenstates and energies
Overview of „Structure of hydrogen“

Goal of this section

Discuss effects in atoms beyond Coulomb interaction between nucleus and electron(s), using hydrogen as simplest possible example

Crucial knowledge for anything involving atoms

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1) Intro
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   - weak B-field
   - strong B-field
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Griffiths 3rd 7.3
7.3
7.5
7.4
7.4.1
7.4.2
7.4.3
Weak-field Zeeman effect $B_{\text{ext}} \ll B_{\text{int}}$

For $B_{\text{ext}} \ll B_{\text{int}}$: $H'_{\text{so}}$ wins $\implies |\psi^0_{nljm_j}\rangle$ good states, perturbed by $H'_{z}$

$$= \frac{\mu_B}{\hbar} (L_z + 2S_z) B_{\text{ext}}$$

Need to determine matrix elements of $H'_{z}$ with basis states $|\Psi^0_n(r)\rangle |\psi^0_{lsm_j}\rangle$

**Simplifications**

- independent of $r$ $\implies$ spatial part of matrix element $\langle \psi^0_n(r)|\Psi^0_n(r)\rangle = 1$
- Dirac energies + Lamb shift different for different $n$ or different $j$. 
Hydrogen with fine-structure

$E_{nj}$

$n = 4$

$j = 7/2$

$j = 5/2$

$j = 3/2$

$j = 1/2$

$n = 3$

$j = 5/2$

$j = 3/2$

$j = 1/2$

$n = 2$

$j = 3/2$

$j = 1/2$

$n = 1$

$j = 1/2$

$l = 0$ (S)

$l = 1$ (P)

$l = 2$ (D)

$l = 3$ (F)

Bohr energies

Dirac energies (relativistic + spin-orbit)

Griffiths Ch. 6, Fig. 9
Weak-field Zeeman effect \( B_{\text{ext}} \ll B_{\text{int}} \)

For \( B_{\text{ext}} \ll B_{\text{int}} \): \( H'_{\text{so}} \) wins \( \implies \left| \psi_{nlsjm}^0 \right> \) good states, perturbed by \( H'_z \)

\[
\frac{\mu_B}{\hbar} (L_z + 2S_z) B_{\text{ext}}
\]

Need to determine matrix elements of \( H'_z \) with basis states \( |\Psi^0_n(r)\rangle |\psi_{lsjm}^0\rangle \)

Simplifications

- independent of \( r \) \( \implies \) spatial part of matrix element \( \langle \Psi^0_n(r) |\psi^0_n(r)\rangle = 1 \)
- Dirac energies + Lamb shift different for different \( n \) or different \( j \).

For weak fields perturbation always less than splitting between \( j \)- and \( n \)-manifolds.

\( \implies \) no mixing of states with different \( j \) or \( n \). Can consider \( (n,j) \)-manifolds individually.
Generalization to \( m \) manifolds

Starting point so far: \( n \) states with same unperturbed energy (1 manifold of \( n \) states)

Now: \( m \) manifolds with \( n_i \) states of energy \( E_i \) each ; \( i \in \{1, \ldots, m\} \)

If mixing matrix elements between two manifolds are all much smaller than energy gap between manifolds (\( |W_{mn}| \ll |\Delta_{nm}| \)), different manifolds can be approximated as independent and treated as discussed.
Weak-field Zeeman effect \( B_{\text{ext}} \ll B_{\text{int}} \)

For \( B_{\text{ext}} \ll B_{\text{int}} \): \( H'_{\text{so}} \) wins \( \implies \left| \psi_{nlsjm}^0 \right> \) good states, perturbed by \( H'_z \)

\[
\frac{\mu_B}{\hbar} (L_z + 2S_z) B_{\text{ext}}
\]

Need to determine matrix elements of \( H'_z \) with basis states \( \left| \psi_{n}^0(r) \right> \left| \psi_{ljsjm}^0 \right> \)

Simplifications

- independent of \( r \) \( \implies \) spatial part of matrix element \( \langle \psi_{n}^0(r) | \psi_{ljsjm}^0 \rangle = 1 \)
- Dirac energies + Lamb shift different for different \( n \) or different \( j \).
  - For weak fields perturbation always less than splitting between \( j \)- and \( n \)-manifolds.
  - \( \implies \) no mixing of states with different \( j \) or \( n \). Can consider \( (n,j) \)-manifolds individually.
- Perturbation operators \( L_z \) and \( S_z \) don’t change \( n, l \) or \( s \).
  - Since for a given \( j \) state \( l \) and \( s \) are fixed, perturbation doesn’t change \( n, l, s \), or \( j \).
  - (Remember: We first chose \( l \) and \( s \), then couple them to some \( j \).)
  - \( \implies \) Off-diagonal matrix elements between states with different \( n, l, s \) or \( j \) are zero.

We can chose \( n, l, s, j \) and consider them fixed.

Only states of the corresponding \( m_j \) manifold can mix and potentially produce off-diagonal elements of the perturbation matrix.

Simplified notation for states of the chosen manifold:

\[
\left| m_j \right>=\left| \psi_{nlsjm}^0 \right>
\text{ for chosen } n, l, s, j
\]
Perturbation matrix

\[ \frac{\mu_B}{\hbar} (L_z + 2S_z) B_{\text{ext}} = \frac{\mu_B}{\hbar} (J_z + S_z) B_{\text{ext}} \]

Perturbation matrix

\[ \mathcal{W} = \langle H'_z \rangle = \frac{\mu_B}{\hbar} (\langle J_z \rangle + \langle S_z \rangle) B_{\text{ext}} \]

\[ \langle J_z \rangle = \langle \tilde{m}_j | J_z | m_j \rangle = \hbar m_j \delta_{\tilde{m}_j m_j} \]

What is \( \langle S_z \rangle = \langle \tilde{m}_j | S_z | m_j \rangle \)?

Expand:

\[ |m_j\rangle = \sum_{m_i m_s} c_{m_i m_s}^{m_j} |m_i m_s\rangle \]

\[ \langle \tilde{m}_j | S_z | m_j \rangle = \sum_{\tilde{m}_i \tilde{m}_s} \sum_{m_i m_s} c_{\tilde{m}_i \tilde{m}_s}^{\tilde{m}_j} c_{m_i m_s}^{m_j} \langle \tilde{m}_i \tilde{m}_s | S_z | m_i m_s \rangle = \sum_{m_i m_s} c_{\tilde{m}_i \tilde{m}_s}^{\tilde{m}_j} c_{m_i m_s}^{m_j} \hbar m_s \]

\[ = \delta_{\tilde{m}_i m_i} \delta_{\tilde{m}_s m_s} \hbar m_s \]

\[ \mathcal{W} = \langle \tilde{m}_j | H'_z | m_j \rangle = \mu_B \left( \delta_{\tilde{m}_j m_j} m_j + \sum_{m_i m_s} c_{\tilde{m}_i \tilde{m}_s}^{\tilde{m}_j} c_{m_i m_s}^{m_j} \hbar m_s \right) B_{\text{ext}} \]

One way to solve problem: look up \( c_{m_i m_s}^{m_j} \), calculate matrix elements and diagonalize matrix
(Here: matrix is already diagonal because of Clebsch-Gordan property \( c_{m_i m_s}^{m_j} = 0 \) if \( m_j \neq m_i + m_s \).)
Perturbation matrix

More elegant and powerful way to calculate $\langle S_z \rangle$ and then $W = \langle H'_z \rangle = \frac{\mu_B}{\hbar} (\langle J_z \rangle + \langle S_z \rangle) B_{ext}$

Use operator identity $J^2 S_z + S_z J^2 = 2J_z(\vec{J} \cdot \vec{S})$ (not proven here)

Express $\vec{J} \cdot \vec{S}$ in more useful way:

$$L^2 = (J-S)^2 = J^2 + S^2 - 2 \vec{J} \cdot \vec{S}$$

$$\rightarrow \vec{J} \cdot \vec{S} = -\frac{1}{2} (L^2 - J^2 - S^2)$$

Using $|\psi^0_{nlsjm_j}\rangle$ states:

$$\langle J^2 S_z \rangle + \langle S_z J^2 \rangle = -\langle J_z (L^2 - J^2 - S^2) \rangle$$

$$\hbar^2 j(j+1) \langle S_z \rangle + \langle S_z \rangle \hbar^2 j(j+1) = -m_j \hbar [\hbar^2 l(l+1) - \hbar^2 j(j+1) - \hbar^2 s(s+1)]$$

$$\langle S_z \rangle = m_j \hbar \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

Perturbation matrix is diagonal:

$$E_z^1 = \frac{\mu_B}{\hbar} \langle J_z + S_z \rangle B = \left[ 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right] m_j \mu_B B$$

$$E_z^1 = g_J m_j \mu_B B \quad ; \quad g_J = \left[ 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right] \text{ Landé g-factor}$$
**Weak-field Zeeman effect**  \( B_{\text{ext}} \ll B_{\text{int}} \)

**Result**

\[ E_z^1 = \mu_B g_J m_J B_{\text{ext}} \]

magnetic moment of atom
not necessarily equal to e\(^{-}\) spin or orbital magnetic moment

**Hydrogen**

\( n^{2S+1}L_J \)

\( 2^2P_{3/2} \)

\( 2^2P_{3/2} \)

\( 2^2S_{1/2} \)

\( 2^2P_{1/2} \)

\( 1^2S_{1/2} \)

**Interpretation**

- L and S strongly coupled to J
- J states split in \( 2J+1 \) \( m_J \) states
- highest magnetic moment of \( 2\mu_B \) reached if e\(^{-}\) spin and orbital magnetic moment parallel
Zeeman effect in multi-electron atoms

In many-electron atoms it is often the case that the valence electron spins and the valence electron orbital angular momenta are strongly coupled.

In that case we have as good observables
• the total spin $S$
• the total orbital angular moment $L$

Zeeman effect is determined the same way.

The only consequence in the result is that Landé g-factor includes the eigenvalues of total angular momenta:

\[ E_z^1 = g_J m_j \mu_B B \quad ; \quad g_J = \left[ 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)} \right] \quad \text{Landé g-factor} \]
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Griffiths 3rd 7.3
7.3
7.4
7.4.1
7.4.2
7.4.3
Strong-field Zeeman effect $B_{\text{ext}} \gg B_{\text{int}}$

$|\psi^0_{nlm_l}m_s\rangle$ good states

Total Hamiltonian

$$H = H^0 + H'_z + H'_{\text{rel}} + H'_{\text{so}}$$

exactly solvable two perturbations

Zeeman shifts:

$$H'_z = \frac{\mu_B}{\hbar} (L_z + g_e S_z) B_{\text{ext}} \quad \rightarrow \quad E^1_z = \mu_B (m_l + g_e m_s) B_{\text{ext}}$$

Calculate perturbation of $H'_{\text{rel}}$ as before (same result since independent of spin).
Relativistic correction in 1\textsuperscript{st} order

\[ E_{r,n}^1 = -\frac{1}{2mc^2} \left[ E_n^2 + 2E_n \left( \frac{e^2}{4\pi\varepsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \left( \frac{e^2}{4\pi\varepsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right] \]

Insert \( \left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2\alpha} \) and \( \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l+\frac{1}{2})n^3\alpha^2} \), simplify:

\[ E_r^1 = -\frac{E_n^2}{2mc^2} \left[ \frac{4n}{l+1/2} - 3 \right] \]

Easily checked, that \( E_r^1 \) is on the order of \( \alpha^2 \) times smaller than \( E_n \).
Strong-field Zeeman effect $B_{\text{ext}} \gg B_{\text{int}}$

$|\psi_{nlm_l m_s}^0\rangle$ good states

Total Hamiltonian

$$H = H^0 + H'_z + H'_{\text{rel}} + H'_{\text{so}}$$

exactly solvable two perturbations

Zeeman shifts:

$$H'_z = \frac{\mu_B}{\hbar} (L_z + g_e S_z) B_{\text{ext}} \quad \rightarrow \quad E^1_z = \mu_B (m_l + g_e m_s) B_{\text{ext}}$$

Calculate perturbation of $H'_{\text{rel}}$ as before (same result since independent of spin).

Calculate perturbation by $H'_{\text{so}}$

$$E^1_{\text{so}} = \left( \frac{e^2}{8\pi\varepsilon_0} \right) \frac{1}{m^2 c^2} \left\langle \frac{1}{r^3} \right\rangle \left\langle \vec{S} \cdot \vec{L} \right\rangle$$

as before
Spin-orbit coupling

\[ H'_{SO} = \left( \frac{e^2}{8\pi \epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} \]

Energy correction in first order perturbation theory

\[ E_{SO}^1 = \langle \psi_{lsjm}^0 | H'_{SO} | \psi_{lsjm}^0 \rangle = \left( \frac{e^2}{8\pi \epsilon_0} \right) \frac{1}{mc^2} \left\langle \frac{1}{r^3} \right\rangle \frac{\hbar^2}{2} [j(j + 1) - l(l + 1) - s(s + 1)] \]

\[ \left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l + 1/2)(l + 1)n^3 a^3} \] (Griffiths)

Energy shift of hydrogen from spin-orbit coupling

\[ E_{SO}^1 = \frac{(E_n)^2}{mc^2} \left[ \frac{n[j(j + 1) - l(l + 1) - 3/4]}{l(l + 1/2)(l + 1)} \right] \] (for \( l \neq 0 \))
Strong-field Zeeman effect  $B_{\text{ext}} \gg B_{\text{int}}$

$|\psi_{nls_{1}m_{s}}^{0}\rangle$ good states

Total Hamiltonian

$$H = H^{0} + H'_{z} + H'_{\text{rel}} + H'_{\text{so}}$$

exactly solvable two perturbations

Zeeman shifts:

$$H'_{z} = \frac{\mu_{B}}{\hbar} (L_{z} + g_{e}S_{z}) B_{\text{ext}} \quad \Rightarrow \quad E^{1}_{z} = \mu_{B} (m_{l} + g_{e}m_{s}) B_{\text{ext}}$$

Calculate perturbation of $H'_{\text{rel}}$ as before (same result since independent of spin).

Calculate perturbation by $H'_{\text{so}}$

$$E^{1}_{\text{so}} = \left( \frac{e^{2}}{8\pi\epsilon_{0}} \right) \frac{1}{m^{2}c^{2}} \left\langle \frac{1}{r^{3}} \right\rangle \left\langle \vec{S} \cdot \vec{L} \right\rangle$$

as before

$$\left\langle \vec{S} \cdot \vec{L} \right\rangle = \left\langle S_{x} \right\rangle \langle L_{x} \rangle + \langle S_{y} \rangle \left\langle L_{y} \right\rangle + \langle S_{z} \rangle \left\langle L_{z} \right\rangle = \hbar^{2} m_{l} m_{s}$$

Sum up both perturbations ($H'_{\text{rel}} + H'_{\text{so}}$):

$$E^{1}_{\text{fs}} = E_{1} \frac{\alpha^{2}}{n^{3}} \left\{ \frac{3}{4n} - \left[ \frac{l(l+1) - m_{l}m_{s}}{l(l+1/2)(l+1)} \right] \right\}$$
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Griffiths 3rd 7.3
7.3
7.5
7.4
7.4.1
7.4.2
7.4.3
Zeeman effect for all $B_{\text{ext}}$

Perturbation can not be separated in small and big contribution

$$\rightarrow \quad H' = H'_{fs} + H'_{z}$$

Degenerate perturbation theory: need to solve

$$W \vec{\alpha} = E^1 \vec{\alpha} ; \quad W_{pq} = \langle \psi^0_p | H' | \psi^0_q \rangle$$

i.e. we need to diagonalize $W$

We are free to chose basis states. $W$ is simpler in basis $\{ |\psi^0_{nlj} \rangle \}$

We already calculated

$$(W_{fs})_{pq} = \langle H'_{fs} \rangle_{pq} = \frac{E_1}{n^4} \alpha^2 \left( \frac{n}{j + 1/2} - \frac{3}{4} \right)$$
Hydrogen with fine-structure

Two contributions to fine structure:

- **relativistic**

\[
E_r^1 = - \frac{E_n^2}{2mc^2} \left[ \frac{4n}{l + 1/2} - 3 \right]
\]

- **spin-orbit coupling**

\[
E_{SO}^1 = \frac{(E_n)^2}{mc^2} \left[ \frac{n[j(j+1) - l(l+1) - 3/4]}{l(l + 1/2)(l + 1)} \right]
\]

Both have same order of magnitude \( \frac{(E_n)^2}{mc^2} \)

Add both fine-structure contributions:

\[
E_{fs}^1 = \frac{(E_n)^2}{2mc^2} \left( 3 - \frac{4n}{j + 1/2} \right)
\]

Energy of hydrogen levels with fine structure

\[
E_{nj} = E_n + E_{fs}^1 = \frac{E_1}{n^2} \left[ 1 + \alpha^2 \left( \frac{n}{j + 1/2} - \frac{3}{4} \right) \right]
\]

\[
E_1 = -\frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\varepsilon_0} \right)^2 \simeq -13.6 \text{ eV}
\]

\[
j = l + s \quad ; \quad \alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \simeq \frac{1}{137.036}
\]
Zeeman effect for all $B_{\text{ext}}$

Perturbation can not be separated in small and big contribution

$$\rightarrow \quad H' = H'_{fs} + H'_z$$

Degenerate perturbation theory: need to solve

$$W\vec{\alpha} = E^1\vec{\alpha} \quad ; \quad W_{pq} = \langle \psi^0_p | H' | \psi^0_q \rangle$$

i.e. we need to diagonalize $W$

We are free to chose basis states. $W$ is simpler in basis $\{|\psi^0_{nlsjm}\rangle\}$

We already calculated

$$\begin{align*}
(W_{fs})_{pq} &= \langle H'_{fs} \rangle_{pq} = \frac{E_1}{n^4}\alpha^2 \left(\frac{n}{j+1/2} - \frac{3}{4}\right) \\
(W_z)_{pq} &= \langle H'_z \rangle_{pq} = \frac{\mu_B}{\hbar} B_{\text{ext}} \langle L_z + 2S_z \rangle_{pq}
\end{align*}$$
Zeeman effect for all $B_{\text{ext}}$

We need

$$ (W_z)_{pq} = \langle H'_z \rangle_{pq} = \frac{\mu_B}{\hbar} B_{\text{ext}} \langle L_z + 2S_z \rangle_{pq} $$

$$ = \hbar (m_l + 2m_s) \text{ in basis } \{|\psi^0_{nlm_lsm_s}\rangle\} $$

Express $|\psi^0_{nlsmjm}\rangle$ in terms of $|\psi^0_{nlsmjm}\rangle$

$$ |\psi^0_{nlsmjm}\rangle = \sum_{m_l, m_s} C^{jm}_{m_l m_s} |\psi^0_{nlm_lsm_s}\rangle $$

calculate

$$ \langle \psi_{nljm}\mid L_z + 2S_z \mid \psi_{nljm}\rangle = \sum_{\tilde{m}_l, \tilde{m}_s} \sum_{m_l, m_s} \tilde{c}^{jm}_{\tilde{m}_l \tilde{m}_s} c^{jm}_{m_l m_s} \langle \psi^0_{nl\tilde{m}_l \tilde{m}_s} \mid L_z + 2S_z \mid \psi^0_{nlm_lsm_s}\rangle $$

$$ = \hbar (m_l + 2m_s) \delta_{\tilde{m}_l m_l} \delta_{\tilde{m}_s m_s} $$

Which gives us

$$ (W_z)_{pq} = \langle H'_z \rangle_{pq} = \frac{\mu_B}{\hbar} B_{\text{ext}} \langle L_z + 2S_z \rangle_{pq} \text{ in basis } \{|\psi^0_{nlsmjm}\rangle\} $$
Perturbation for all $B_{\text{ext}}$

Perturbation can not be separated in small and big contribution

$$H' = H'_f + H'_z$$

Degenerate perturbation theory: need to solve

$$W \alpha = E^1 \alpha ; \quad W_{pq} = \langle \psi_0^* \mid H' \mid \psi_0 \rangle$$

i.e. we need to diagonalize $W$

We are free to chose basis states. $W$ is simpler in basis \( \{ |\psi_{nlsjm}^0 \rangle \} \)

We already calculated

$$\left( W_f \right)_{pq} = \langle H'_f \rangle_{pq} = \frac{E_1}{n^4} \alpha^2 \left( \frac{n}{j + 1/2} - \frac{3}{4} \right)$$

And now we have

$$\left( W_z \right)_{pq} = \langle H'_z \rangle_{pq} = \frac{\mu B}{\hbar} B_{\text{ext}} \langle L_z + 2S_z \rangle_{pq} \quad \text{in basis} \quad \{ |\psi_{nlsjm}^0 \rangle \}$$

$$= \sum_{m_l, m_s} c_{\tilde{m} \tilde{m} s} c_{m_l m_s} \tilde{h}(m_l + 2m_s)$$
To note down matrix $W$, we need to specify order of basis states.

We limit ourselves to the $n=2$ states of hydrogen.
Hydrogen with fine-structure

\[ E_{nj} \]

- \( n = 4 \)
- \( n = 3 \)
- \( n = 2 \)
- \( n = 1 \)

Bohr energies

Dirac energies (relativistic + spin-orbit)

\( j = 7/2 \)
\( j = 5/2 \)
\( j = 3/2 \)
\( j = 1/2 \)

\[ l = 0 \] (S)
\[ l = 1 \] (P)
\[ l = 2 \] (D)
\[ l = 3 \] (F)
Zeeman effect for H \( n = 2 \) states

To note down matrix \( W \), we need to specify order of basis states.

We limit ourselves to the \( n=2 \) states of hydrogen

\[
|jm_j\rangle = \sum_{m_l,m_s} c_{m_l m_s} |lm_l\rangle |sm_s\rangle
\]

exact eigenstates for zero field

\[
\begin{align*}
\psi_1 & \equiv \frac{1}{2} |\frac{1}{2}\rangle = |00\rangle |\frac{1}{2}\rangle, \\
\psi_2 & \equiv \frac{1}{2} |\frac{-1}{2}\rangle = |00\rangle |\frac{-1}{2}\rangle,
\end{align*}
\]

exact eigenstates for infinite field

\[
\begin{align*}
\psi_3 & \equiv \frac{3}{2} |\frac{3}{2}\rangle = |11\rangle |\frac{1}{2}\rangle, \\
\psi_4 & \equiv \frac{3}{2} |\frac{-3}{2}\rangle = |1-1\rangle |\frac{-1}{2}\rangle, \\
\psi_5 & \equiv |1\frac{1}{2}\rangle = \sqrt{2/3} |10\rangle |\frac{1}{2}\rangle + \sqrt{1/3} |11\rangle |\frac{-1}{2}\rangle, \\
\psi_6 & \equiv |\frac{1}{2}\rangle = -\sqrt{1/3} |10\rangle |\frac{1}{2}\rangle + \sqrt{2/3} |11\rangle |\frac{-1}{2}\rangle, \\
\psi_7 & \equiv |\frac{3}{2}\frac{-1}{2}\rangle = \sqrt{1/3} |1-1\rangle |\frac{1}{2}\rangle + \sqrt{2/3} |10\rangle |\frac{-1}{2}\rangle, \\
\psi_8 & \equiv |\frac{1}{2}\frac{-1}{2}\rangle = -\sqrt{2/3} |1-1\rangle |\frac{1}{2}\rangle + \sqrt{1/3} |10\rangle |\frac{-1}{2}\rangle.
\end{align*}
\]

notice: \( m_j = m_L + m_S \) for each component

With this rule you can find the components that can contribute
Perturbation for all $B_{\text{ext}}$

Perturbation can not be separated in small and big contribution

\[ H' = H'_{fs} + H'_{z} \]

Degenerate perturbation theory: need to solve

\[ W \tilde{\alpha} = E^{1} \tilde{\alpha} ; \quad W_{pq} = \langle \psi^{0}_{p} | H' | \psi^{0}_{q} \rangle \]

i.e. we need to diagonalize $W$

We are free to chose basis states. $W$ is simpler in basis \[ \{|\psi^{0}_{nlsjm_{j}}\rangle\} \]

We already calculated

\[ (W_{fs})_{pq} = \langle H'_{fs} \rangle_{pq} = \frac{E_{1}}{n^4} \alpha^{2} \left( \frac{n}{j + 1/2} - \frac{3}{4} \right) \]

And now we have

\[ (W_{z})_{pq} = \langle H'_{z} \rangle_{pq} = \frac{\mu B}{\hbar} B_{\text{ext}} \langle L_{z} + 2S_{z} \rangle_{pq} \text{ in basis } \{|\psi^{0}_{nlsjm_{j}}\rangle\} \]

\[ = \sum_{m_{l}, m_{s}} c^{\tilde{j} m_{j}^{*}} c^{j m_{j}} \bar{c}_{m_{l} m_{s}} \bar{c}_{m_{l} m_{s}} \hbar (m_{l} + 2m_{s}) \]
First order perturbation theory

Perturbation matrix:

\[ W = W_{fs} + W_z \]

\[
\Psi_A = \begin{pmatrix} 5\gamma - \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5\gamma + \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \gamma - 2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma + 2\beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \gamma - \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma - \frac{1}{3}\beta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \gamma + \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma + \frac{1}{3}\beta & \Psi_B \end{pmatrix}
\]

with

\[ \gamma \equiv \left( \frac{\alpha}{8} \right)^2 E_1 \quad ; \quad \beta \equiv \mu_B B_{ext} \]

To obtain first order energy shifts \( \vec{\alpha} \) and eigenstates of perturbed system \( |\Psi^0 > = \sum_{i=1}^{n} \alpha_i^0 |\Psi_i^0 > \)
solve

\[ W \vec{\alpha} = E^1 \vec{\alpha} \]
### Zeeman effect for H \( n = 2 \) states

**Interpretation in weak field**
- \( L \) and \( S \) strongly coupled to \( J \)
- \( J \) states split in \( 2J+1 \) \( m_J \) states

(Lamb shift not included in calculation)

**Compare to weak field result:**

- \( n^{2S+1}L_J \)
- \( 2^2P_{3/2} \)
- \( 2^2S_{1/2} \)
- \( 2^2P_{1/2} \)

(Lamb shift included)

\[ m_J \]
- \(+3/2\)
- \(+1/2\)
- \(-1/2\)
- \(-3/2\)

Griffiths Fig. 6.12
Zeeman effect for H $n = 2$ states

Interpretation in strong field

- L and S strongly coupled to B-field
- spin and orbital magnetic momenta just add up

\[ E_Z^1 = \mu_B (m_l + g_e m_s) B_{ext} \]

- spin: $m_s = 1/2$ and $g_e = 2$ \( m_s g_e = 1 \)
- maximum orbital: $m_L = 1$ and $g_L = 1$ \( m_L g_L = 1 \)
**Summary: corrections intrinsic to atom**

**Fine structure**

1) relativistic correction:
   instead of classical expression use relativistic expression for kinetic energy

2) spin-orbit coupling:
   in electrons frame of motion, nucleus moving around it, creating magnetic field.
   This field couples to magnetic moment of electron.

**Lamb shift**

Vacuum fluctuations of electric field push $e^-$ around. Changed $e^-$ trajectory through
Coulomb field of nucleus leads to energy shift.

**Hyperfine structure**

1) nuclear magnetic moment creates B-field
   $e^-$ magnetic moment couples to that field, leading to energy shift

2) electric quadrupole moment of nucleus experiences energy shift in
   electric field gradient created by $e^-$.  

3) finite size of nucleus
Summary: corrections by external fields

Zeeman effect
B-field couples to magnetic moment of atom

Stark effect
E-field induces electric dipole moment in atom
Polarized atom experiences energy shift in that field

These are all static effects. In addition effects from time-dependent fields (AC-Stark effect, photon absorption and emission)

→ time-dependent perturbation theory (next lecture)
Overview of course

Part 1: 7 lectures in January (Piet Mulders)
- Basics of quantum mechanics
- Spin states
- Addition of angular momentum
- Identical particles
- Basic structure of atom

Part 2: 7 lectures in February and March (Florian Schreck)
- Structure of atoms & the periodic table
- Crystalline solids
- Time-independent perturbation theory
- Structure of hydrogen
- Variational principle
- Time-dependent perturbation theory, atom-light interaction

today

Lecture notes, problem sets and link to video recordings of C0.110 lectures available on Canvas

Questions: schreck@StrontiumBEC.com
Overview of "Variational principle"

Goal of this section

Determine approximate solutions for ground-state wavefunction and energy

Plan of this section

1) General principle

2) Examples
   - harmonic oscillator
   - delta function potential

3) Applications
   - helium atom
   - hydrogen molecule ion
The variational principle

Goals

determine

• upper bound of ground state energy \( E_{gs} \)
• which one of several trial wave functions \( |\psi_i\rangle \) approximates ground state wave function best.

Theorem

For any normalized wave function \( |\psi\rangle \)

\[
E_{gs} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle
\]

Expectation value of Hamiltonian always greater than or equal to ground-state energy.
The variational principle

**Theorem**

For any normalized wave function $|\psi\rangle$: 

$$E_{gs} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle$$

**Proof**

Let $\{ |\psi_n\rangle \}$ be a complete, orthonormal basis; 

$$H |\psi_n\rangle = E_n |\psi_n\rangle$$

Then

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle$$

Normalization:

$$1 = \langle \psi | \psi \rangle = \sum_{n,m} c_n^* c_m \langle \psi_n | \psi_m \rangle = \sum_n |c_n|^2 \delta_{n,m}$$

Expectation value of $H$

$$\sum_{n,m} c_n^* c_m \langle \psi_n | H | \psi_m \rangle = \sum_{n,m} c_n^* c_m E_m \langle \psi_n | \psi_m \rangle \geq E_{gs} \sum_n |c_n|^2 = E_{gs}$$

$$E_{gs} \leq E_n \text{ for all } n$$

Q.E.D.
Example 1: the harmonic oscillator ground state

\[ H = T + V \quad ; \quad T = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad ; \quad V = \frac{1}{2} m\omega^2 x^2 \]

Trial wave functions, parametrized by \( b \):

\[ \psi(x) = Ae^{-bx^2} \]

Normalization:

\[ 1 = A^2 \int e^{-2bx^2} \, dx = A^2 \sqrt{\frac{\pi}{2b}} \quad \Rightarrow \quad A = \left( \frac{2b}{\pi} \right)^{1/4} \]

\[ \langle H \rangle : \]

\[ \langle T \rangle = -\frac{\hbar^2}{2m} A^2 \int e^{-bx^2} \frac{d^2}{dx^2} \left( e^{-bx^2} \right) \, dx = \frac{\hbar^2 b}{2m} \]

\[ \langle V \rangle = \frac{1}{2} m\omega^2 A^2 \int e^{-2bx^2} x^2 \, dx = \frac{m\omega^2}{8b} \]

\[ \Rightarrow \quad \langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b} \]
Example 1: the harmonic oscillator ground state

\[
\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}
\]

Minimize \( \langle H \rangle \):

\[
\frac{d}{db} \langle H \rangle = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \quad \implies \quad b = \frac{m\omega}{2\hbar}
\]

\[
\implies \langle H \rangle_{\text{min}} = \frac{1}{2} \hbar \omega
\]

\[
\psi_{\text{min}}(x) = \left( \frac{m\omega}{\pi \hbar} \right)^{1/4} \exp \left( -\frac{m\omega}{2\hbar} x^2 \right)
\]

Since we started with gaussian, we even were able to find true ground state.
Example 2: delta function potential

\[ H = T + V ; \quad T = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} ; \quad V(x) = -\alpha \delta(x) \]

Trial wave function: again gaussian

\[ \langle V \rangle = -\alpha A^2 \int e^{-xb^2} \delta(x) \, dx = -\alpha \sqrt{\frac{2b}{\pi}} \]

\[ \Rightarrow \quad \langle H \rangle = \frac{\hbar^2 b}{2m} - \alpha \sqrt{\frac{2b}{\pi}} \]

Minimize:

\[ \frac{d}{db} \langle H \rangle = \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} = 0 \quad \Rightarrow \quad b = \frac{2m^2 \alpha^2}{\pi \hbar^4} \]

\[ \Rightarrow \quad \langle H \rangle_{\text{min}} = -\frac{m\alpha^2}{\pi \hbar^2} \]

Indeed higher than true ground-state energy \[ E_{gs} = -\frac{m\alpha^2}{2\hbar^2} \]
Example 2: delta function potential

- Exact solution determined in Griffiths section 2.5.2
- Gaussian approximation determined by variational principle
Overview of "Variational principle"

Goal of this section

Determine approximate solutions for ground-state wavefunction and energy

Plan of this section

1) General principle
2) Examples
   - harmonic oscillator
   - delta function potential
3) Applications
   - helium atom
   - hydrogen molecule ion
The ground state of Helium

\[ H = -\frac{\hbar^2}{2m} \left( \nabla_1^2 + \nabla_2^2 \right) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) \]

Neglecting difficult e\(^{-}\) - e\(^{-}\) interaction

\[ V_{ee} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \]

exact solution is hydrogen wavefunction for each electron (with q = +2e nuclear charge)

\[ \psi_0 (\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a} \]

Ground-state energy: \( E = 8E_1 = -109 \text{ eV} \) (see also Griffiths section 5.2.1.)
Variational principle & first-order perturbation

Now: don’t neglect $V_{ee}$

No exact solution.

Determine upper bound of ground-state energy by $E_{gs} \leq \langle H \rangle$ using $\Psi_0 (\vec{r}_1, \vec{r}_2)$

$$H \Psi_0 = (8E_1 + V_{ee}) \Psi_0$$

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle$$

$$\langle V_{ee} \rangle = \frac{e^2}{4\pi \varepsilon_0} \left( \frac{8}{\pi a^3} \right)^2 \int \frac{e^{-4(r_1+r_2)/a}}{|\vec{r}_1 - \vec{r}_2|} d^3\vec{r}_1 d^3\vec{r}_2 = \frac{5}{4a} \frac{e^2}{4\pi \varepsilon_0} = -\frac{5}{2}E_1$$

check for yourself

$$\langle H \rangle = \frac{16}{2}E_1 - \frac{5}{2}E_1 = \frac{11}{2}E_1 = -75 \text{ eV}$$

Compare to measured value $E_{gs} = -79 \text{ eV} : 5\%$ off.

Remark: another way to think about this calculation:

correction to ground-state energy using first-order perturbation theory on $\Psi_0 (\vec{r}_1, \vec{r}_2)$ with $V_{ee}$ as perturbation.
Can we do better?

**Idea:** one electron shields nuclear charge for other electron and vice versa.

Effectively each electron sees slightly reduced nuclear charge.

→ Use nuclear charge $Z$ as variational parameter.

Ground state wave function of hydrogen-like atom (ion) with nuclear charge $Z$:

$$\psi_0(\vec{r}_1) = \sqrt{\frac{Z^3}{\pi a^3}} e^{-Zr_1/a} ; \quad E = Z^2 E_1$$

Trial wavefunction for He:

$$\psi_1(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}$$

which is eigenstate of

$$H_Z(\vec{r}_1) + H_Z(\vec{r}_2)$$

where $H_Z$ is hamiltonian for hydrogen-like atom (ion) with nuclear charge $Z$.
write Hamiltonian

\[
H = -\frac{\hbar^2}{2m} \left( \nabla_1^2 + \nabla_2^2 \right) - \frac{e^2}{4\pi \varepsilon_0} \left( \frac{Z}{r_1} + \frac{Z}{r_2} \right) + \frac{e^2}{4\pi \varepsilon_0} \left( \frac{(Z - 2)}{r_1} + \frac{(Z - 2)}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right)
\]

Hamiltonian of hydrogen-like atom with charge \(Z\) for each electron

everything remaining for He Hamiltonian

Upper limit for ground state energy:

\[
\langle H \rangle = 2Z^2 E_1 + 2(Z - 2) \left( \frac{e^2}{4\pi \varepsilon_0} \right) \langle \frac{1}{r} \rangle + \langle V_{ee} \rangle
\]

\[
\langle \frac{1}{r} \rangle = \frac{Z}{a} \quad ; \quad \langle V_{ee} \rangle = -\frac{5Z}{4} E_1
\]

\[
\langle H \rangle = \left[ 2Z^2 - 4Z(Z - 2) - \frac{5}{4}Z \right] E_1 = \left[ -2Z^2 + \frac{27}{4} Z \right] E_1
\]

Minimize

\[
\frac{d}{dZ} \langle H \rangle = \left[ -4Z + \frac{27}{4} \right] E_1 \overset{!}{=} 0 \quad \Rightarrow \quad Z = \frac{27}{16} \simeq 1.69
\]

\[
\Rightarrow \quad \langle H \rangle = \frac{1}{2} \left( \frac{3}{2} \right)^6 E_1 \simeq -77.5 \text{ eV} \quad \text{compare to measured value } E_{gs} = -79 \text{ eV : 2% off.}
\]

Continue with ever more sophisticated trial wave functions.
Overview of „Variational principle“

Goal of this section

Determine approximate solutions for ground-state wavefunction and energy

Plan of this section

1) General principle
2) Examples
   - harmonic oscillator
   - delta function potential
3) Applications
   - helium atom
   - hydrogen molecule ion

Griffiths 3\textsuperscript{rd} 8.1

example 8.1

example 8.2

8.2

8.3
The hydrogen molecule ion

\[ \text{H}_2^+ \text{ ion:} \]

\[ \text{proton} \quad q = +e \]

\[ \text{proton} \quad q = +e \]

Heisenberg uncertainty principle

\[ \Delta x \Delta p \geq \frac{\hbar}{m} \quad \rightarrow \quad \Delta v \geq \frac{\hbar}{m \Delta x} \]

Mass of e\(^-\) 1836 times lighter than mass of proton

\[ \rightarrow \quad \text{e}^- \text{ wave function adapts quickly to slow change of positions of nuclei} \]

Born-Oppenheimer approximation

separate total molecular wavefunction into nuclear and e- wavefunction:

\[ \Psi_{\text{tot}} = \Psi_{\text{el}} \Psi_{\text{nuc}} \]

Our goal: approximate \( \Psi_{\text{el}} \), determine energy of e\(^-\) and then of ion
Can $\text{H}_2^+$ ion exist?

i.e. what is energetically favorable

H atom and free proton

Strategy to find answer

For each $R$:
- chose trial wavefunction $\Psi_{\text{trial}}$ for $\Psi_{\text{el}}$
- calculate upper limit of $e^-$ energy using variational principle: $E_{gs} \leq \langle \Psi_{\text{trial}} | H_{el} | \Psi_{\text{trial}} \rangle$
- determine total energy: electron energy + proton-proton repulsion

$$E_{\text{tot}}(R) = E_{\text{el}}(R) + E_{p-p}(R)$$

If $E_{\text{tot}} < E_1$ for some value of $R$, then $\text{H}_2^+$ has chance of existing.
Trial wavefunction

**Electron Hamiltonian** (consider $R$ fixed)

$$H_{el} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi \varepsilon_0} \left( \frac{1}{|\vec{r}|} + \frac{1}{|\vec{r} - \vec{R}|} \right)$$

**Trial wavefunction**

Hydrogen ground-state \( \psi_0(\vec{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \quad ; \quad a = \text{Bohr radius} \)

Good approximation for e- around one proton and the other at huge distance $R$.

But don’t know which proton \( \quad \rightarrow \quad \) try superposition state

$$\psi_{\text{trial}} = A[\psi_0(|\vec{r}|) + \psi_0(|\vec{r} - \vec{R}|)]$$

At least if $R$ big, this should be a good wavefunction, since second proton doesn’t disturb too much.

This approach is called „Linear Combination of Atomic Orbitals“ (LCAO)
Normalization

\[ 1 = \int |\psi_{\text{trial}}|^2 d^3 \vec{r} = A^2 \left[ \int |\psi_0(|\vec{r}|)|^2 d^3 \vec{r} + \int |\psi_0(|\vec{r} - \vec{R}|)|^2 d^3 \vec{r} \right] = 1 + 1 \]

\[ + 2 \int \psi_0(|\vec{r}|)\psi_0(|\vec{r} - \vec{R}|) d^3 \vec{r} \]

\[ \equiv I \quad \text{overlap integral} \]

\[ I = \frac{1}{\pi a^3} \int e^{-|\vec{r}|/a} e^{-|\vec{r} - \vec{R}|/a} d^3 \vec{r} \]

\[ = \frac{1}{\pi a^3} \int e^{-r/a} e^{-\sqrt{r^2 + R^2 - 2rr\cos\Theta}} r^2 \sin\Theta dr d\Theta d\phi \]

\[ = \ldots = e^{-R/a} \left[ 1 + \left( \frac{R}{a} \right) + \frac{1}{3} \left( \frac{R}{a} \right)^2 \right] \]

Notice: \( I \xrightarrow{R \to 0} 1 \) and \( I \xrightarrow{R \to \infty} 0 \)

\[ \Rightarrow A^2 = \frac{1}{2(1 + I)} \]
Electron ground-state energy

Variational principle

\[ E_{gs} \leq \langle \Psi_{\text{trial}} | H_{el} | \Psi_{\text{trial}} \rangle \]

First step:

\[
H_{el} \Psi_{\text{trial}} = \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{|\vec{r}|} + \frac{1}{|\vec{r} - \vec{R}|} \right) \right] A \left[ \Psi_0(|\vec{r}|) + \Psi_0(|\vec{r} - \vec{R}|) \right]
\]

\[ = E_1 A \Psi_0(|\vec{r}|) \]

\[ - A \frac{e^2}{4\pi\varepsilon_0} \left[ \frac{1}{|\vec{r} - \vec{R}|} \Psi_0(|\vec{r}|) + \frac{1}{|\vec{r}|} \Psi_0(|\vec{r} - \vec{R}|) \right] \]

reminder

\[ \Psi_{\text{trial}} = A \left[ \Psi_0(|\vec{r}|) + \Psi_0(|\vec{r} - \vec{R}|) \right] \]

with (from hydrogen):

\[ \left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r} \right) \Psi_0(r) = E_1 \Psi_0(r) \]

shifted Hydrogen Schrödinger equation
Electron ground-state energy

\[ H_{\text{el}} \psi_{\text{trial}} = E_1 \psi_{\text{trial}} - |A| \frac{e^2}{4\pi \varepsilon_0} \left[ \frac{1}{|\vec{r} - \vec{R}|} \psi_0(|\vec{r}|) + \frac{1}{|\vec{r}|} \psi_0(|\vec{r} - \vec{R}|) \right] \]

\[ \langle \psi_{\text{trial}} | H_{\text{el}} | \psi_{\text{trial}} \rangle = E_1 - 2 |A|^2 \frac{e^2}{4\pi \varepsilon_0} \left[ \langle \psi_0(|\vec{r}|) | \frac{1}{|\vec{r} - \vec{R}|} | \psi_0(|\vec{r}|) \rangle + \langle \psi_0(|\vec{r}|) | \frac{1}{|\vec{r}|} | \psi_0(|\vec{r} - \vec{R}|) \rangle \right] \]

Intergrals like D and X appear 2 times each. To make equal to D and X, change coordinates by exploiting mirror symmetry of molecule.

\[ D = \frac{a}{R} - \left( 1 + \frac{a}{R} \right) e^{-2R/a} \]
\[ X = \left( 1 + \frac{R}{a} \right) e^{-R/a} \]

\[ \langle \psi_{\text{trial}} | H_{\text{el}} | \psi_{\text{trial}} \rangle = \left[ 1 + 2 \frac{D + X}{1 + I} \right] E_1 \]

In addition: energy from proton-proton repulsion

\[ V_{p-p} = \frac{e^2}{4\pi \varepsilon_0} \frac{1}{R} = -\frac{2a}{R} E_1 \]

Result: upper limit for ground-state energy

\[ E(x) = -E_1 \left[ -1 + \frac{2}{x} \left\{ \frac{(1 - (2/3)x^2)e^{-x} + (1 + x)e^{-2x}}{1 + (1 + x + (1/3)x^2)e^{-x}} \right\} \right] \quad ; \quad x \equiv \frac{R}{a} \]
Molecular potential

To do: solve Schrödinger equation of nuclear motion in molecular potential and show that potential is deep enough to contain bound state

You’ll find a bound state.
The two protons in $\text{H}_2^+$ are held together by the electron.
Goal of this section

Determine approximate solutions for ground-state wavefunction and energy

Plan of this section

1) General principle
2) Examples
   - harmonic oscillator
   - delta function potential
3) Applications
   - helium atom
   - hydrogen molecule ion

Griffiths 3rd 8.1
example 8.1
example 8.2
8.2
8.3
Overview of course

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Questions: schreck@StrontiumBEC.com
Overview of „Time-dependent perturbation theory“

Goal of this section

Describe the reaction of a system to a time-dependent perturbation, especially absorption and emission of photons by atoms.

Plan of this section

1) Introduction
2) Two-level system with time-dependent $H$
   - time-dependent perturbation theory
   - sinusoidal perturbation
3) Emission and absorption of radiation
   - absorption, stimulated emission, spontaneous emission
   - spontaneous emission
   - incoherent perturbation
   - Einstein's A and B coefficients
   - lifetime of excited state
   - selection rules
4) Fermi's golden rule
So far: „quantum statics“

Hamiltonian **independent** of time

i.e. potential \( V(\vec{r}, t) = V(\vec{r}) \)

Example: **static** harmonic oscillator

Now: „quantum dynamics“

Hamiltonian **dependent** of time

Example: **driven** harmonic oscillator
Even if Hamiltonian time-independent, quantum system evolves over time. 

\[ H \Psi = i \hbar \frac{\partial \Psi}{\partial t} \]

has solutions

\[ \Psi_n(\vec{r}, t) = \Psi_n(\vec{r})e^{-iE_n t/\hbar} \]

with \( \Psi_n(\vec{r}), E_n \) satisfying

\[ H \Psi_n(\vec{r}) = E_n \Psi_n(\vec{r}) \]

and general solution

\[ \Psi(\vec{r}, t) = \sum_n c_n \Psi_n(\vec{r})e^{-iE_n t/\hbar} \]

**Eigenstates**

Density distributions & energy don’t evolve

\[ n_n(\vec{r}) = |\Psi_n(\vec{r}, t)|^2 = |\Psi_n(\vec{r})|^2 \]

**Superposition states**

Density distribution can evolve

Energy doesn’t evolve

Probability to measure \( E_n \) is \( |c_n|^2 \)

\[ \langle H \rangle \] is constant
Time evolution for time-dependent $H$

If Hamiltonian is time-dependent then energy can be injected into system or removed from system by drive.

Example: driven harmonic oscillator
Overview of "Time-dependent perturbation theory"

Goal of this section

Describe the reaction of a system to a time-dependent perturbation, especially absorption and emission of photons by atoms.

Plan of this section

1) Introduction

2) Two-level system with time-dependent $H$
   - time-dependent perturbation theory
   - sinuosidal perturbation

3) Emission and absorption of radiation
   - absorption, stimulated emission, spontaneous emission
   - spontaneous emission
     - incoherent perturbation
     - Einstein's A and B coefficients
     - lifetime of excited state
   - selection rules

4) Fermi's golden rule
Two level system with time-dependent $H$

\[ E_b \quad |\Psi_b\rangle \quad \Delta E \quad H \Psi_i = E_i \Psi_i \quad ; \quad \langle \Psi_i | \Psi_j \rangle = \delta_{ij} \quad ; \quad i, j \in \{a, b\} \quad \]

\[ E_a \quad |\Psi_a\rangle \]

Initial state: $\Psi(t = 0) = c_a(0) \Psi_a + c_b(0) \Psi_b \quad |c_a(0)|^2 + |c_b(0)|^2 = 1$

Later state: (solution of $H \Psi = i\hbar \frac{\partial \Psi}{\partial t}$)

Time-independent $H = H^0$

$\Psi(t) = c_a(0)e^{-iE_a t/\hbar} \Psi_a + c_b(0)e^{-iE_b t/\hbar} \Psi_b$

Time-dependent $H = H^0 + H'(t)$

$\Psi(t) = c_a(t)e^{-iE_a t/\hbar} \Psi_a + c_b(t)e^{-iE_b t/\hbar} \Psi_b \quad |c_a(t)|^2 + |c_b(t)|^2 = 1$

Task: (approximately) find $c_a(t)$ and $c_b(t)$
Two level system with time-dependent $H$

$$H = H^0 + H'(t)$$

- time-dependent part of Hamiltonian (not necessarily small)

Solve $H \Psi = i\hbar \frac{\partial \Psi}{\partial t}$ with ansatz $\Psi(t) = c_a(t)e^{-iE_a t/\hbar}\Psi_a + c_b(t)e^{-iE_b t/\hbar}\Psi_b$

$$c_a[H^0\Psi_a]e^{-iE_a t/\hbar} + c_b[H^0\Psi_b]e^{-iE_b t/\hbar} + c_a[H'\Psi_a]e^{-iE_a t/\hbar} + c_b[H'\Psi_b]e^{-iE_b t/\hbar}$$

$$= i\hbar \left[ \dot{c}_a \Psi_a e^{-iE_a t/\hbar} + \dot{c}_b \Psi_b e^{-iE_b t/\hbar} + c_a \Psi_a \left( \frac{-iE_a}{\hbar} \right) e^{iE_a t/\hbar} + c_b \Psi_b \left( \frac{-iE_b}{\hbar} \right) e^{iE_b t/\hbar} \right]$$

$$c_a[H'\Psi_a]e^{-iE_a t/\hbar} + c_b[H'\Psi_b]e^{-iE_b t/\hbar} = i\hbar \left[ \dot{c}_a \Psi_a e^{-iE_a t/\hbar} + \dot{c}_b \Psi_b e^{-iE_b t/\hbar} \right]$$

$$\langle \Psi_a | H' | \Psi_a \rangle e^{-iE_a t/\hbar} + c_b \langle \Psi_a | H' | \Psi_b \rangle e^{-iE_b t/\hbar} = i\hbar \dot{c}_a e^{-iE_a t/\hbar}$$

$$H'_{ij} = \langle \Psi_i | H' | \Psi_j \rangle :$$

$$\dot{c}_a = -\frac{i}{\hbar} \left[ c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a) t/\hbar} \right]$$

$$\dot{c}_b = -\frac{i}{\hbar} \left[ c_a H'_{ba} e^{i(E_b - E_a) t/\hbar} + c_b H'_{bb} \right]$$

Matrix notation:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = \begin{pmatrix} \frac{H'_{aa}}{H'_{ba} e^{i(E_b - E_a) t/\hbar}} & \frac{H'_{ab} e^{-i(E_b - E_a) t/\hbar}}{H'_{bb}} \\ \frac{H'_{ba} e^{i(E_b - E_a) t/\hbar}}{H'_{bb}} & \frac{H'_{bb}}{H'_{ba} e^{i(E_b - E_a) t/\hbar}} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix}$$
Two level system with time-dependent $H$

\[
H = H^0 + H'(t) \\
\text{static} \quad \text{time-dependent part of Hamiltonian (not necessarily small)}
\]

Solve $H \Psi = i\hbar \frac{\partial \Psi}{\partial t}$ with ansatz $\Psi(t) = c_a(t)e^{-iE_a t/\hbar} \Psi_a + c_b(t)e^{-iE_b t/\hbar} \Psi_b$

\[
\begin{align*}
\dot{c}_a &= -\frac{i}{\hbar} \left[c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a) t/\hbar}\right] \\
\dot{c}_b &= -\frac{i}{\hbar} \left[c_a H'_{ba} e^{i(E_b - E_a) t/\hbar} + c_b H'_{bb}\right]
\end{align*}
\]

Often $H'_{aa} = H'_{bb} = 0$:

\[
\begin{align*}
\dot{c}_a &= -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \\
\dot{c}_b &= -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a
\end{align*}
\]

with $\omega_0 = \frac{E_b - E_a}{\hbar}$
Overview of "Time-dependent perturbation theory"

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Griffiths 3rd 11.0
11.1
11.2 - 3
Time-dependent perturbation theory

\[ H = H^0 + H'(t) \]

static \[ \text{small time-dependent perturbation} \]

Initial condition: system in ground state \[ c_a(0) = 1 \,, \quad c_b(0) = 0 \]

Iteratively solve

\[ \begin{align*}
\dot{c}_a &= -\frac{i}{\hbar} H'_a b e^{-i\omega_0 t} c_b \\
\dot{c}_b &= -\frac{i}{\hbar} H'_b a e^{i\omega_0 t} c_a
\end{align*} \]

true solution

would be nice to have, but too complicated to calculate

zeroth order: \[ c_a(t) = 1 \,, \quad c_b(t) = 0 \]

not that far away from true solution

Idea: use zeroth order solution to calculate \( \dot{c}_a(0)(t) \) & \( \dot{c}_b(0)(t) \),

which should not be far away from true values since zeroth order already pretty good.

Integrate to find first order solutions.

first order: \[ c_a^{(1)}(t) \,, \quad c_b^{(1)}(t) \]

less far away from true solution

Idea: iterate this process

should lead to ever better solution

second order: \[ c_a^{(2)}(t) \,, \quad c_b^{(2)}(t) \]

even less far away from true solution

Note: there is no need to add up \( c_a^{(0)}(t) + c_a^{(1)}(t) + \ldots + c_a^{(n)}(t) \) is already the full \( n^{th} \) order solution.
Time-dependent perturbation theory

\[ H = H^0 + H'(t) \]

static \[ \text{small} \] time-dependent perturbation

Initial condition: system in ground state \[ c_a(0) = 1 \, , \, c_b(0) = 0 \]

Iteratively solve
\[ \dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \]
\[ \dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a \]

Zeroth Order: \( (H' = 0) \)
\[ c_a^{(0)}(t) = 1 \, , \, c_b^{(0)}(t) = 0 \]

First Order:
\[ \dot{c}_a^{(1)} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b^{(0)} = 0 \implies c_a^{(1)}(t) = 1 \]
\[ \dot{c}_b^{(1)} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a^{(0)} \implies c_b^{(1)}(t) = -\frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \]

Second Order:
\[ \dot{c}_a^{(2)} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} \left( -\frac{i}{\hbar} \right) \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \]
\[ \implies c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2} \int_0^t \left[ \int_0^{t'} H'_{ab}(t'') e^{-i\omega_0 t''} dt'' \right] dt' \]
\[ \dot{c}_b^{(2)} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a^{(1)} \implies c_b^{(2)}(t) = c_b^{(1)}(t) \]

Note: \( |c_a^{(1)}(t)|^2 + |c_b^{(1)}(t)|^2 = 1 + \mathcal{O}(H'_{ab})^2 \neq 1 \)
Interpretation

Probability amplitude to find system in $|\Psi_b\rangle$ after time $t$ in second order:

$$c_b^{(1)}(t) = -\frac{i}{\hbar} \int_0^t H'_{ba}(t')e^{i\omega_0 t'} dt'$$

with $\omega_0 = \frac{E_b-E_a}{\hbar}$

rewrite:

$$c_b^{(1)}(t)e^{-iE_b t/\hbar} = -\frac{i}{\hbar} \int_0^t e^{-iE_b(t-t')/\hbar} H'_{ba}(t')e^{-iE_a t'/\hbar} dt'$$

(read from right to left)

Interpretation: probability amplitude to transition from $|\Psi_a\rangle$ to $|\Psi_b\rangle$ is sum over all possibilities

System is in $|\Psi_a\rangle$ up to time $t'$ and then transitions to $|\Psi_b\rangle$.

Total transition amplitude = sum over all possibilities, i.e. times $t'$.

See also: Feynman path integral.
Interpretation

Probability amplitude to find system in $|\Psi_a\rangle$ after time $t$ in second order:

$$c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2} \int_0^t H_{ab}'(t') e^{-i\omega_0 t'} \left[ \int_0^{t'} H_{ba}'(t'') e^{i\omega_0 t''} dt'' \right] dt'$$

with

$$\omega_0 = \frac{E_b - E_a}{\hbar}$$

rewrite:

$$c_a^{(2)}(t) e^{-iE_a t/\hbar} = e^{-iE_a t/\hbar} + \left( \frac{i}{\hbar} \right)^2 \int_0^t \int_0^{t'} e^{-iE_a(t-t')/\hbar} H_{ab}'(t') e^{-iE_b(t'-t'')/\hbar} H_{ba}'(t'') e^{-iE_a t''/\hbar} dt'' dt'$$

Interpretation: probability amplitude to transition from $|\Psi_a\rangle$ to $|\Psi_b\rangle$ to $|\Psi_a\rangle$ is sum over all possibilities

Zeroth Order:

$$|\Psi_a\rangle$$

Second Order:

$$|\Psi_a\rangle$$

Total transition amplitude = sum over all possibilities.
Let’s invert: start by drawing graphs and read off equation from them. Huge shortcut on calculation. Probability amplitude to transition from $|\Psi_a\rangle$ to $|\Psi_b\rangle$ in second order and in presence of $N$ states.

First Order:

Second Order:

$$c_b^{(2)}(t) e^{-iE_b t / \hbar} = + \left( -\frac{i}{\hbar} \right) \int_0^t e^{-iE_b (t - \tilde{t}) / \hbar} H'_{ba}(\tilde{t}) e^{-iE_a \tilde{t} / \hbar} d\tilde{t}$$

$$+ \sum_n \left( -\frac{i}{\hbar} \right)^2 \int_0^t \int_0^{t'} e^{-iE_b (t - t') / \hbar} H'_{bn}(t') e^{-iE_n (t' - t'') / \hbar} H'_{na}(t'') e^{-iE_a t'' / \hbar} dt'' dt'$$
Overview of „Time-dependent perturbation theory“

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Griffiths 3rd 11.0
11.1
11.2 - 3
Sinusoidal perturbation

\[ H = H^0 + H'(t) \]

\[ \text{static } \quad \text{small time-dependent perturbation } \quad H'(t) = V \cos(\omega t) \]

Initial condition: system in ground state \[ c_a(0) = 1, \quad c_b(0) = 0 \]

Iteratively solve \[ \dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \]
\[ \dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a \]

First Order: \[ H'_{ij}(t) \equiv V_{ij} \cos(\omega t) \]
\[ c_a(t) \approx 1 \]
\[ c_b(t) \approx -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t') e^{i\omega_0 t'} dt' = -\frac{i V_{ba}}{2\hbar} \int_0^t \left[ e^{i(\omega_0 + \omega) t'} + e^{i(\omega_0 - \omega) t'} \right] dt' \]
\[ = -\frac{V_{ba}}{2\hbar} \left[ \frac{e^{i(\omega_0 + \omega) t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0 - \omega) t} - 1}{\omega_0 - \omega} \right] \]

Simplifying assumption: \( \omega_0 + \omega \gg |\omega_0 - \omega| = |\delta| \), i.e. detuning small compared to transition frequency

\[ c_b(t) \approx -\frac{V_{ba}}{2\hbar} \frac{e^{i(\omega_0 - \omega) t/2}}{\omega_0 - \omega} \left[ e^{i(\omega_0 - \omega) t/2} - e^{-i(\omega_0 - \omega) t/2} \right] \]
\[ = -i \frac{V_{ba}}{\hbar} \frac{\sin[(\omega_0 - \omega) t/2]}{\omega_0 - \omega} e^{i(\omega_0 - \omega) t/2} \]
Transition probability

\[ P_{a \rightarrow b}(t) = |c_b(t)|^2 \propto \frac{|V_{ba}|^2 \sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \]

\[ \frac{|V_{ba}|^2}{\hbar^2} \ll 1 \text{ for perturbation theory to be valid} \]

Spectrum:

\[ P(t) = \left( \frac{|V_{ba}|^2}{\hbar^2} \right) \]

Probability to be in \( |\Psi_b\rangle \) higher if detuning \( \delta \) small. Resonance becomes narrower and higher over time.

Rescaling collapses resonances for all times on one graph:
Transition probability

\[ P_{a \rightarrow b}(t) = |c_b(t)|^2 \approx \frac{|V_{ba}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \]

\[ \frac{|V_{ba}|^2}{\hbar^2} \ll 1 \text{ for perturbation theory to be valid} \]

Spectrum:

Probability to be in \( |\Psi_b\rangle \) higher if detuning \( \delta \) small. Resonance becomes narrower and higher over time.

On resonance (\( \delta = 0 \)):

\[ P(t) = \left( \frac{|V_{ba}|^2}{\hbar^2} \right) \]

Probability to be in \( |\Psi_b\rangle \) increases with \( t^2 \).

Off resonance:

\[ \delta = 2\pi \times 1 \text{ Hz} \]

Probability to be in \( |\Psi_b\rangle \) oscillates.
Transition probability

\[ P_{a \rightarrow b}(t) = |c_b(t)|^2 \cong \frac{|V_{ba}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \]

\[ \frac{|V_{ba}|^2}{\hbar^2} \ll 1 \text{ for perturbation theory to be valid} \]

Spectrum:

\[ P(t) \left( \frac{|V_{ba}|^2}{\hbar^2} \right) \]

<table>
<thead>
<tr>
<th>Time (t)</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 s</td>
<td>0.5</td>
</tr>
<tr>
<td>2 s</td>
<td>1.0</td>
</tr>
<tr>
<td>3 s</td>
<td>2.0</td>
</tr>
</tbody>
</table>

On resonance (\( \delta = 0 \)):

Probability to be in \(|\Psi_b\rangle\) increases with \(t^2\).

Off resonance:

Probability to be in \(|\Psi_b\rangle\) oscillates.

Rescaling collapses graph:

\[ \frac{\hbar \delta}{\hbar (\omega_0 - \omega)} \]

\[ \hbar\omega \quad \hbar\omega_0 \equiv E_b - E_a \]

\[ |\Psi_b\rangle \quad |\Psi_a\rangle \]

Resonance becomes narrower and higher over time.
Overview of „Time-dependent perturbation theory“

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   - Einstein’s A and B coefficients
   - lifetime of excited state
   - selection rules

4) Fermi’s golden rule
Meet the players

Atom
|e⟩
|g⟩

Laser beam

EM field modes
Atom-light interaction
Electromagnetic waves

Linearly polarized plane wave

- Electric field: $\mathbf{E}_0$
- Magnetic field: $\mathbf{B}_0$
- Wavevector: $\mathbf{k'} = \frac{2\pi}{\lambda_L} \mathbf{e}_L$

- Frequency: $f_L = \frac{c}{\lambda_L}$
- Angular frequency: $\omega_L = 2\pi \times f_L$
- Intensity: $I = \frac{E_0^2}{2\mu_0 c}$
- Energy of photon: $E_L = hf_L$
- Momentum of photon: $\mathbf{p} = \hbar \mathbf{k'}$

- Electric field: $\mathbf{E} = \mathbf{E}_0 \cos \left( \mathbf{k'} \cdot \mathbf{r} - \omega_L t + \varphi_L \right)$
- Magnetic field: magnitude $B_0 = \frac{E_0}{c}$
A plane wave fills all of space.
Atomic transitions

Electromagnetic radiation can drive different types of transitions in atoms:

Example: hydrogen

$n = 2$

\[ ^2P_{3/2} \]

\[ ^2S_{1/2} \]

\[ ^2P_{1/2} \]

$n = 1$

Coulomb

Fine structure

Lamb shift

Hyperfine splitting

Zeeman Shift

$F = 1$

$F = 0$

$m_F$

$+1$

$0$

$-1$

$0$
Hydrogen with fine-structure

$E_{nj}$

$n=4$

$n=3$

$n=2$

$n=1$

$l = 0$ (S)

$l = 1$ (P)

$l = 2$ (D)

$l = 3$ (F)

Griffiths Ch. 6, Fig. 9
Atomic transitions

Electromagnetic radiation can drive different types of transitions in atoms:

Example: hydrogen

$n = 2$

- $^2\text{P}_{3/2}$
- $^2\text{S}_{1/2}$
- $^2\text{P}_{1/2}$

$n = 1$

- $^2\text{S}_{1/2}$

Coulomb  Fine structure  Lamb shift  Hyperfine splitting  Zeeman Shift

principal quantum number changing transitions
100 ... 10000 THz
(includes visible light)

hyperfine state changing transitions
0.1 ... 10 GHz

Zeeman state changing transitions
1 kHz ... 1 GHz
for lab B-fields

In the following: principal quantum number changing transitions
Principal quantum number changing transition

(Valence) electron has to change its orbital

We need a force acting on the electron

Strongest force: E-field of light acting on charge of electron
(others: e.g. B-field gradient acting on electron magnetic moment)
Electric dipole transitions

E-field of light acting on charge of electron

E-field of monochromatic, linearly polarized plane wave:

\[ \overrightarrow{E}_L(\overrightarrow{r}, t) = \overrightarrow{E}_0 \cos \left( \overrightarrow{k} \cdot \overrightarrow{r} - \omega_L t + \varphi_l \right) \]

Force on electron \[ \overrightarrow{F} = -\overrightarrow{E}_0 e \]

(Force on nucleus has negligible effect since nucleus is much heavier than electron.)

Time-dependent perturbation

Energy \[ E = -e \overrightarrow{r}_e \cdot \overrightarrow{E}_L(\overrightarrow{r}_e, t) \]

\[ \overrightarrow{E}_L(\overrightarrow{r}, t) \sim \overrightarrow{E}_L(\overrightarrow{r}_n, t) \]

Simplifications:

- wavelength of light much larger than size of atom (blue: 400 nm, red: 700 nm; Bohr radius: 0.05 nm)

- chose z-axis parallel to E-field polarization

- atom position fixed in space during transition → no Doppler effect

- light phase \( \varphi_L \) chosen such that \( \overrightarrow{k} \cdot \overrightarrow{r}_n + \varphi_l = 0 \)

\[ E = -eE_0 \cos(\omega_L t) z_e \equiv H' \]

throughout derivation:
Sakurai 5.7, Cohen-Tannoudji A_{x_iii, ...}
Hamiltonian of valence e\(^{-}\) and E-field

\[
\hat{H}(\vec{r}, t) = \frac{1}{2m_e} \left[ \hat{\vec{p}} + e \hat{\vec{A}}(\vec{r}, t) \right]^2 - e\Phi(\vec{r}, t) + V(\vec{r}) - \frac{e}{m_e} \hat{\vec{S}} \cdot \hat{\vec{B}}(\vec{r}, t)
\]

\(\hat{\vec{A}}\)  vector potential

\(\Phi\)  scalar potential

\(V\)  Coulomb potential of nucleus and inner electrons on valence electron

\(-e\)  electron charge

\(m_e\)  electron mass

\(\hat{\vec{S}}\)  electron spin operator

See Sakurai "Advanced Quantum Mechanics", section 3.2 for deeper insights.
Dipole approximation

\[ \hat{H}(\vec{r}, t) = \frac{1}{2m_e} \left[ \frac{\hat{p}}{p} + e\vec{A}(\vec{r}, t) \right]^2 - e\Phi(\vec{r}, t) + V(r) - \frac{e}{m_e} \vec{S} \cdot \vec{B}(\vec{r}, t) \]

Calculation steps and approximations

- Find gauge of EM field that simplifies Hamiltonian.
- Show that terms \( \propto \vec{A}^2 \) can be neglected.
- Show that interaction between electron magnetic moment and B field can be neglected.
- Note that spatial extend of electron wavefunction much smaller than wavelength of transition.

  Typical diameter of atom: < 1 nm
  Typical wavelength of atomic transition: several 100 nm

EM field that electron experiences can be approximated by the field at the location of the nucleus.

Replace \( \vec{A}(\vec{r}, t) \) and \( \Phi(\vec{r}, t) \) by \( \vec{A}(\vec{0}, t) \) and \( \Phi(\vec{0}, t) \).

Result

\[ \hat{H} = \hat{H}_{\text{at}} + \hat{H}_{\text{int}} \]
\[ \hat{H}_{\text{at}} = \frac{\hat{p}^2}{2m} + V(r) \]
\[ \hat{H}_{\text{int}} = -e \vec{E}(\vec{r} = \vec{0}, t) \cdot \vec{r} = -eE_0 \cos(\omega_L t + \varphi_L) \hat{x} \]
Two-level approximation

Atoms have many internal states.

At energy $E_3$, states are barely populated during the dynamics and can be neglected.

Proof: transition probability spectrum of sine-perturbation

We assume that atom initially in state $|g\rangle$ or $|e\rangle$.

We want to describe transitions between states by light with frequency $\omega_L \sim \omega_0$.

States besides $|e\rangle$ and $|g\rangle$ are barely populated during the dynamics and can be neglected.

Proof: transition probability spectrum of sine-perturbation
Atom-light interaction

Summary:

\[ \hbar \delta = \hbar (\omega_L - \omega_0) \]

\[ \hbar \omega_L \]

\[ \hbar \omega_0 = E_e - E_g \]

\[ E_e \]

\[ E_g \]

\[ H = H^0 + H'(t) \]

\[ H'(t) = -eE_0 \cos(\omega_L t) z_e \]

\[ H^0 |i\rangle = E_i |i\rangle \quad ; \quad \langle i | j \rangle = \delta_{ij} \quad ; \quad i, j \in \{g, e\} \]

Compare to calculation „Sinuosidal perturbation“
Sinusoidal perturbation

\[ H = H^0 + H'(t) \]

Static \( \int \) \quad Small time-dependent perturbation \( H'(t) = V \cos(\omega t) \)

Initial condition: system in ground state \( c_a(0) = 1 \), \( c_b(0) = 0 \)

Iteratively solve \( \dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \); \( \dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a \)

First Order: \( H'_{ij}(t) \equiv V_{ij} \cos(\omega t) \)

\[ c_a(t) \approx 1 \]

\[ c_b(t) \approx -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t') e^{i\omega_0 t'} dt' = -\frac{i V_{ba}}{2\hbar} \int_0^t \left[ e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'} \right] dt' \]

\[ = -\frac{V_{ba}}{2\hbar} \left[ \frac{e^{i(\omega_0+\omega)t/2} - 1}{\omega_0+\omega} + \frac{e^{i(\omega_0-\omega)t/2} - 1}{\omega_0-\omega} \right] \]

Simplifying assumption: \( \omega_0 + \omega \gg |\omega_0 - \omega| = |\delta| \), i.e. detuning small compared to transition frequency

\[ c_b(t) \approx -\frac{V_{ba}}{2\hbar} \frac{e^{i(\omega_0-\omega)t/2}}{\omega_0-\omega} \left[ e^{i(\omega_0-\omega)t/2} - e^{-i(\omega_0-\omega)t/2} \right] \]

\[ = -i \frac{V_{ba}}{\hbar} \frac{\sin[(\omega_0-\omega)t/2]}{\omega_0-\omega} e^{i(\omega_0-\omega)t/2} \]
Summary:

\[ H = H^0 + H'(t) \]

\[ H'(t) = -e E_0 \cos(\omega_L t) z_e \]

\[ H^0 |i\rangle = E_i |i\rangle \quad ; \quad \langle i | j \rangle = \delta_{ij} \quad ; \quad i, j \in \{g, e\} \]

Compare to calculation „Sinuosidal perturbation“

\[ \rightarrow V_{ab} = -\mathcal{M} E_0 \quad \text{with „transition dipole moment“} \quad \mathcal{M} \equiv e \langle e | z_e | g \rangle \]

Perturbation theory transition probability (valid if \( P \ll 1 \))

Atom starts in \(|g\rangle\). Probability of transition to \(|e\rangle\):

\[ P_{g \rightarrow e}(t) \approx \left( \frac{\mathcal{M} E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{((\omega_0 - \omega_L)^2} \]
Transition probability

\[ P_{a \rightarrow b}(t) = |c_b(t)|^2 \approx \left| \frac{V_{ba}}{\hbar^2} \right|^2 \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \]

\[ \left| \frac{V_{ba}}{\hbar^2} \right|^2 \ll 1 \] for perturbation theory to be valid

Spectrum:

\[ P(t) \left( \frac{|V_{ba}|^2}{\hbar^2} \right) \]

Probability to be in \( |\Psi_b\rangle \) higher if detuning \( \delta \) small.
Resonance becomes narrower and higher over time.

Rescaling collapses resonances for all times on one graph:
Basic atom-light interaction processes

Absorption

\[ |g\rangle \quad \xrightarrow{\text{resonant light beam populated by}} \quad |e\rangle \]

N photons
atom absorbs photon from light mode
N-1 photons
momentum conservation lets atom absorb photon momentum, i.e.
atom accelerates in direction of light

Probability

\[ P(\omega) \]

\[ (\omega_0 - 2\pi/t) \quad (\omega_0 + 2\pi/t) \]
Summary:

\[ E_e \quad \delta = \hbar \omega_L - \hbar \omega_0 \quad \left\langle e \right\rangle \]

\[ E_g \quad \hbar \omega_0 = E_e - E_g \quad \left\langle g \right\rangle \]

\[ H = H^0 + H'(t) \]

\[ H'(t) = -eE_0 \cos(\omega_L t) z_e \]

\[ H^0 \left| i \right\rangle = E_i \left| i \right\rangle \quad ; \quad \left\langle i \mid j \right\rangle = \delta_{ij} \quad ; \quad i, j \in \{g, e\} \]

Compare to calculation „Sinuosidal perturbation“

\[ \rightarrow \quad V_{ab} = -\mathcal{Q} E_0 \quad \text{with „transition dipole moment“} \quad \mathcal{Q} \equiv e \left\langle e \mid z_e \mid g \right\rangle \]

Perturbation theory transition probability \( (\text{valid if } P \ll 1) \)

Atom starts in \( \left| g \right\rangle \). Probability of transition to \( \left| e \right\rangle \): \( P_{g \rightarrow e}(t) \approx \left( \frac{\mathcal{Q} E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2} \)

Atom starts in \( \left| e \right\rangle \). Probability of transition to \( \left| g \right\rangle \): \( P_{e \rightarrow g}(t) \approx \left( \frac{\mathcal{Q} E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2} \)
Stimulated emission

Stimulated emission

N photons
resonant light beam populated by N photons incident on excited-state atom
atom emits photon into light mode
momentum conservation lets atom recoil in direction opposite to photon momentum, i.e. opposite to light direction

\( P(\omega) \)
emission probability

\( (\omega_0 - 2\pi/t) \quad \omega_0 \quad (\omega_0 + 2\pi/t) \)
Rabi oscillations

The figure shows a graph of $P(t)$ versus $t$, with oscillations that indicate absorption and emission dominance at different times. The mathematical expression for the oscillations includes terms involving $V_{ab}$, $\hbar$, $\omega_0$, and $\omega$.
Meet the players

Atom

\[ |e \rangle \quad |g \rangle \]

Laser beam

EM field modes
In a finite volume (e.g. a hollow metal cube) only discrete modes of the EM field possible.

Hollow metal cube with volume $V = l^3$
E-field zero at wall

Eigenmodes: standing waves

$$\overrightarrow{E} = \overrightarrow{E}_0 \sin \left( \frac{n_x \pi x}{l} \right) \sin \left( \frac{n_y \pi y}{l} \right) \sin \left( \frac{n_z \pi z}{l} \right) \sin (\omega t)$$

Example shown:
red lines symbolize sine term along respective direction
$n_x = n_y = 1$ and $n_z = 8$

Two polarizations $\overrightarrow{E}_{1,2}$:
e.g. linear with $\overrightarrow{E}_{1,2} \perp \overrightarrow{k}$ and $\overrightarrow{E}_1 \perp \overrightarrow{E}_2$

Each mode can be populated with $n = 0 \ldots \infty$ photons.

The energy of each mode is $E = \left( \frac{1}{2} + n \right) \hbar \omega$ (just like harmonic oscillator)

\[\text{quantum fluctuations of vacuum}\]

The electromagnetic vacuum $|0\rangle$ consists of these modes in their groundstate, $n = 0$ for every mode.
Spontaneous emission is stimulated emission driven by vacuum fluctuations of EM field modes.

Momentum conservation lets atom recoil in direction opposite to photon momentum.
Quantum mechanics 3
Structure of matter
Lecture 14

Piet Mulders
Florian Schreck
University of Amsterdam
Overview of course

Part 1: 7 lectures in January  (Piet Mulders)
- Basics of quantum mechanics
- Spin states
- Addition of angular momentum
- Identical particles
- Basic structure of atom

Part 2: 7 lectures in February and March  (Florian Schreck)
- Structure of atoms & the periodic table
- Crystalline solids
- Time-independent perturbation theory
- Structure of hydrogen
- Variational principle
- Time-dependent perturbation theory, atom-light interaction

Lecture notes, problem sets and link to video recordings of C0.110 lectures available on Canvas

Questions: schreck@StrontiumBEC.com
Overview of „Time-dependent perturbation theory“

**Goal of this section**

Describe the reaction of a system to a time-dependent perturbation, especially absorption and emission of photons by atoms.

**Plan of this section**

1) Introduction

2) Two-level system with time-dependent $H$
   - time-dependent perturbation theory
   - sinuosidal perturbation

3) Emission and absorption of radiation
   - absorption, stimulated emission, spontaneous emission
   - spontaneous emission
     - incoherent perturbation
     - Einstein's A and B coefficients
     - lifetime of excited state
     - selection rules

4) Fermi's golden rule
Atom-light interaction

Summary:

\[ E_e \quad \Downarrow \quad \hbar \delta = \hbar \omega_L - \hbar \omega_0 \]

\[ E_g \quad \Downarrow \quad \hbar \omega_0 = E_e - E_g \]

\[ H = H^0 + H'(t) \]

\[ H'(t) = -eE_0 \cos(\omega_L t) z_e \]

\[ H^0 |i\rangle = E_i |i\rangle \quad ; \quad \langle i | j \rangle = \delta_{ij} \quad ; \quad i, j \in \{ g, e \} \]

Compare to calculation „Sinuosidal perturbation“

\[ \rightarrow V_{ab} = -\varpi E_0 \quad \text{with „transition dipole moment“} \quad \varpi \equiv e \langle e | z_e | g \rangle \]

Perturbation theory transition probability \( (\text{valid if } P \ll 1) \)

Atom starts in \( |g\rangle \). Probability of transition to \( |e\rangle \):

\[ P_{g\rightarrow e}(t) \approx \left( \frac{\varpi E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0-\omega_L)t/2]}{(\omega_0-\omega_L)^2} \]

Atom starts in \( |e\rangle \). Probability of transition to \( |g\rangle \):

\[ P_{e\rightarrow g}(t) \approx \left( \frac{\varpi E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0-\omega_L)t/2]}{(\omega_0-\omega_L)^2} \]
Basic atom-light interaction processes

Absorption

\[ \hbar \vec{k} \quad \langle g \rangle \quad \rightarrow \quad \langle e \rangle \quad \hbar \vec{k} \]

Stimulated emission

\[ \hbar \vec{k} \quad \langle e \rangle \quad \rightarrow \quad \langle g \rangle \quad \hbar \vec{k} \]

Spontaneous emission

\[ \hbar \vec{k} \quad \langle e \rangle \quad \rightarrow \quad \langle g \rangle \quad \hbar \vec{k} \]
Laser amplifier

LASER: Light Amplification by Stimulated Emission of Radiation

gain medium full of excited two-level systems
stimulated emission leads to increase of photon number in light beam

Excited two-level systems are created
- optically („optical pumping“)
- electronically (laser diode)
- chemically (excimer laser)

Optical pumping

optical pumping transition
fast, spontaneous decay
stimulated emission „lasing“
driven by flash lamp, LED, laser
LASER: Light Amplification by Stimulated Emission of Radiation

- Laser beam
- Optical resonator (=cavity) around gain medium
- Gain medium full of excited two-level systems
- Stimulated emission leads to increase of photon number in light beam
- Photons travel many times forwards and backwards, each time leading to amplification by spontaneous emission
- Lasing process starts by spontaneous emission
- Lasing only possible on modes of the electromagnetic field that are resonant with cavity

Small fraction of in-cavity light transmitted by "outcoupling" mirror
Laser diode

- Lens
- Junction
- n-type
- p-type
- Light emerges from polished end
- -ve terminal
- +ve terminal

Bonus material
Light-emitting Diode (LED)

Placing n-doped and p-doped semiconductor next to each other leads to one-way conductor for current. Light can be emitted at interface.

Current flows if voltage connected as shown.

In LEDs energy of electron combining with hole liberated as photon.
Laser diode

Laser diode components:
- Lens
- Junction
- n-type
- p-type
- Light emerges from polished end
- -ve terminal
- +ve terminal

Diagram showing:
- Laser diode
- Heat sink
- Protective can
- Window
- Monitor photodiode

Bonus material

Images from:
- visiblelasers.com
- newport.com
- wikipedia.com

www.explainthatstuff.com
Red laser pointer

![Diagram of a red laser pointer showing battery, LD driver, and LD module.](http://repairfaq.cis.upenn.edu/sam/laserpic/glpdpics.htm)
Green laser pointer

Edmund Scientific L54-101 Green DPSS Laser Pointer
Components of green laser pointer
20W frequency doubled Nd:YAG laser

Coherent Verdi DPSS Laser Cavity with Components Labeled
Overview of “Time-dependent perturbation theory”

Goal of this section

Describe the reaction of a system to a time-dependent perturbation, especially absorption and emission of photons by atoms.

Plan of this section

1) Introduction
   
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   - time-dependent perturbation theory
   - sinuosidal perturbation
   
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   - absorption, stimulated emission, spontaneous emission
   - spontaneous emission
   - incoherent perturbation
   - Einstein’s A and B coefficients
   - lifetime of excited state
   - selection rules
   
4) Fermi’s golden rule

Griffiths 3rd 11.0

11.1

11.2 - 3
Spontaneous emission limits lifetime of $|e\rangle$

Goals:

Understand spontaneous emission better.
Derive lifetime of excited state.

An atom would stay forever in excited state if truly undisturbed, i.e. even no vacuum fluctuations.

In reality atom decays by spontaneous emission driven by vacuum fluctuations.

Vacuum fluctuations happen in each electromagnetic field mode, not just one.

Need to calculate transition probability of atom in such an electromagnetic field, an incoherent field.
Incoherent perturbation

So far: coherent, monochromatic, electromagnetic plane wave

Energy density: \[ u = \frac{\varepsilon_0}{2} E_0^2 \]

Energy density in range \( d\omega \) is \( \rho(\omega)d\omega \)
Atom-light interaction

Summary:

\[ H = H^0 + H'(t) \]

\[ H'(t) = -eE_0 \cos(\omega_L t) z_e \]

\[ H^0 |i\rangle = E_i |i\rangle \quad ; \quad \langle i | j \rangle = \delta_{ij} \quad ; \quad i, j \in \{g, e\} \]

Compare to calculation "Sinuosidal perturbation"

\[ V_{ab} = -\zeta \bar{E}_0 \quad \text{with "transition dipole moment"} \quad \zeta \equiv e \langle e | z_e | g \rangle \]

Perturbation theory transition probability \( \text{(valid if } P \ll 1) \)

Atom starts in \(|g\rangle\). Probability of transition to \(|e\rangle\):

\[ P_{g\rightarrow e}(t) \approx \left( \frac{\zeta |\bar{E}_0|}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2} \]

Atom starts in \(|e\rangle\). Probability of transition to \(|g\rangle\):

\[ P_{e\rightarrow g}(t) \approx \left( \frac{\zeta |\bar{E}_0|}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2} \]
Incoherent perturbation

So far: coherent, monochromatic, electromagnetic plane wave

Energy density: \[ u = \frac{\varepsilon_0}{2} E_0^2 \]

Transition probability, expressed using energy density:

\[ P_{e \to g}(t) = \frac{2u}{\varepsilon_0 \hbar^2} |\phi|^2 \int_0^{\infty} \rho(\omega) \left\{ \frac{\sin^2[(\omega_0-\omega_L)t/2]}{(\omega_0-\omega_L)^2} \right\} d\omega \]

Incoherent electromagnetic wave:

\[ P_{e \to g}(t) = \frac{2}{\varepsilon_0 \hbar^2} |\phi|^2 \int_0^{\infty} \rho(\omega) \left\{ \frac{\sin^2[(\omega_0-\omega_L)t/2]}{(\omega_0-\omega_L)^2} \right\} d\omega \]

\[ = \frac{2}{\varepsilon_0 \hbar^2} |\phi|^2 \rho(\omega_0) \int_0^{\infty} \frac{\sin^2[(\omega_0-\omega_L)t/2]}{(\omega_0-\omega_L)^2} d\omega \]

\[ \approx \frac{\pi |\phi|^2}{\varepsilon_0 \hbar^2} \rho(\omega_0) t \]

Transition rate:

\[ R_{e \to g}(t) \equiv \frac{dP_{e \to g}(t)}{dt} = \frac{\pi}{\varepsilon_0 \hbar^2} |\phi|^2 \rho(\omega_0) \]

energy density in range \( d\omega \) is \( \rho(\omega) d\omega \)

atom absorbs resonantly around \( \omega_0 \)

\[ \rho(\omega) \]

\[ \rho(\omega_0) \]

known (electromagnetism or deduced from Boltzmann formula, see later)

to calculate
Radiation from all directions, with all polarizations

Transition rate:

\[ R_{e \rightarrow g}(t) \equiv \frac{dP_{e \rightarrow g}(t)}{dt} = \frac{\pi}{\varepsilon_0 \hbar^2} |\varphi|^2 \rho(\omega_0) \]

So far: single plane wave, polarized along \( z \) direction

\[ |\varphi|^2 \text{ calculated with } \varphi = e \langle e | z_e | g \rangle ; \ V_{ge} = -\varphi E_0 ; \ H'_{eg}(t) = V_{eg} \cos(\omega t) \]

Now: radiation from all directions, all polarization directions per mode

Todo: Average over \( |\varphi|^2 \) calculated for all directions and polarizations

First: Generalize \( |\varphi|^2 \) to one wave with wavevector \( \vec{k} \) and polarization direction \( \hat{n} \).

i.e. repeat calculation „sinusoidal perturbation“, but keep polarization general.

Perturbation \( H'(t) = -e \vec{r} \cdot \vec{E}_L(\vec{r}, t) \)
Electric dipole transitions

E-field of light acting on charge of electron

E-field of monochromatic, linearly polarized plane wave:

\[ \vec{E}_L(\vec{r}, t) = \vec{E}_0 \cos \left( \vec{k} \cdot \vec{r} - \omega_L t + \varphi_l \right) \]

Force on electron

\[ \vec{F} = -\vec{E}_0 e \]

(Force on nucleus has negligible effect since nucleus is much heavier than electron.)

Time-dependent perturbation

\[ E = -e \vec{r}_e \cdot \vec{E}_L(\vec{r}_e, t) \]

valence electron position

Simplifications:

- Wavelength of light much larger than size of atom
  (blue: 400 nm, red: 700 nm; Bohr radius: 0.05 nm)

  \[ \rightarrow \text{E-field homogeneous across atom} \]

  \[ \vec{E}_L(\vec{r}, t) \sim \vec{E}_L(\vec{r}_n, t) \]

- Chose z-axis parallel to E-field polarization

- Atom position fixed in space during transition

  \[ \rightarrow \text{no Doppler effect} \]

- Light phase \( \varphi_L \) chosen such that \( \vec{k} \cdot \vec{r}_n + \varphi_l = 0 \)

Energy

\[ E = -eE_0 \cos (\omega_L t) \approx H' \]

thorough derivation: Sakurai 5.7, Cohen-Tannoudji A_{XIII}...
Radiation from all directions, with all polarizations

Transition rate:

\[ R_{e\rightarrow g}(t) \equiv \frac{dP_{e\rightarrow g}(t)}{dt} = \frac{\pi}{\varepsilon_0 h^2} |\mathcal{O}|^2 \rho(\omega_0) \]

So far: single plane wave, polarized along \( z \) direction

\[ |\mathcal{O}|^2 \text{ calculated with } \mathcal{O} = e \langle e | z_e | g \rangle ; \quad V_{ge} = -\mathcal{O} E_0 ; \quad H'_{eg}(t) = V_{eg} \cos(\omega t) \]

Now: radiation from all directions, all polarization directions per mode

Todo: Average over \( |\mathcal{O}|^2 \) calculated for all directions and polarizations

First: Generalize \( |\mathcal{O}|^2 \) to one wave with wavevector \( \overrightarrow{k} \) and polarization direction \( \hat{n} \).

i.e. repeat calculation „sinusoidal perturbation“, but keep polarization general.

Perturbation

\[ H'(t) = -e \overrightarrow{r}_e \cdot \overrightarrow{E}_L(\overrightarrow{r}_e, t) = -e \overrightarrow{r}_e \cdot \hat{n} E_0 \cos(\omega_L t) \]

Note: direction of light \( \overrightarrow{k} \) doesn’t influence atom-light interaction, only polarization \( \hat{n} \) does.

Perturbation matrix element \( V_{ge} \), keeping in mind \( H'_{eg}(t) = V_{eg} \cos(\omega t) \):

\[ V_{ge} = -\mathcal{O} \cdot \hat{n} E_0 \quad \text{with} \quad \mathcal{O} \equiv e \langle e | \overrightarrow{r}_e | g \rangle \]
Sinusoidal perturbation

\[ H = H^0 + H'(t) \]

Static \( \int \) \text{ small} time-dependent perturbation \( H'(t) = V \cos(\omega t) \)

Initial condition: system in ground state \( c_a(0) = 1 \), \( c_b(0) = 0 \)

Iteratively solve
\[
\begin{align*}
\dot{c}_a &= -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \\
\dot{c}_b &= -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a
\end{align*}
\]

First Order:
\[ H'_{ij}(t) \equiv V_{ij} \cos(\omega t) \]

\[ c_a(t) \cong 1 \]

\[ c_b(t) \cong -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t') e^{i\omega_0 t'} dt' = -\frac{iV_{ba}}{2\hbar} \int_0^t \left[ e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'} \right] dt' \]

\[ = -\frac{V_{ba}}{2\hbar} \left[ \frac{e^{i(\omega_0+\omega)t} - 1}{i(\omega_0+\omega)} + \frac{e^{i(\omega_0-\omega)t} - 1}{i(\omega_0-\omega)} \right] \]

Simplifying assumption: \( \omega_0 + \omega \gg |\omega_0 - \omega| = |\delta| \), i.e. detuning small compared to transition frequency

\[ c_b(t) \cong -\frac{V_{ba}}{2\hbar} \frac{e^{i(\omega_0-\omega)t/2}}{\omega_0-\omega} \left[ e^{i(\omega_0-\omega)t/2} - e^{-i(\omega_0-\omega)t/2} \right] \]

\[ = -i \frac{V_{ba}}{\hbar} \frac{\sin[(\omega_0-\omega)t/2]}{\omega_0-\omega} e^{i(\omega_0-\omega)t/2} \]
Radiation from all directions, with all polarizations

Transition rate:

\[ R_{e\rightarrow g}(t) \equiv \frac{dP_{e\rightarrow g}(t)}{dt} = \frac{\pi}{\epsilon_0 c \hbar^2} |\mathcal{A}|^2 \rho(\omega_0) \]

**So far:** single plane wave, polarized along \( z \) direction

|\( \mathcal{A}^2 \) calculated with | \( \mathcal{A} = e \langle e | z_e | g \rangle \); \( V_{ge} = -\mathcal{A} E_0 \); \( H'_{eg}(t) = V_{eg} \cos(\omega t) \)

**Now:** radiation from all directions, all polarization directions per mode

**Todo:** Average over |\( \mathcal{A}^2 \) calculated for all directions and polarizations

**First:** Generalize |\( \mathcal{A}^2 \) to one wave with wavevector \( \hat{k} \) and polarization direction \( \hat{n} \).

i.e. repeat calculation „sinusoidal perturbation“, but keep polarization general.

Perturbation

\[ H'(t) = -e \vec{r}_e \cdot \vec{E}_L(\vec{r}_e, t) = -e \vec{r}_e \cdot \hat{n} E_0 \cos(\omega_L t) \]

Note: direction of light \( \vec{k} \) doesn’t influence atom-light interaction, only polarization \( \hat{n} \) does.

Perturbation matrix element \( V_{ge} \), keeping in mind \( H'_{ij}(t) \equiv V_{ij} \cos(\omega t) \):

\[ V_{ge} = -\mathcal{A} \cdot \hat{n} E_0 \quad \text{with} \quad \mathcal{A} \equiv e \langle e | \vec{r}_e | g \rangle \]

**Next:** Average over |\( \mathcal{A} \cdot \hat{n} \)² calculated for all directions and all polarizations
Radiation from all directions, with all polarizations

Next: Average over $|\vec{\mathcal{E}} \cdot \hat{n}|^2$ calculated for all directions and all polarizations

\[ \vec{\mathcal{E}} \cdot \hat{n} = \mathcal{E} \cos \theta \]

Hold $\vec{\mathcal{E}}$ fixed and average over all orientations $\vec{k}$ and $\hat{n}$ with $\vec{k} \perp \hat{n}$. Equivalent to holding $\vec{k}$ and $\hat{n}$ fixed as in figure and averaging over all $\vec{\mathcal{E}}$.

\[
|\vec{\mathcal{E}} \cdot \hat{n}|^2_{\text{average}} = \frac{1}{4\pi} \int |\mathcal{E}|^2 \cos^2 \theta \sin \theta d\theta d\phi
\]

\[
= \frac{|\mathcal{E}|^2}{4\pi} \left( -\frac{\cos^3 \theta}{3} \right) \bigg|_0^\pi (2\pi) = \frac{1}{3} |\mathcal{E}|^2
\]

Final result: transition rate

\[
R_{e\rightarrow g}(t) = \frac{\pi}{3\varepsilon_0 \hbar^2} |\mathcal{E}|^2 \rho(\omega_0)
\]
Incoherent perturbation

Energy density of monochromatic, electromagnetic plane wave:

\[ u = \frac{\varepsilon_0}{2} E_0^2 \]

Transition probability:

\[ P_{e \rightarrow g}(t) = \frac{2u}{\varepsilon_0 \hbar^2} |\varphi|^2 \int_0^\infty \rho(\omega) \left[ \frac{\sin^2 \left( (\omega_0 - \omega_L) t/2 \right)}{(\omega_0 - \omega_L)^2} \right] d\omega \]

Incoherent electromagnetic wave:

\[ P_{e \rightarrow g}(t) = \frac{2}{\varepsilon_0 \hbar^2} |\varphi|^2 \int_0^\infty \rho(\omega) \left[ \frac{\sin^2 \left( (\omega_0 - \omega_L) t/2 \right)}{(\omega_0 - \omega_L)^2} \right] d\omega \]

\[ = \frac{2}{\varepsilon_0 \hbar^2} |\varphi|^2 \rho(\omega_0) \int_0^\infty \frac{\sin^2 \left( (\omega_0 - \omega_L) t/2 \right)}{(\omega_0 - \omega_L)^2} d\omega \]

\[ = \frac{\pi |\varphi|^2}{\varepsilon_0 \hbar^2} \rho(\omega_0) t \]

Transition rate:

\[ R_{e \rightarrow g}(t) \equiv \frac{dP_{e \rightarrow g}(t)}{dt} = \frac{\pi}{\varepsilon_0 \hbar^2} |\varphi|^2 \rho(\omega_0) \]

\[ \rho(\omega) \]

energy density in range \( d\omega \) is \( \rho(\omega)d\omega \)

atom absorbs resonantly around \( \omega_0 \)

\[ \rho(\omega_0) \]

\[ \rho(\omega) \]

known (electromagnetism or deduced from Boltzmann formula, now)
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Goal of this section

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1) Introduction
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   - time-dependent perturbation theory
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   - spontaneous emission
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     - lifetime of excited state
     - selection rules
4) Fermi's golden rule

Griffiths 3rd 11.0
11.1 11.2 - 3
Spontaneous emission rate after Einstein

Goal: derive spontaneous emission rate

Einstein’s derivation from 1917, before quantum mechanics. Quantization enters via Planck’s blackbody formula from 1900.

Consider box filled with blackbody radiation and two-level systems.

\[ \frac{dN_b}{dt} = -N_b A - N_b B_{ba} \rho(\omega_0) \]

- spontaneous emission
- stimulated emission

\[ B_{ba} = \frac{\pi |\Phi|^2}{3\varepsilon_0 \hbar^2} \]

\[ N_a \] two-level systems in lower state \( |a\rangle \)

\[ N_b \] two-level systems in upper state \( |b\rangle \)
Radiation from all directions, with all polarizations

Next: Average over $|\vec{\Phi} \cdot \hat{n}|^2$ calculated for all directions and all polarizations

Hold $\vec{\Phi}$ fixed and average over all orientations $\vec{k}$ and $\hat{n}$ with $\vec{k} \perp \hat{n}$. Equivalent to holding $\vec{k}$ and $\hat{n}$ fixed as in figure and averaging over all $\vec{\Phi}$.

$$|\vec{\Phi} \cdot \hat{n}|^2 = \Phi \cos \theta$$

$$\frac{1}{4\pi} \int |\Phi|^2 \cos^2 \theta \sin \theta d\theta d\phi$$

$$= \frac{|\Phi|^2}{4\pi} \left( -\frac{\cos^3 \theta}{3} \right) \bigg|_0^\pi (2\pi) = \frac{1}{3} |\Phi|^2$$

factor 1/3 different from before.

Final result: transition rate

$$R_{e\rightarrow g}(t) = \frac{\pi}{3\epsilon_0 \hbar^2} |\Phi|^2 \rho(\omega_0)$$
Spontaneous emission rate after Einstein

**Goal:** derive spontaneous emission rate

Einstein’s derivation from 1917, before quantum mechanics. Quantization enters via Planck’s blackbody equation from 1900.

Consider box filled with blackbody radiation and two-level systems.

\( N_a \) two-level systems in lower state \( |a\rangle \)
\( N_b \) two-level systems in upper state \( |b\rangle \)

Change of number of two-level systems in upper state:

\[
\frac{dN_b}{dt} = -N_b A
\]

spontaneous emission

\[-N_b B_{ba} \rho(\omega_0)\]

stimulated emission

\[+N_a B_{ab} \rho(\omega_0)\]

stimulated absorption

\[
B_{ba} = \frac{\pi|\Phi|^2}{3\varepsilon_0 \hbar^2}
\]

In equilibrium:

\[
\frac{dN_b}{dt} = 0
\]

\[
\rho(\omega_0) = \frac{A}{(N_a/N_b)B_{ab} - B_{ba}}
\]
Spontaneous emission rate after Einstein

Goal: derive spontaneous emission rate

Einstein’s derivation from 1917, before quantum mechanics. Quantization enters via Planck’s blackbody equation from 1900.

\[ \rho(\omega_0) = \frac{A}{(N_a/N_b)B_{ab} - B_{ba}} \]

From statistical mechanics we know that occupation proportional to Boltzmann factor \( e^{-E/k_BT} \):

\[ \frac{N_a}{N_b} = \frac{e^{-E_a/k_BT}}{e^{-E_b/k_BT}} = e^{\hbar\omega_0/k_BT} \]

\[ \rho(\omega_0) = \frac{A}{e^{\hbar\omega_0/k_BT}B_{ab} - B_{ba}} \]

Compare to Planck’s blackbody formula, which also gives energy density of thermal radiation \( \rho(\omega) \):

\[ \rho(\omega) = \frac{\hbar}{\pi^2c^3} \frac{\omega^3}{e^{\hbar\omega/k_BT} - 1} \]

\[ B_{ba} = B_{ab} , \quad A = \frac{\omega_0^3\hbar}{\pi^2c^3} B_{ba} \]

, where we know \( B_{ba} = \frac{\pi |\Phi|^2}{3\epsilon_0\hbar^2} \)

\[ \frac{dN_b}{dt} = -AN_b \quad \text{with spontaneous emission rate} \quad A = \frac{\omega_0^3|\Phi|^2}{3\pi\epsilon_0\hbar c^3} \]

Spontaneous emission

Note: modern symbol \( \Gamma \) instead of \( A \)
Lifetime of excited state

Prepare $N_b$ emitters in state $|b\rangle$

Spontaneous emission decreases number of excited emitters over time.

Assuming emitters don’t reabsorb emitted photons (e.g. emitters are dilute and in finite volume)

$$\frac{dN_b}{dt} = -AN_b$$

Number of excited emitters over time:

$$N_b(t) = N_b(0)e^{-t/\tau} \quad \text{with} \quad \tau = 1/A$$

Rate of photon emission:

$$N_{\Gamma}(t) = AN_b(t)$$

In case there are several lower states:

$$\tau = \frac{1}{A_1 + A_2 + A_3 + \ldots}$$
Basic atom-light interaction processes

Absorption

\[ \hbar \kappa \]

\[ |g\rangle \rightarrow |e\rangle \]

\[ \hbar \kappa \]

Stimulated emission

\[ \hbar \kappa \]

\[ |e\rangle \rightarrow |g\rangle \]

\[ -\hbar \kappa \]

Spontaneous emission

\[ -\hbar \kappa \]

\[ |e\rangle \rightarrow |g\rangle \]

\[ \hbar \kappa \]

Reminder
All together now: fluorescence

Typical resonance in scattering rate

Minimum linewidth \( \Gamma = 1/\tau \)

Linewidth often broadened by
- Doppler effect
- collisions
- saturation of resonance
Overview of “Time-dependent perturbation theory“

Goal of this section

Describe the reaction of a system to a time-dependent perturbation, especially absorption and emission of photons by atoms.

Plan of this section

1) Introduction

2) Two-level system with time-dependent $H$
   - time-dependent perturbation theory
   - sinuosidal perturbation

3) Emission and absorption of radiation
   - absorption, stimulated emission, spontaneous emission
   - spontaneous emission
     - incoherent perturbation
     - Einstein's A and B coefficients
     - lifetime of excited state
   - selection rules

4) Fermi's golden rule
Selection rules

Angular momentum needs to be conserved during photon absorption and emission.

This fact limits the possible electric dipole transitions to a small fraction of all imaginable transitions in an atom or molecule.

Strength of electric dipole transition proportional to dipole matrix element:

\[ \vec{\mathcal{M}} = e \langle a | \vec{r}_e | b \rangle \]

It is often obvious from angular momentum conservation that \( \langle a | \vec{r}_e | b \rangle \) is zero, eliminating the need of a calculation.

Todo: derive rules that select which transitions are allowed by angular momentum conservation.

Consider hydrogen-like atom. Neglect fine and hyperfine structure.

Eigenstates: \( |n l m \rangle \)

\[ \langle a | \vec{r}_e | b \rangle = \langle n' l' m' | \vec{r}_e | n l m \rangle \]
Selection rules involving $m$ and $m'$

Commutators between angular momentum and position:

\[
[L_z, x] = i\hbar y, \quad [L_z, y] = -i\hbar x, \quad [L_z, z] = 0
\]

\[
[L_z, z] = 0:
0 = \langle n'l'm'|[L_z, z]|nlm\rangle = \langle n'l'm'|L_z z - z L_z|nlm\rangle = (m' - m)\hbar \langle n'l'm'|z|nlm\rangle
\]

\[\rightarrow \text{ either } m' = m \text{ or } \langle n'l'm'|z|nlm\rangle = 0\]

\[
[L_z, x] = i\hbar y:
\langle n'l'm'|[L_z, x]|nlm\rangle = (m' - m)\hbar \langle n'l'm'|x|nlm\rangle = i\hbar \langle n'l'm'|y|nlm\rangle
\]

\[
\text{Note: can calculate } \langle n'l'm'|x|nlm\rangle \text{ from } \langle n'l'm'|y|nlm\rangle
\]

\[
[L_z, y] = -i\hbar x:
\langle n'l'm'|[L_z, y]|nlm\rangle = (m' - m)\hbar \langle n'l'm'|y|nlm\rangle = -i\hbar \langle n'l'm'|x|nlm\rangle
\]

\[
(m' - m)^2 \langle n'l'm'|x|nlm\rangle = i(m' - m) \langle n'l'm'|y|nlm\rangle = \langle n'l'm'|x|nlm\rangle
\]

\[\rightarrow \text{ either } (m' - m) = 1 \text{ or } \langle n'l'm'|x|nlm\rangle = \langle n'l'm'|y|nlm\rangle = 0\]

Selection rule for $m$:

No electric dipole transitions occur unless $\Delta m = \pm 1$ or $0$.

Interpretation:

Angular momentum projection conservation under emission/absorption of photon, which has spin 1.
Selection rules involving $l$ and $l'$

Yet another commutator involving angular momentum and position:

$$\left[ L^2, \left[ L^2, \vec{r} \right] \right] = 2\hbar^2 \left( \vec{r} \cdot L^2 + L^2 \vec{r} \right)$$

(no proof here)

$$\langle n'l'm'| \left[ L^2, \left[ L^2, \vec{r} \right] \right] |nlm \rangle = 2\hbar^2 \langle n'l'm'| (\vec{r} \cdot L^2 + L^2 \vec{r}) |nlm \rangle$$

\[ \equiv \]

$$2\hbar^4[l(l + 1) + l'(l' + 1)] \langle n'l'm'| \vec{r} |nlm \rangle$$

$$\hbar^4[l'(l' + 1) - l(l + 1)]^2 \langle n'l'm'| \vec{r} |nlm \rangle$$

\[ \equiv \]

either \[ 2[l(l + 1) + l'(l' + 1)] = [l'(l' + 1) - l(l + 1)]^2 \] or \[ \langle n'l'm'| \vec{r} |nlm \rangle = 0 \]

\[ \equiv \]

equivalent (see Griffiths)

$$[(l' + l + 1)^2 - 1][(l' - l)^2 - 1] = 0$$

true if \[ \Delta l = l' - l = \pm 1 \]

(or \[ l' = l = 0 \], but then \[ \langle n'l'm'| \vec{r} |nlm \rangle = 0 \], see Griffiths)

Selection rule for $l$:

No electric dipole transitions occur unless \[ \Delta l = \pm 1 \].

Interpretation:

Angular momentum conservation under emission/absorption of photon, which has spin 1.

Note: \[ \Delta l = 0 \] would be allowed by angular momentum conservation, but isn’t for dipole transitions.
Neglecting electron and nuclear spin

\[ l = 0 \quad l = 1 \quad l = 2 \quad l = 3 \]

\[ n = 4 \quad n = 3 \quad n = 2 \quad n = 1 \]

\( \Delta l = \pm 1 \)

\( 2S \) is metastable state:
- doesn’t decay through electric dipole transition
- can decay through other processes (collisions, multiphoton emission)
$m_l$ selection rules in hydrogen

Neglecting electron and nuclear spin

$\begin{align*}
\Delta l &= \pm 1 \\
\Delta m &= 0, \pm 1
\end{align*}$
Overview of "Time-dependent perturbation theory"

Goal of this section

Describe the reaction of a system to a time-dependent perturbation, especially absorption and emission of photons by atoms.

Plan of this section

1) Introduction

2) Two-level system with time-dependent $H$
   - time-dependent perturbation theory
   - sinusoidal perturbation

3) Emission and absorption of radiation
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   - spontaneous emission
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     - selection rules

4) Fermi's golden rule
Fermi's golden rule

So far: transitions between two discrete states
Example: transition of e\(^-\) from H ground state to higher orbital

\[ E_f \quad \Downarrow \quad \Delta E \quad \Uparrow \quad E_i \]

Transition probability:
\[ P = \frac{|V_{ba}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{\omega_0 - \omega} \]

Now: transition between discrete state and continuum
Example: transition of e\(^-\) from H ground state to an unbound e\(^-\), i.e. photoionization of atom

\[ E_f \quad \Downarrow \quad \Delta E \quad \Uparrow \quad E_i \]

density of final states \( \rho(E) \)

Transition probability:
\[ P = \int_{E_f - \Delta E/2}^{E_f + \Delta E/2} \frac{|V_{in}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{\omega_0 - \omega} \rho(E_n) dE_n \]
Incoherent perturbation

Energy density of monochromatic, electromagnetic plane wave:

\[
u = \frac{\varepsilon_0}{2} E_0^2\]

Transition probability:

\[
P_{e \rightarrow g}(t) = \frac{2\nu}{\varepsilon_0 h^2} |\psi|^2 \frac{\sin^2[(\omega_0 - \omega_L) t / 2]}{(\omega_0 - \omega_L)^2}\]

Incoherent electromagnetic wave:

\[
P_{e \rightarrow g}(t) = \frac{2}{\varepsilon_0 h^2} |\psi|^2 \int_0^\infty \rho(\omega) \left\{ \frac{\sin^2[(\omega_0 - \omega_L) t / 2]}{(\omega_0 - \omega_L)^2} \right\} d\omega\]

\[
\approx \frac{2}{\varepsilon_0 h^2} |\psi|^2 \rho(\omega_0) \int_0^\infty \frac{\sin^2[(\omega_0 - \omega_L) t / 2]}{(\omega_0 - \omega_L)^2} d\omega\]

\[
\approx \frac{\pi |\psi|^2}{\varepsilon_0 h^2} \rho(\omega_0) t\]

Transition rate:

\[
R_{e \rightarrow g}(t) \equiv \frac{dP_{e \rightarrow g}(t)}{dt} = \frac{\pi}{\varepsilon_0 h^2} |\psi|^2 \rho(\omega_0)\]

Reminder

energy density in range \(d\omega\) is \(\rho(\omega) d\omega\)

atom absorbs resonantly around \(\omega_0\)

Attention

don't confuse with incoherent perturbation
Fermi’s golden rule

Now: transition between discrete state and continuum
Example: transition of $e^-$ from H ground state to an unbound $e^-$, i.e. photoionization of atom

Transition probability:

$$P = \int_{E_f - \Delta E/2}^{E_f + \Delta E/2} \frac{|V_{in}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \rho(E_n) dE_n$$

because of peak ( ):

$$\simeq \frac{|V_{if}|^2}{\hbar^2} \rho(E_f) \int_{-\infty}^{\infty} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} dE_n$$

$$= \frac{2\pi}{\hbar} \left| \frac{V_{if}}{2} \right|^2 \rho(E_f) t$$

Transition rate:

$$R = \frac{2\pi}{\hbar} \left| \frac{V_{if}}{2} \right|^2 \rho(E_f)$$

Fermi’s golden rule
Overview of "Time-dependent perturbation theory"

Goal of this section

Describe the reaction of a system to a time-dependent perturbation, especially absorption and emission of photons by atoms.

Plan of this section

1) Introduction
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     - lifetime of excited state
   - selection rules
4) Fermi's golden rule
Overview of course

Part 1: 7 lectures in January (Piet Mulders)
- Basics of quantum mechanics
- Spin states
- Addition of angular momentum
- Identical particles
- Basic structure of atom

Part 2: 7 lectures in February and March (Florian Schreck)
- Structure of atoms & the periodic table
- Crystalline solids
- Time-independent perturbation theory
- Structure of hydrogen
- Variational principle
- Time-dependent perturbation theory, atom-light interaction

Lecture notes, problem sets and link to video recordings of C0.110 lectures available on Canvas

Questions: schreck@StrontiumBEC.com
Bonus material
Overview of „Time-dependent perturbation theory“

Goal of this section

Describe the reaction of a system to a time-dependent perturbation, especially absorption and emission of photons by atoms.

Plan of this section

1) Introduction
2) Two-level systems
   - time-dependent perturbation theory
   - sinuosidal perturbation
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   - absorption, stimulated emission, spontaneous emission
   - spontaneous emission
     - incoherent perturbation
     - Einstein’s A and B coefficients
     - lifetime of excited state
   - selection rules
   - Fermi’s golden rule
Goal: calculate dynamics of two-level system under sinusoidal perturbation without perturbation theory, for arbitrary times and perturbation strengths

Let’s review what we did so far
Two level system

\[ E_b \quad \uparrow \quad |\Psi_b\rangle \]
\[ \Delta E \quad H \Psi_i = E_i \Psi_i \quad ; \quad \langle \Psi_i | \Psi_j \rangle = \delta_{ij} \quad ; \quad i, j \in \{a, b\} \]
\[ E_a \quad \downarrow \quad |\Psi_a\rangle \]

Initial state: \[ \Psi(t = 0) = c_a(0) \Psi_a + c_b(0) \Psi_b \quad |c_a(0)|^2 + |c_b(0)|^2 = 1 \]

Later state: (solution of \[ H \Psi = i\hbar \frac{\partial \Psi}{\partial t} \])

Time-independent \[ H = H^0 \]
\[ \Psi(t) = c_a(0)e^{-iE_a t/\hbar} \Psi_a + c_b(0)e^{-iE_b t/\hbar} \Psi_b \]

Time-dependent \[ H = H^0 + H'(t) \]
\[ \Psi(t) = c_a(t)e^{-iE_a t/\hbar} \Psi_a + c_b(t)e^{-iE_b t/\hbar} \Psi_b \quad |c_a(t)|^2 + |c_b(t)|^2 = 1 \]

**Task:** (approximately) find \( c_a(t) \) and \( c_b(t) \)
Perturbed system

\[ H = H^0 + H'(t) \]

\[ \text{static} \quad \text{time-dependent perturbation (not necessarily small)} \]

Solve \( H \Psi = i\hbar \frac{\partial \Psi}{\partial t} \) with ansatz \( \Psi(t) = c_a(t)e^{-iE_at/\hbar}\Psi_a + c_b(t)e^{-iE_bt/\hbar}\Psi_b \)

\[
c_a[H^0\Psi_a]e^{-iE_at/\hbar} + c_b[H^0\Psi_b]e^{-iE_bt/\hbar} + c_a[H'\Psi_a]e^{-iE_at/\hbar} + c_b[H'\Psi_b]e^{-iE_bt/\hbar} = i\hbar \left[ \dot{c}_a \Psi_a e^{-iE_at/\hbar} + \dot{c}_b \Psi_b e^{-iE_bt/\hbar} + c_a \Psi_a \left( -\frac{iE_at}{\hbar} \right) e^{-iE_at/\hbar} + c_b \Psi_b \left( -\frac{iE_bt}{\hbar} \right) e^{-iE_bt/\hbar} \right]
\]

\[
c_a[H'\Psi_a]e^{-iE_at/\hbar} + c_b[H'\Psi_b]e^{-iE_bt/\hbar} = i\hbar \left[ \dot{c}_a \Psi_a e^{-iE_at/\hbar} + \dot{c}_b \Psi_b e^{-iE_bt/\hbar} \right]
\]

\[
\langle \Psi_a | : \quad c_a \langle \Psi_a | H' | \Psi_a \rangle e^{-iE_at/\hbar} + c_b \langle \Psi_b | H' | \Psi_b \rangle e^{-iE bt/\hbar} = i\hbar \dot{c}_a e^{-iE_at/\hbar}
\]

\[
H_{ij} = \langle \Psi_i | H' | \Psi_j \rangle : \quad \dot{c}_a = -\frac{i}{\hbar} \left[ c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b-E_a)t/\hbar} \right]
\]

\[
\langle \Psi_b | : \quad \dot{c}_b = -\frac{i}{\hbar} \left[ c_a H'_{ba} e^{i(E_b-E_a)t/\hbar} + c_b H'_{bb} \right]
\]

Matrix notation:
\[
i\hbar \frac{\partial}{\partial t} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = \begin{pmatrix} H'_{aa} & H'_{ab} e^{-i(E_b-E_a)t/\hbar} \\ H'_{ba} e^{i(E_b-E_a)t/\hbar} & H'_{bb} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix}
\]
Perturbed system

\[ H = H^0 + H'(t) \]

- time-dependent perturbation (not necessarily small)
- static

Solve \[ H \Psi = i\hbar \frac{\partial \Psi}{\partial t} \] with ansatz \[ \Psi(t) = c_a(t)e^{-iE_a t/\hbar}\Psi_a + c_b(t)e^{-iE_b t/\hbar}\Psi_b \]

\[
\dot{c}_a = -\frac{i}{\hbar} \left[ c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar} \right]
\]

\[
\dot{c}_b = -\frac{i}{\hbar} \left[ c_a H'_{ba} e^{i(E_b - E_a)t/\hbar} + c_b H'_{bb} \right]
\]

Often \[ H'_{aa} = H'_{bb} = 0 \] :

\[
\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \quad \text{with} \quad \omega_0 = \frac{E_b - E_a}{\hbar}
\]

\[
\dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a
\]
Time-dependent perturbation theory

\[ H = H^0 + H'(t) \]

static \(\square\) small time-dependent perturbation

Initial condition: system in ground state \( c_a(0) = 1 \), \( c_b(0) = 0 \)

Iteratively solve

\[ \dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \]
\[ \dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a \]

Zeroth Order: \( (H' = 0) \)

\[ c_a^{(0)}(t) = 1 \quad , \quad c_b^{(0)}(t) = 0 \]

First Order:

\[ \dot{c}_a^{(1)} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b^{(0)} = 0 \quad \Rightarrow \quad c_a^{(1)}(t) = 1 \]
\[ \dot{c}_b^{(1)} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a^{(0)} \quad \Rightarrow \quad c_b^{(1)}(t) = -\frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \]

Second Order:

\[ \dot{c}_a^{(2)} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} \left( -\frac{i}{\hbar} \right) \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \]
\[ \Rightarrow \quad c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2} \int_0^t H'_{ab}(t') e^{-i\omega_0 t'} \left[ \int_0^{t'} H'_{ba}(t'') e^{i\omega_0 t''} dt'' \right] dt' \]
\[ \dot{c}_b^{(2)} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a^{(1)} \quad \Rightarrow \quad c_b^{(2)}(t) = c_b^{(1)}(t) \]

Note: \( |c_a^{(1)}(t)|^2 + |c_b^{(1)}(t)|^2 = 1 + \mathcal{O}(H'_{ab}^2) \neq 1 \)}

etc.
Sinusoidal perturbation

\[ H = H^0 + H'(t) \]

**Static**  \( \quad \) **Small** time-dependent perturbation \( H'(t) = V \cos(\omega t) \)

Initial condition: system in ground state \( c_a(0) = 1 \), \( c_b(0) = 0 \)

Iteratively solve

\[ \dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \quad ; \quad \omega_0 \equiv \frac{E_b - E_a}{\hbar} \]

\[ \dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a \]

First Order: \( H'_{ij}(t) \equiv V_{ij} \cos(\omega t) \)

\[ c_a(t) \approx 1 \]

\[ c_b(t) \approx -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t') e^{i\omega_0 t'} dt' = -\frac{i V_{ba}}{2\hbar} \int_0^{t'} \left[ e^{i(\omega_0 + \omega) t'} + e^{i(\omega_0 - \omega) t'} \right] \]

\[ = -\frac{V_{ba}}{2\hbar} \left[ \frac{e^{i(\omega_0 + \omega) t'} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0 - \omega) t'} - 1}{\omega_0 - \omega} \right] \]

Simplifying assumption: \( \omega_0 + \omega \gg |\omega_0 - \omega| \)

\[ c_b(t) \approx -\frac{V_{ba}}{2\hbar} \frac{e^{i(\omega_0 - \omega) t'}}{\omega_0 - \omega} \left[ e^{i(\omega_0 - \omega) t'/2} - e^{i(\omega_0 + \omega) t'/2} \right] \]

\[ = -\frac{V_{ba}}{\hbar \omega_0 - \omega} \sin[(\omega_0 - \omega) t/2] e^{i(\omega_0 - \omega) t/2} \]
**Rotating wave approximation**

**Goal:** calculate dynamics of two-level system under sinusoidal perturbation without perturbation theory, for arbitrary times and perturbation strengths

Let’s review what we did so far

We first derived time evolution equations for
Then performed perturbation theory
Then specialized to sinusoidal perturbation
Then made approximation \( \omega_0 + \omega \gg |\omega_0 - \omega| \)

**Result:** evolution for short times and small perturbation

We can do better:

We first derive time evolution equations for
Then specialize to sinusoidal perturbation
Then make approximation \( \omega_0 + \omega \gg |\omega_0 - \omega| \)

We will find that perturbation theory is not needed.

**Result:** evolution for arbitrary times and arbitrary perturbation
Perturbed system

\[ H = H^0 + H'(t) \]
\[ \text{static} \]
\[ \text{time-dependent perturbation (not necessarily small)} \]

Solve \[ H \Psi = i\hbar \frac{\partial \Psi}{\partial t} \]
with ansatz \[ \Psi(t) = c_a(t)e^{-iE_a t/\hbar} \Psi_a + c_b(t)e^{-iE_b t/\hbar} \Psi_b \]

\[ \dot{c}_a = -\frac{i}{\hbar} \left[ c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b-E_a)t/\hbar} \right] \]
\[ \dot{c}_b = -\frac{i}{\hbar} \left[ c_a H'_{ba} e^{i(E_b-E_a)t/\hbar} + c_b H'_{bb} \right] \]

Often \[ H'_{aa} = H'_{bb} = 0 : \]

\[ \dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \]
with \[ \omega_0 = \frac{E_b - E_a}{\hbar} \]

\[ \dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a \]
Rotating wave approximation

Starting point:

\[ \dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \]

\[ \dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a \]  

with  \[ \omega_0 \equiv \frac{E_b - E_a}{\hbar} \]
Solve differential equations

\[ i\hbar \frac{\partial}{\partial t} \begin{pmatrix} c_e \\ c_g \end{pmatrix} = \begin{pmatrix} 0 & \frac{\hbar \Omega}{2} e^{-i\delta t} \\ \frac{\hbar \Omega^*}{2} e^{i\delta t} & 0 \end{pmatrix} \begin{pmatrix} c_e \\ c_g \end{pmatrix} \]

Solve this set of differential equations for

- atom in \( |g\rangle \) at \( t = 0 \)
- laser phase \( \varphi = 0 \)

\[ c_e(t) = -i \frac{\Omega}{\Omega'} \sin \frac{\Omega' t}{2} e^{-i\delta t/2} \]

\[ c_g(t) = \left( \cos \frac{\Omega' t}{2} - i \frac{\delta}{\Omega'} \sin \frac{\Omega' t}{2} \right) e^{i\delta t/2} \]

with \( \Omega' = \sqrt{\Omega^2 + \delta^2} \)

Probability of finding atom in \( |e\rangle \):

\[ P_e(t) = |c_e(t)| = \left( \frac{\Omega}{\Omega'} \sin \frac{\Omega' t}{2} \right)^2 \]
Resonant behavior

\[ P_e(t) = |c_e(t)| = \left( \frac{\Omega}{\Omega'} \sin \frac{\Omega' t}{2} \right)^2 \]

with \( \Omega' \equiv \sqrt{\Omega^2 + \delta^2} \)

On resonance: \( P_e(t) = \sin^2 \frac{\Omega t}{2} \)

Sine oscillations with period \( 2\pi/\Omega \).

Absorption dominates emission dominates
Experiment: ion qubit


The coherence of qubits based on single Ca⁺ ions

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Excitation probability to D₅₂ state against Time (µs)
Off resonant behavior

\[ P_e(t) = |c_e(t)| = \left( \frac{\Omega}{\Omega'} \sin \frac{\Omega' t}{2} \right)^2 \quad \text{with} \quad \Omega' = \sqrt{\Omega^2 + \delta^2} \]

- Oscillations faster.
- Atom never fully in excited state.
Resonance

Excitation probability by square pulse with duration $t = \pi / \Omega$ in dependence of detuning:

$$P_e(t) = |c_e(t)| = \left(\frac{\Omega}{\Omega'} \sin \frac{\Omega' t}{2}\right)^2$$

with $\Omega' \equiv \sqrt{\Omega^2 + \delta^2}$
The Bloch sphere

Let's find an intuitive description.

Observation:

\[ |\Psi\rangle = c_e |e\rangle + c_g |g\rangle \]

\(c_e\) and \(c_g\) are complex numbers
\[ \rightarrow \text{four real parameters.} \]

Normalization \(|c_e|^2 + |c_g|^2 = 1\) removes one parameter.

Overall phase is unimportant.
\[ \rightarrow \text{only two relevant real parameters.} \]

Express \(|\Psi\rangle\) with two real parameters, \(\varphi_{at}\) and \(z\):

\[
|\Psi\rangle = \sqrt{\frac{1+z}{2}} e^{i\varphi_{at}/2} |e\rangle + \sqrt{\frac{1-z}{2}} e^{-i\varphi_{at}/2} |g\rangle \quad \text{with} \quad z \equiv |c_e|^2 - |c_g|^2
\]

Can be represented as a point on a unit sphere!
The Bloch sphere

We will show that the equation of motion is

\[ |\Psi\rangle = \sqrt{\frac{1+z}{2}} e^{i\varphi_{at}/2} |e\rangle + \sqrt{\frac{1-z}{2}} e^{-i\varphi_{at}/2} |g\rangle \]

Represent |\Psi\rangle by Bloch vector

\[ \vec{R} = \begin{pmatrix} \sqrt{1-z^2} \cos(-\varphi_{at}) \\ \sqrt{1-z^2} \sin(-\varphi_{at}) \\ z \end{pmatrix} \]

We will show that the equation of motion is

\[ \frac{\partial \vec{R}}{\partial t} = \vec{\Omega} \times \vec{R} \]

with field vector

\[ \vec{\Omega} = \begin{pmatrix} |\Omega| \cos \varphi_L \\ |\Omega| \sin \varphi_L \\ -\delta \end{pmatrix} \]

Surface of Bloch sphere represents the Hilbert space of the two-level system.

© Wikipedia

R. Feynman et al. J. Appl. Phys. 28, 49 (1957)
The Bloch sphere

Equation of motion of Bloch vector:

\[
\frac{\partial \vec{R}}{\partial t} = \vec{\Omega} \times \vec{R}
\]

The Bloch vector moves under the influence of a driving field in the direction orthogonal to the field vector and the Bloch vector itself.

This is analogous to the evolution of an angular momentum under the influence of a torque.

\[
\begin{align*}
\vec{R} &= \begin{pmatrix}
\sqrt{1-z^2} \cos(-\varphi_{at}) \\
\sqrt{1-z^2} \sin(-\varphi_{at}) \\
z
\end{pmatrix} \\
\vec{\Omega} &= \begin{pmatrix}
|\Omega| \cos \varphi_L \\
|\Omega| \sin \varphi_L \\
-\delta
\end{pmatrix}
\end{align*}
\]
Examples

\[ \pi \text{-pulse} \]

Switch laser on for as long as necessary to bring atom to excited state.

For weaker laser, longer time needed.

\[ \pi / 2 \text{-pulse} \]

(differs starting conditions)

\[ \pi \text{-pulse} \]

Switch laser on for as long as necessary to bring atom to excited state.

For weaker laser, longer time needed.
Rabi oscillations

Resonant Rabi oscillations

Off-resonant Rabi oscillations

Compare to our calculation from before:

\[
P_e(t)\]

Resonant Rabi oscillations

Off-resonant Rabi oscillations

Time \( (1/\Omega) \)
Stationary states

If Bloch vector is parallel or antiparallel to the Rabi vector, the atomic state only acquires a phase.

These are the eigenstates of the system.
Applications

The Bloch vector picture gives intuitive insight into many applications.

- Nuclear magnetic resonance
- Quantum computation
- Atomic clocks
- Atom interferometers in general

Everything we derived is valid for any two-level transition driven by EM wave.

Especially useful if pulse shorter than the lifetime of the excited level, so that spontaneous emission is negligible.

In the radiofrequency domain this is always the case on experimental timescales. In the optical domain this requires short laser pulses.

Bloch vector picture can be generalized to include spontaneous emission and to describe an ensemble of many atoms.  

next lecture
Basic structure of any clock

clockwork
gearwheels
do something useful
display elapsed time on dial

frequency reference
pendulum
Atomic clock

Highest accuracy

- High transition frequency $\rightarrow$ optical transitions
- Narrow transition $\rightarrow$ mHz linewidth
- Large signal $\rightarrow$ use many atoms
- Undisturbed by other atoms $\rightarrow$ use gas of atoms
- Observe for long time $\rightarrow$ cool atoms to standstill
Atomic clock

Definition of second:
9 192 631 770 periods of the radiation corresponding to the transition between the cesium hyperfine levels

Challenge: measure this transition precisely

Use Ramsey spectroscopy:

\[
\begin{align*}
|g\rangle & \xrightarrow{\pi/2\text{-pulse}} (|e\rangle + |g\rangle)/\sqrt{2} \\
\text{atomic beam} & \xrightarrow{\pi/2\text{-pulse}} \\
\text{detector} & \text{for } P_e(t)
\end{align*}
\]
Ramsey spectroscopy on resonance

\[ \pi/2 \text{-pulse} \quad \text{wait time} \quad \pi/2 \text{-pulse} \quad \text{result} \]
Ramsey spectroscopy off resonance

\[
\pi/2\text{-pulse} \quad \text{wait time} \quad \pi/2\text{-pulse} \quad \text{result}
\]

\[
\begin{align*}
|e\rangle & \quad \to \quad |g\rangle \\
|e\rangle & \quad \text{after } x \\
|e\rangle & \quad \text{after } y \\
|e\rangle & \quad \text{after } z
\end{align*}
\]

Frequency difference between rf source and atomic transition leads to phase shift between \( \overrightarrow{\Omega} \) and \( \overrightarrow{R} \), in this example by \( \pi \).
To determine if rf source is too low or too high in frequency, execute two measurements, with frequencies slightly above and below the rf source frequency.
Fountain clock

Long interrogation time (~1s) through slow (few cm/s), ultracold (few µK) atoms.
Ultracold fridge
Ultracold strontium atoms
Sr transitions

2 mm

\[ {^1S_0} \rightarrow {^1P_1} \rightarrow {^3P_J} \]

blue cooling 461 nm 30 MHz
red cooling 689 nm 7.4 kHz
clock 698 nm 1 mHz

blue laser cooling hot gas \( T \sim 1 \text{ mK} \)
red laser cooling cold gas \( T \sim 1 \mu\text{K} \)
Optical clock scheme

Frequency reference
ultracold Sr atoms in lattice

Clockwork
optical frequency comb
translates optical frequency into microwave frequency
Optical clock scheme

Frequency reference
ultracold Sr atoms in lattice

Flywheel
optical resonator
keeps clock ticking while ultracold atoms are prepared

Clockwork
optical frequency comb
translates optical frequency into microwave frequency

Blue laser cooling
Red laser cooling
Interrogate

Interrogate
Blue laser cooling
Red laser cooling
...
Time and gravity

Reference clock

Movable clock

compare

lift clock by 33cm

Are the „constants of nature“ constant?

Clock using Sr

Clock using Yb

compare

Frequency difference

Time (years)

?
Overview of course

Part 1: 7 lectures in January (Piet Mulders)
- Basics of quantum mechanics
- Spin states
- Addition of angular momentum
- Identical particles
- Basic structure of atom

Part 2: 7 lectures in February and March (Florian Schreck)
- Structure of atoms & the periodic table
- Solids
- Time-independent perturbation theory
- Structure of hydrogen
- Variational principle
- Time-dependent perturbation theory, atom-light interaction

today → Time-dependent perturbation theory, atom-light interaction

Lecture notes, problem sets and link to video recordings of C0.05 lectures available on Canvas

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