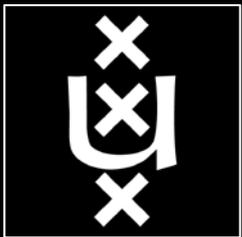
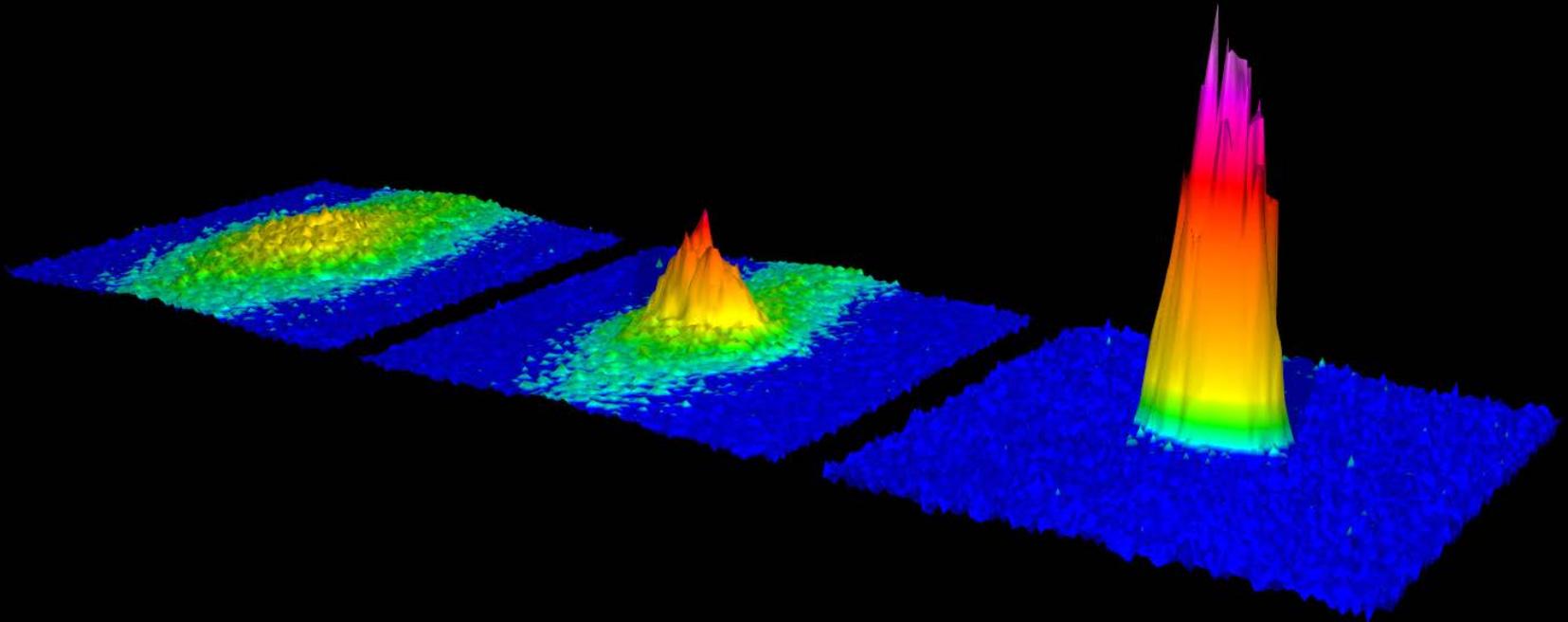


Quantum mechanics 3

Structure of matter

Lecture 8



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

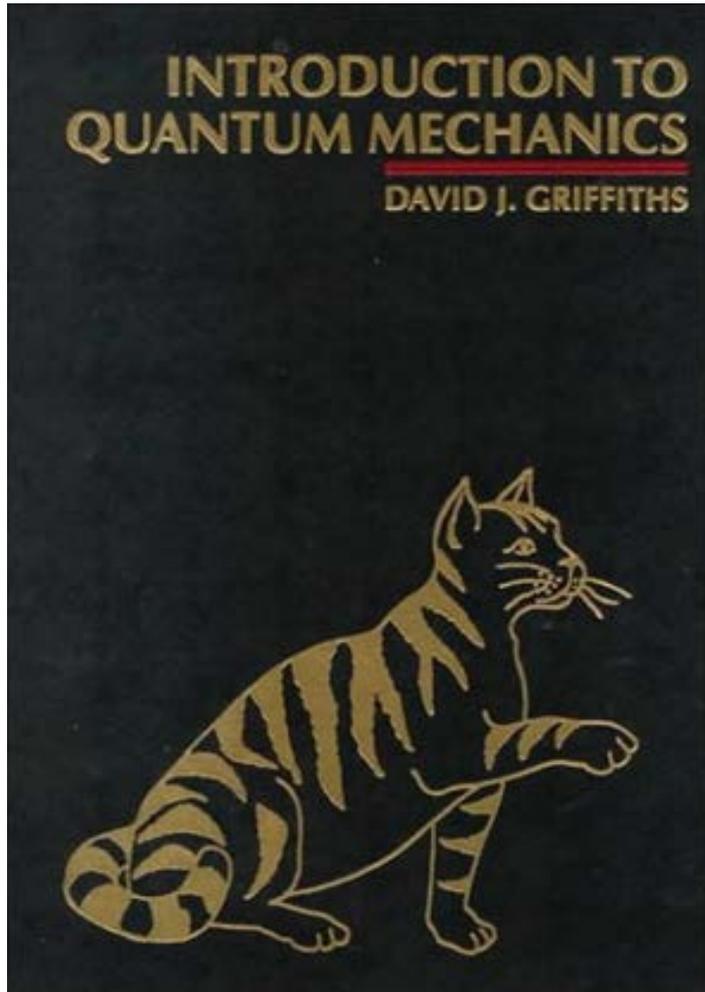
Part 2: 7 lectures in February and March (Florian Schreck)

today	→	Structure of atoms & the periodic table	Griffiths 3 rd 5.1, 5.2
		Crystalline solids	5.3.2
		Time-independent perturbation theory	7.1, 7.2
		Structure of hydrogen	7.3 – 7.5
		Variational principle	8.1 – 8.3
		Time-dependent perturbation theory, atom-light interaction	11.1 – 11.4

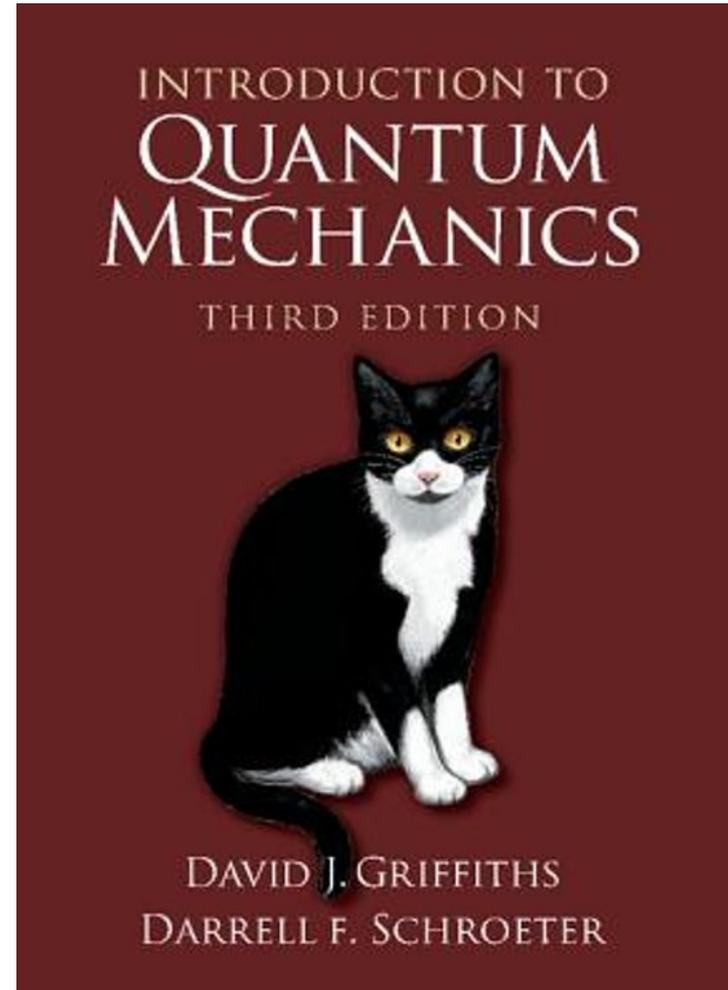
Lecture notes, problem sets and link to video recordings of C0.110 lectures available on Canvas

Questions: schreck@StrontiumBEC.com

Literature part 2

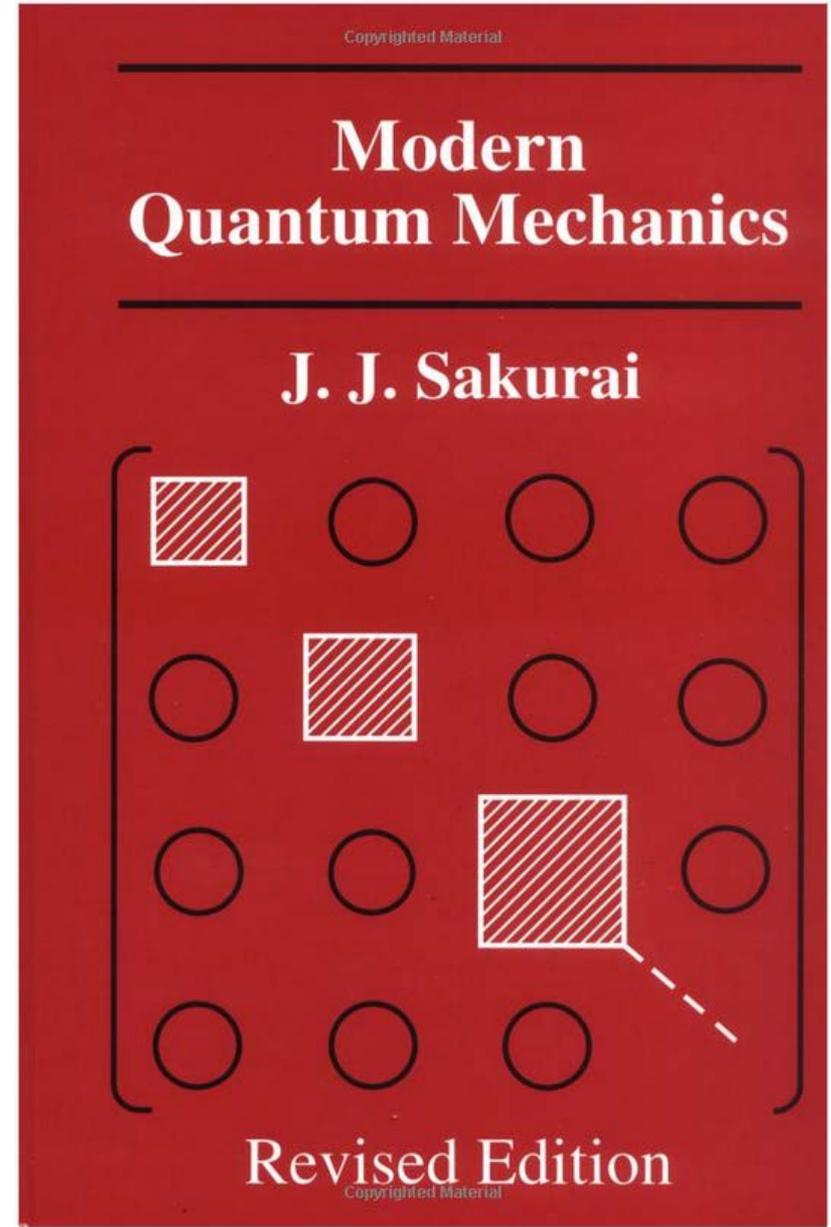
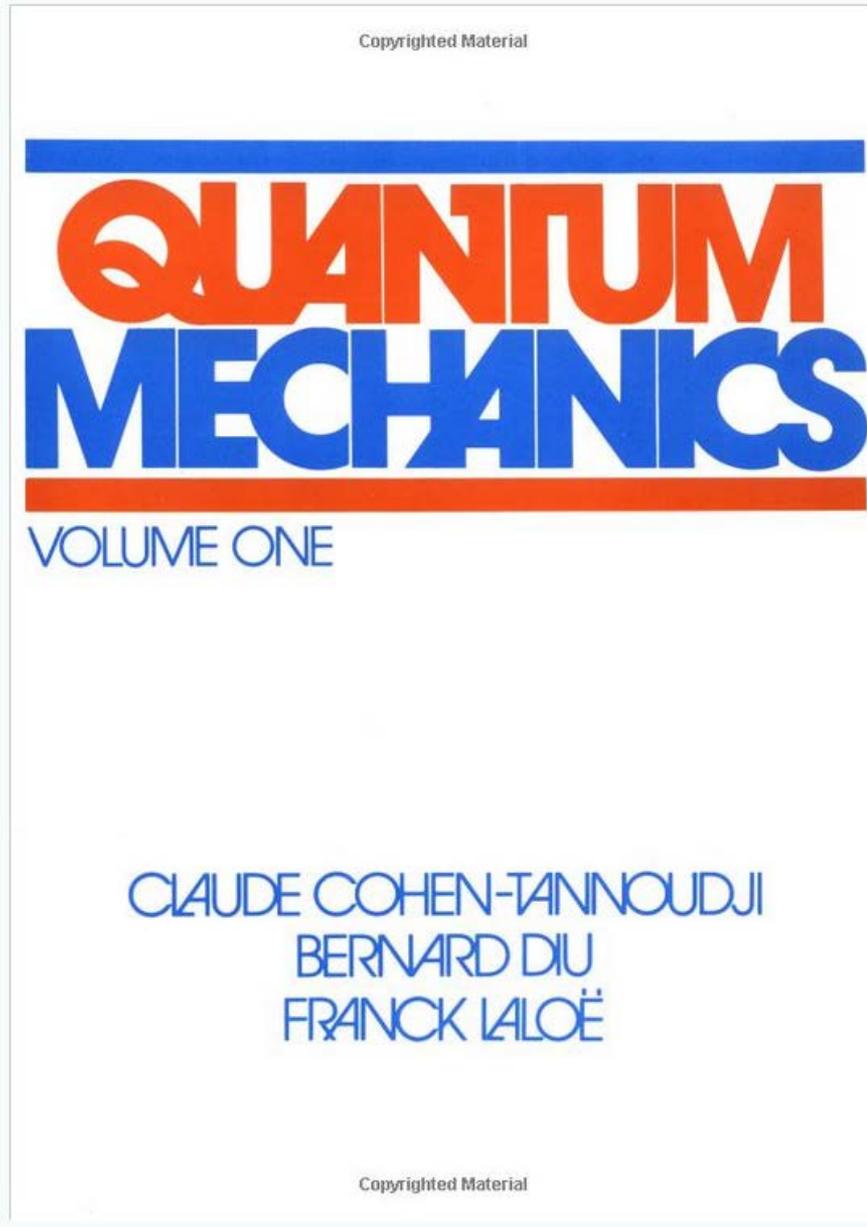


Griffiths (2nd edition)
Chapters 5, 6, 7, 9



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

Other literature



Overview of course

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Basic structure of atom

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Overview „Structure of atoms & the periodic table“

Outline

- • Reminder of Piet's lecture on orbital and spin structure of atoms Griffiths 3rd 5.2.2
- Energy structure of He 5.2.1
 - „exchange energy“ 5.1.2
 examples: He, covalent bonds, magnetism
 - shielding of nuclear charge by inner shell electrons 5.2.2
- Energy structure of atoms with many electrons 5.2.2
 - Hund's rules
 - the periodic table

Orbital and spin structure of atoms

Atom with nuclear charge Z and Z electrons:

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

electron-electron repulsion

- 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

$$\Psi \dots (\vec{r}_1, \dots, \vec{r}_Z) = \mathcal{A} \left(\prod_{i=1}^Z \underbrace{\phi_{n_i l_i m_{l_i}}(\vec{r}_i)}_{\text{orbital wavefunction}} \cdot \underbrace{\chi_{s_i m_{s_i}}}_{\text{spin state}} \right)$$

Label: Term symbol

orbital wavefunction

spin state

2 states for each e^- $|1/2, m_s\rangle$

Antisymmetrize under electron exchange!

shorthand: $|\uparrow\rangle$

$|\downarrow\rangle$

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

perturbation

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

Example: Helium atom

2 electrons $\longrightarrow Z = 2$

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

Energies without ee repulsion

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

configurations	E/E_R
$(1s)^2$	$-8 = 109 \text{ eV}$
$(1s)(2s)$	-5
$(1s)(2p)$	-5
$(2s)(2p)$	-2
$(2s)^2$	-2
$(2p)^2$	-2
$(1s)(3d)$	\dots

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

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

Explanation: Chapter „variational principle“

He wavefunctions

Wavefunction of the 2 He electrons

$$\Psi(\vec{r}_1, \vec{r}_2) = \underbrace{\Phi_{n_1 l_1 m_{l_1}}(\vec{r}_1) \Phi_{n_2 l_2 m_{l_2}}(\vec{r}_2)}_{\Phi(\vec{r}_1, \vec{r}_2)} \underbrace{\chi_{s_1 m_{s_1}} \chi_{s_2 m_{s_2}}}_{\chi} \quad \text{must be antisymmetric!}$$

Groundstate of He

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

Φ_0 is symmetric $\rightarrow \chi_0$ must be antisymmetric: singlet

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

Excited states of He

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

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

Φ_e can be both: symmetric or antisymmetric!

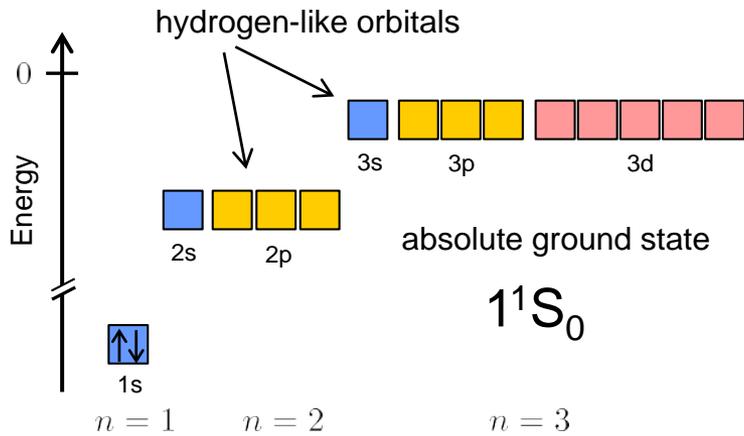
If Φ_e symmetric $\rightarrow \chi_e$ antisymmetric: singlet „parahelium“

If Φ_e antisymmetric $\rightarrow \chi_e$ symmetric: triplet „orthohelium“

$$\chi_e = \begin{cases} |\uparrow_1\rangle |\uparrow_2\rangle & \equiv |t_{+1}\rangle \\ (|\uparrow_1\rangle |\downarrow_2\rangle + |\downarrow_1\rangle |\uparrow_2\rangle) / \sqrt{2} & \equiv |t_0\rangle \\ |\downarrow_1\rangle |\downarrow_2\rangle & \equiv |t_{-1}\rangle \end{cases}$$

Examples of He states

singlet
 $S=0$
„parahelium“

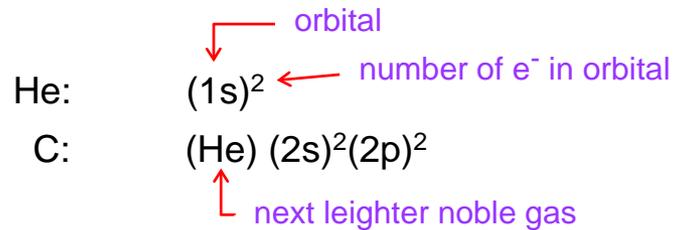


Term symbols

$$n^{2S+1}L_J$$

e.g. 2^3P_0 : $n = 2$, $S = 1$, $L = 1$, $J = 0$

n : longform:



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 $L = |l_1 - l_2|, |l_1 - l_2| + 1, \dots, |l_1 + l_2|$

$L = 0, 1, 2, 3, \dots$
 written as S,P,D,F,G,H,J,K...

↖ skip „I“

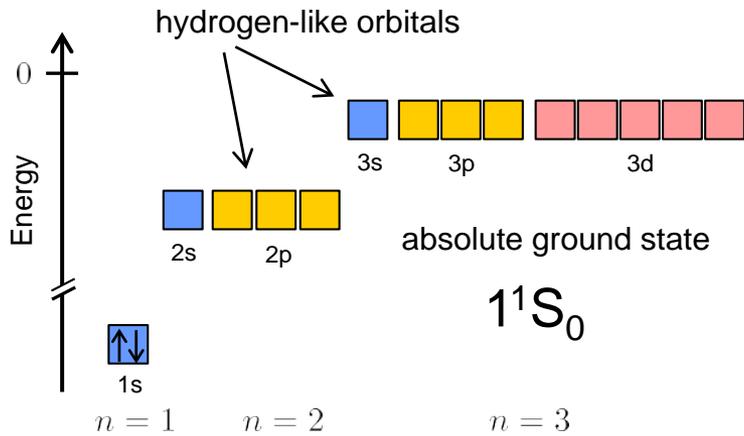
J : total angular momentum quantum number

$J = |L - S|, |L - S| + 1, \dots, |L + S|$

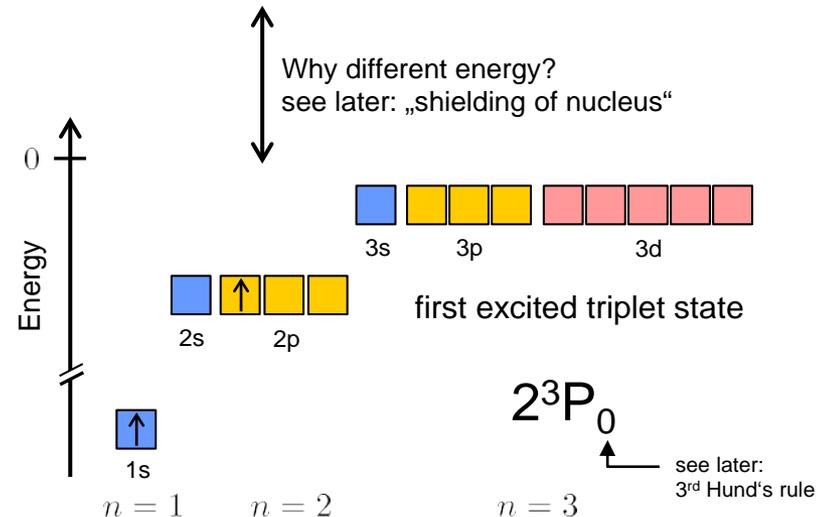
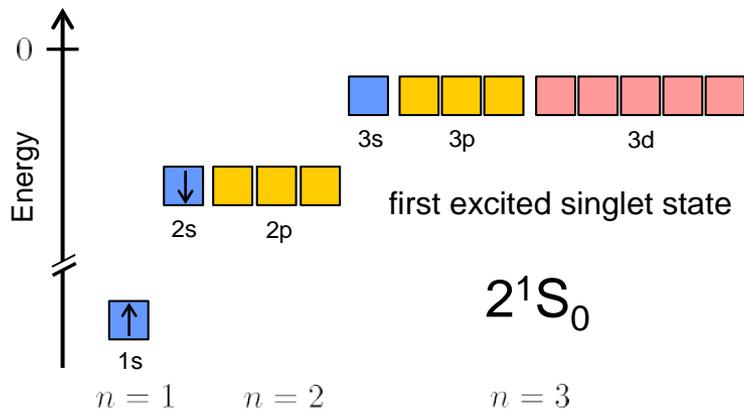
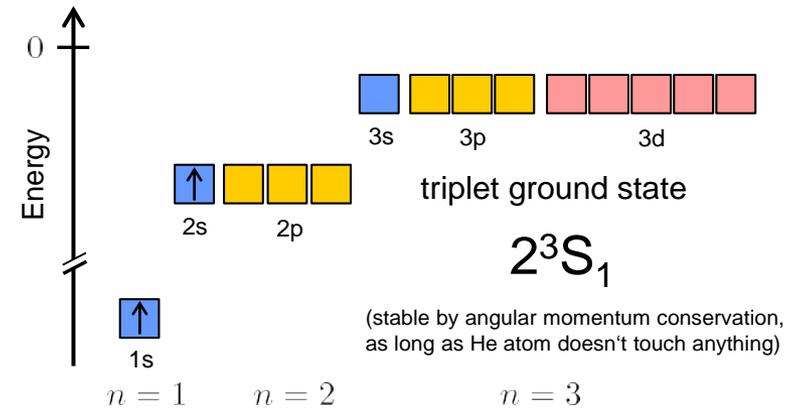
angular momentum = \hbar angular momentum quantum number

Examples of He states

singlet
 $S=0$
 „parahelium“



triplet
 $S=1$
 „orthohelium“



Helium states

Antisymmetrization and termsymbols

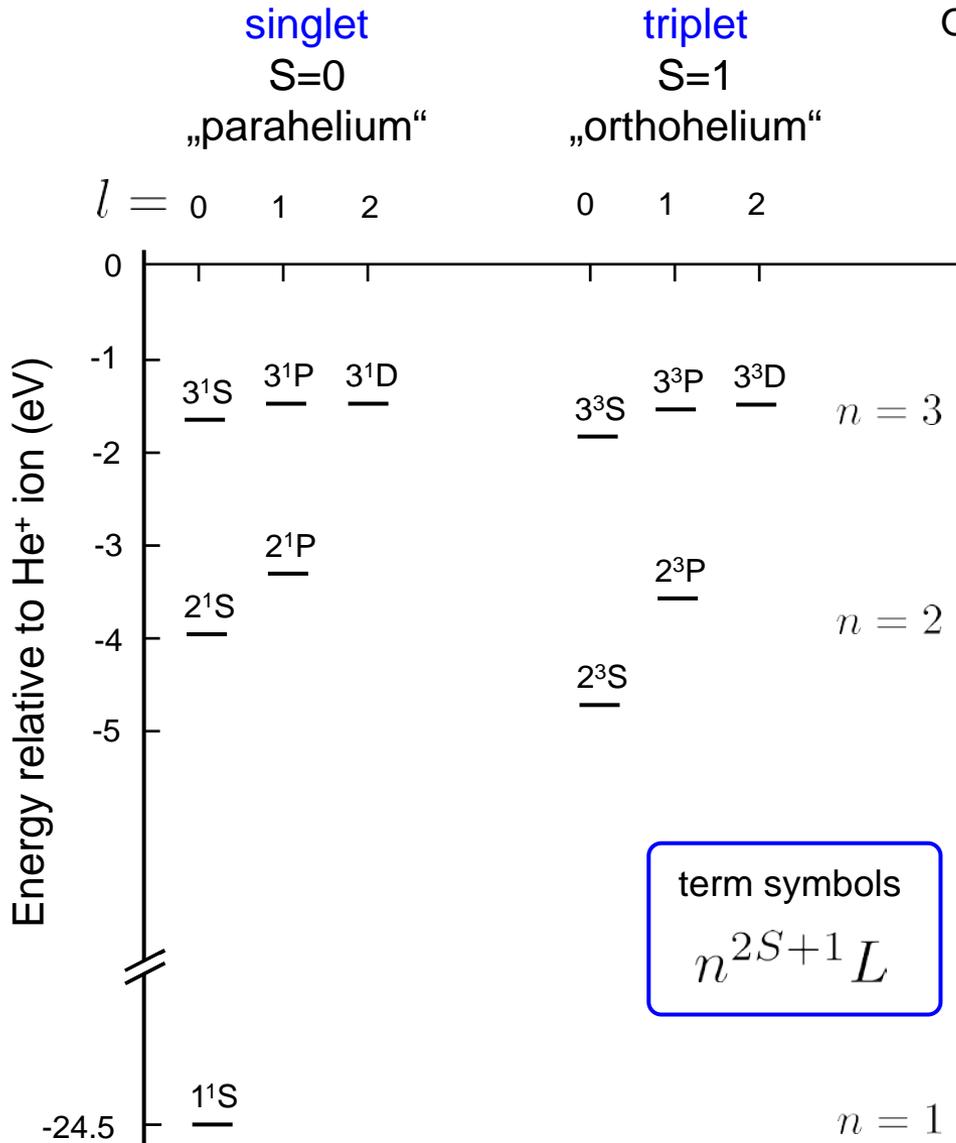
config.	E/E_R	Parity	L (sym)	S (sym)	Term symbol	J	# states
$(1s)^2$	-8	+	0 (S)	0 (A) 1 (S)	$(1s)^2$ 1S	1S_0	1
$(1s)(2p)$ & $(2p)(1s)$	-5	-	1 (A) 1 (S)	0 (A) 1 (S) 0 (A) 1 (S)	$(1s)(2p)$ 1P $(1s)(2p)$ 3P	1P_1 $^3P_{0,1,2}$	3 9
$(1s)(2s)$ & $(2s)(1s)$	-5	+	0 (A) 0 (S)	0 (A) 1 (S) 0 (A) 1 (S)	$(1s)(2s)$ 3S $(1s)(2s)$ 1S	3S_1 1S_0	3 1
$(2p)^2$	-2	+	0 (S) 1 (A) 1 (S) 2 (S)	0 (A) 1 (S) 0 (A) 1 (S) 0 (A) 1 (S)	$(2p)^2$ 1S $(2p)^2$ 3P $(2p)^2$ 1D	1S_0 $^3P_{0,1,2}$ 3D_2	1 9 5

So far:
Which states are allowed?

Now:
Energy shifts between states?

see Piet 6.2

He energy levels



Orbital wavefunctions:

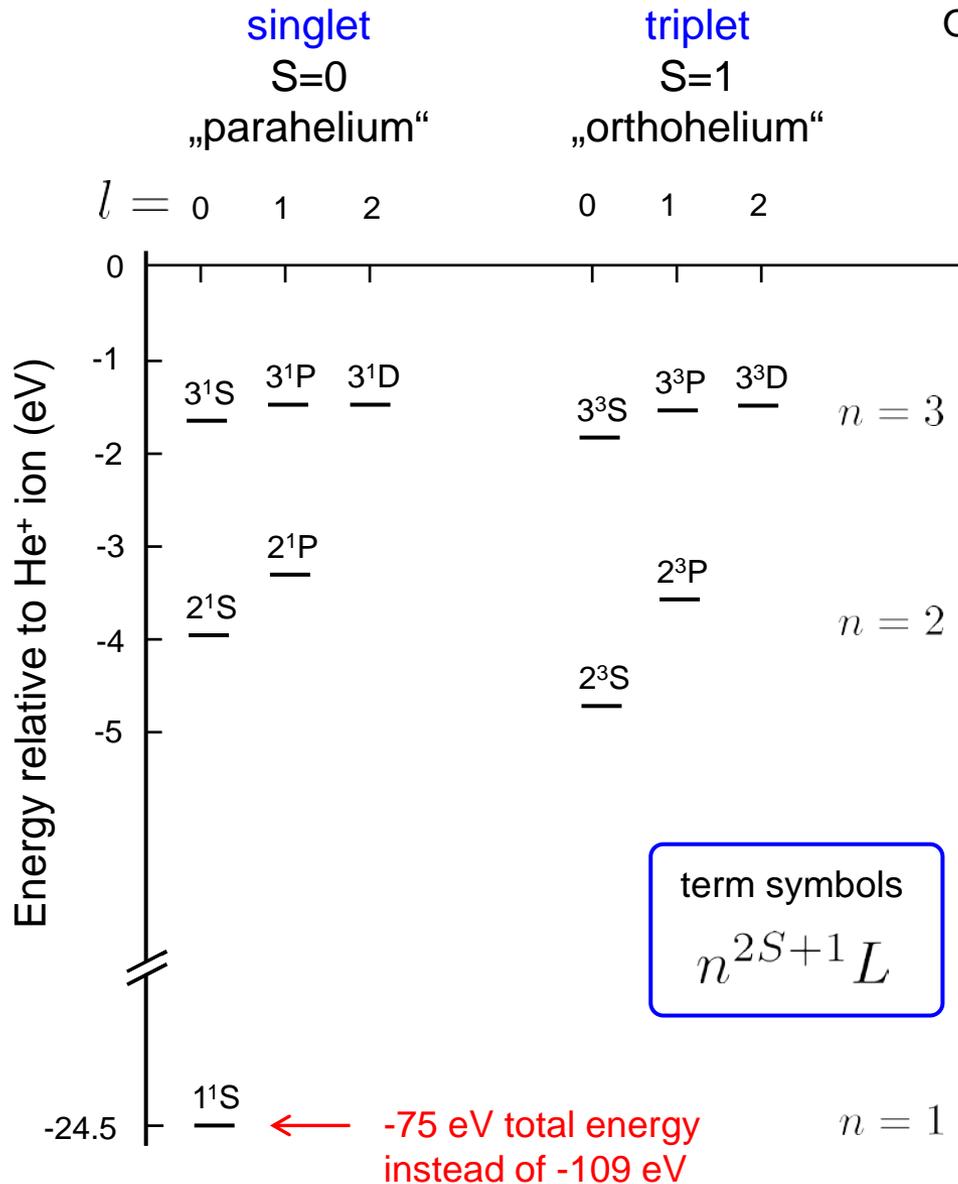
$$\Phi_e(\vec{r}_1, \vec{r}_2) =$$

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

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

Observations

He energy levels



Orbital wavefunctions:

$$\Phi_e(\vec{r}_1, \vec{r}_2) =$$

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

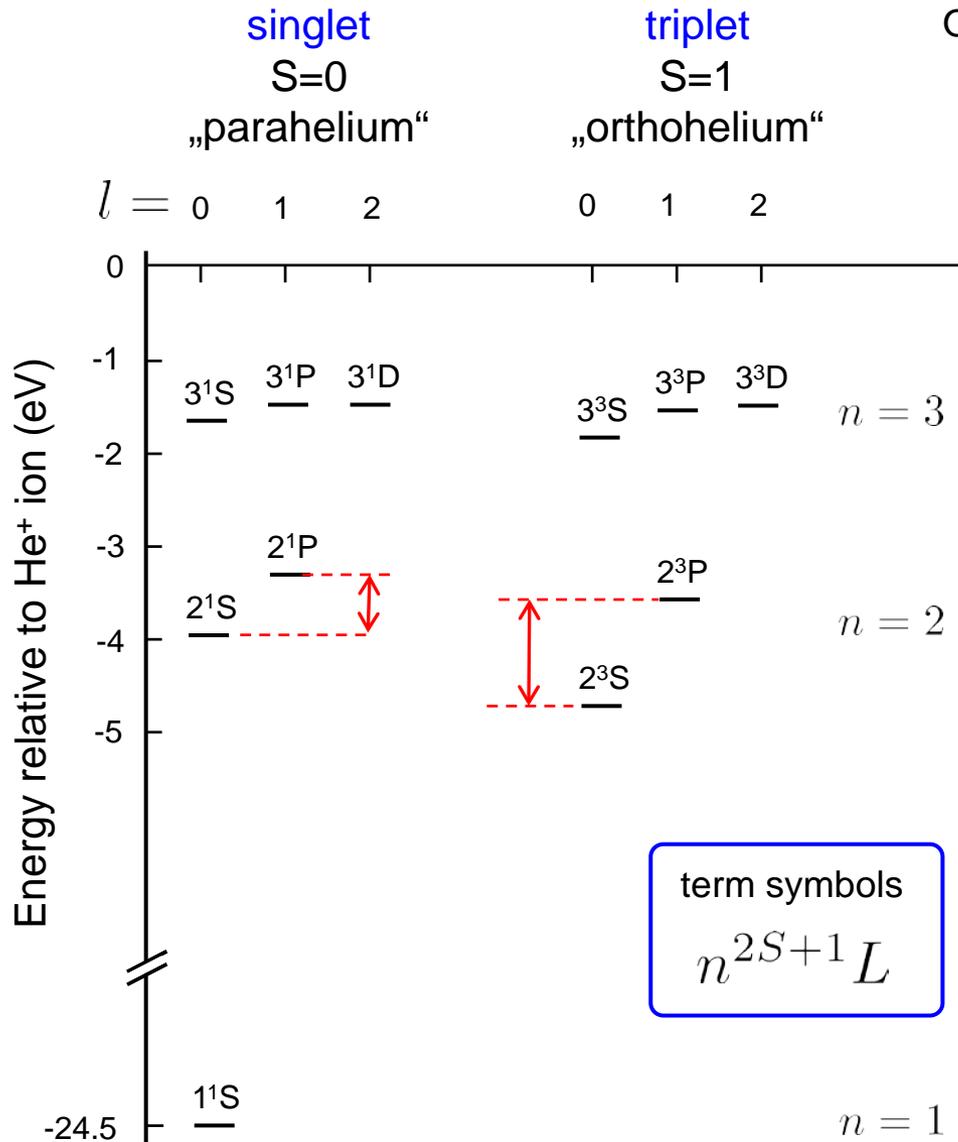
$$\Phi_0(\vec{r}_1, \vec{r}_2) = \Phi_{100}(\vec{r}_1)\Phi_{100}(\vec{r}_2)$$

Observations

Ground state binding energy lower than predicted

See chapter „variational principle“

He energy levels



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

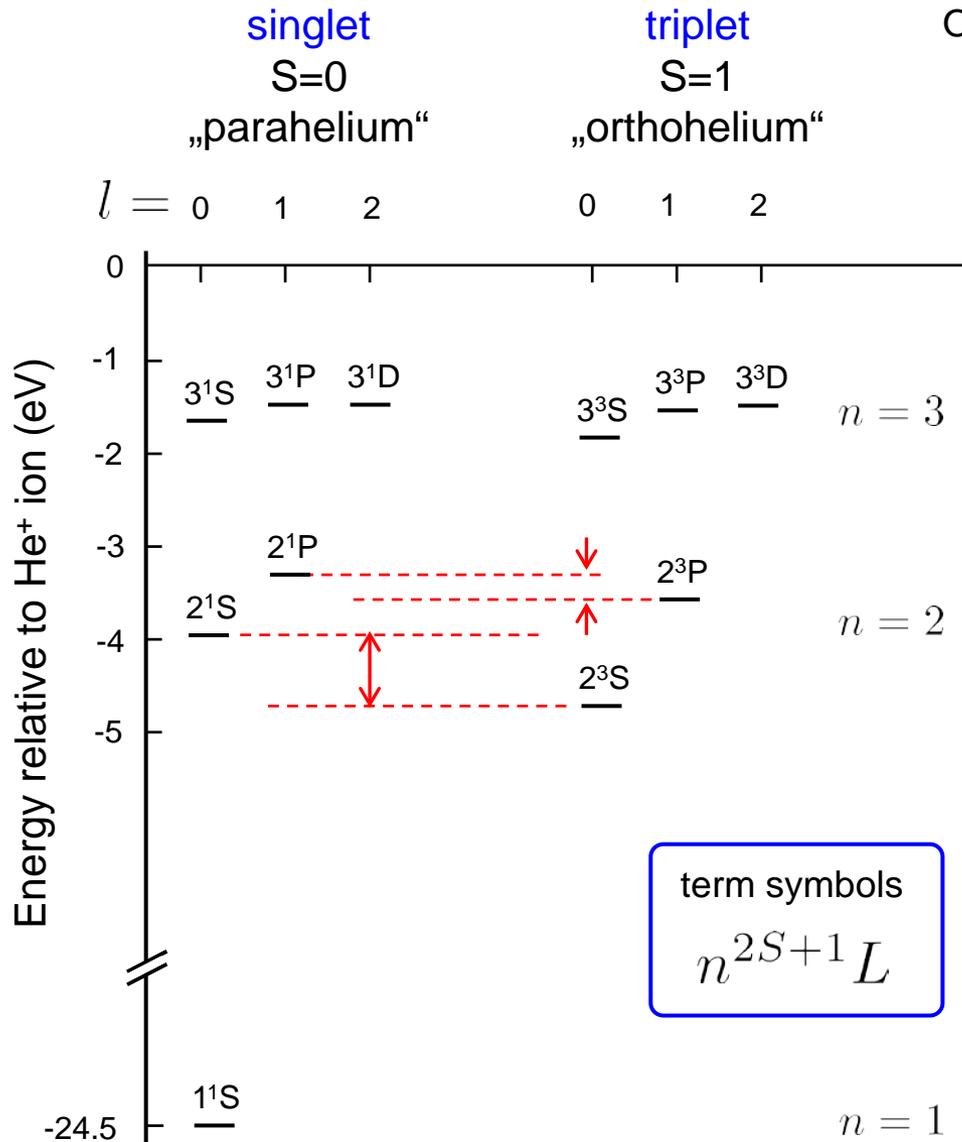
Ground state binding energy lower than predicted

See chapter „variational principle“

P levels always higher than S levels

Shielding of nuclear charge

He energy levels



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“

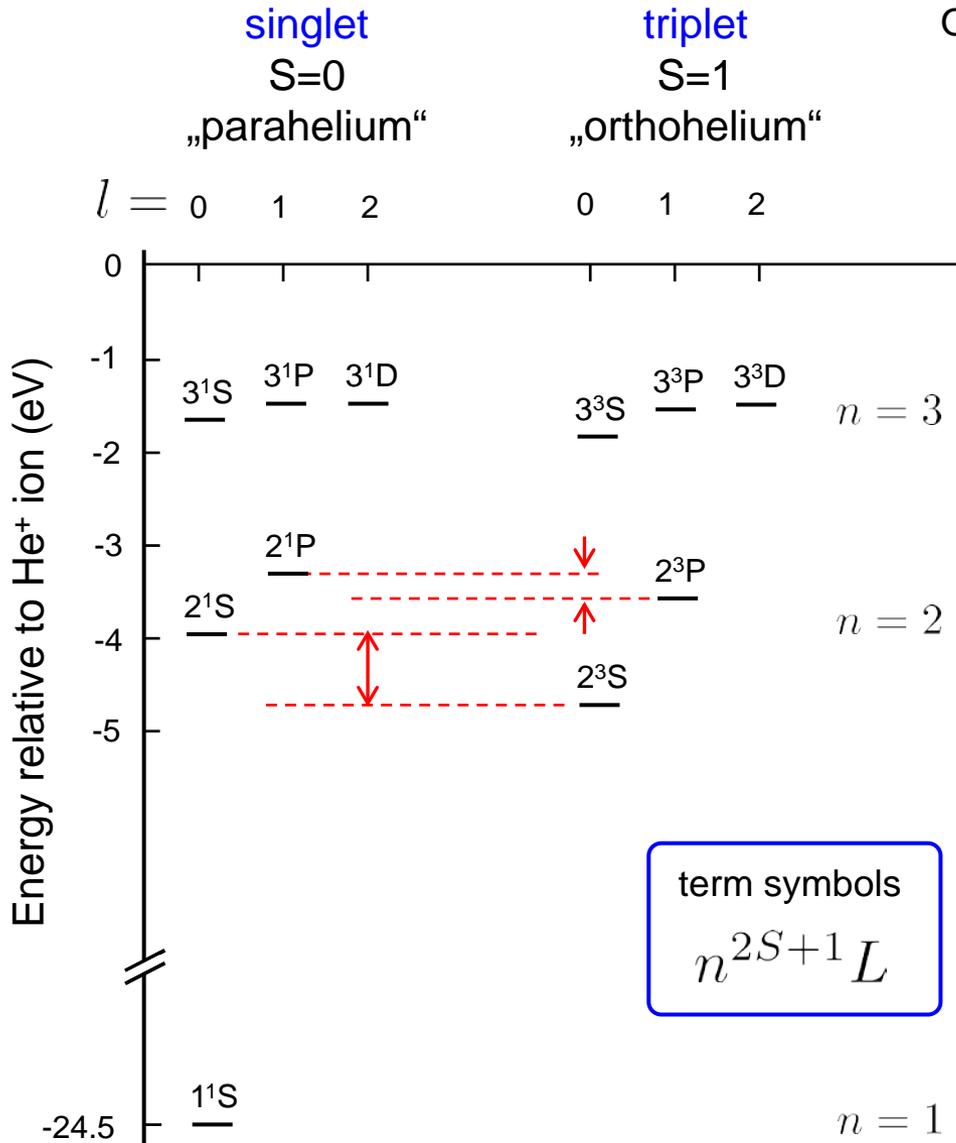
P levels always higher than S levels

Shielding of nuclear charge

Singlet levels always higher than triplet levels

Reason: „exchange energy“

He energy levels



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“

Exchange energy

Energy shifts depend on spin state

(1) If spin state χ $\left\{ \begin{array}{l} \text{singlet: antisymmetric} \\ \text{triplet: symmetric} \end{array} \right\} \implies$ orbital wavefunc. Φ $\left\{ \begin{array}{l} \text{symmetric} \\ \text{antisymmetric} \end{array} \right\}$

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

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

Energy different for singlet and triplet

$$\begin{array}{ll} \chi = |s\rangle & \longrightarrow E = E_s \\ \chi = |t_{-1,0,+1}\rangle & \longrightarrow E = E_t \end{array} \quad ; \quad E_s \neq E_t$$

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 Φ sym.

First: [handwaving argument](#)

Coulomb energy strongest when e^- very close.

What is probability amplitude for e^- to be at same location for symmetric or antisymmetric wavefunction?

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

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

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

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

$$\begin{array}{llll} \chi = |s\rangle & \longrightarrow & \Phi^+ & \longrightarrow & E = E_s \\ \chi = |t_{-1,0,+1}\rangle & \longrightarrow & \Phi^- & \longrightarrow & E = E_t \end{array} \quad \text{with } E_s \neq E_t$$

Coulomb energy dependence on Φ sym.

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

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

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

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

$$= \underbrace{[\langle \Phi_a(x_1) | x_1^2 | \Phi_a(x_1) \rangle]}_{\equiv \langle x_1^2 \rangle_a} \underbrace{[\langle \Phi_b(x_2) | \Phi_b(x_2) \rangle]}_{=1} + \underbrace{[\langle \Phi_b(x_1) | x_1^2 | \Phi_b(x_1) \rangle]}_{\equiv \langle x_1^2 \rangle_b} \underbrace{[\langle \Phi_a(x_2) | \Phi_a(x_2) \rangle]}_{=1}$$

$$\pm \underbrace{[\langle \Phi_a(x_1) | x_1^2 | \Phi_b(x_1) \rangle]}_{=0} \underbrace{[\langle \Phi_b(x_2) | \Phi_a(x_2) \rangle]}_{=0} \pm \underbrace{[\langle \Phi_b(x_1) | x_1^2 | \Phi_a(x_1) \rangle]}_{=0} \underbrace{[\langle \Phi_a(x_2) | \Phi_b(x_2) \rangle]}_{=0} / 2$$

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

Independent of symmetry:

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

Since electron 1 identical to electron 2:

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

Coulomb energy dependence on Φ sym.

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

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

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

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

$$= \left[\underbrace{\langle \Phi_a(x_1) | x_1 | \Phi_a(x_1) \rangle}_{= \langle x \rangle_a} \underbrace{\langle \Phi_b(x_2) | x_2 | \Phi_b(x_2) \rangle}_{= \langle x \rangle_b} + \underbrace{\langle \Phi_b(x_1) | x_1 | \Phi_b(x_1) \rangle}_{= \langle x \rangle_b} \underbrace{\langle \Phi_a(x_2) | x_2 | \Phi_a(x_2) \rangle}_{= \langle x \rangle_a} \right]$$

$$\pm \left[\underbrace{\langle \Phi_a(x_1) | x_1 | \Phi_b(x_1) \rangle}_{\equiv \langle x \rangle_{ab}} \underbrace{\langle \Phi_b(x_2) | x_2 | \Phi_a(x_2) \rangle}_{= \langle x \rangle_{ba}} \pm \underbrace{\langle \Phi_b(x_1) | x_1 | \Phi_a(x_1) \rangle}_{= \langle x \rangle_{ba}} \underbrace{\langle \Phi_a(x_2) | x_2 | \Phi_b(x_2) \rangle}_{= \langle x \rangle_{ab}} \right] / 2$$

$$= \underbrace{\langle x \rangle_{ab}}_{\text{blue}}^2 \quad \quad \quad = \underbrace{\langle x \rangle_{ba}}_{\text{blue}}^2$$

$$= \langle x \rangle_a \langle x \rangle_b \pm \underbrace{|\langle x \rangle_{ab}|^2}_{\text{blue}}$$

Coulomb energy dependence on Φ sym.

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

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

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with $\underbrace{\langle x_1^2 \rangle_+} = \langle x_1^2 \rangle_-$

$$\underbrace{\langle x_2^2 \rangle_+} = \langle x_2^2 \rangle_-$$

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

Difference between symmetric and antisymmetric wavefunction:

$$\begin{aligned} \langle (\Delta x)^2 \rangle_+ - \langle (\Delta x)^2 \rangle_- &= \cancel{\langle x_1^2 \rangle_+} + \cancel{\langle x_2^2 \rangle_+} - 2 \langle x_1 x_2 \rangle_+ \\ &\quad - \cancel{\langle x_1^2 \rangle_-} - \cancel{\langle x_2^2 \rangle_-} + 2 \langle x_1 x_2 \rangle_- \\ &= -2(\cancel{\langle x \rangle_a \langle x \rangle_b} + |\langle x \rangle_{ab}|^2) \\ &\quad + 2(\cancel{\langle x \rangle_a \langle x \rangle_b} - |\langle x \rangle_{ab}|^2) \\ &= -4 |\langle x \rangle_{ab}|^2 \end{aligned}$$

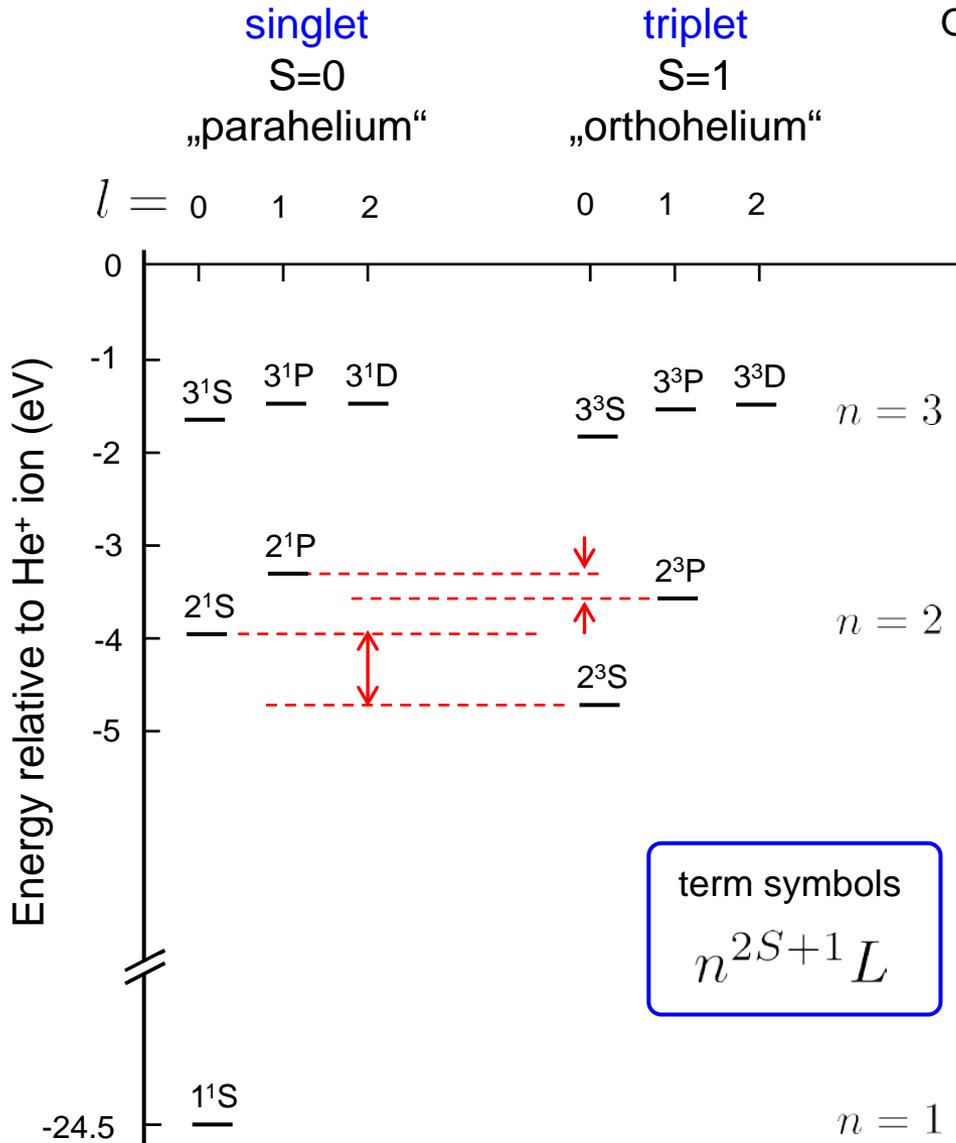
$$\langle x \rangle_{ab} = \int \Phi_a^*(x) x \Phi_b(x) dx$$

Effect plays only a role if wavefunctions overlap

Average electron distance smaller for symmetric than for antisymmetric wavefunction

→ For He: leads to higher Coulomb energy for symmetric wavefunction

He energy levels



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“

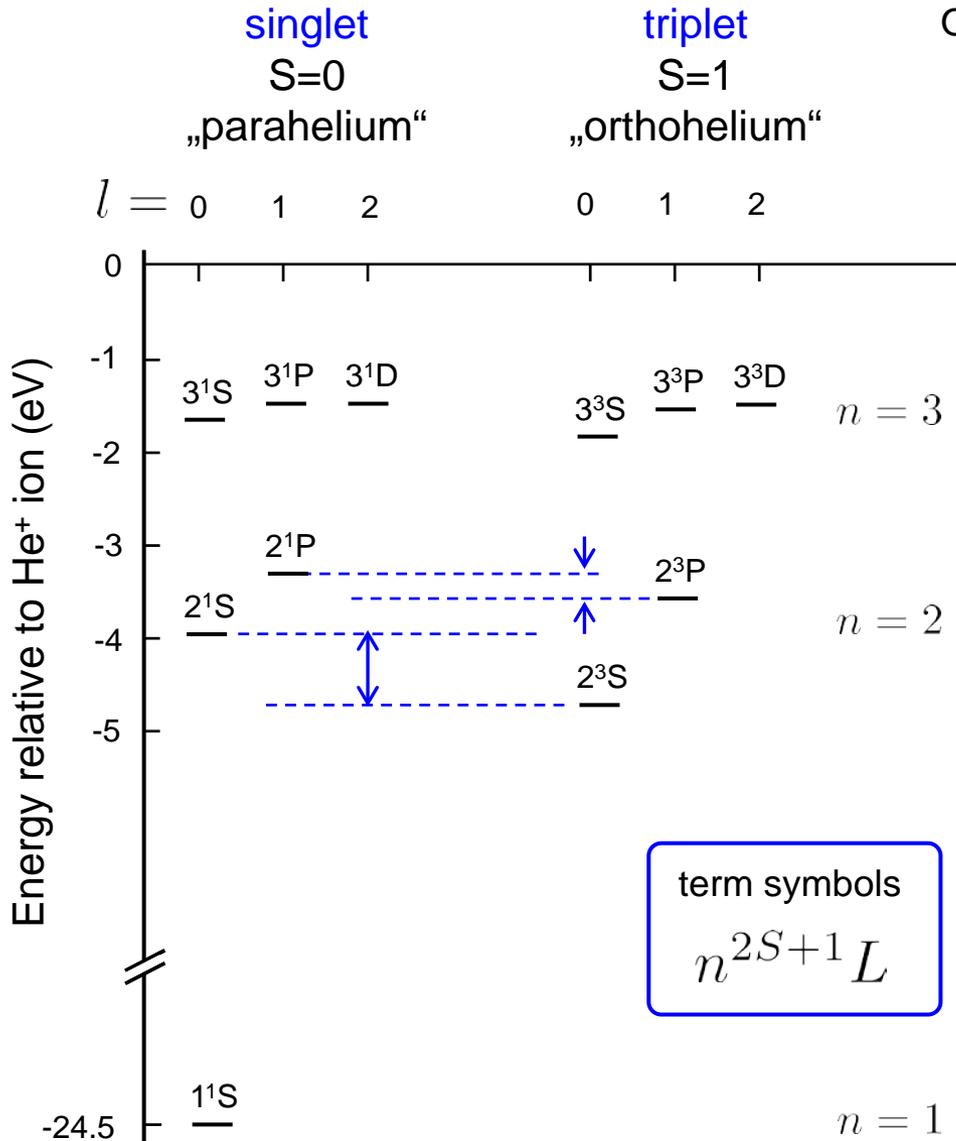
P levels always higher than S levels

Shielding of nuclear charge

Singlet levels always higher than triplet levels

Reason: „exchange energy“

He energy levels



Orbital wavefunctions:

$$\Phi_e(\vec{r}_1, \vec{r}_2) =$$

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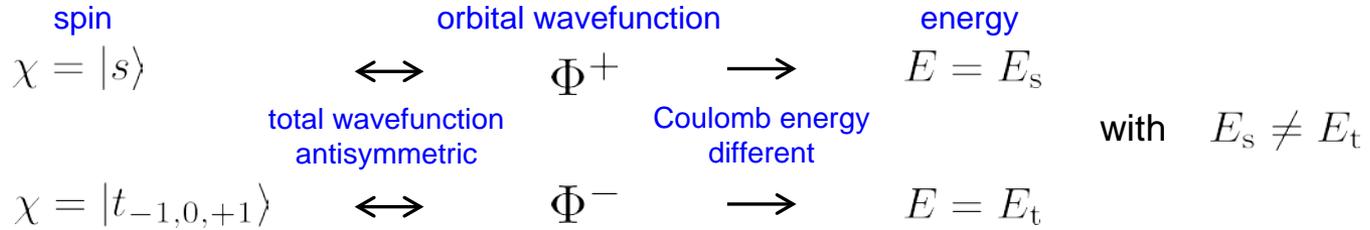
Singlet levels always higher than triplet levels

Reason: „exchange energy“



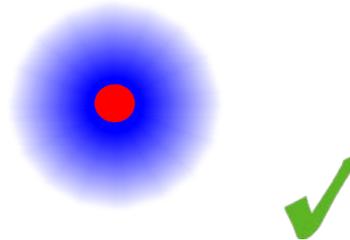
Exchange energy

Exchange energy between two electrons

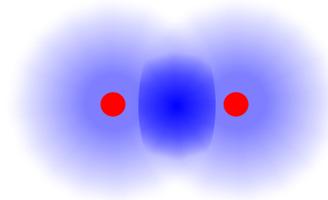


Three examples

singlet – triplet shift
in He

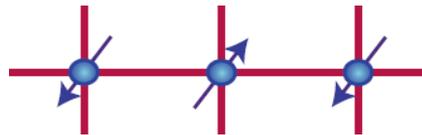


covalent bond
in H₂



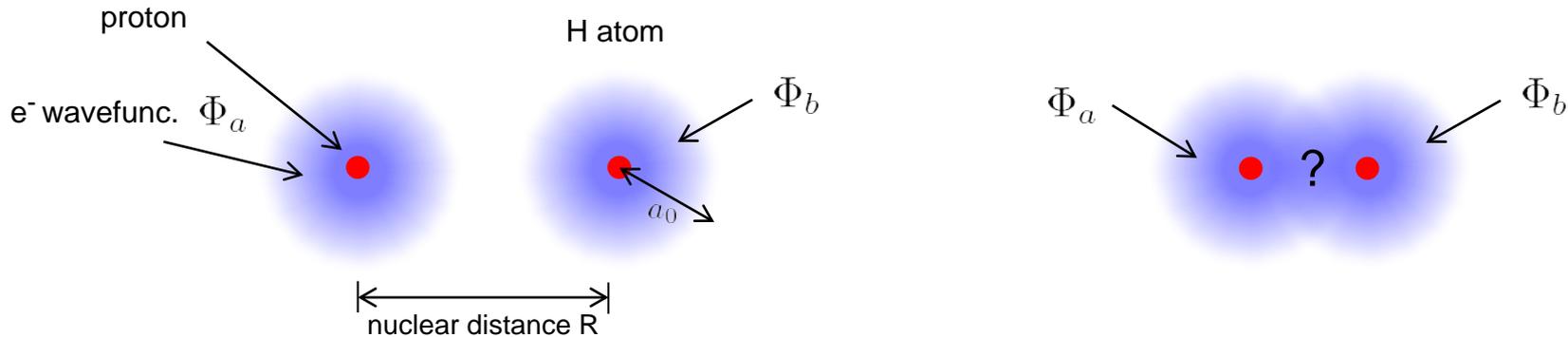
Bonus material

magnetic order



Example 2: covalent bonds

Example: H_2 molecule



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

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

Hydrogen orbital wavefunction:

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

here: Φ_a and Φ_b spatially shifted H groundstate, i.e. real and positive functions

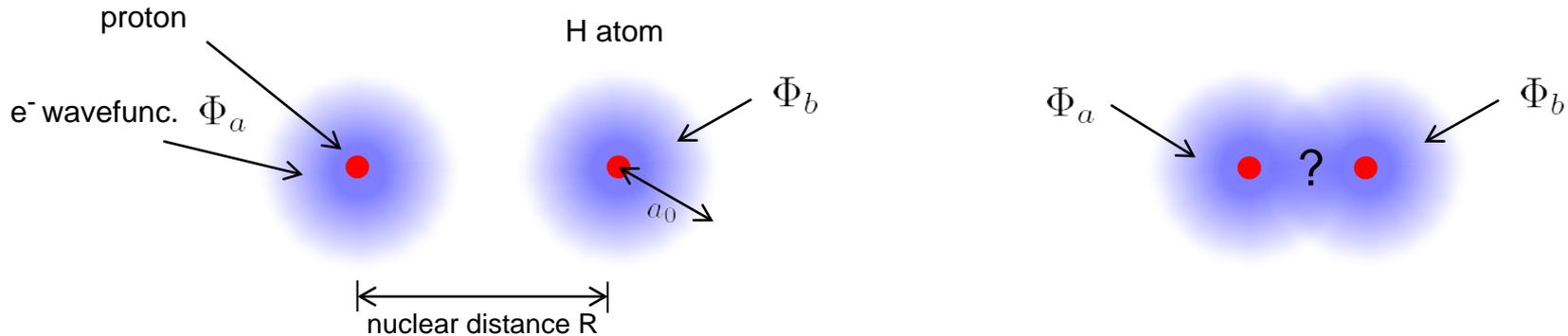
Density distribution of electron 1:

$$\begin{aligned} n^\pm(\vec{r}_1) &= \int |\Phi^\pm(\vec{r}_1, \vec{r}_2)|^2 d\vec{r}_2 \propto |\Phi_a(\vec{r}_1)|^2 \int |\Phi_b(\vec{r}_2)|^2 d\vec{r}_2 + |\Phi_b(\vec{r}_1)|^2 \int |\Phi_a(\vec{r}_2)|^2 d\vec{r}_2 \\ &\quad \pm \Phi_a^*(\vec{r}_1)\Phi_b(\vec{r}_1) \int \Phi_b^*(\vec{r}_2)\Phi_a(\vec{r}_2) d\vec{r}_2 \pm \Phi_b^*(\vec{r}_1)\Phi_a(\vec{r}_1) \int \Phi_a^*(\vec{r}_2)\Phi_b(\vec{r}_2) d\vec{r}_2 \\ &\propto |\Phi_a(\vec{r}_1)|^2 + |\Phi_b(\vec{r}_1)|^2 \pm (\text{function that is positive in overlap region and approaches zero outside}) \end{aligned}$$

Same for electron 2.

Example 2: covalent bonds

Example: H_2 molecule



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

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

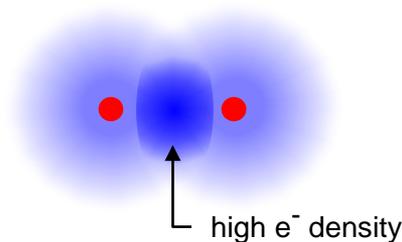
Density distribution of electron 1 and 2:

$$n^\pm(\vec{r}_1) \propto |\Phi_a(\vec{r}_1)|^2 + |\Phi_b(\vec{r}_1)|^2 \pm \text{(function that is positive in overlap region and close to zero outside)}$$

Singlet

symmetric orbital wavefunction

n^+

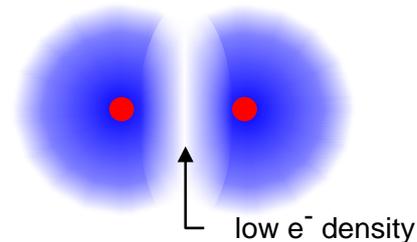


- in average e^- closer together

Triplet

antisymmetric orbital wavefunction

n^-



- in average e^- farther apart

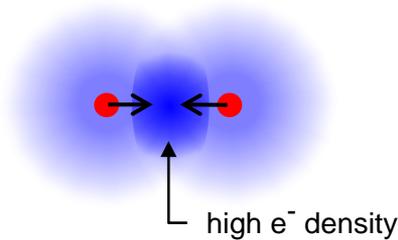
Example 2: covalent bonds

Example: H_2 molecule

Singlet

symmetric orbital wavefunction

n^+



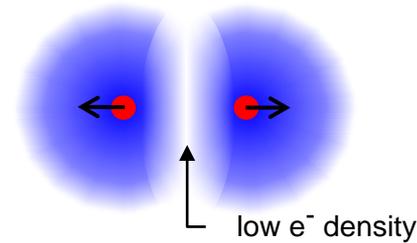
attractive „exchange force“ between protons
for $R \sim a_0$

lower energy

Triplet

antisymmetric orbital wavefunction

n^-



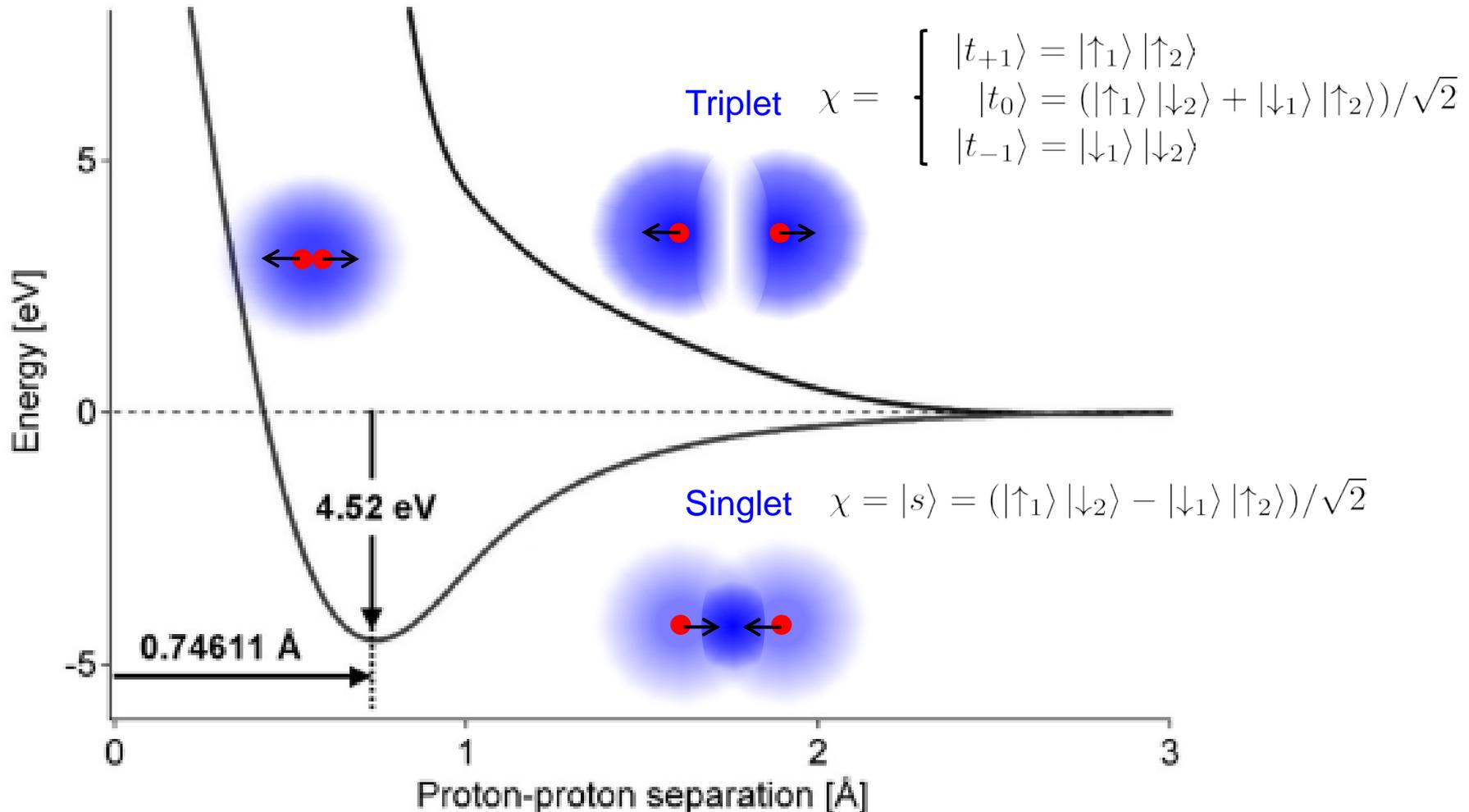
repulsive „exchange force“ between protons

higher energy

Protons in H_2 are bound by „covalent bond“
established by electrons in singlet state

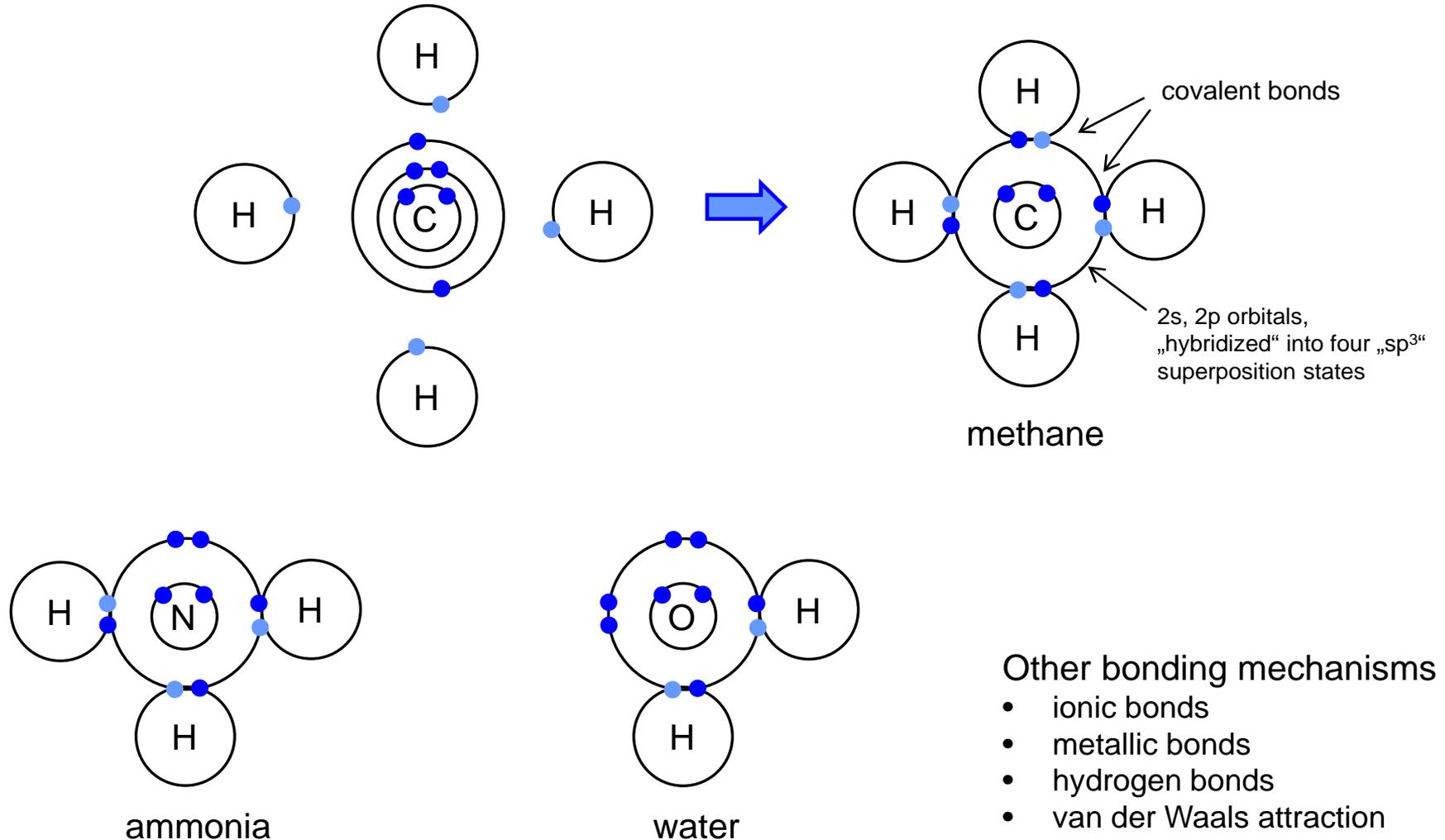
Example 2: covalent bonds

Potential energy curves of H₂ molecule



Example 2: covalent bonds

Fundamental bonding mechanism in many molecules, e.g.



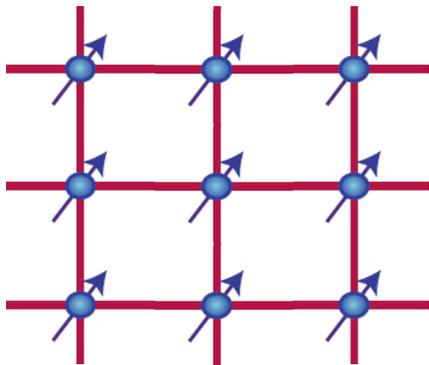
Example 3: magnetism

Bonus material

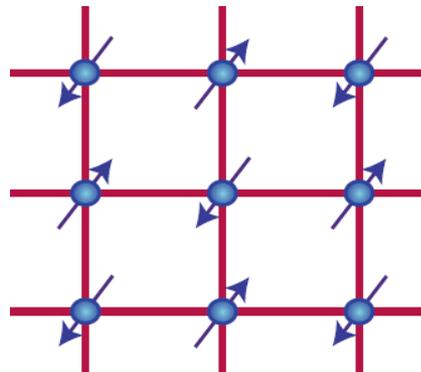
Insulators of some materials have **lattice of localized electrons**

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

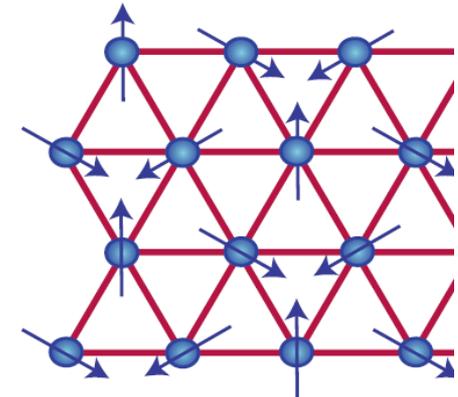
Ferromagnetic order



Antiferromagnetic order



on square lattice



on triangular lattice

Origin of magnetic order

Bonus material

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

- Is magnetic dipole-dipole interaction between e^- origin of magnetic order?

distance of $e^- \sim 2 \text{ \AA}$

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

→ magnetism would only occur below 1K,
therefore it must have different origin

- typical Coulomb interaction between e^- :

$$U_{\text{el}} \sim 1 \text{ eV} \sim 1000 \text{ K}$$

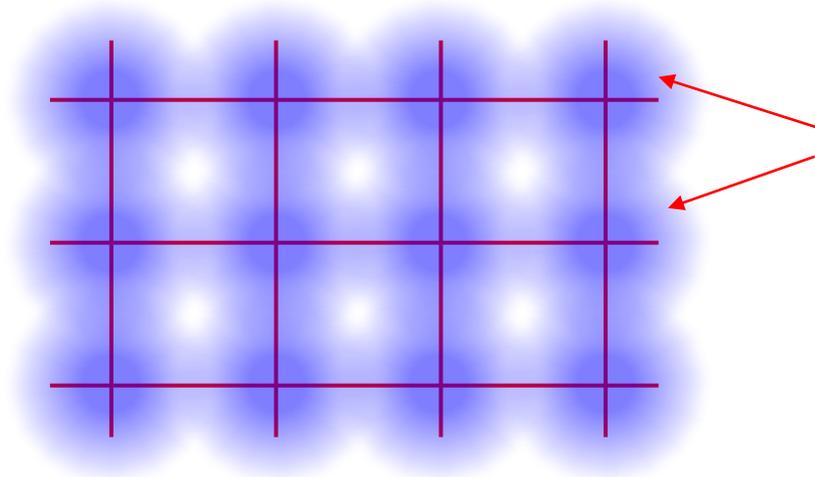
Coulomb interaction strong enough,
but not spin dependent

Is there a mechanism that renders Coulomb interaction spin dependent?

Yes, [exchange interaction](#)!

Exchange interaction

Bonus material



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

Wavefunctions of these electrons on neighboring atoms overlap

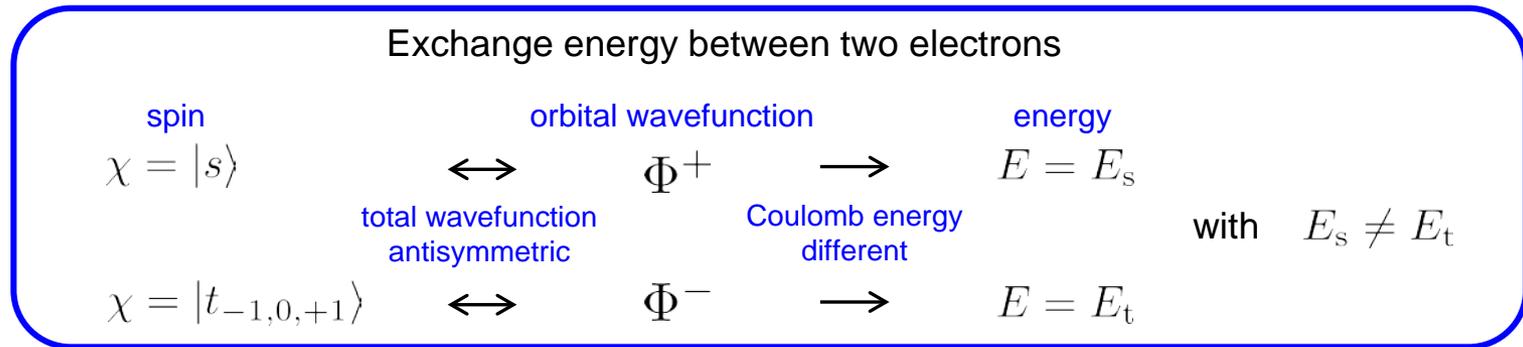
Exchange energy shift between singlet and triplet spin configuration

If $E_t < E_s$: ferromagnetic interaction

If $E_s < E_t$: antiferromagnetic interaction

Effective interactions

Bonus material



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

→ simplified *effective* Hamiltonian

Effective spin Hamiltonian

Bonus material

Spin Hamiltonian

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

has eigenvectors and -values as required for exchange interaction!

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

Check: eigenvectors and -values of $\hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2$

$$\hat{\vec{S}}^2 = (\hat{\vec{S}}_1 + \hat{\vec{S}}_2)^2 = \hat{\vec{S}}_1^2 + \hat{\vec{S}}_2^2 + 2\hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2$$

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

\uparrow difference of $\hbar^2\hat{1}$

$$\begin{matrix} \uparrow & \uparrow & \uparrow \\ \frac{3}{4}\hbar^2\hat{1} & \frac{3}{4}\hbar^2\hat{1} & \frac{3}{4}\hbar^2\hat{1} \\ \uparrow & \uparrow & \uparrow \\ S(S+1)\hbar^2\hat{1} & \left\{ \begin{array}{l} 0 \\ 2\hbar^2\hat{1} \end{array} \right. & \left\{ \begin{array}{l} 0 \\ 2\hbar^2\hat{1} \end{array} \right. \end{matrix} \begin{matrix} \text{for singlet} \\ \text{for triplet} \end{matrix}$$

Heisenberg Hamiltonian

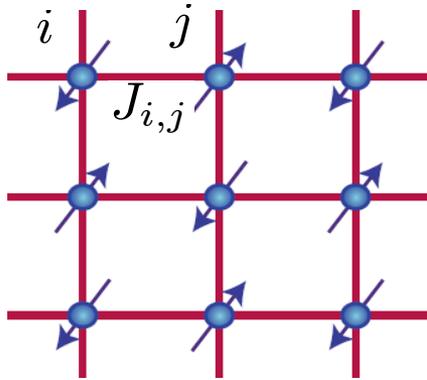
Bonus material

Many spins with pairwise interactions:

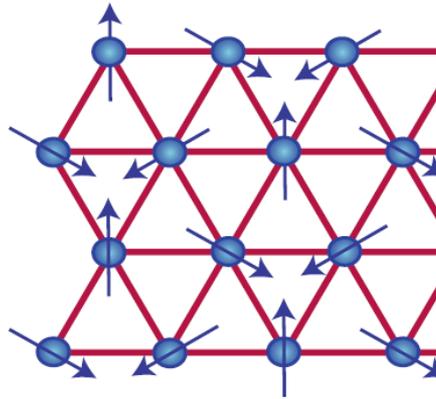
$$\hat{H} = -\frac{1}{2} \sum_{i,j;i \neq j} J_{i,j} \hat{\vec{S}}_i \cdot \hat{\vec{S}}_j$$

↑ i, j are indices enumerating the lattice sites

Examples:

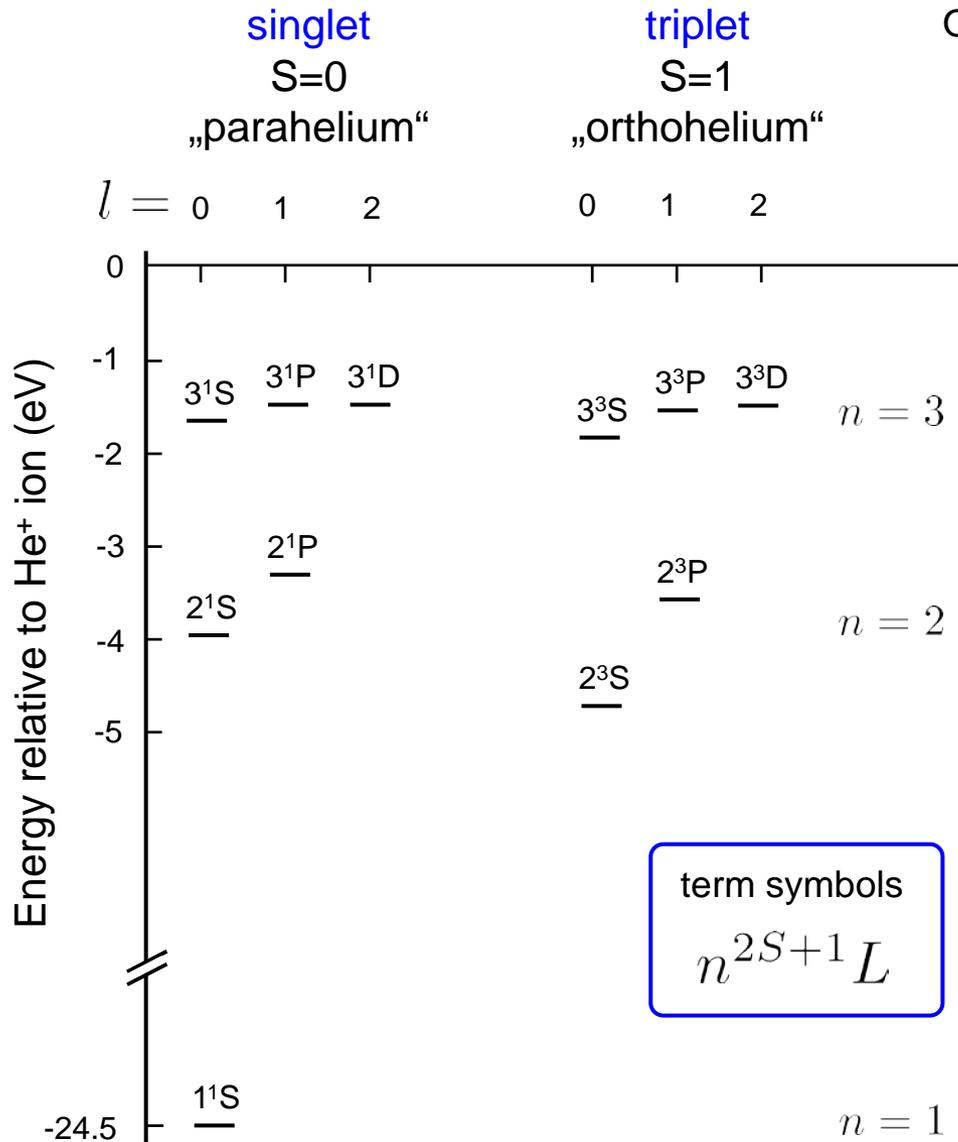


Square lattice



Triangular lattice

He energy levels



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

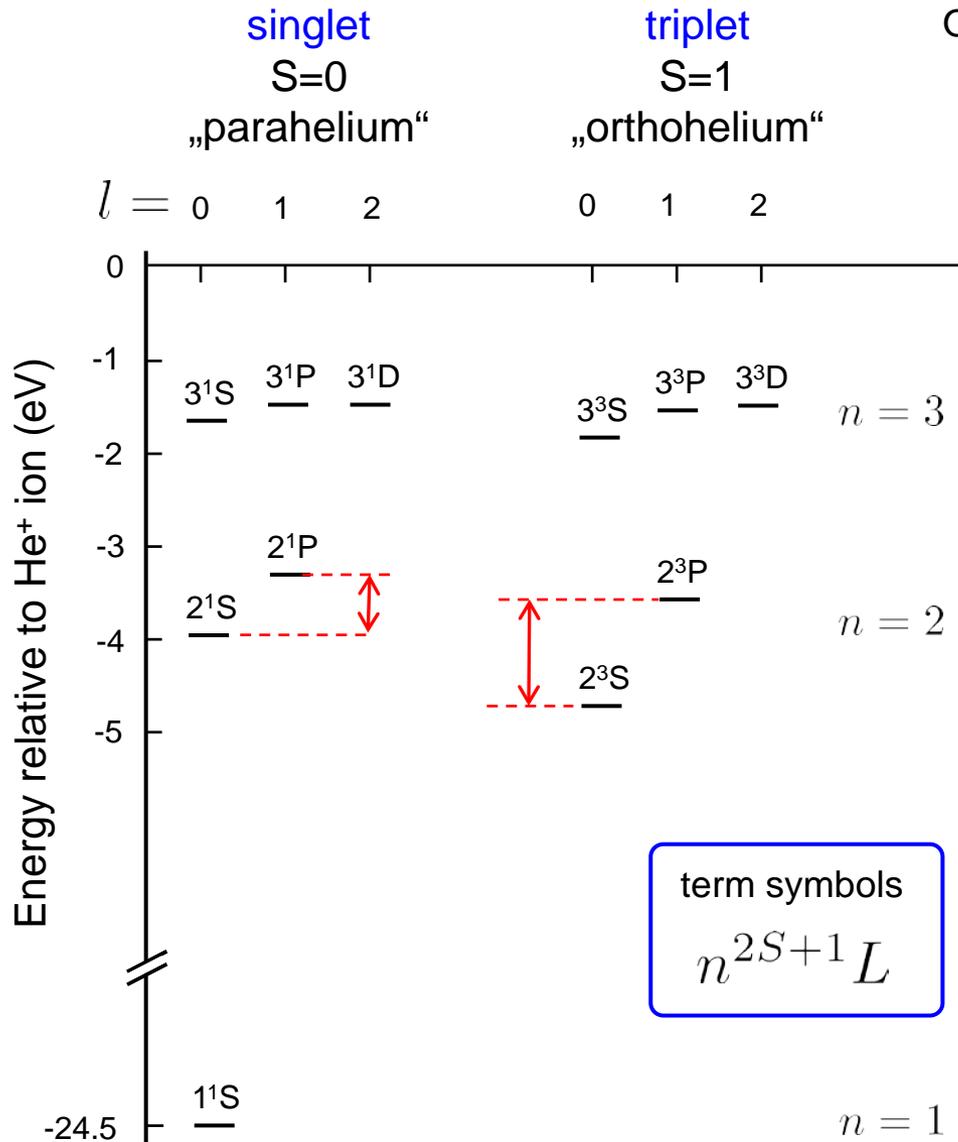
Shielding of nuclear charge

Singlet levels always higher than triplet levels

Reason: „exchange energy“



He energy levels



Observations

Ground state binding energy lower than predicted

See chapter „variational principle“

P levels always higher than S levels

Shielding of nuclear charge

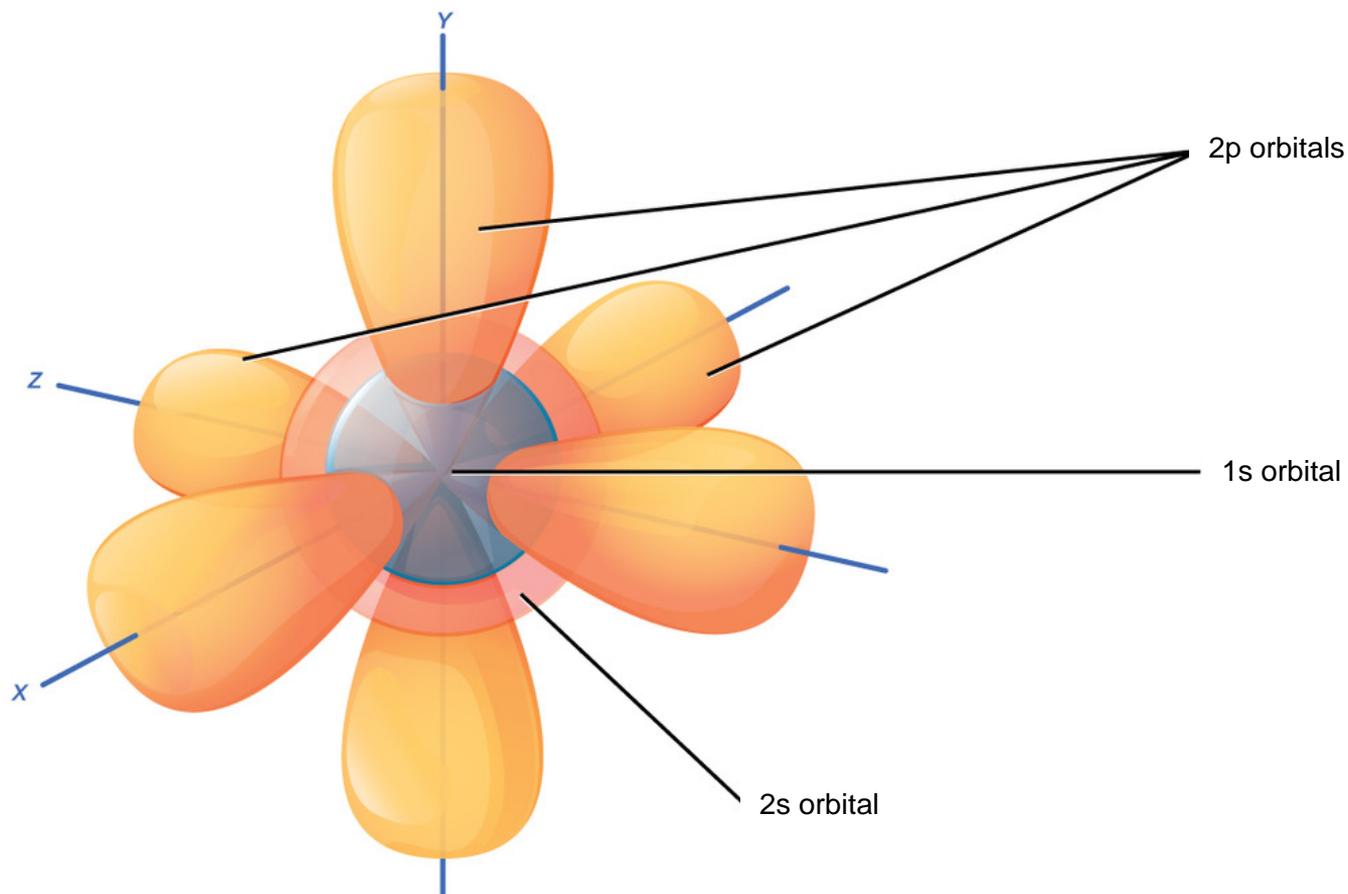
Singlet levels always higher than triplet levels

Reason: „exchange energy“



Shielding of nuclear charge

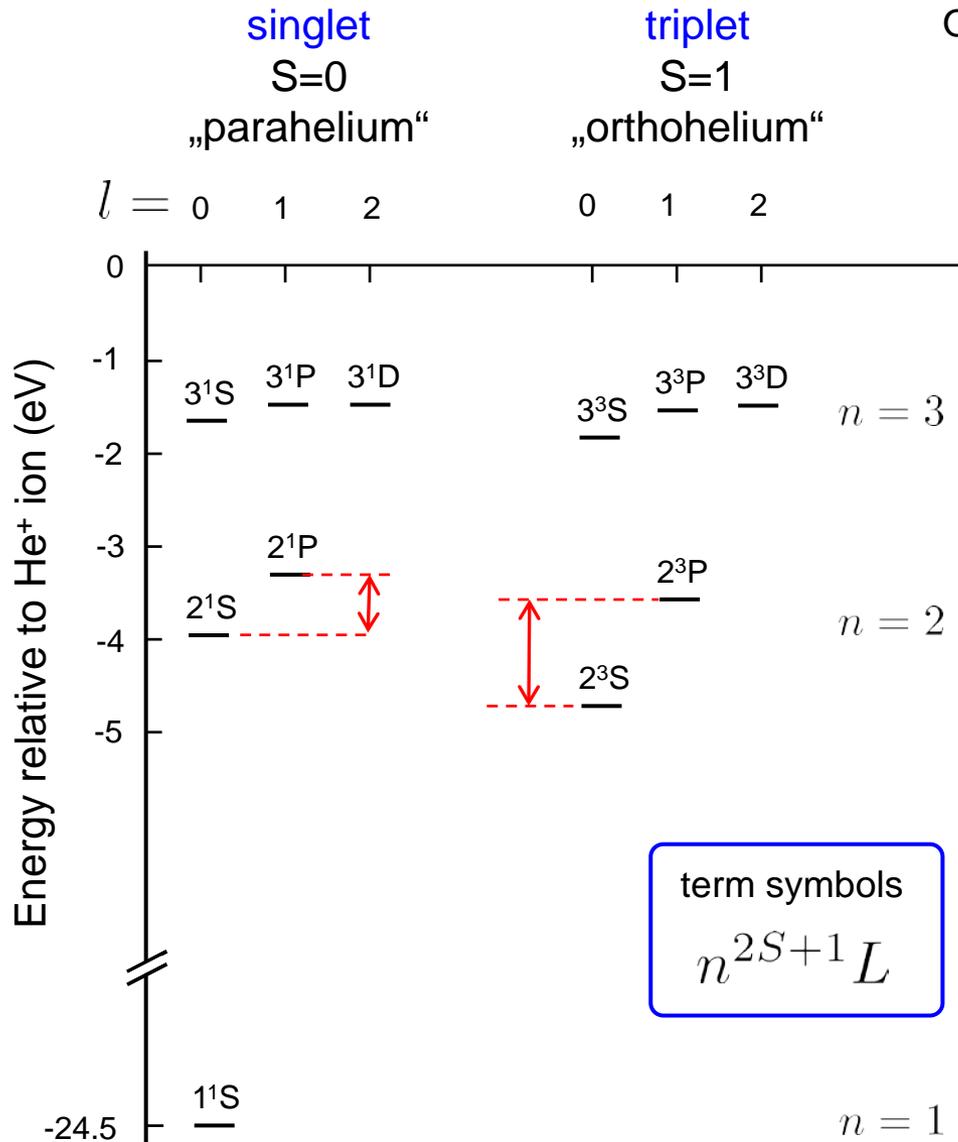
Inner shell e^- shield nuclear charge and reduce Coulomb potential experienced by far away e^-



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

} better shielding \rightarrow less binding energy

He energy levels



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

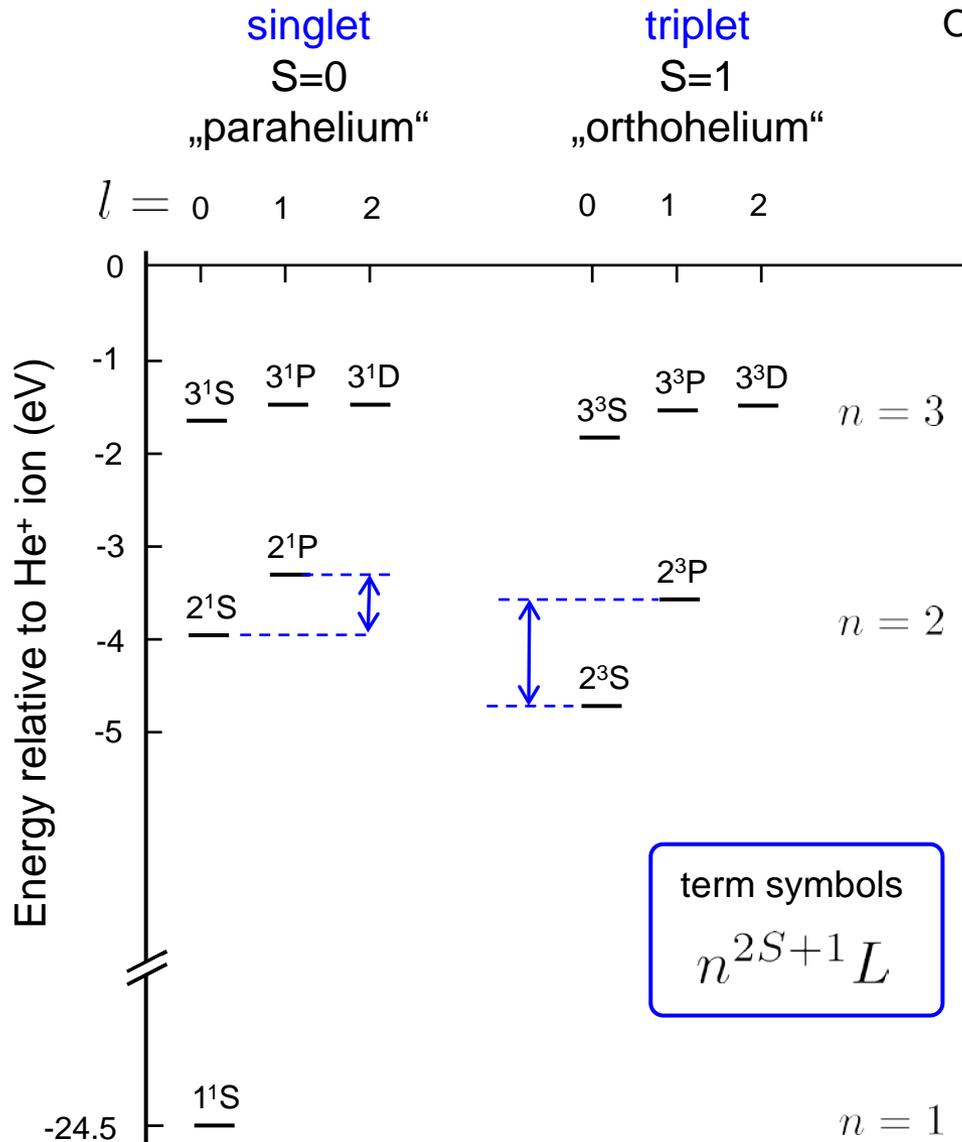
Shielding of nuclear charge

Singlet levels always higher than triplet levels

Reason: „exchange energy“



He energy levels



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 Griffiths 3rd 5.2.2
- Energy structure of He 5.2.1
 - „exchange energy“ 5.1.2
 - examples: He, covalent bonds, magnetism
 - shielding of nuclear charge by inner shell electrons 5.2.2
- • Energy structure of atoms with many electrons 5.2.2
 - Hund's rules
 - the periodic table

The periodic table

Our goals

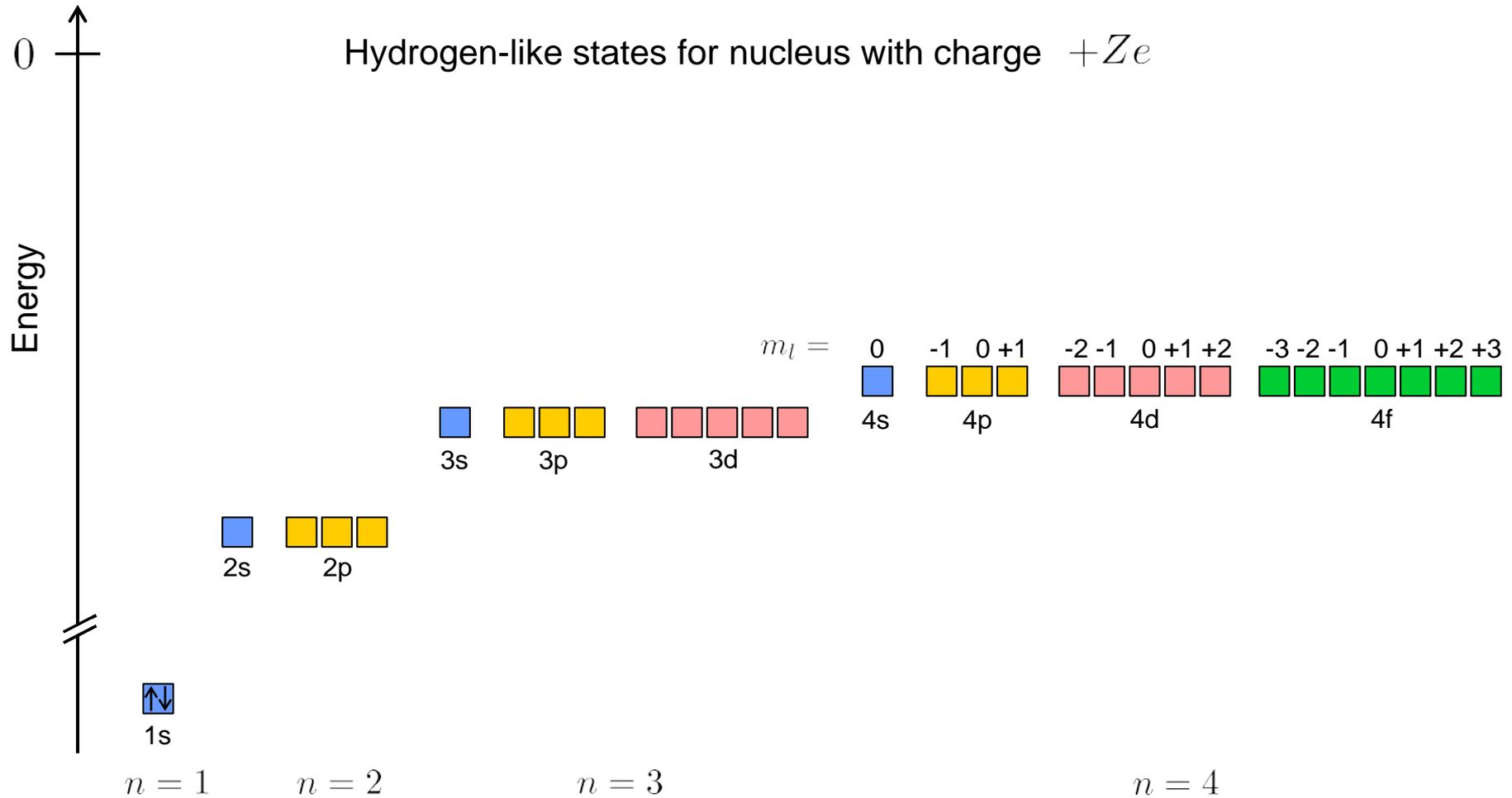
- understand structure of periodic table
- determine groundstate e^- configuration

1 H Hydrogen 1.008																	18 He Helium 4.003
3 Li Lithium 6.941	2 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Actinides	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

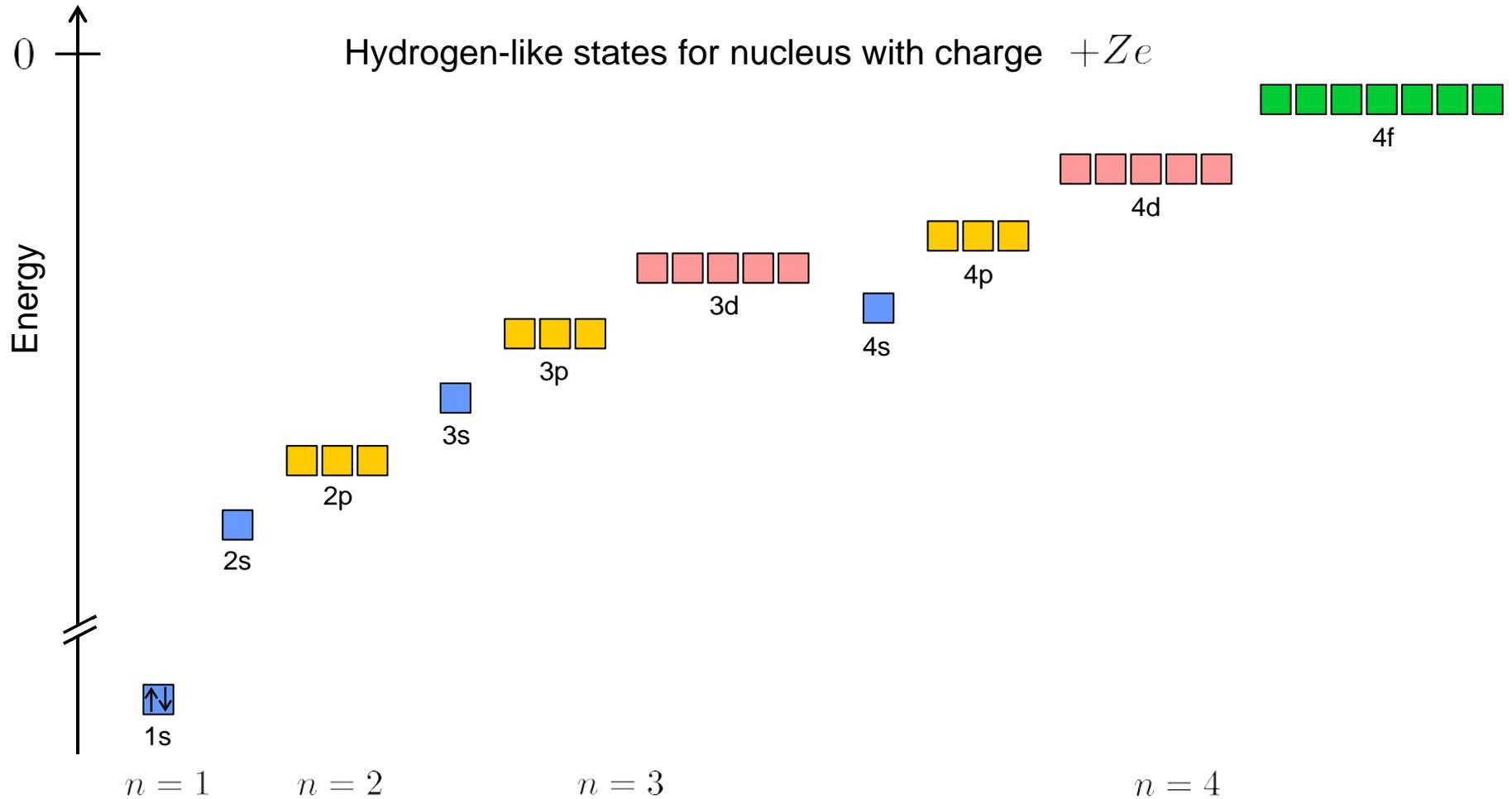
Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide
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Starting point: hydrogen states

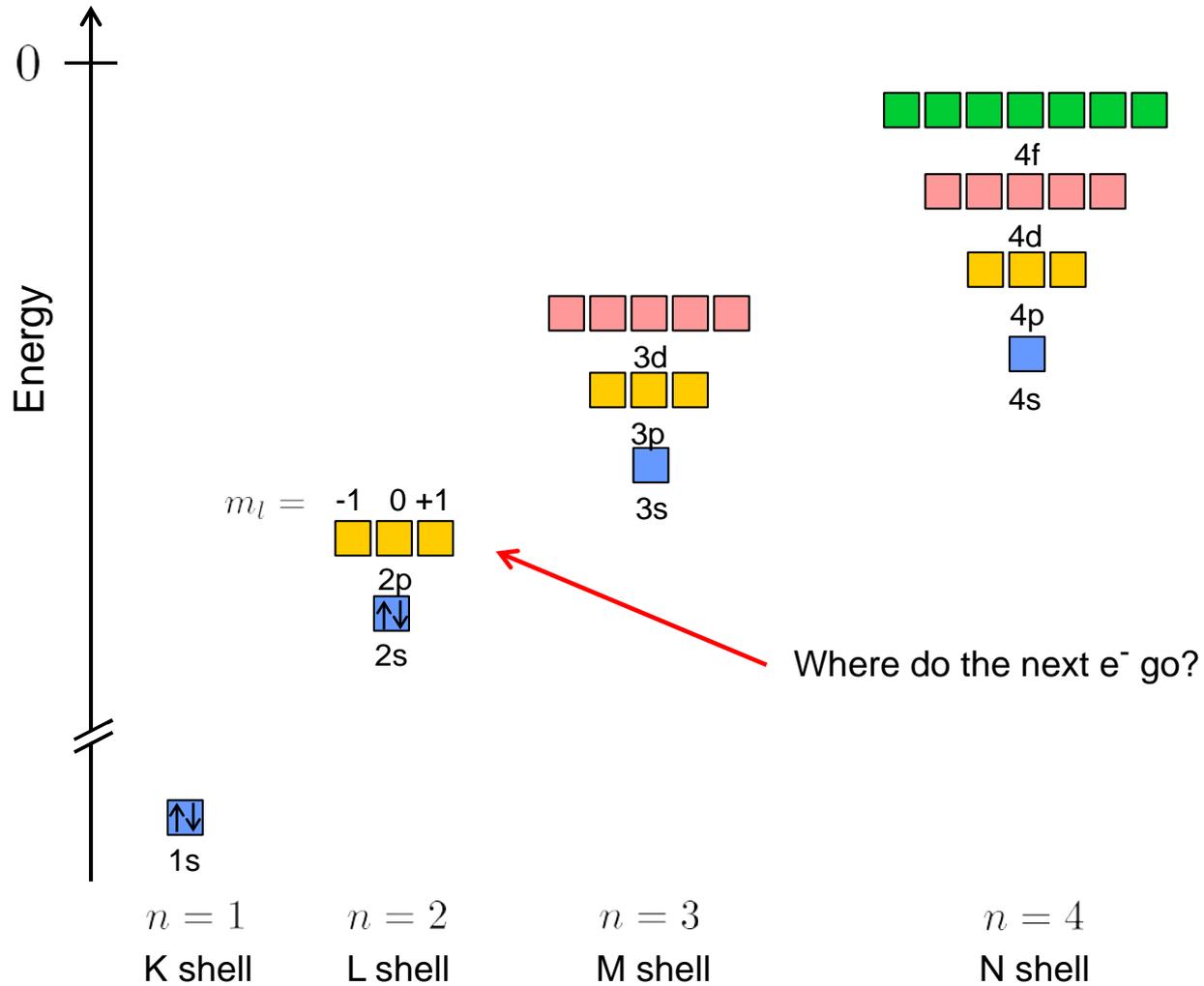


- maximally two e^- per state, spin \uparrow and spin \downarrow
- in groundstate of multi- e^- atoms, e^- occupy lowest possible states

Energy shifts by shielding



Filling in more electrons



Hund's rules

1st Hund's rule: maximize total e⁻ spin S

Reason: $m_l = -1 \ 0 \ +1$
 has higher energy than or because of increased shielding of nuclear charge (and increased repulsion between e⁻ in the same orbital)

has higher energy than or because of exchange interaction

Handwaving arguments:

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

Handwaving argument:

$m_l = -2 \ -1 \ 0 \ +1 \ +2$
 has lower energy than e.g.

because e⁻ „rotate in same direction“ and encounter each other less often → less Coulomb repulsion

3rd Hund's rule:

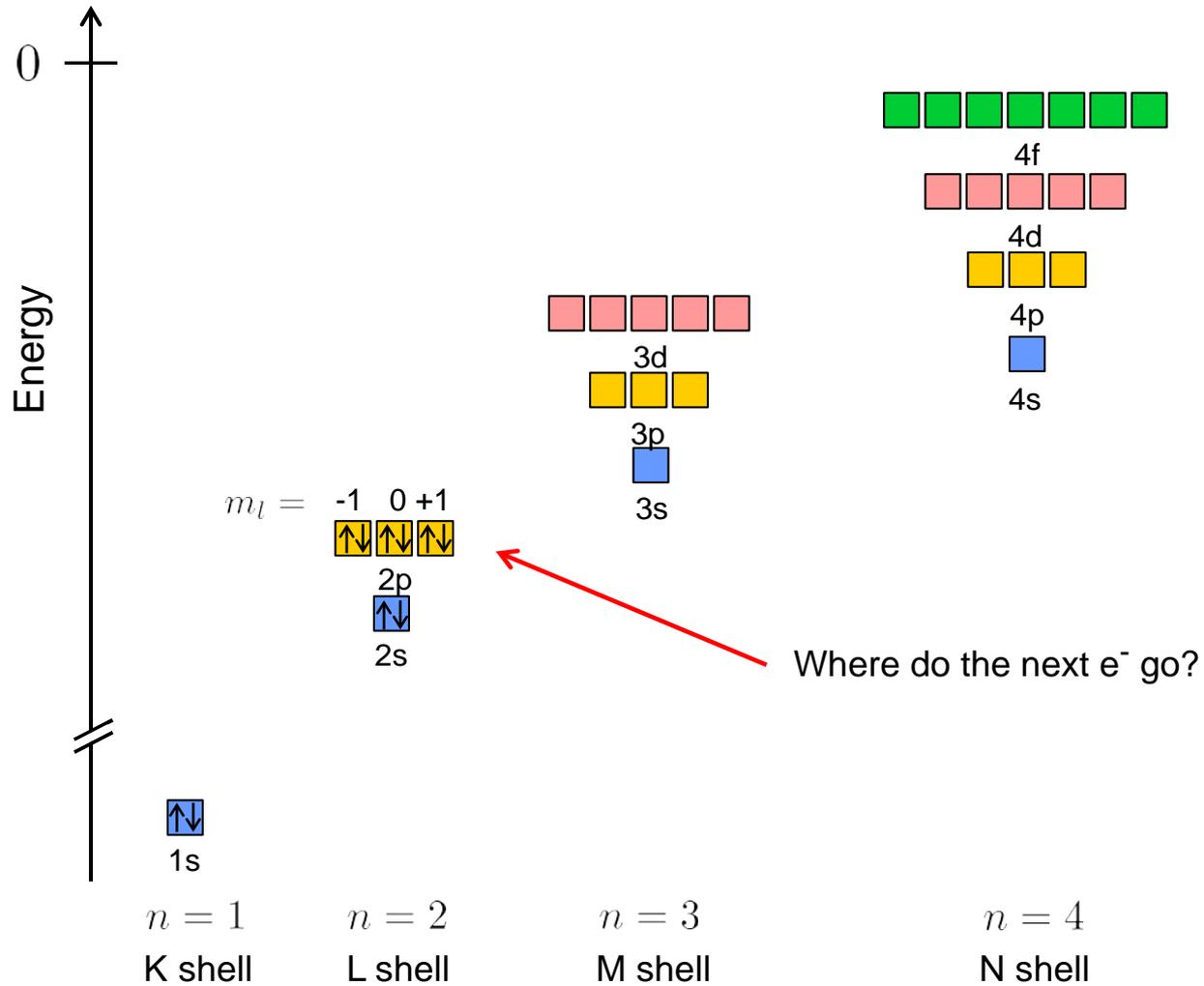
Total electronic angular momentum projection (spin + orbit) J

is $J = |L - S|$ if last orbital no more than half filled

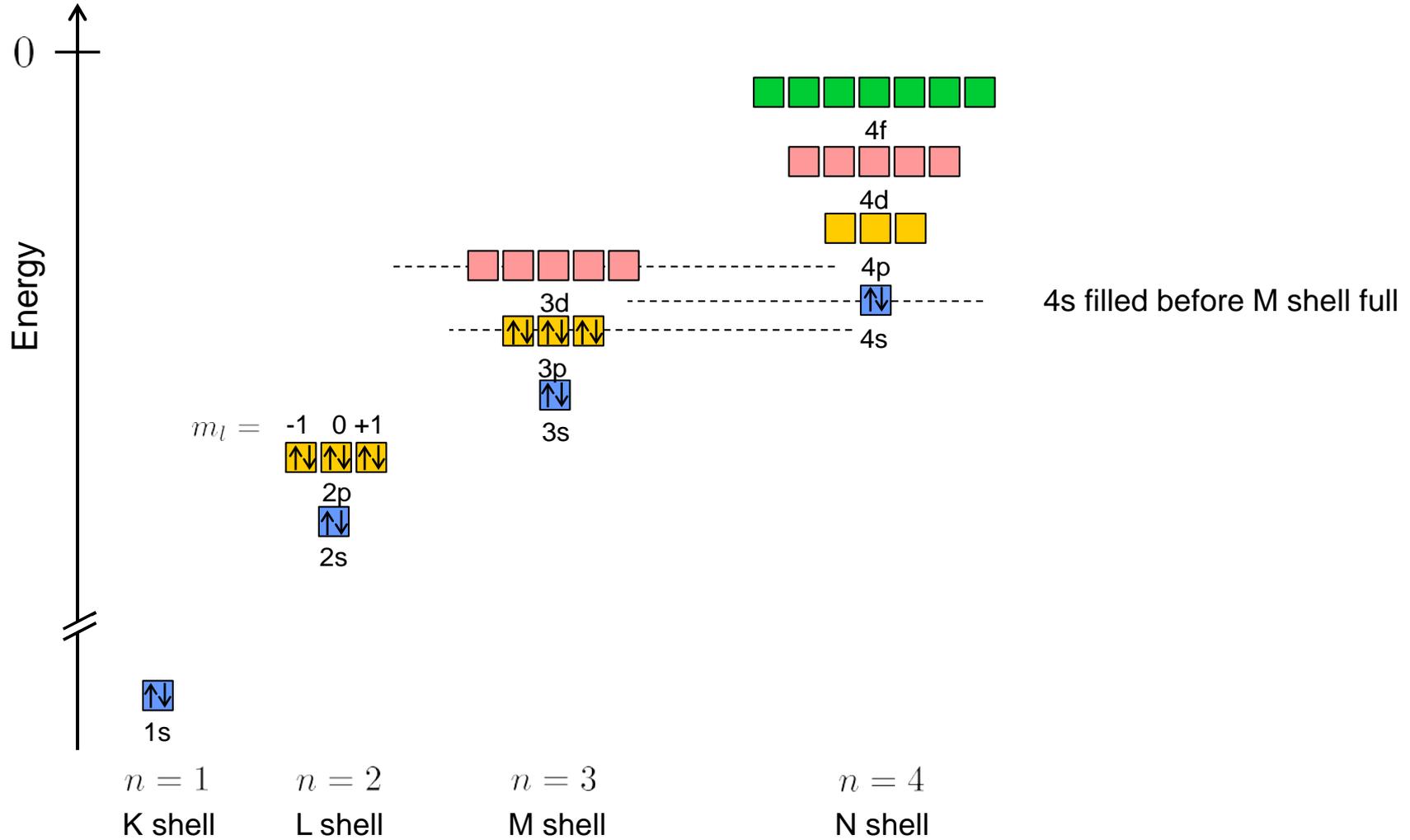
and $J = |L + S|$ if last orbital more than half filled

Reason: spin-orbit coupling (see later)

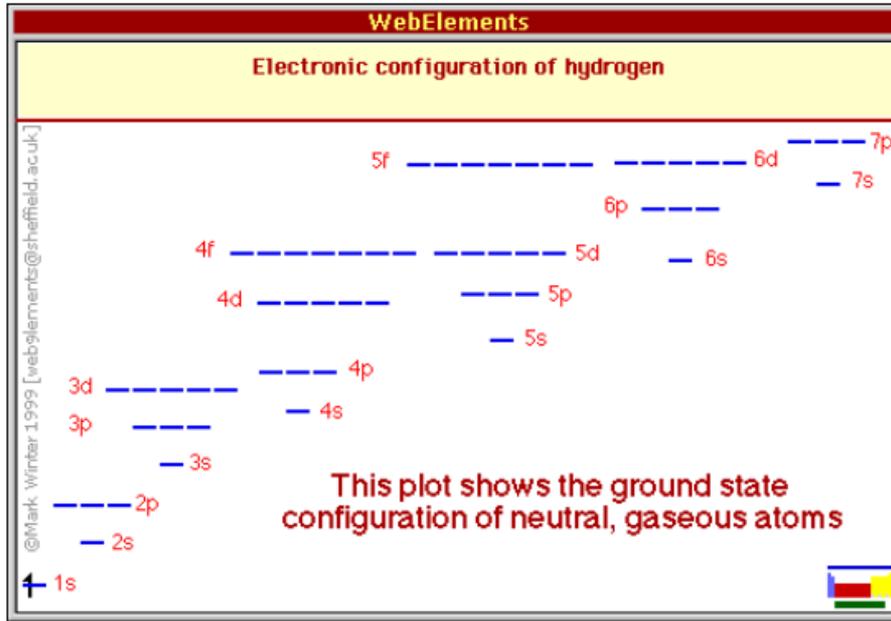
Filling in more electrons



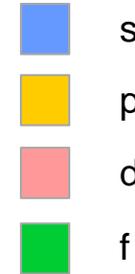
Filling in more electrons



The periodic table



highest orbital with e⁻



Group	1	2
Period 1	1 H 1.008	
2	3 Li 6.94	4 Be 9.0122
3	11 Na 22.990	12 Mg 24.305
4	19 K 39.098	20 Ca 40.078
5	37 Rb 85.468	38 Sr 87.62
6	55 Cs 132.91	56 Ba 137.33
7	87 Fr [223.02]	88 Ra [226.03]

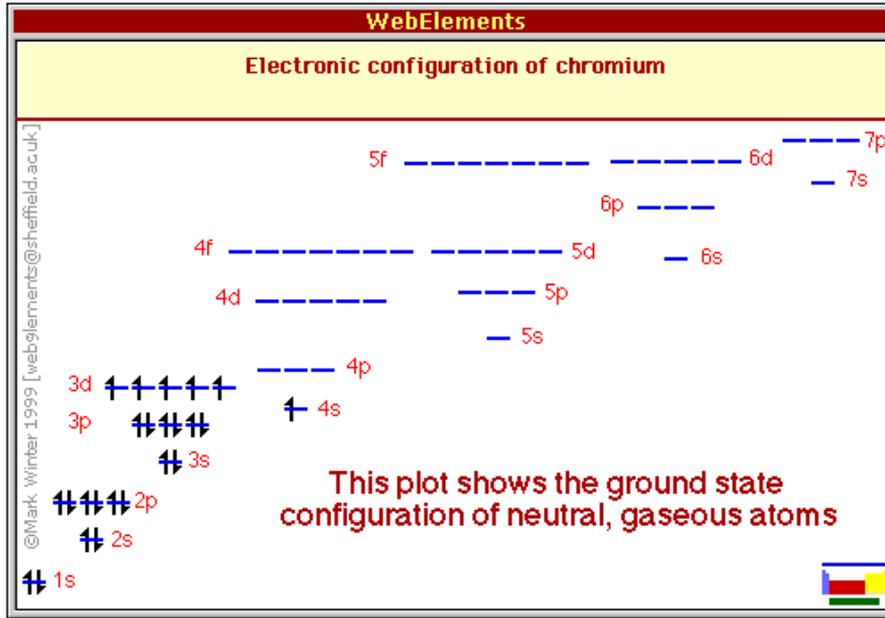
21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798
39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc [97.91]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [208.98]	85 At [209.99]	86 Rn [222.02]
103 Lr [262.11]	104 Rf [265.12]	105 Db [268.13]	106 Sg [271.13]	107 Bh [270]	108 Hs [277.15]	109 Mt [276.15]	110 Ds [281.16]	111 Rg [280.16]	112 Cn [285.17]	113 Nh [284.18]	114 Fl [289.19]	115 Mc [288.19]	116 Lv [293]	117 Ts [294]	118 Og [294]

*Lanthanoids

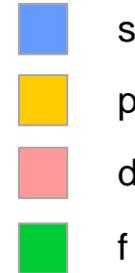
57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [144.91]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05
89 Ac [227.03]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237.05]	94 Pu [244.06]	95 Am [243.06]	96 Cm [247.07]	97 Bk [247.07]	98 Cf [251.08]	99 Es [252.08]	100 Fm [257.10]	101 Md [258.10]	102 No [259.10]

**Actinoids

The periodic table



highest orbital with e⁻



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39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc [97.91]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [208.98]	85 At [209.99]	86 Rn [222.02]
103 Lr [262.11]	104 Rf [265.12]	105 Db [268.13]	106 Sg [271.13]	107 Bh [270]	108 Hs [277.15]	109 Mt [276.15]	110 Ds [281.16]	111 Rg [280.16]	112 Cn [285.17]	113 Nh [284.18]	114 Fl [289.19]	115 Mc [288.19]	116 Lv [293]	117 Ts [294]	118 Og [294]

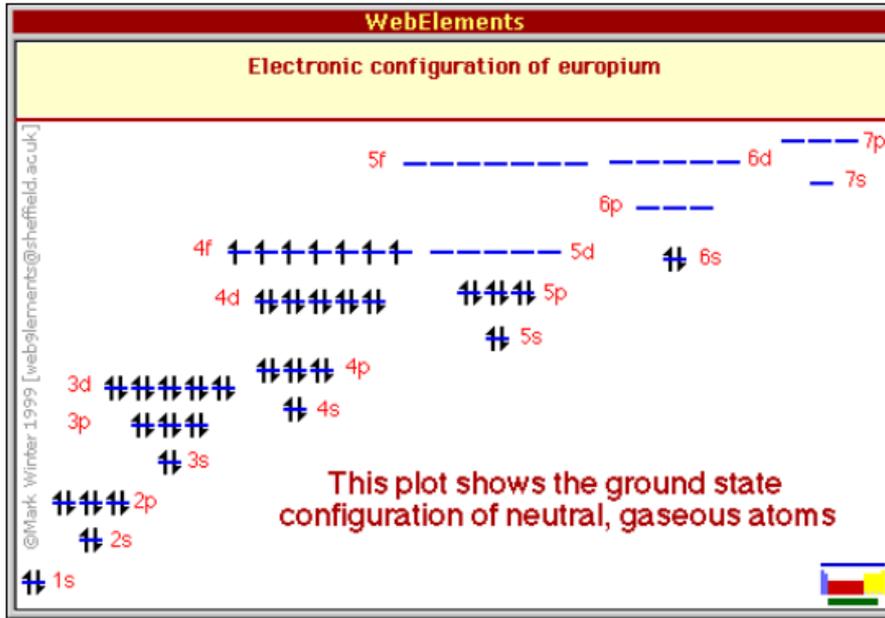
*Lanthanoids

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [144.91]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05
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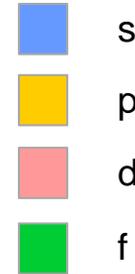
**Actinoids

89 Ac [227.03]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237.05]	94 Pu [244.06]	95 Am [243.06]	96 Cm [247.07]	97 Bk [247.07]	98 Cf [251.08]	99 Es [252.08]	100 Fm [257.10]	101 Md [258.10]	102 No [259.10]
-----------------------------	---------------------------	---------------------------	--------------------------	-----------------------------	-----------------------------	-----------------------------	-----------------------------	-----------------------------	-----------------------------	-----------------------------	------------------------------	------------------------------	------------------------------

The periodic table



highest orbital with e⁻



Group	1	2
Period 1	1 H 1.008	
2	3 Li 6.94	4 Be 9.0122
3	11 Na 22.990	12 Mg 24.305
4	19 K 39.098	20 Ca 40.078
5	37 Rb 85.468	38 Sr 87.62
6	55 Cs 132.91	56 Ba 137.33
7	87 Fr [223.02]	88 Ra [226.03]

21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	2 He 4.0026
39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc [97.91]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	5 B 10.81
71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	6 C 12.011
103 Lr [262.11]	104 Rf [265.12]	105 Db [268.13]	106 Sg [271.13]	107 Bh [270]	108 Hs [277.15]	109 Mt [276.15]	110 Ds [281.16]	111 Rg [280.16]	112 Cn [285.17]	7 N 14.007
31 Ga 69.723	32 Ge 72.63	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	8 O 15.999
81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [208.98]	85 At [209.99]	86 Rn [222.02]	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [208.98]	9 F 18.998
113 Nh [284.18]	114 Fl [289.19]	115 Mc [288.19]	116 Lv [293]	117 Ts [294]	118 Og [294]	113 Nh [284.18]	114 Fl [289.19]	115 Mc [288.19]	116 Lv [293]	10 Ne 20.180

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**Actinoids	89 Ac [227.03]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237.05]	94 Pu [244.06]	95 Am [243.06]	96 Cm [247.07]	97 Bk [247.07]	98 Cf [251.08]	99 Es [252.08]	100 Fm [257.10]	101 Md [258.10]	102 No [259.10]

Overview „Structure of atoms & the periodic table“

Outline

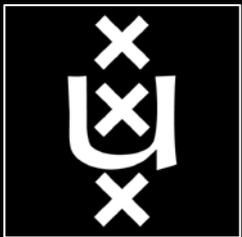
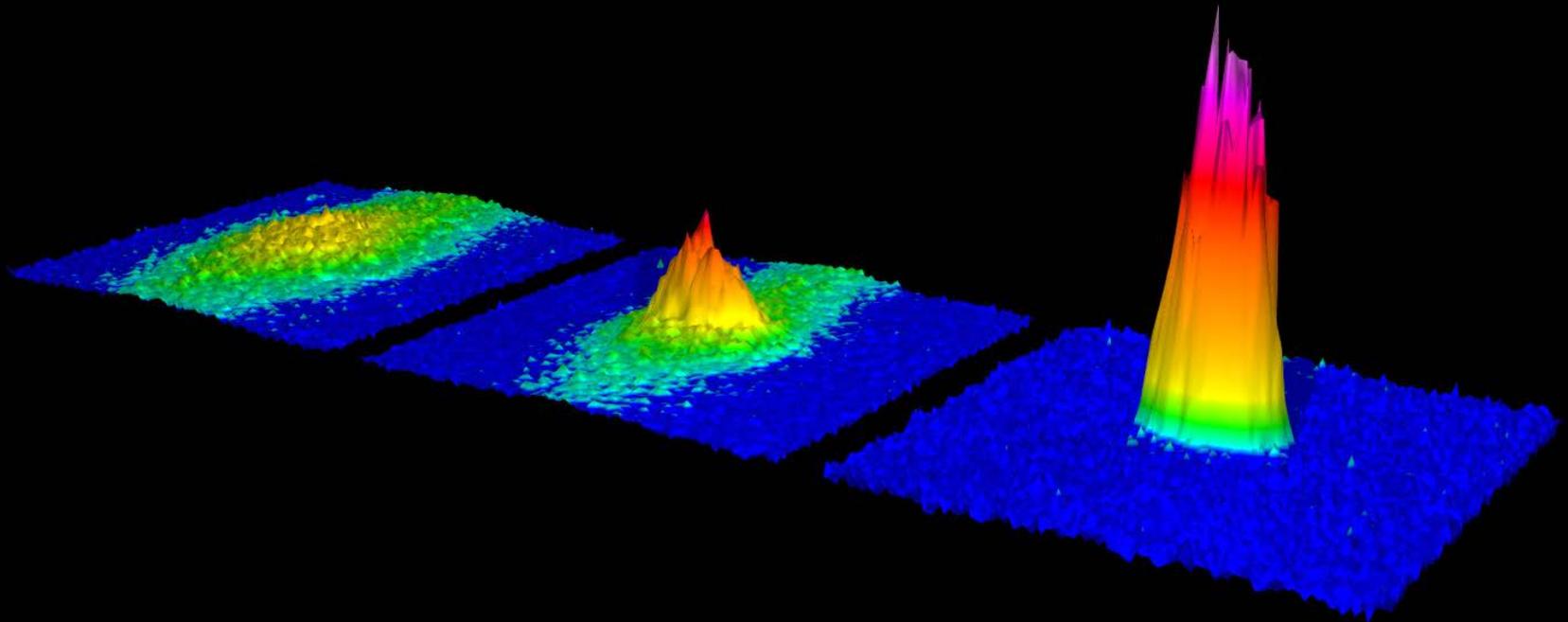
- Reminder of Piet's lecture on orbital and spin structure of atoms Griffiths 3rd 5.2.2
- Energy structure of He 5.2.1
 - „exchange energy“ 5.1.2
 - examples: He, covalent bonds, magnetism
 - shielding of nuclear charge by inner shell electrons 5.2.2
- Energy structure of atoms with many electrons 5.2.2
 - 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)

last
lecture



Structure of atoms & the periodic table

Griffiths 3rd 5.1, 5.2

Crystalline solids

5.3.2

Time-independent perturbation theory

7.1, 7.2

Structure of hydrogen

7.3 – 7.5

Variational principle

8.1 – 8.3

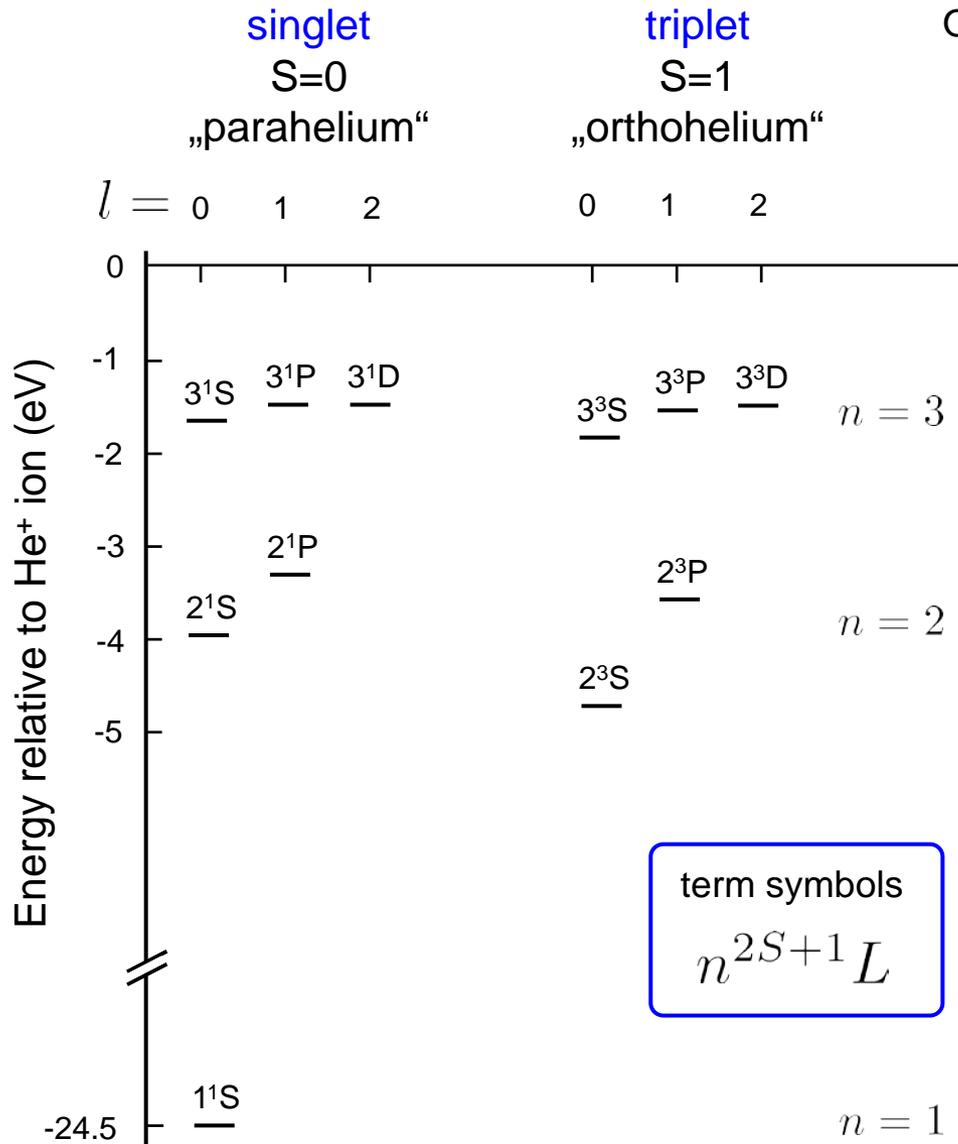
Time-dependent perturbation theory, atom-light interaction

11.1 – 11.4

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

Questions: schreck@StrontiumBEC.com

He energy levels



Orbital wavefunctions:

$$\Phi_e(\vec{r}_1, \vec{r}_2) =$$

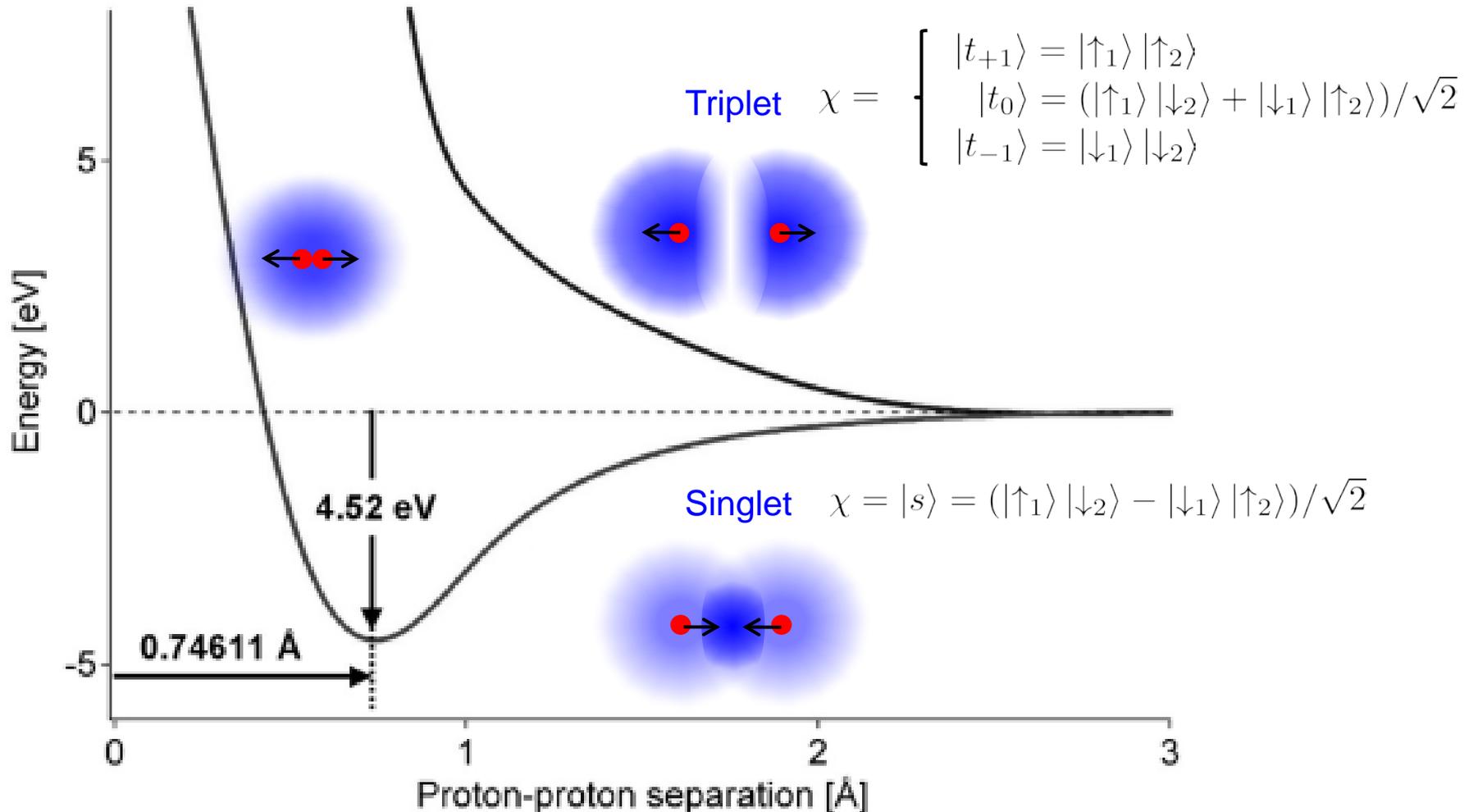
$$(\Phi_{100}(\vec{r}_1)\Phi_{nlm}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2)\Phi_{nlm}(\vec{r}_1))/\sqrt{2}$$

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

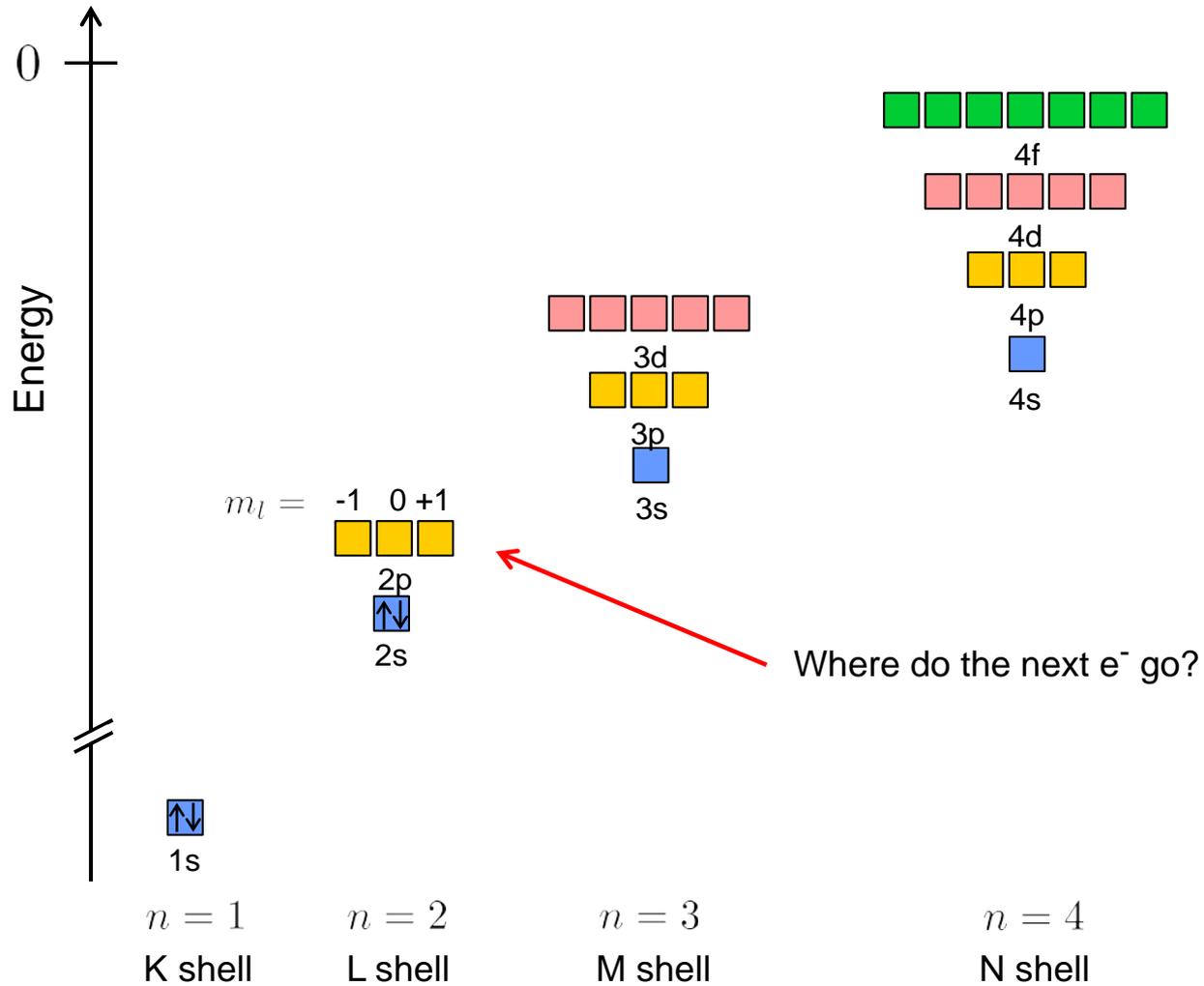
Observations

Example 2: covalent bonds

Potential energy curves of H₂ molecule



Filling in more electrons



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	Griffiths 3 rd 5.1, 5.2	
today {	Crystalline solids	5.3.2	
	Time-independent perturbation theory	7.1, 7.2	
	Structure of hydrogen	7.3 – 7.5	
	Variational principle	8.1 – 8.3	
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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

Griffiths 5.3.1

simple model describing metals

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

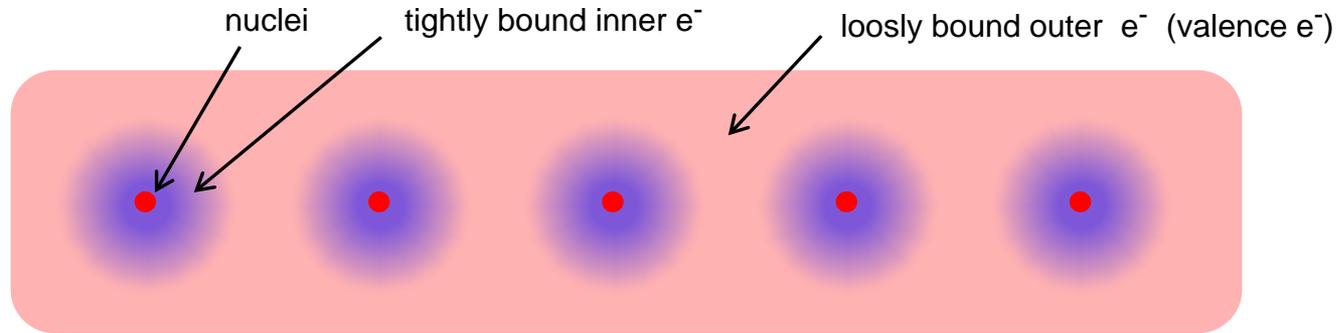
- white dwarfs
- neutron stars
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Plan of section

- • 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

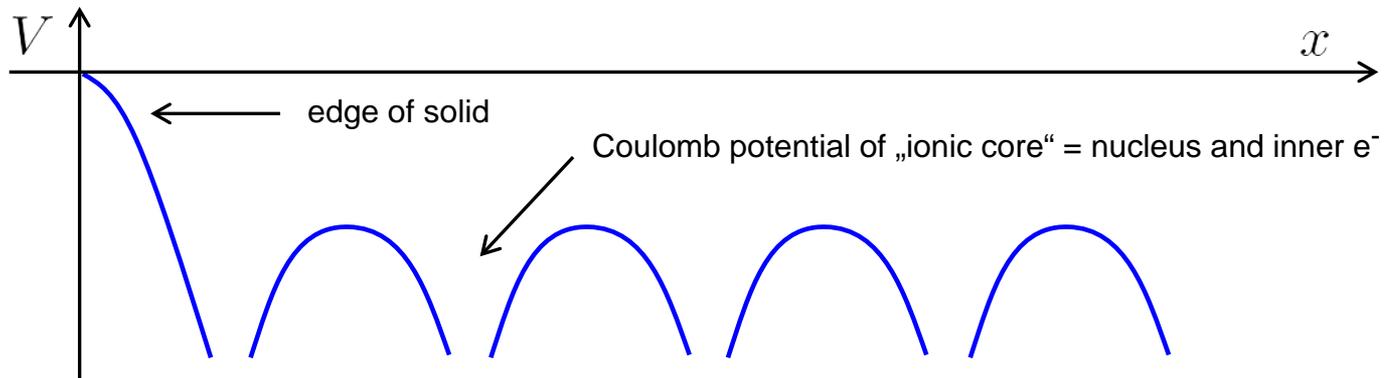
Structure



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

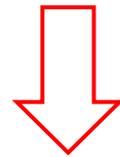
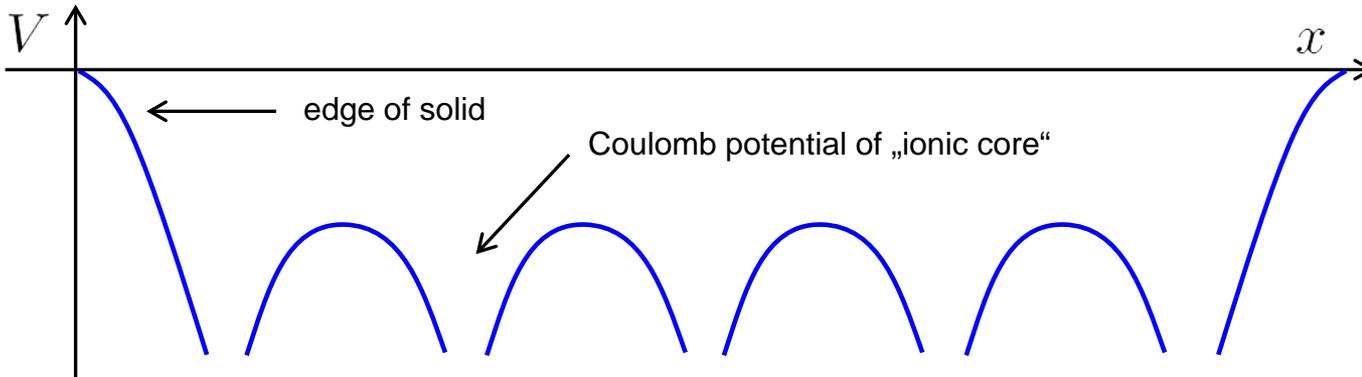
Here only interested in behavior of valence e^-

Potential seen by valence e^- :

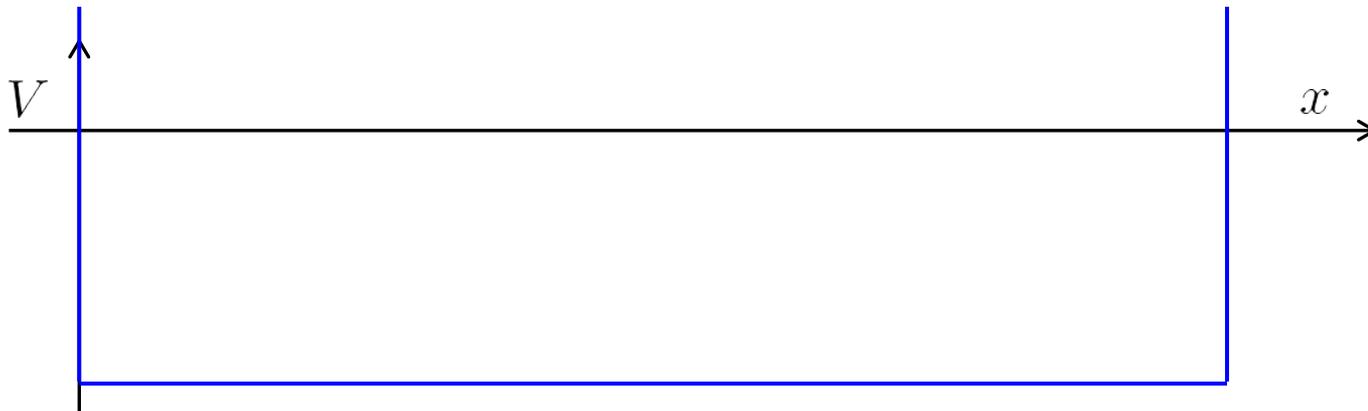


The free electron gas

Potential seen by valence e^- :



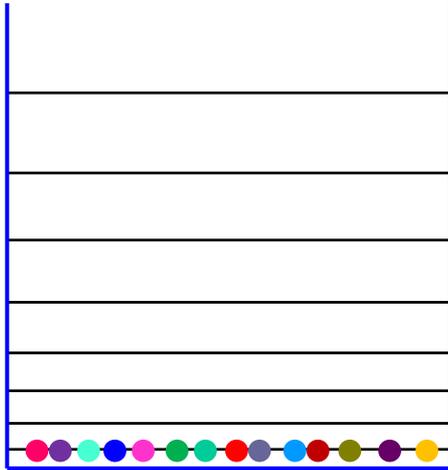
simplified description:
 e^- in box potential



Preview of first essential result

Compare distinguishable particles and e^- , both at zero temperature

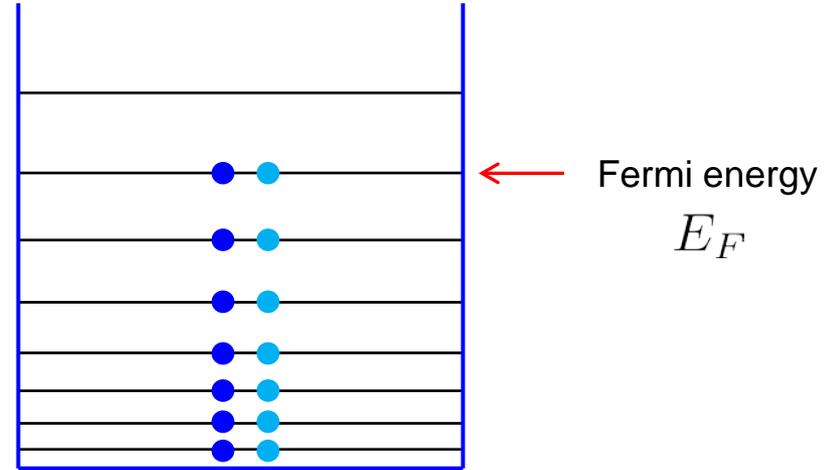
distinguishable
particles



number of particles times
energy of lowest state

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

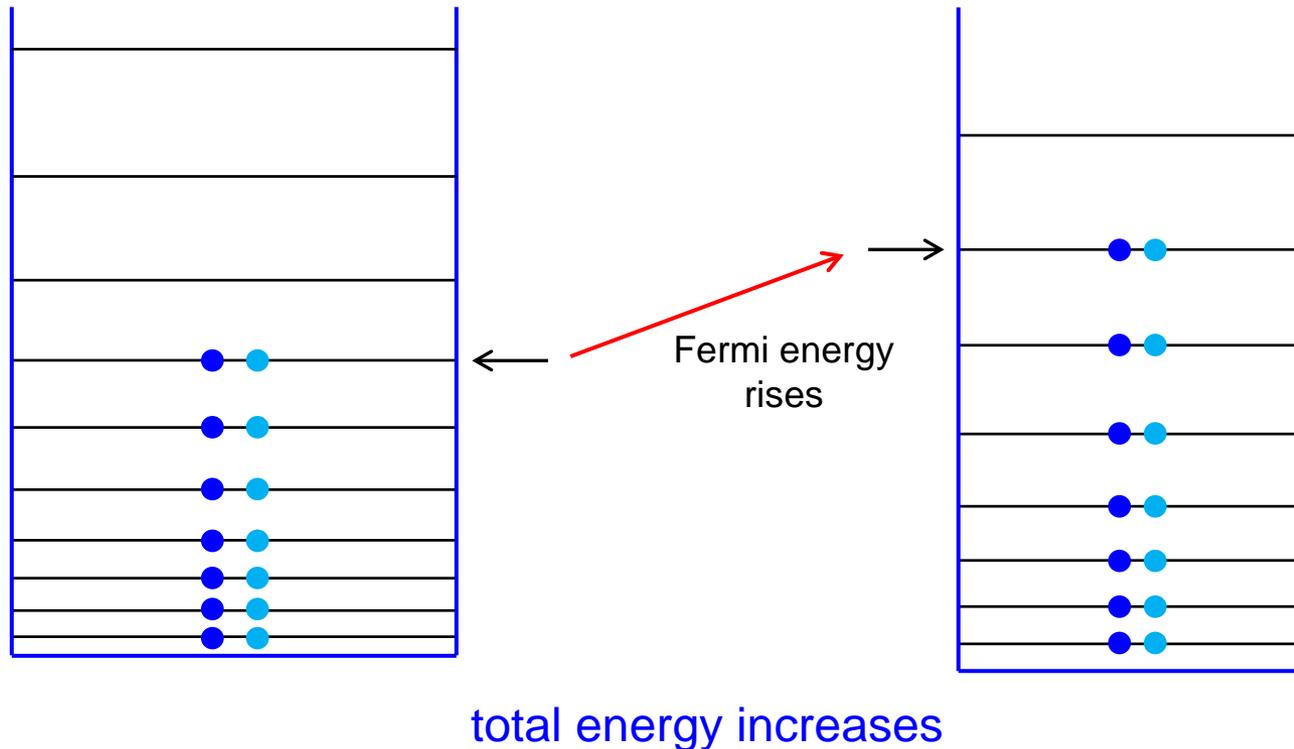
iron: $E_F = 11\text{eV} = k_B \times 10^5 \text{ K}$; $v_F = 2 \times 10^6 \text{ m/s}$

always the case if we have many
identical fermions, not only for e^-

total
energy:

Preview of second essential result

Compare same number of e^- in boxes of different size,
always at zero temperature



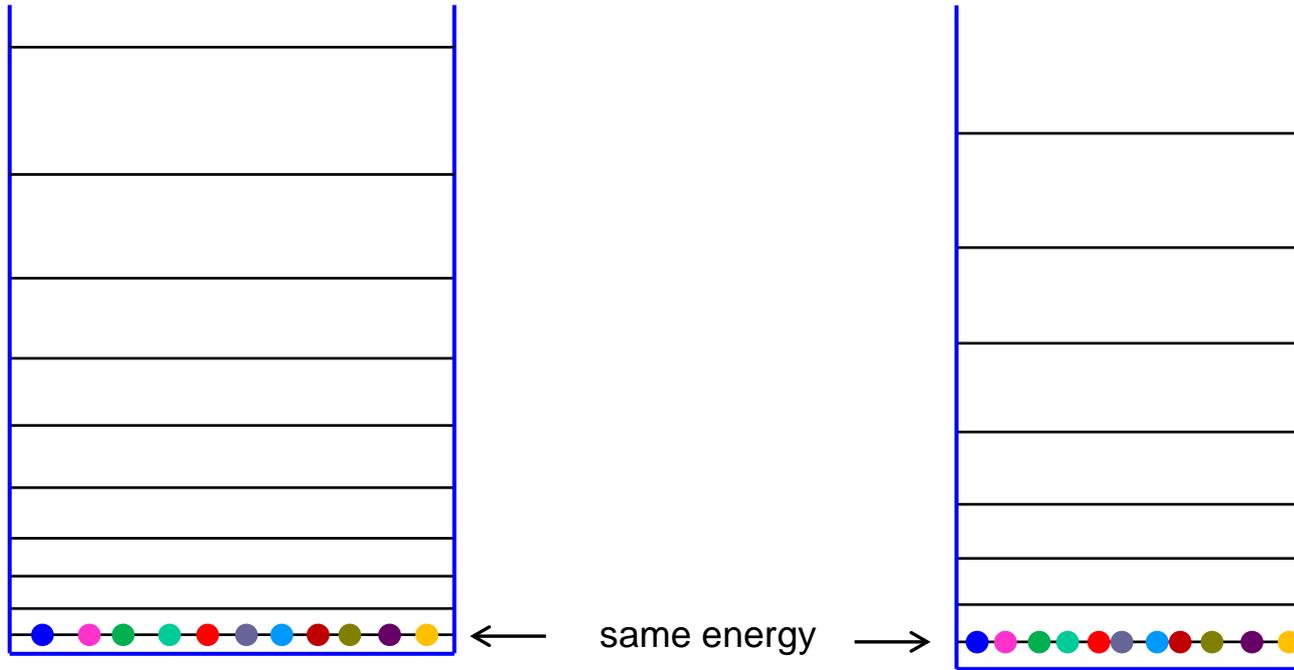
identical fermions do not „like“ to be compressed

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 collapse.
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^- 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

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

Schrödinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) = E \psi(\vec{r}) \quad ; \quad \psi(\vec{r}) = 0 \quad \text{outside solid}$$

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

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

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

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Boundary conditions: $\phi_i(0) = 0$ imposes $B_i = 0$

$\phi_i(l_i) = 0$ imposes quantization $k_i = n_i \pi / l_i$, with $n_i \in \{1, 2, \dots\}$.

$$\text{Energies: } E_{\{n_i\}} = \frac{\hbar^2}{2m} \sum_i k_i^2 = \frac{\hbar^2}{2m} |\vec{k}|^2, \quad \vec{k} = \begin{pmatrix} k_1 \\ k_2 \\ k_3 \end{pmatrix} \quad \text{“wavevector”}$$

Sidenote: Why only positive k_i ?

We used standing waves as ansatz.

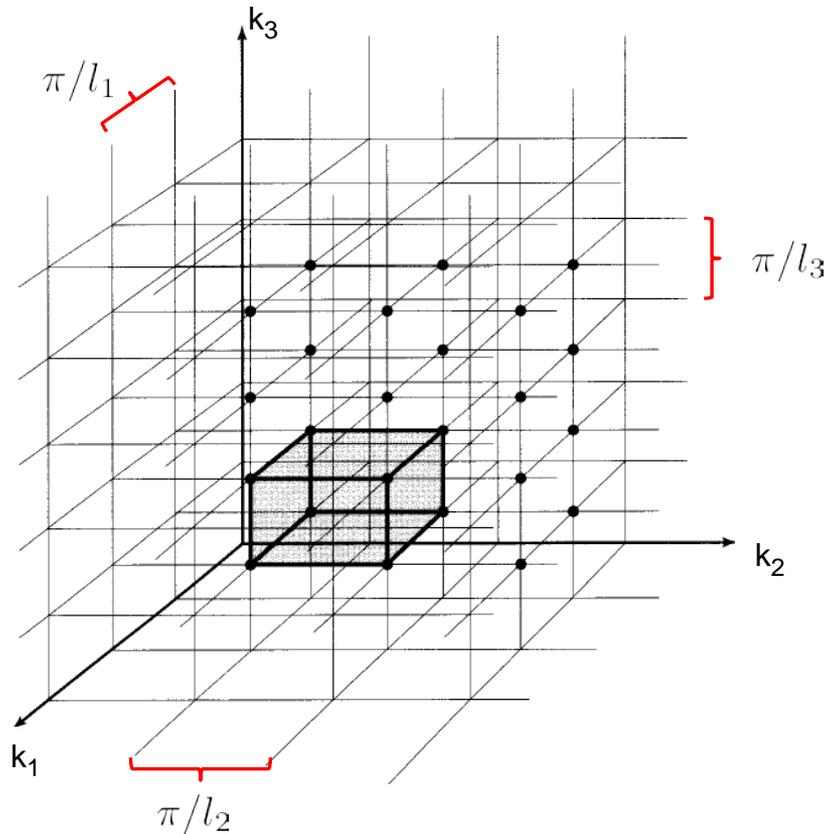
For them $-k_i$ leads after normalization to same wavefunction as k_i .

\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

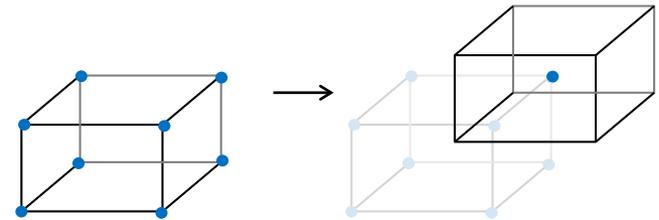
Allowed points in k -space form a grid:



$$k_i = n_i \frac{\pi}{l_i}, \text{ with } n_i \in \{1, 2, \dots\}$$

1 grid point per box:

easier to see if you shift box



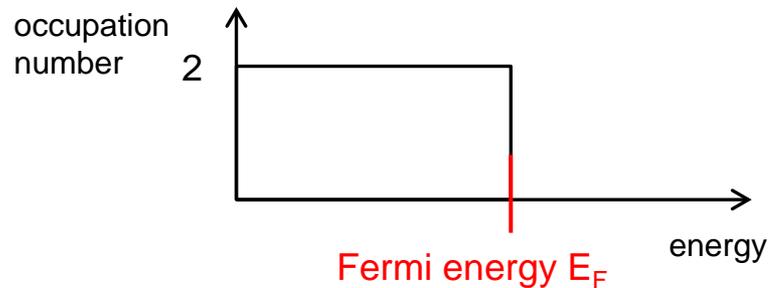
8 times
1/8 grid point
per box

1 grid point
per box

- 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

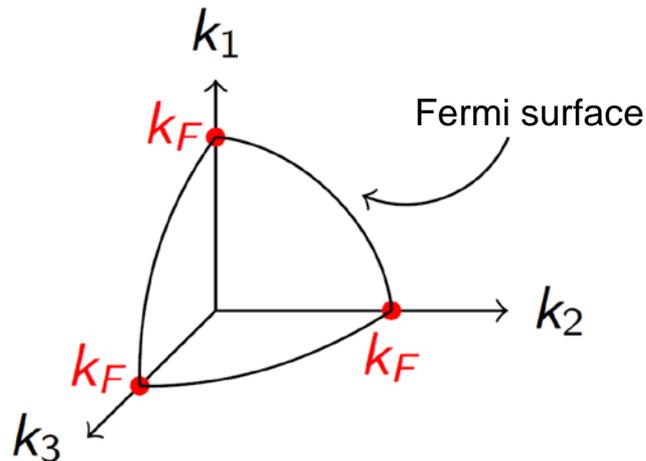
Zero temperature Fermi gas

Fill up lowest energy states with 2 e⁻ each until all Nq valence e⁻ are distributed



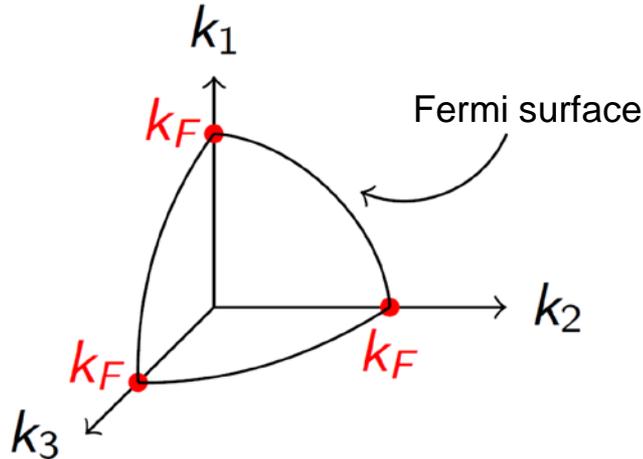
Since $E = \frac{\hbar^2}{2m}k^2$, occupied states fill 1/8 of a sphere in \vec{k} -space up to

$k_F = \sqrt{2mE_F}/\hbar$, the Fermi wave vector.



Number of occupied states

k-space volume to be filled:



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^-
- $N_e = Nq$ valence e^- exist in metal

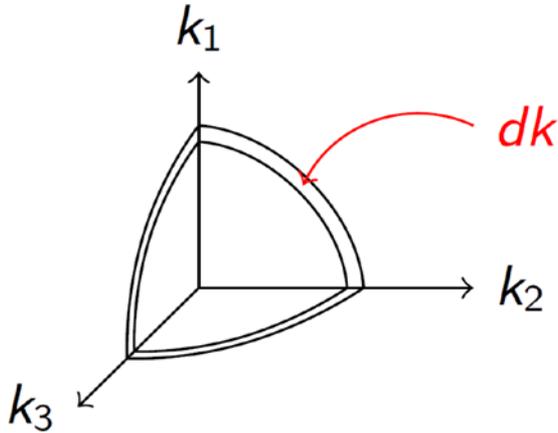
states to be filled: $N_k = \frac{\text{Volume of 1/8 sphere in k space with radius } k_F}{\text{Volume of k-space per state}}$

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

fill states with e^- : $N_e = 2N_k = \frac{1}{3} k_F^3 V / \pi^2$
 \parallel
 Nq

$$k_F^3 = 3\pi^2 \frac{Nq}{V} \quad \longrightarrow \quad k_F = (3\pi^2 \rho)^{1/3} \quad \text{with } e^- \text{ density } \rho = \frac{Nq}{V}$$

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

$$\begin{aligned} n(k) &= \frac{\#e^- \text{ in shell as shown in figure}}{dk} \\ &= \frac{\text{Volume of shell as drawn}}{\text{Volume of } \vec{k}\text{-space per state}} \cdot \frac{2(\text{for spin})}{dk} \\ &= \frac{2}{8} (4\pi k^2) \frac{dk}{dk} / \frac{\pi^3}{V} = V \frac{k^2}{\pi^2} \end{aligned}$$

Energy density:

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

Energy:

$$E = \epsilon V = \underbrace{\frac{\hbar^2 (3\pi^2 Nq)^{5/3}}{10\pi^2 m}}_{\equiv C} V^{-2/3} = CV^{-2/3}$$

$$\uparrow k_F = (3\pi^2 \rho)^{1/3}$$

Overview „The free electron gas“

1) The free electron gas

Griffiths 5.3.1

simple model describing metals

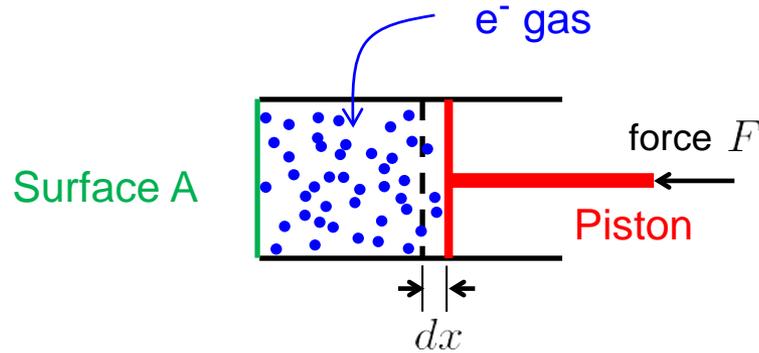
explains why solid objects cannot easily be compressed
essentially the same model describes shape of

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

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:

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

Reminder
energy of e^- gas: $E = CV^{-2/3}$

This energy was used to move piston outwards, doing work

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

$$dW \stackrel{!}{=} -dE$$

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

“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.

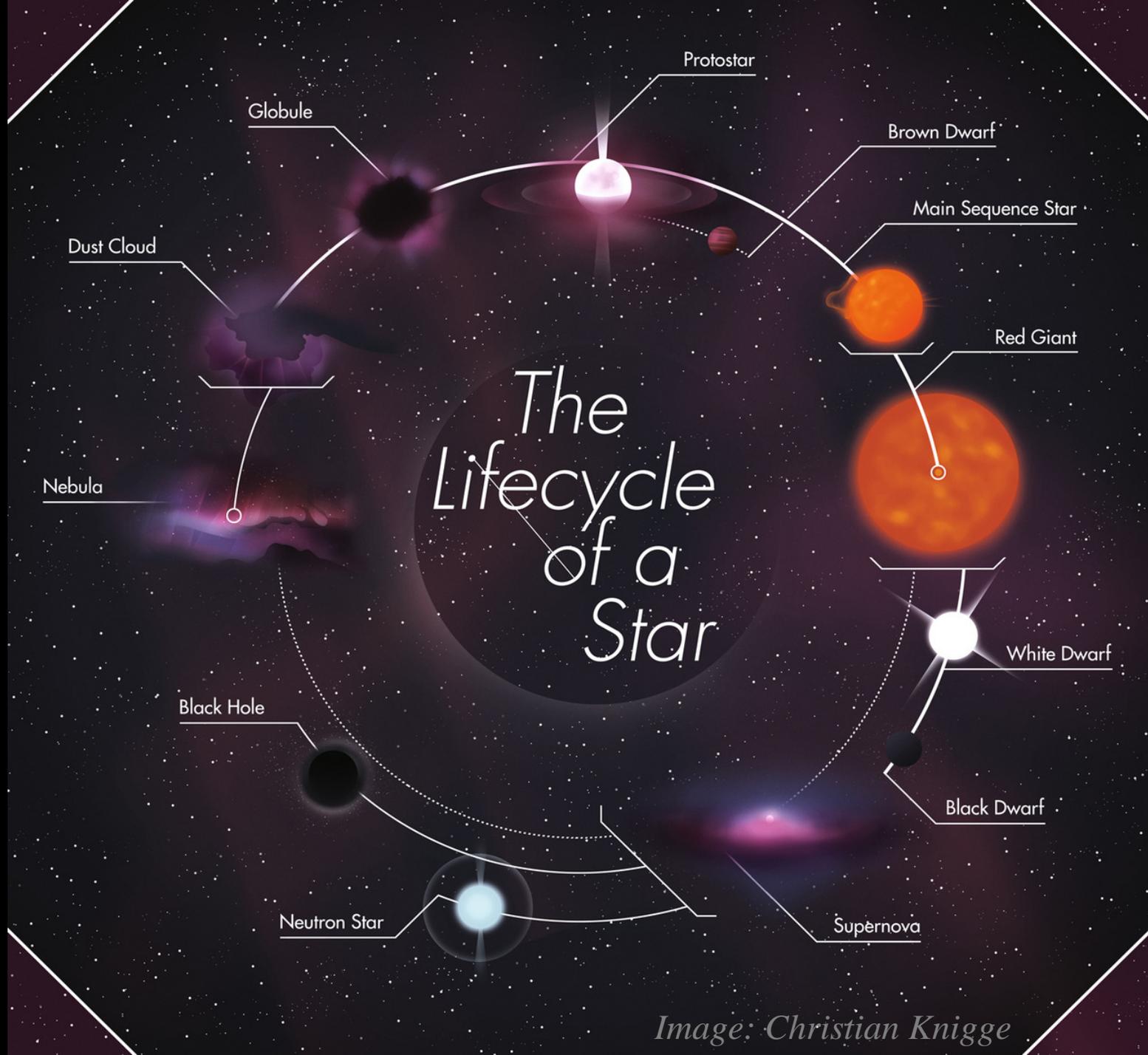
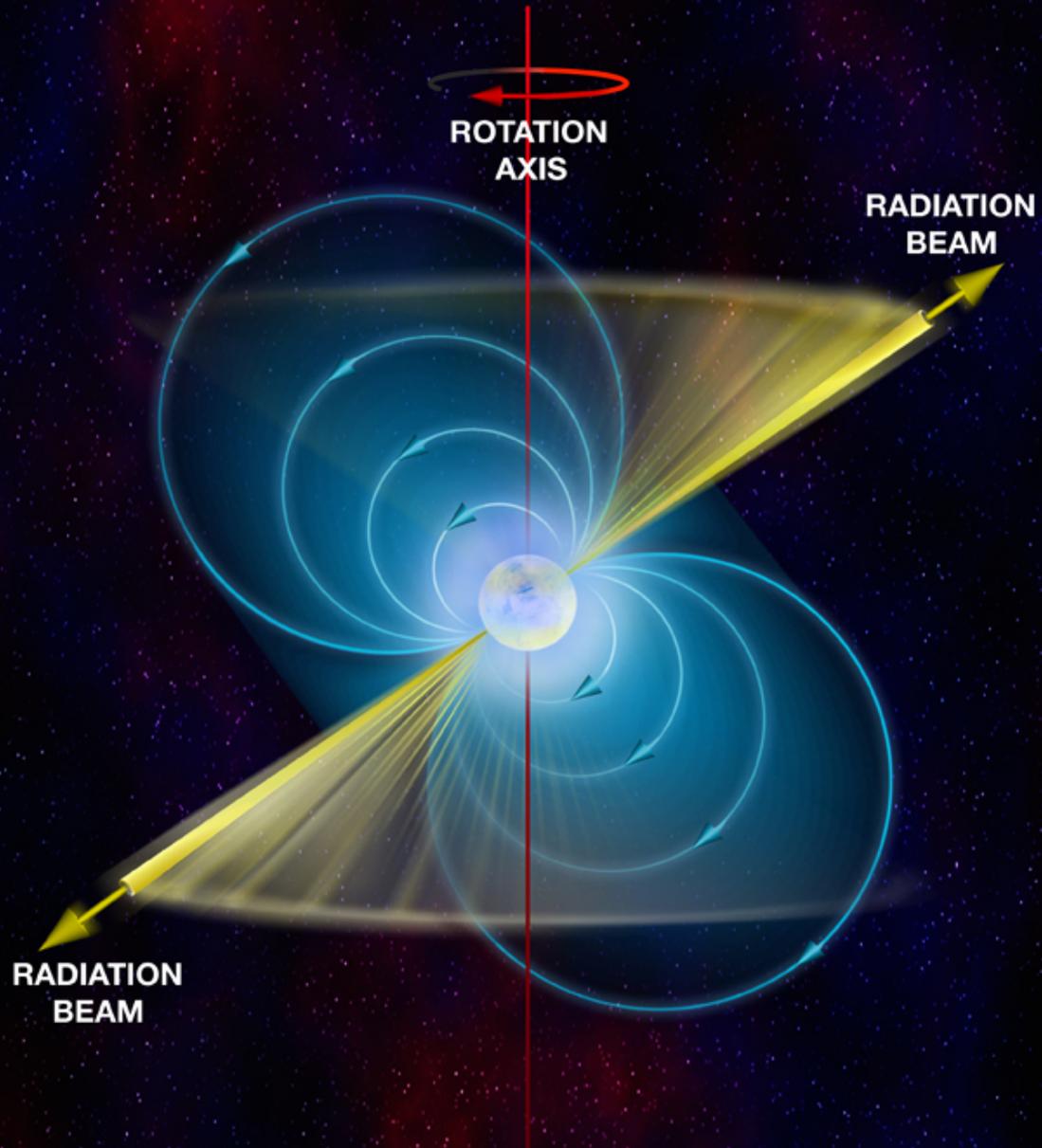
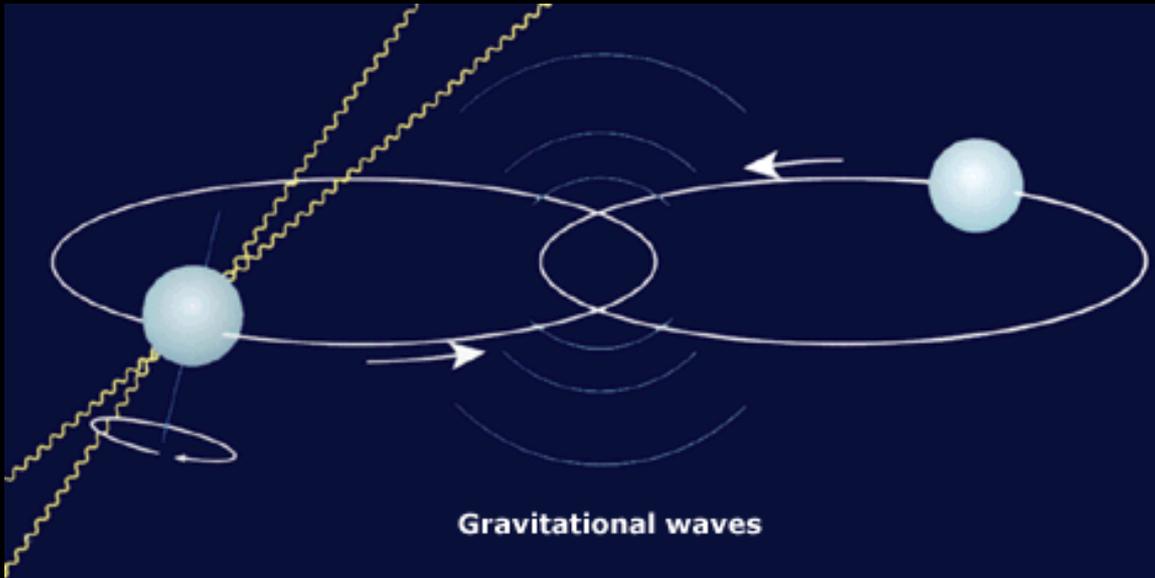


Image: Christian Knigge



Indirect detection of gravitational waves



**Nobel prize
1993**



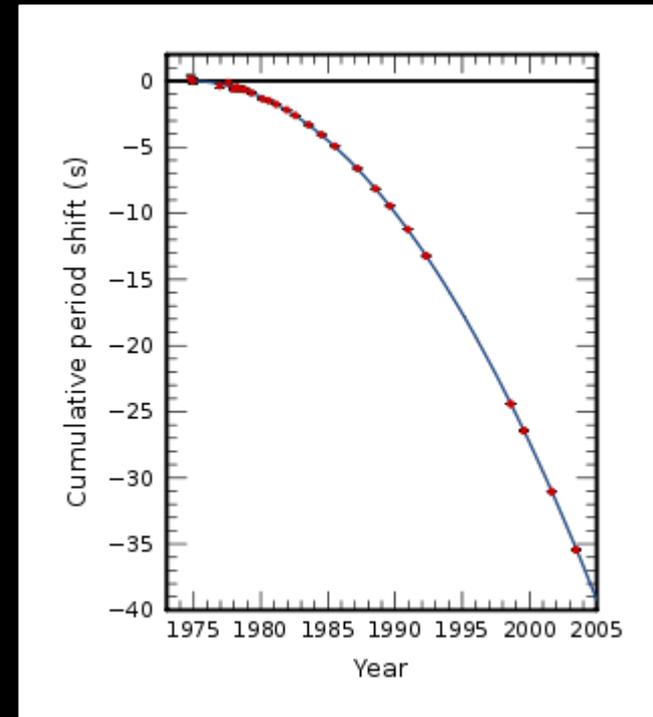
Russell A. Hulse
Prize share: 1/2



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"*

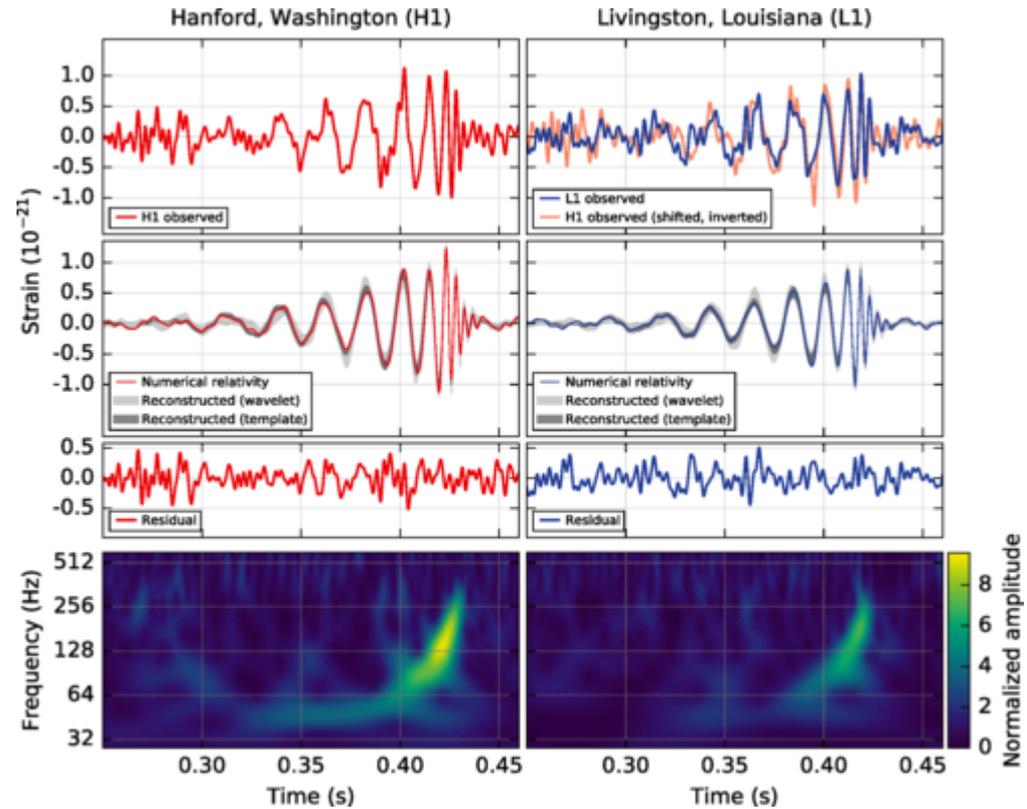
Photos: Copyright © The Nobel Foundation



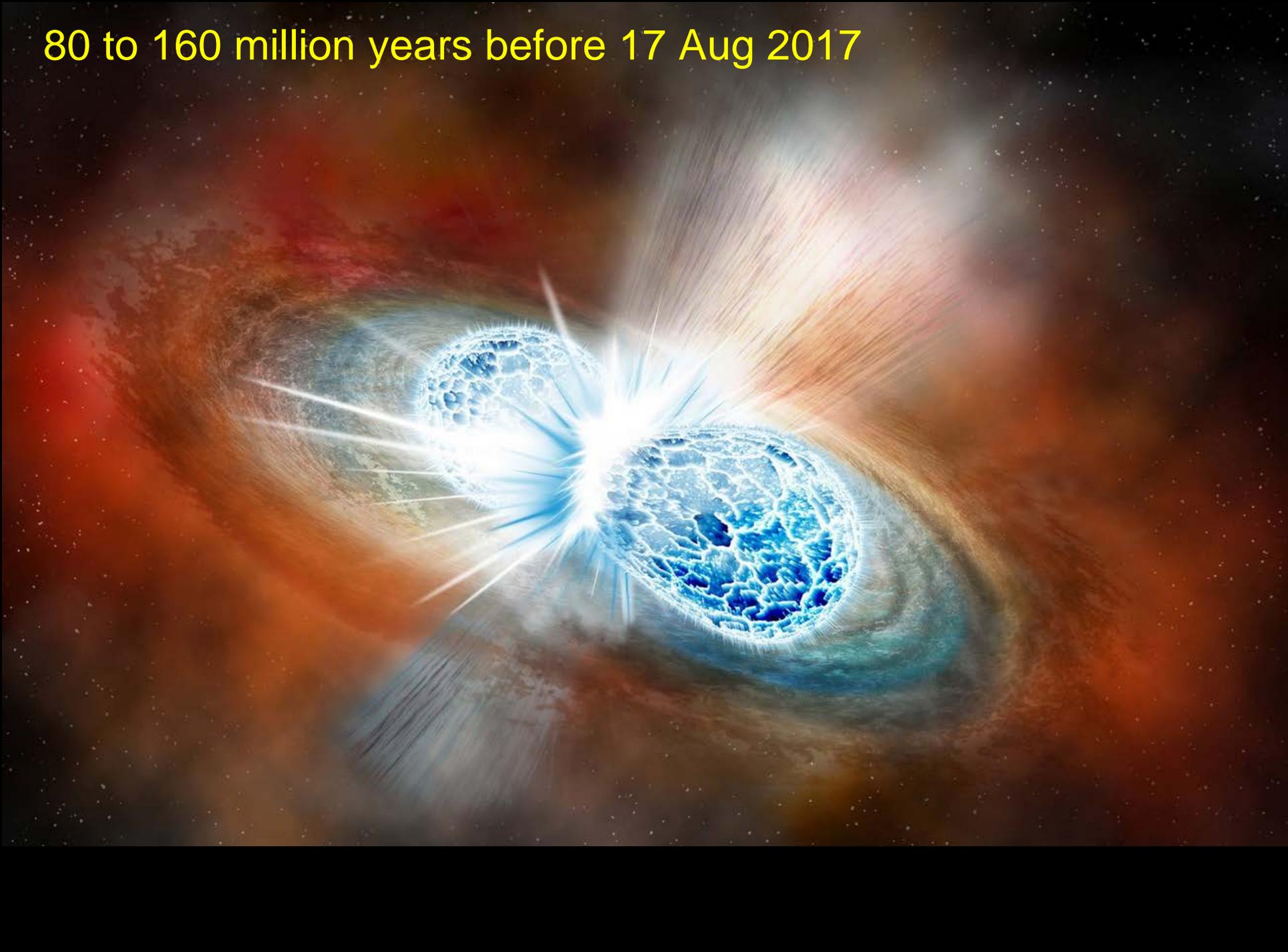
Direct detection of gravitational waves

LIGO interferometer

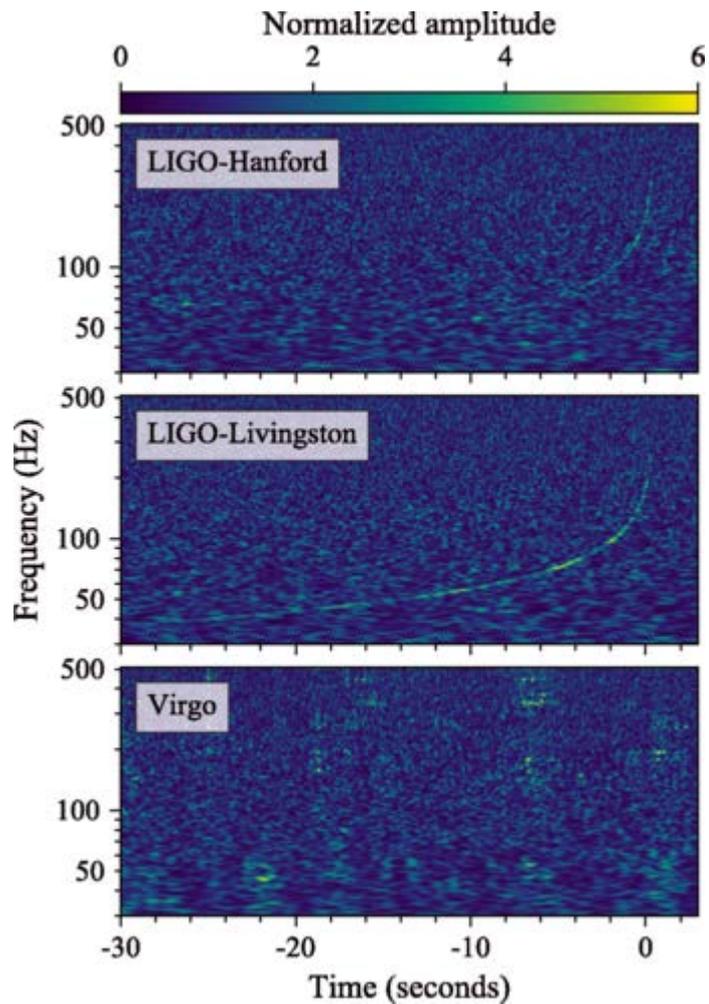
Black hole merger, 14.9.2015



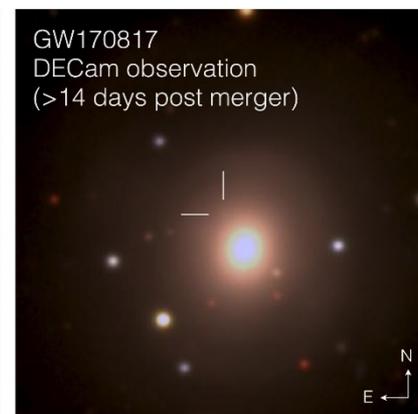
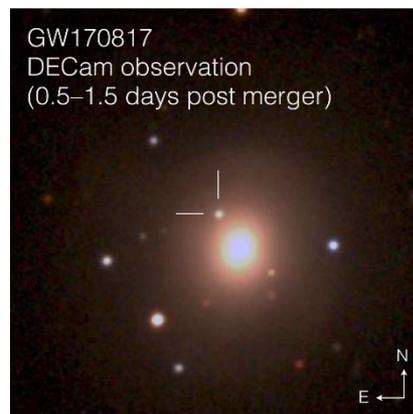
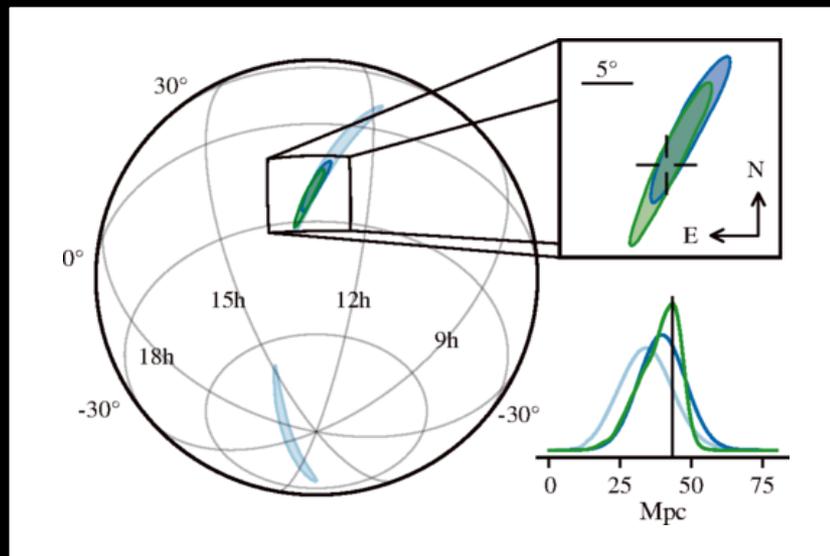
80 to 160 million years before 17 Aug 2017



Neutron star merger, 17 Aug 2017



Phys. Rev. Lett. 119, 161101 (2017)



The Astrophysical Journal Letters, 848, 7 (2017)

Direct detection of gravitational waves

LIGO interferometer

The Nobel Prize in Physics 2017



Photo: Bryce Vickmark
Rainer Weiss
Prize share: 1/2

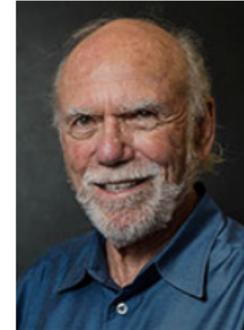


Photo: Caltech
Barry C. Barish
Prize share: 1/4



Photo: Caltech Alumni Association
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**

Griffiths 3rd 5.3.2

simple model describing crystals

explains under which conditions a solid is a

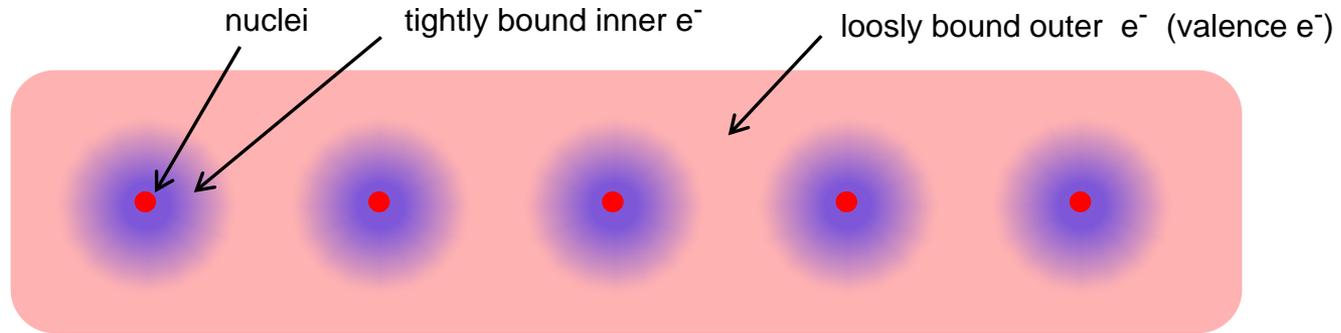
- conductor
- semiconductor
- insulator

Applications

- LED
- solar cell
- transistor

Solids

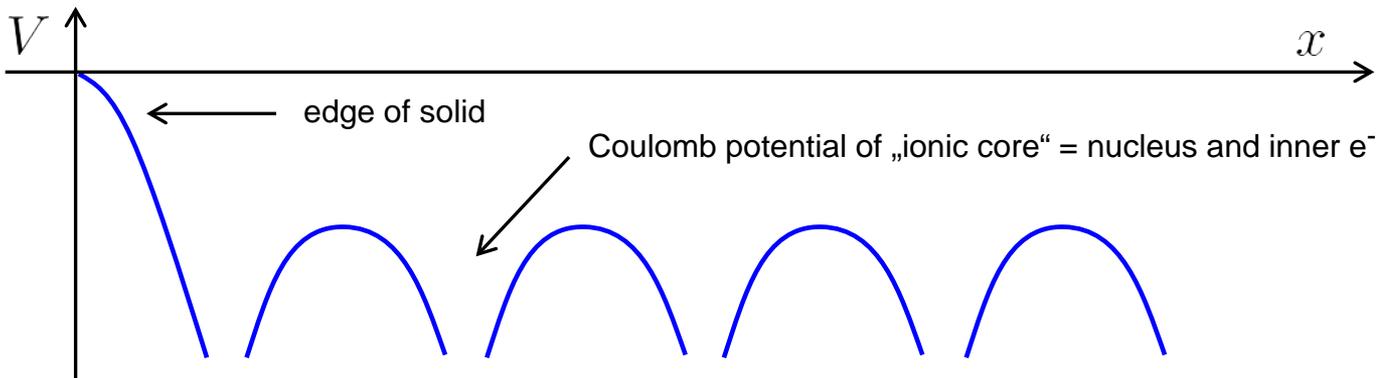
Structure



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^- :

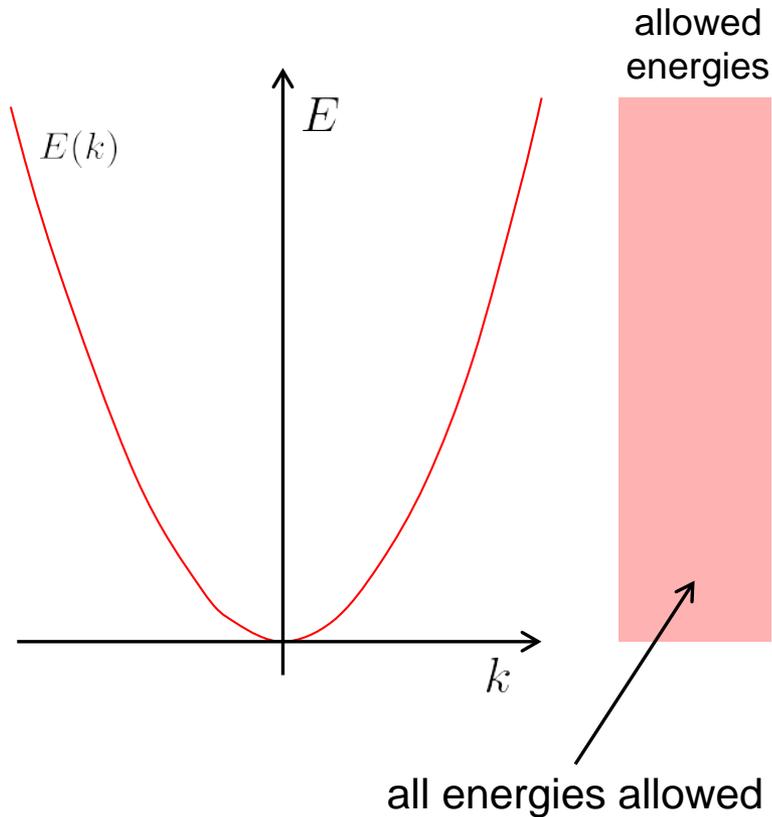


Goal of “Electrons in periodic potentials”

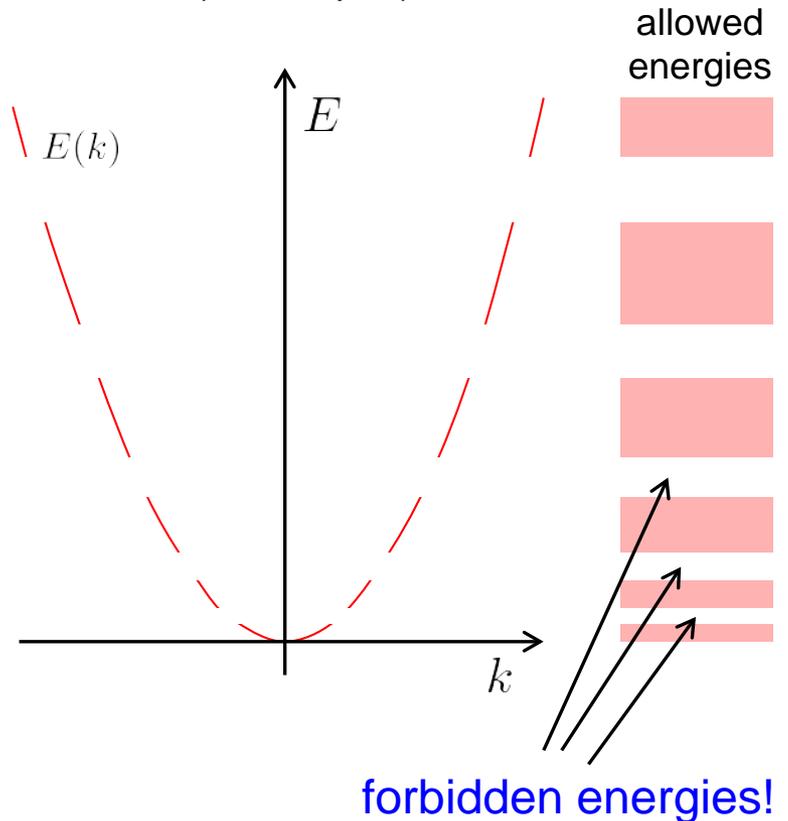
Goal of this section

energy level structure of electron in periodic potential

e^- in free space

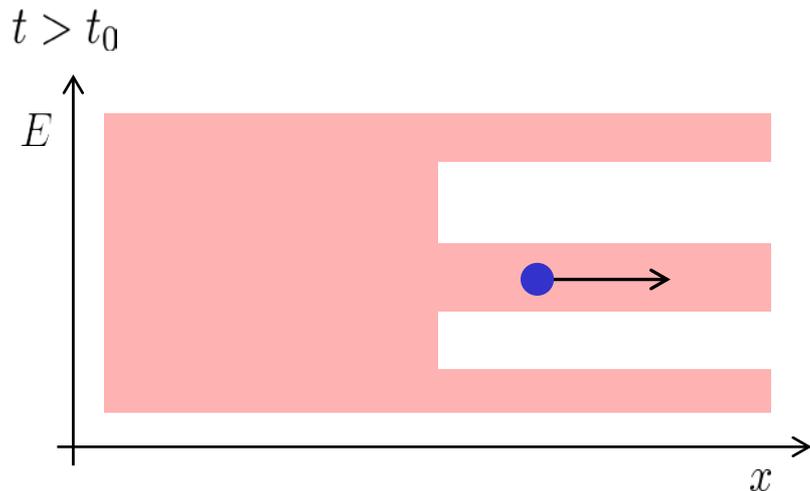
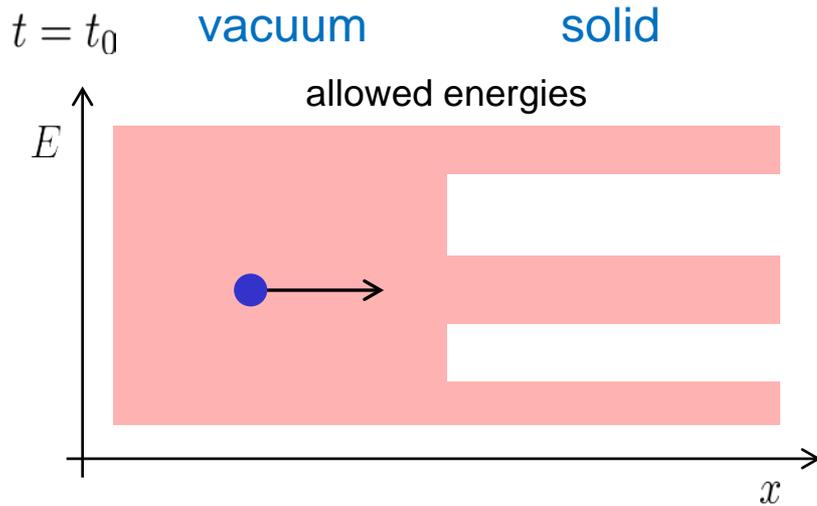


e^- in periodic potential
(this chapter)



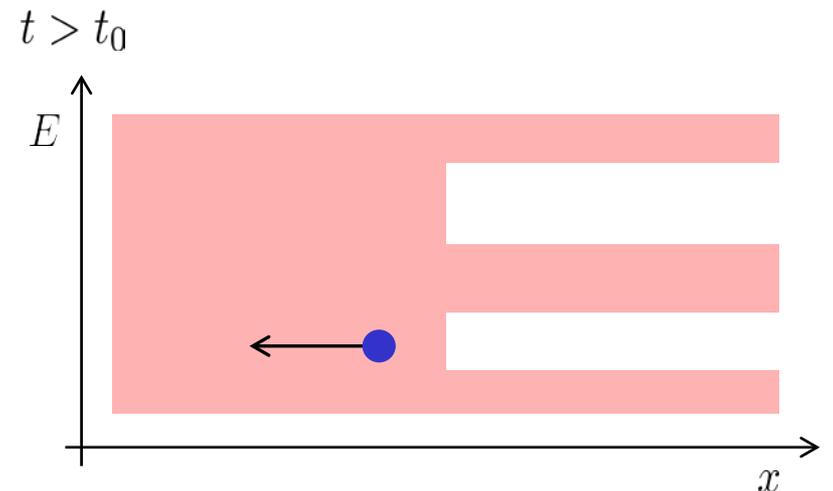
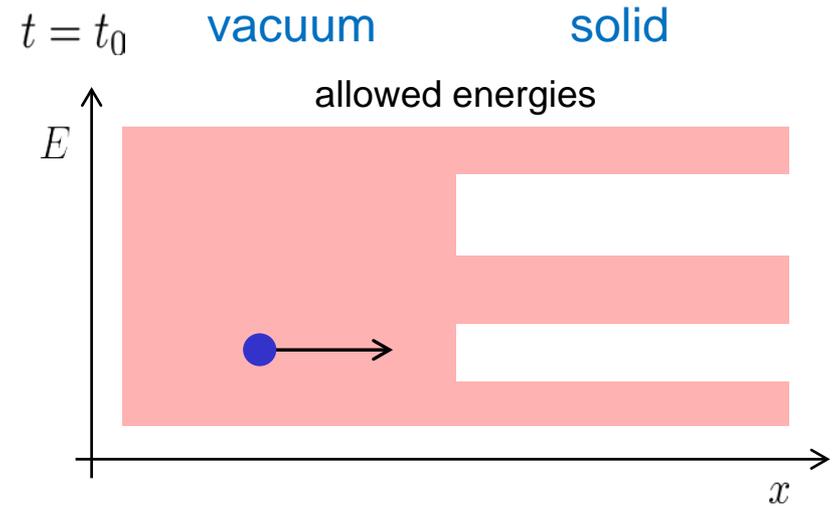
Shooting an electron onto a solid

Case 1: Energy within allowed band



Electron continues to propagate in solid

Case 2: Energy within band gap



Electron unable to propagate through solid.
(It is reflected.)

Band gaps in optics of visible light

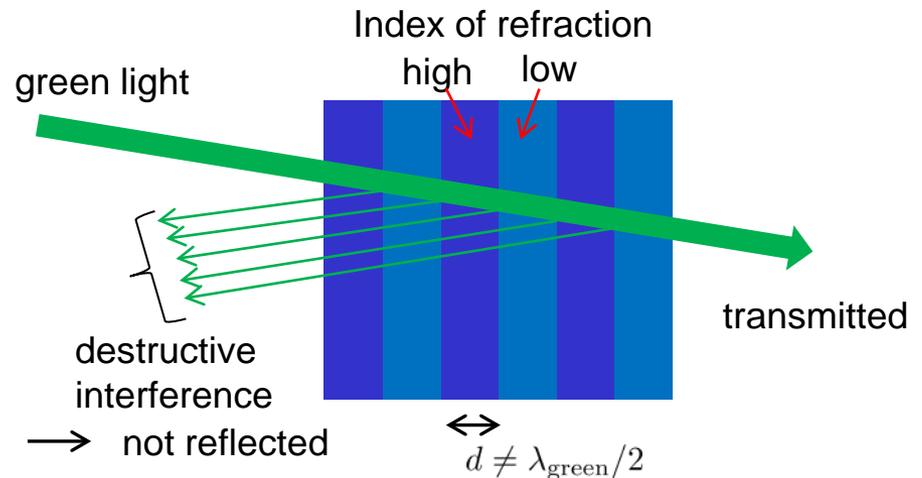
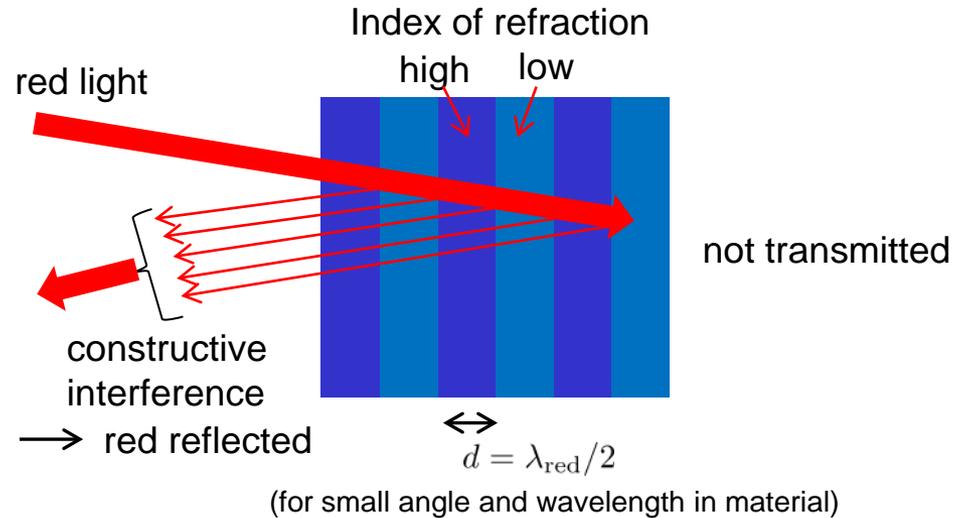
Dichroic mirror

red reflected
green-blue transmitted



Wavelength dependent
reflection and transmission

Dielectric dichroic mirror

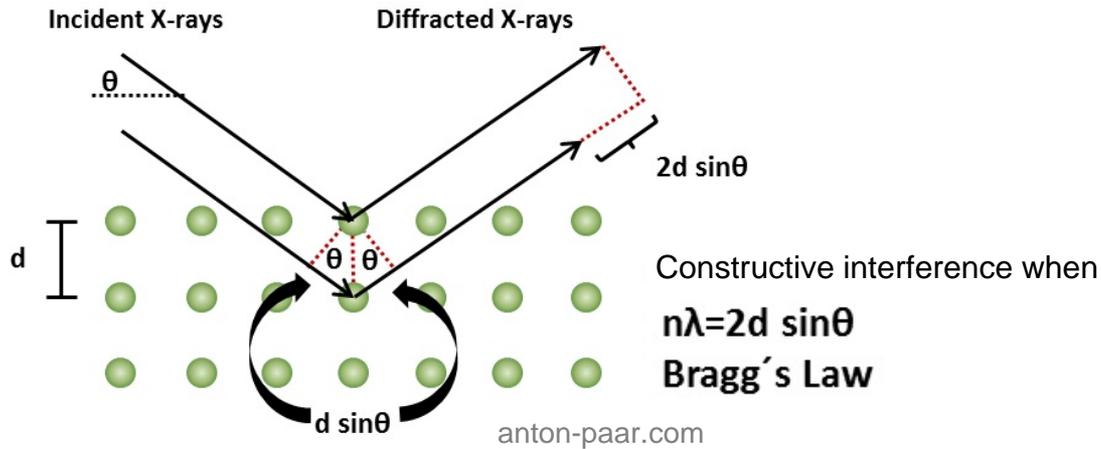


Lattice spacing: $\sim \lambda/2 \sim \text{few } 100 \text{ nm} \sim 100\text{s of lattice spacings}$

X-ray diffraction

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

X rays are scattered by atoms

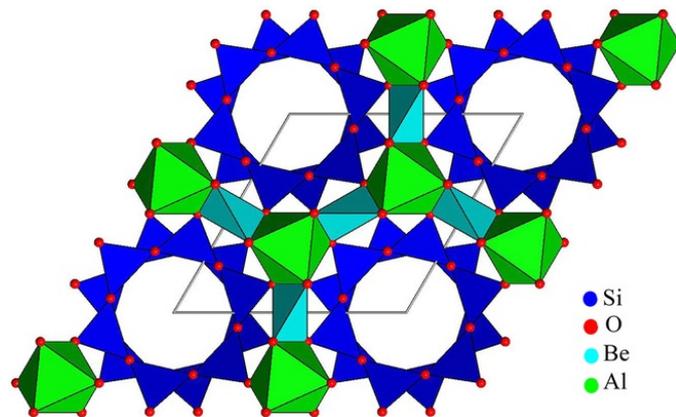
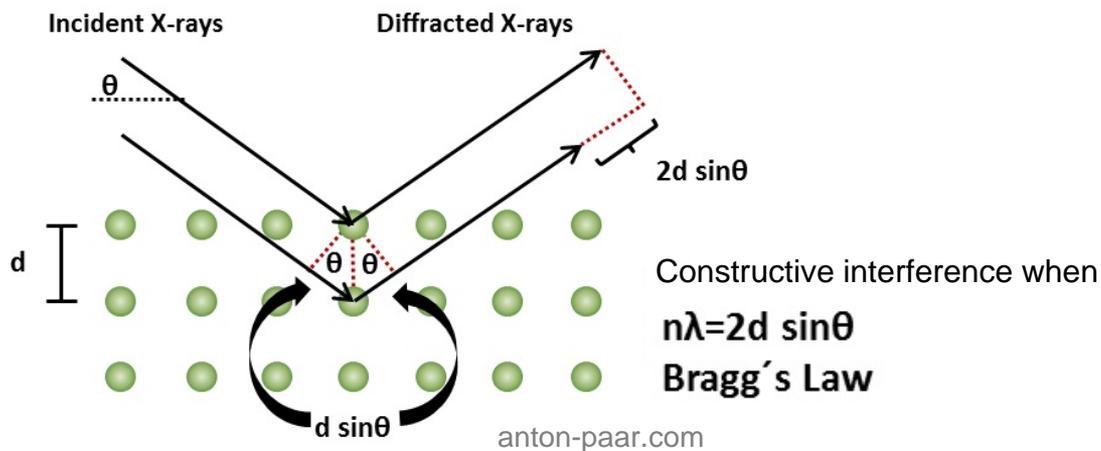


Emerald, a beryl crystal

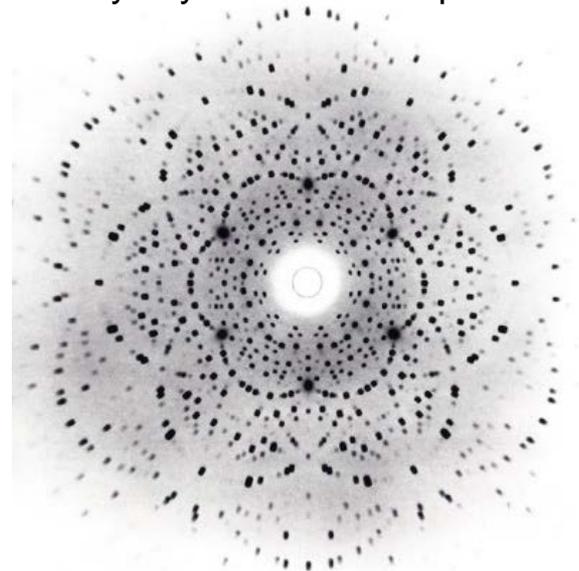
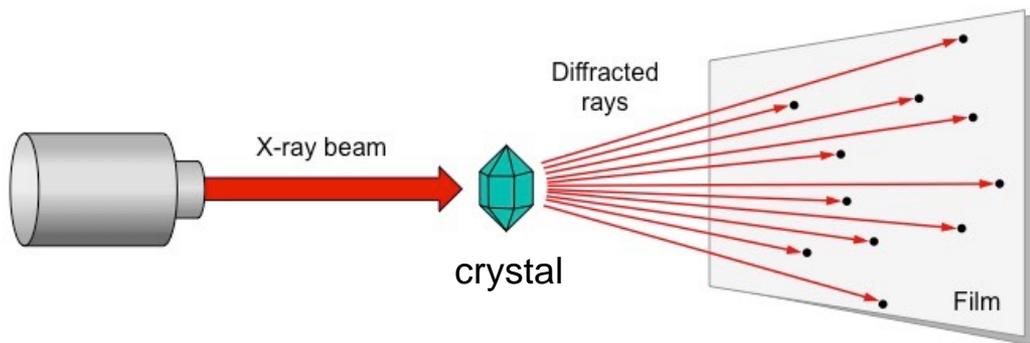
X-ray diffraction

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

X rays are scattered by atoms

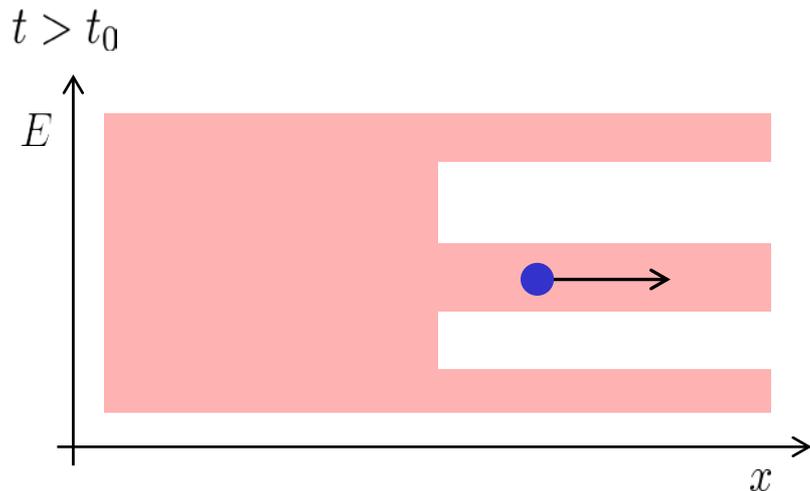
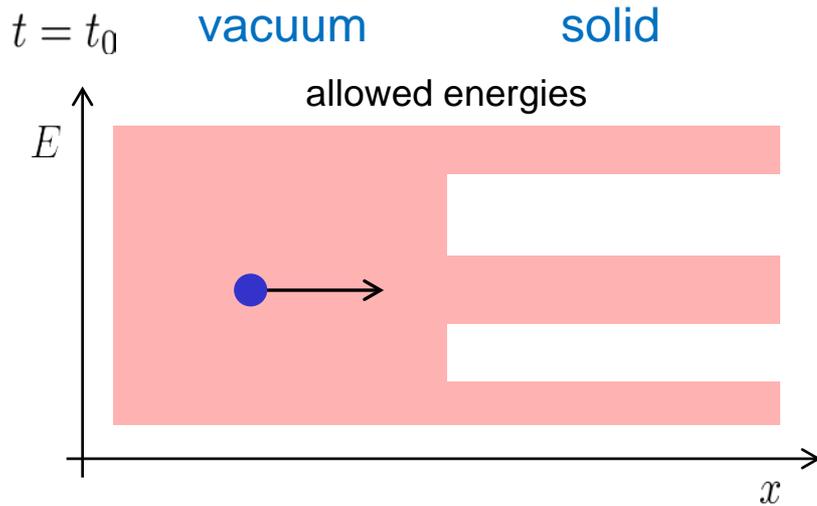


Beryl crystal diffraction pattern



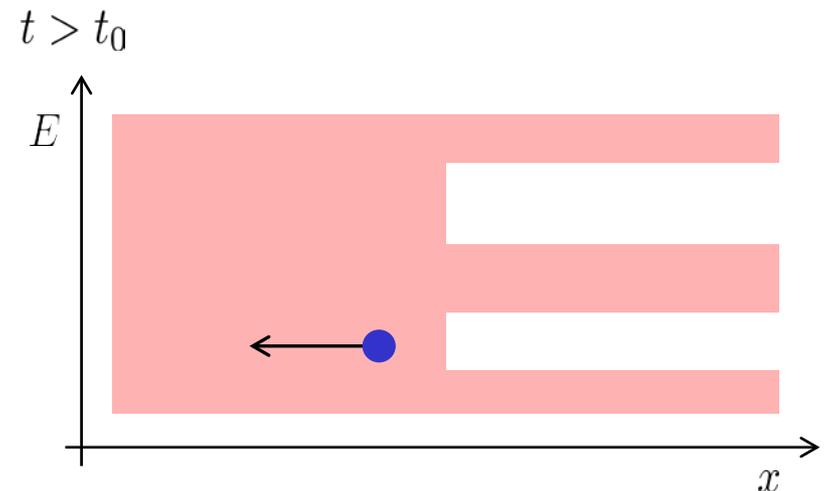
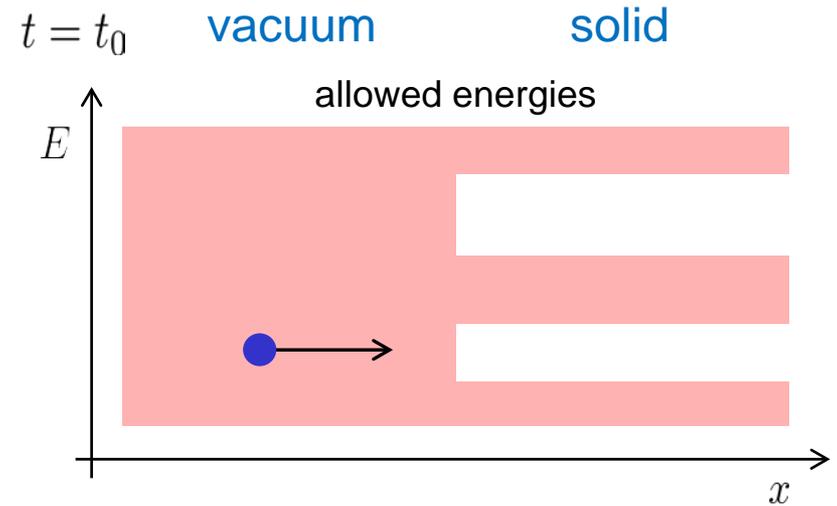
Shooting an electron onto a solid

Case 1: Energy within allowed band



Electron continues to propagate in solid

Case 2: Energy within band gap

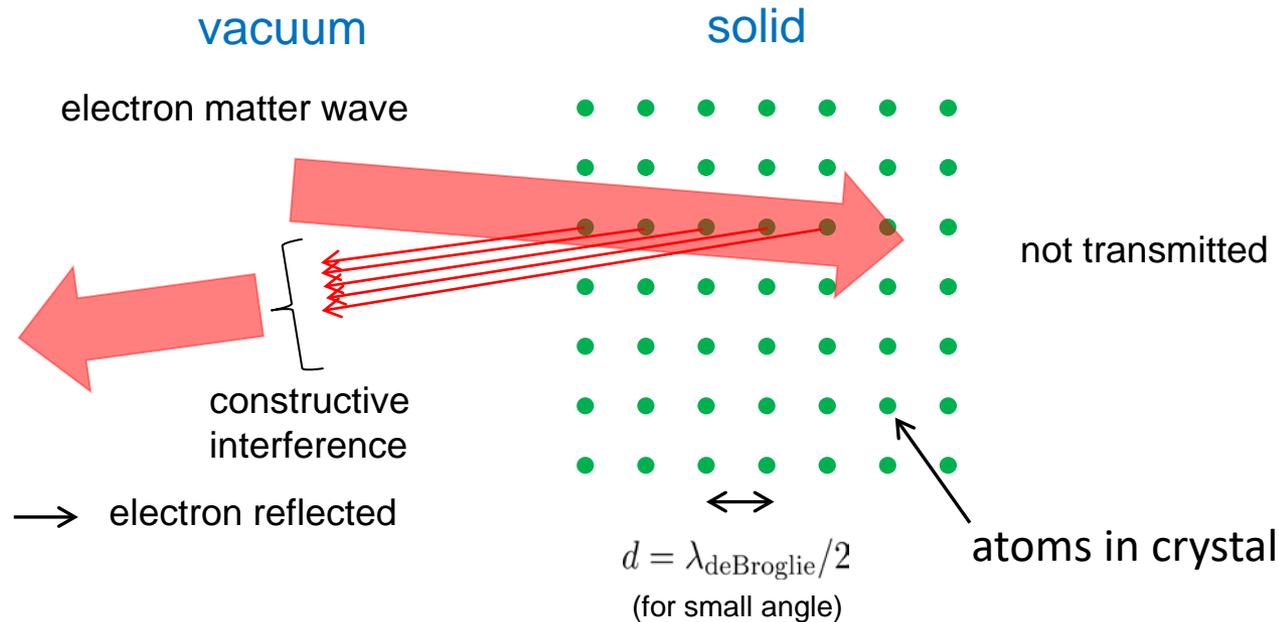


Electron unable to propagate through solid.
(It is reflected.)

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



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

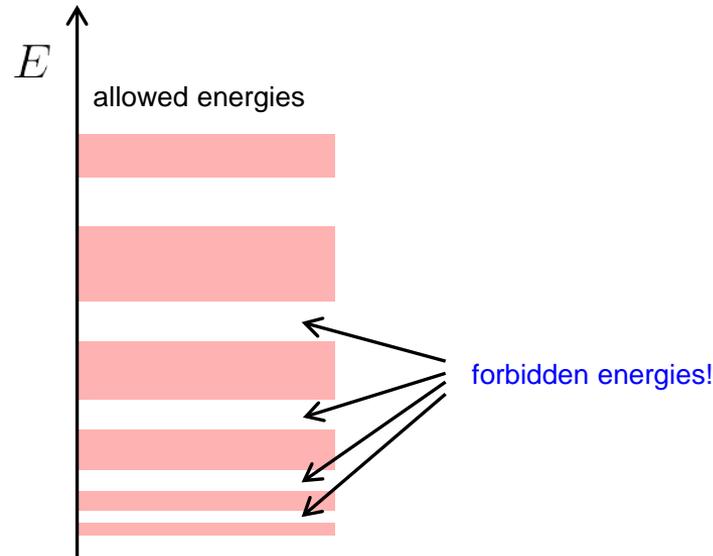
e^- with the corresponding momentum and energy can't exist in crystal

→ 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



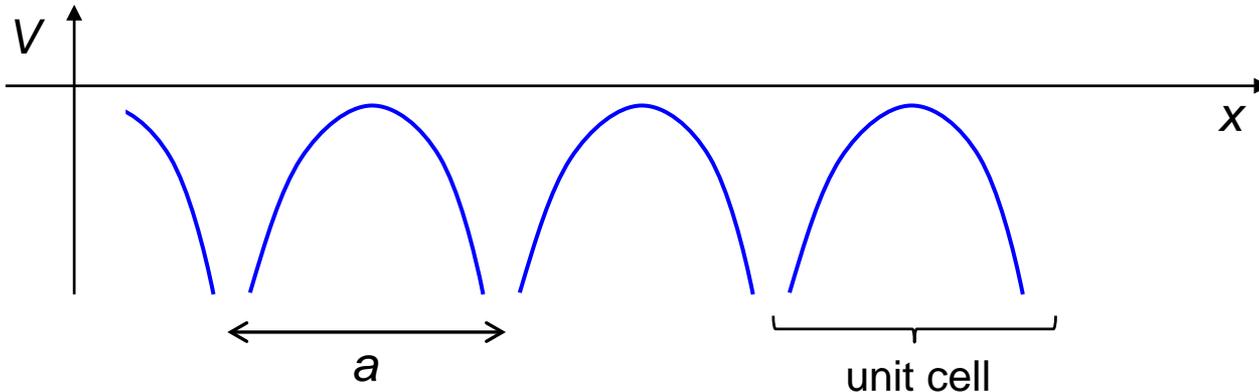
- Bloch's theorem
- solve Schrödinger equation of 1 particle in periodic potential

2) Discussion:

- Placing many particles in that potential
- Is a material an insulator or a conductor?

Bloch's theorem

Potential of ion cores on valence electrons:



We assume ion cores form periodic structure

$$\longrightarrow V(x + a) = V(x)$$

Bloch's theorem

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

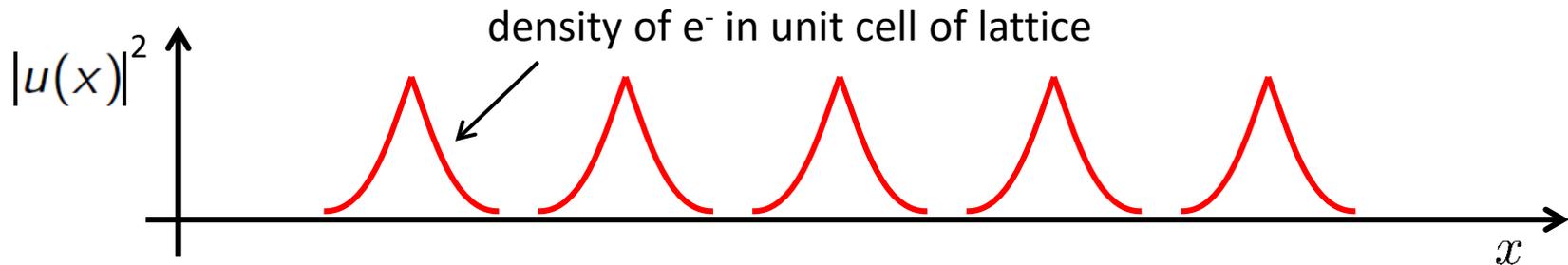
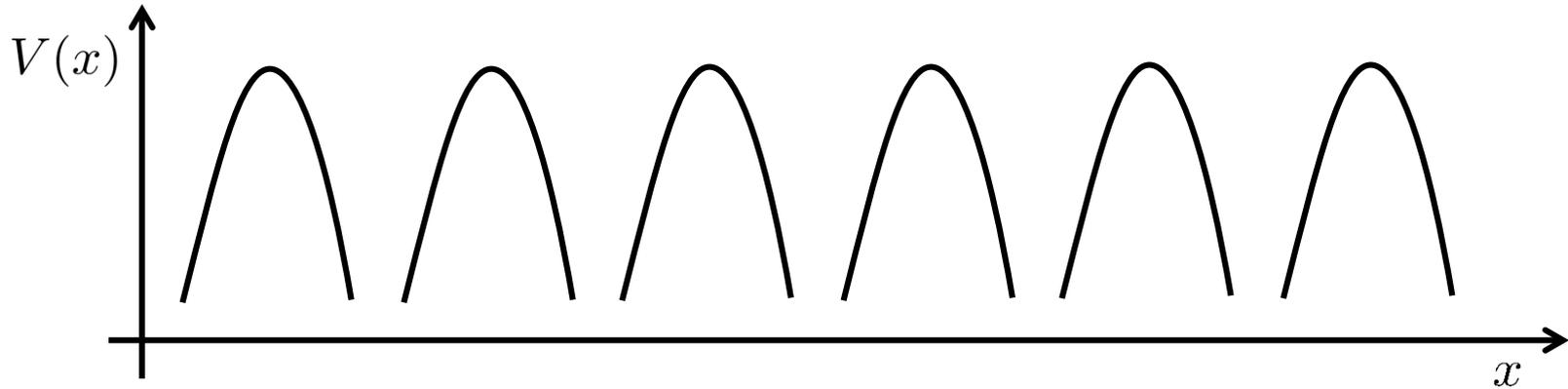
$$\hat{H}\psi(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x)\psi(x) = E\psi(x)$$

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

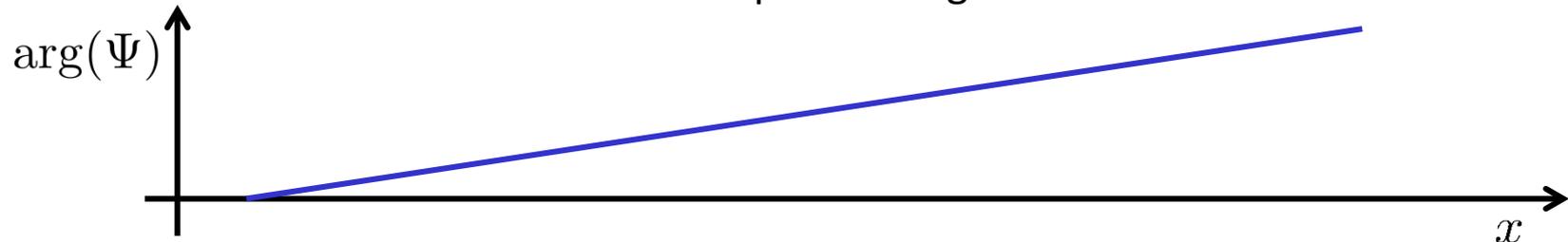
and (II) $\psi(x) = e^{iKx} u(x)$ with periodic function $u(x + a) = u(x)$

Meaning of (II): Bloch wavefunction

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

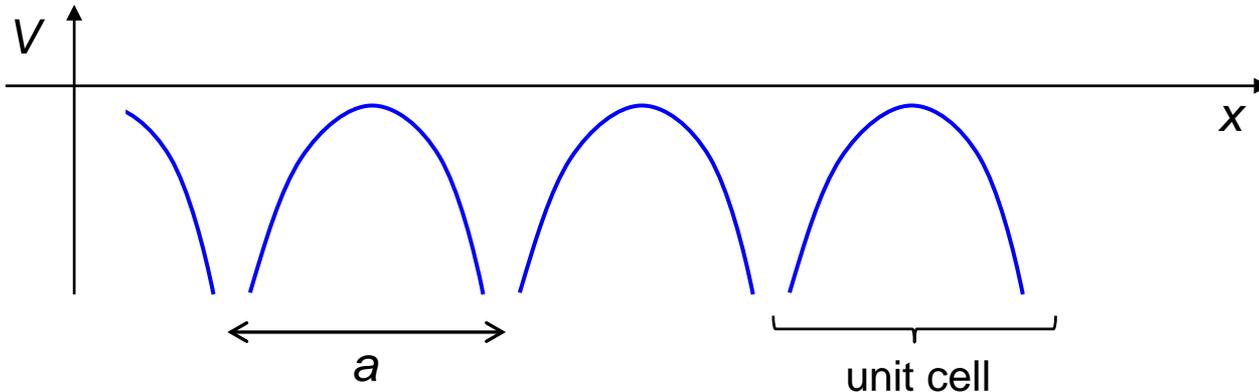


e^{iKx} describes transport through lattice with momentum K



Bloch's theorem

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Bloch's theorem

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

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)

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

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

Prove (II) \longrightarrow (I):

$$\Psi(x + a) \underset{\substack{\uparrow \\ \text{use (II)}}}{=} e^{iK(x+a)} u(x + a) \underset{\substack{\uparrow \\ u(x+a) = u(x)}}{=} e^{iKa} e^{iKx} u(x) \underset{\substack{\uparrow \\ \text{use (II)}}}{=} e^{iKa} \Psi(x) \longrightarrow (I)$$

□

Equivalence of (I) and (II)

Show equivalence of (I) and (II)

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

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

Prove (I) \longrightarrow (II):

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

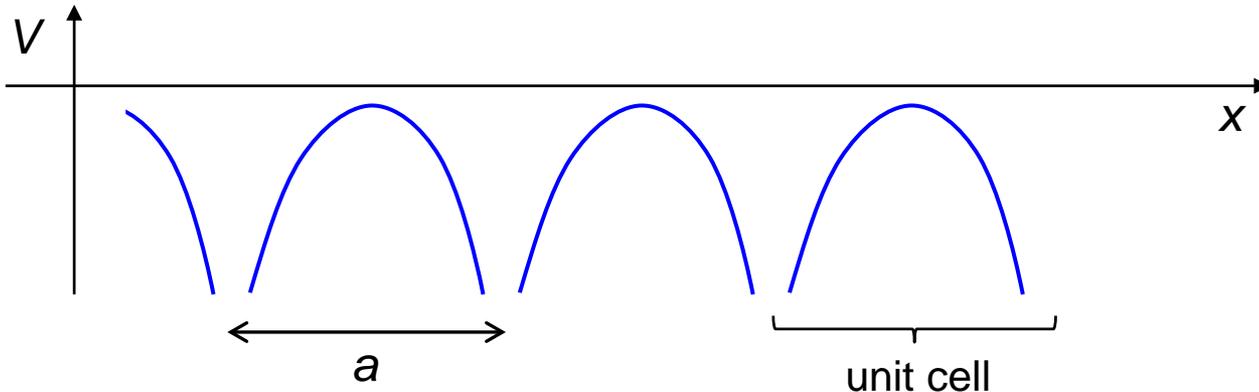
Is $u(x)$ periodic?

$$(I) \longrightarrow \parallel \left. \begin{array}{l} \Psi(x+a) = e^{iK(x+a)} u(x+a) \\ e^{iKa} \Psi(x) = e^{iKa} e^{iKx} u(x) \end{array} \right\} u(x+a) = u(x)$$

$$\longrightarrow (II) \quad \psi(x) = e^{iKx} u(x) \quad \text{with periodic function } u(x+a) = u(x) \quad \square$$

Bloch's theorem

Potential of ion cores on valence electrons:



We assume ion cores form periodic structure

$$\longrightarrow V(x + a) = V(x)$$

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 $u(x + a) = u(x)$

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

$$[\hat{D}, \hat{H}] = 0$$

Proof

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

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

$$\hat{D} V(x) f(x) = V(x + a) f(x + a) = V(x) f(x + a) = V(x) \hat{D} f(x) \quad \square$$

$\implies \hat{D}$ and \hat{H} commute and therefore have common basis.

Commuting observables have common basis

Wikipedia entry „Complete set of commuting observables“

reminder

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 ψ be eigenvector of \hat{D} with eigenvalue $\lambda \in \mathbb{C}$.

$$\hat{D}\psi(x) = \lambda\psi(x) \quad \longrightarrow \quad \psi(x + a) = \lambda\psi(x)$$

Which values of λ are allowed?

λ can be written as

$$\lambda = Ae^{iKa}, \quad A, K \in \mathbb{R}. \quad (\lambda = 0 \longrightarrow \psi(x) = 0, \text{ not interesting})$$

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

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



$$\left. \begin{array}{l} \psi(x + Na) = \psi(x) \\ \parallel \\ \lambda^N \psi(x) \end{array} \right\}$$

$$\lambda^N = A^N e^{iNKa} = 1 \implies A = 1 \longrightarrow \text{(I)} \quad \square$$

$$\implies NKa = 2\pi j; \quad j \in \mathbb{Z} \implies$$

allowed K values

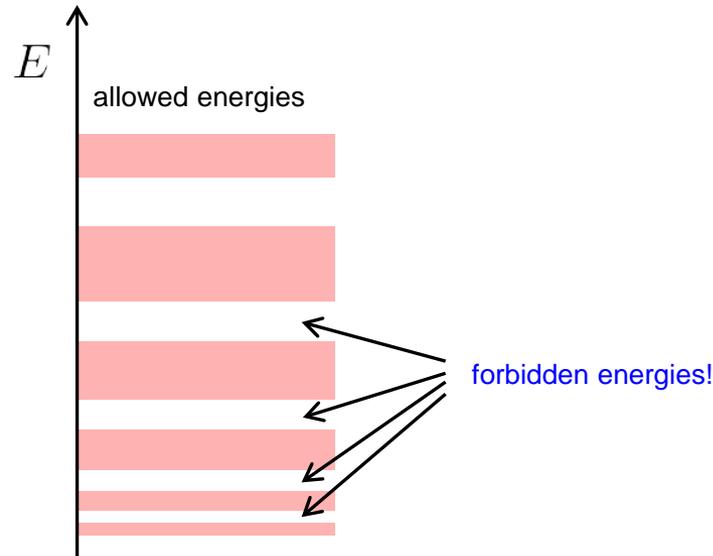
$$K_j = \frac{2\pi}{aN} j$$

Only $j \in \{0, 1, \dots, N-1\}$ need to be considered. Beyond that interval $\lambda = e^{iK_j a}$ values just repeat.

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

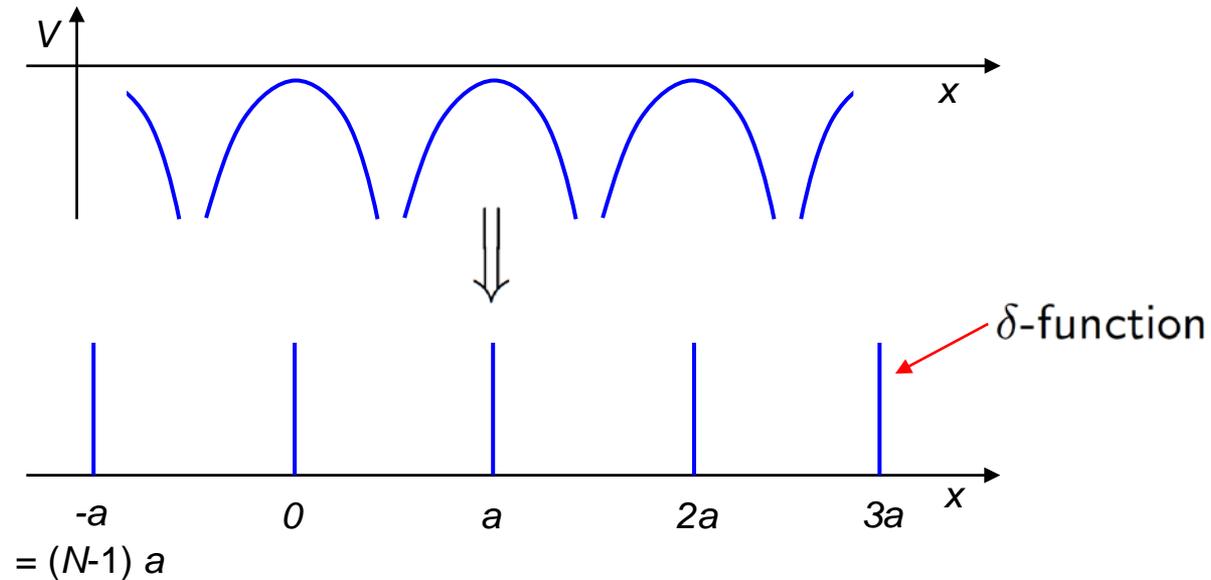
2) Discussion:

- Placing many particles in that potential
- Is a material an insulator or a conductor?

Solve Schr. eqn. for periodic potential

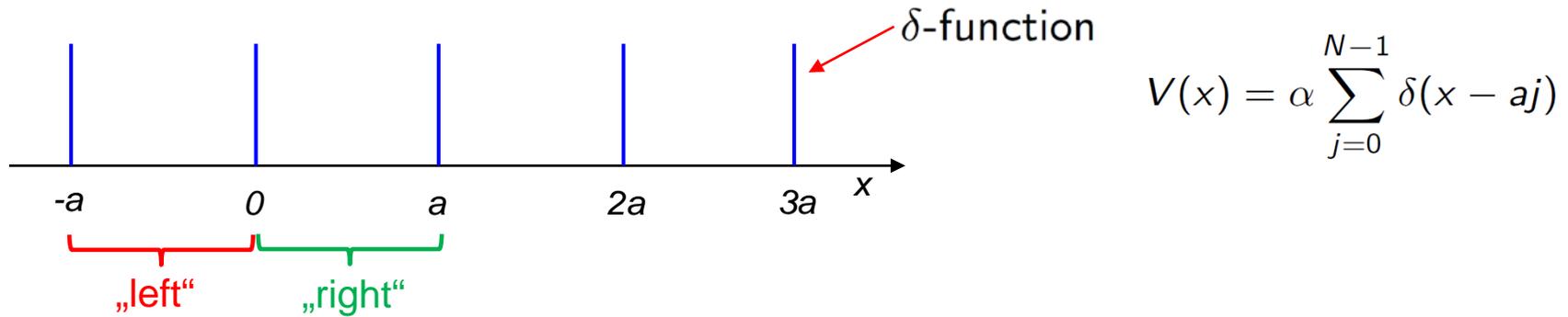
Goal: find allowed energies for electron in periodic potential

Model potential: Dirac comb with periodic boundaries



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

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)

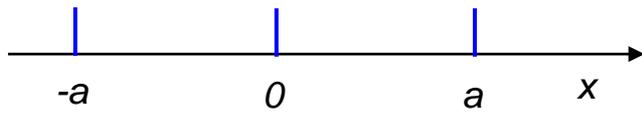
Use Bloch's theorem to find solution in „left“ interval $-a < x < 0$

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

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

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

Solve Schr. eqn. for periodic potential



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

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

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

$$V(x) = \alpha \delta(x)$$

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

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

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

$$(b) \quad kA - e^{-iKa} k [A \cos(ka) - B \sin(ka)] = \frac{2m\alpha}{\hbar^2} B$$

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

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

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

$$(**) \quad \cos(Ka) = f(z)$$

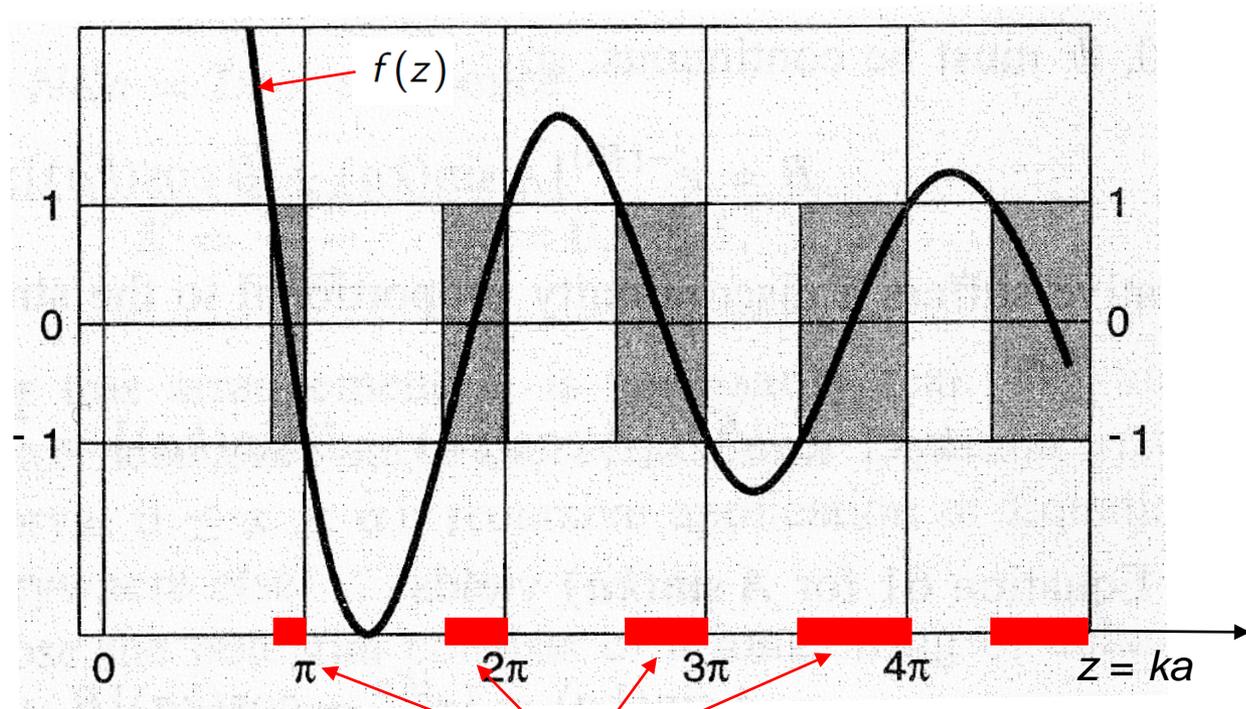
Solve Schr. eqn. for periodic potential

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 $K_j = \frac{2\pi}{aN}j \quad ; \quad j \in \{0, 1, \dots, N-1\}$

Find solutions of (**) graphically:

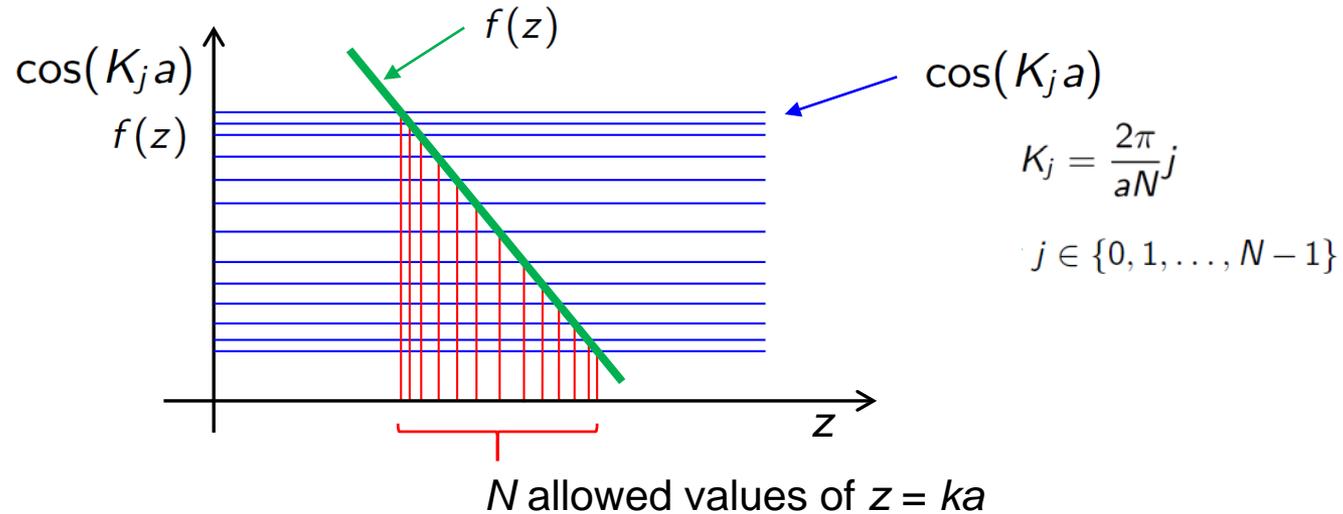


Solutions exist for these intervals of z values.

Griffiths Fig. 5.6

Solve Schr. eqn. for periodic potential

Let's zoom into one interval of allowed values:



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

Since

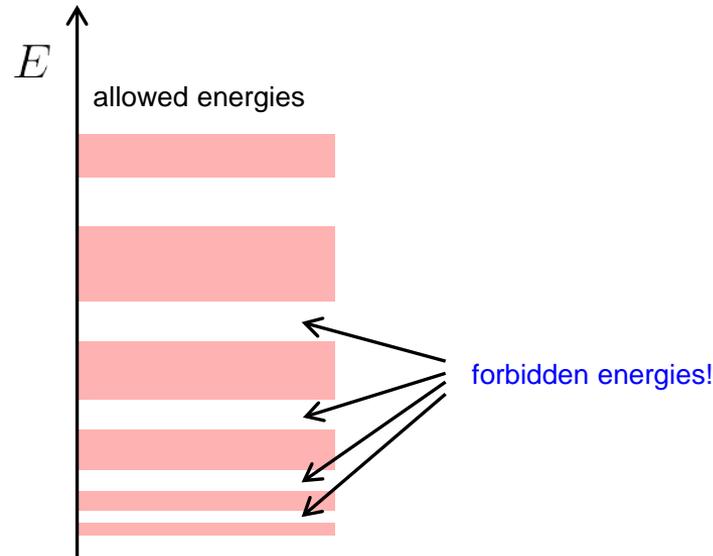
$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{z}{a}\right)^2$$

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

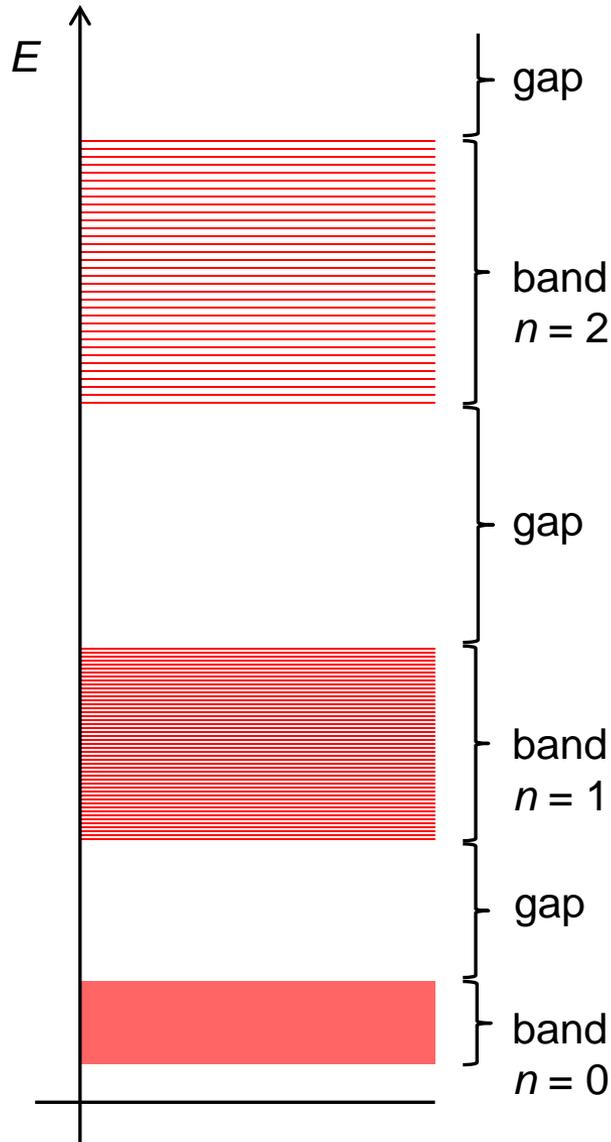
energy level structure of electron in periodic potential



Plan of this section

- 1) Derive allowed and forbidden energies
 - Bloch's theorem
 - 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?

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

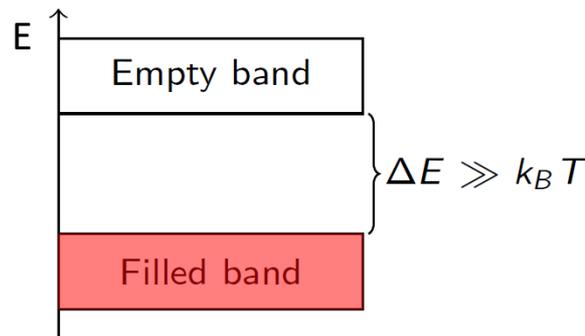
The solutions $\psi(x)$ we found contain equal amounts of left & right moving waves, e.g. $\sin(kx) = (e^{ikx} - e^{-ikx})/2i$.

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:

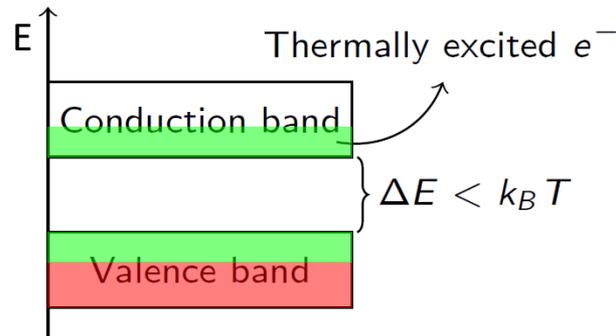
q even



no excitations possible

Insulator

q even

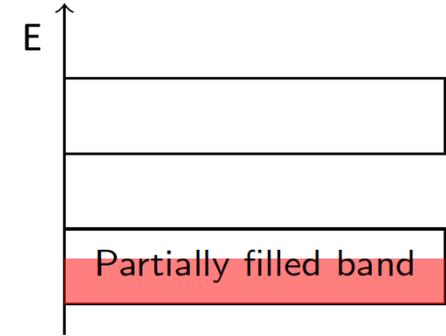


e^- in conduction band and empty states („holes“) in valence band can easily move

Semiconductor

Conducts better for higher T

q odd



Vanishingly small energy needed for excitation around Fermi energy. Many e^- can easily move

Conductor

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

lower q

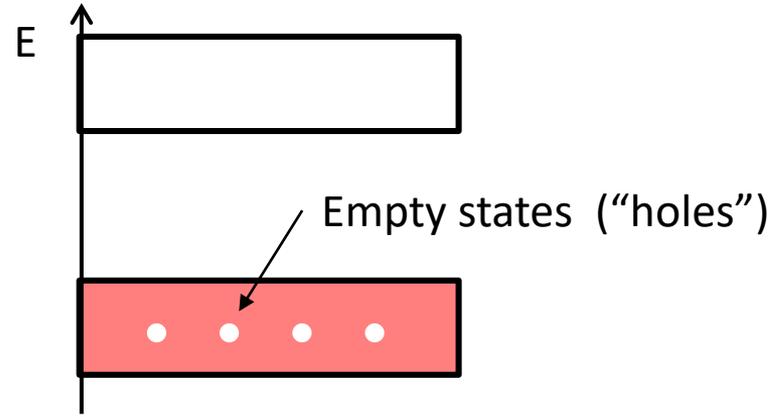
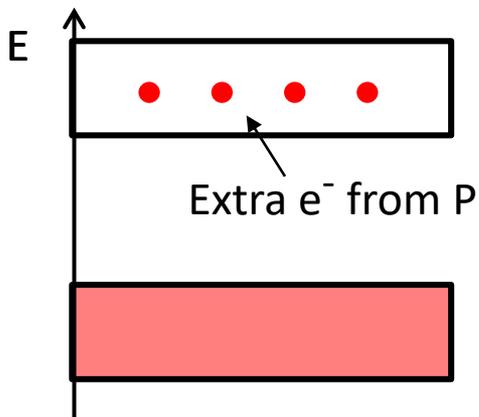
e.g.

Si ($q = 2$)

Si ($q = 2$)

doped with P ($q = 3$)

doped with Al ($q = 1$)



n - doped

p - doped

e⁻ in conduction band
carry current

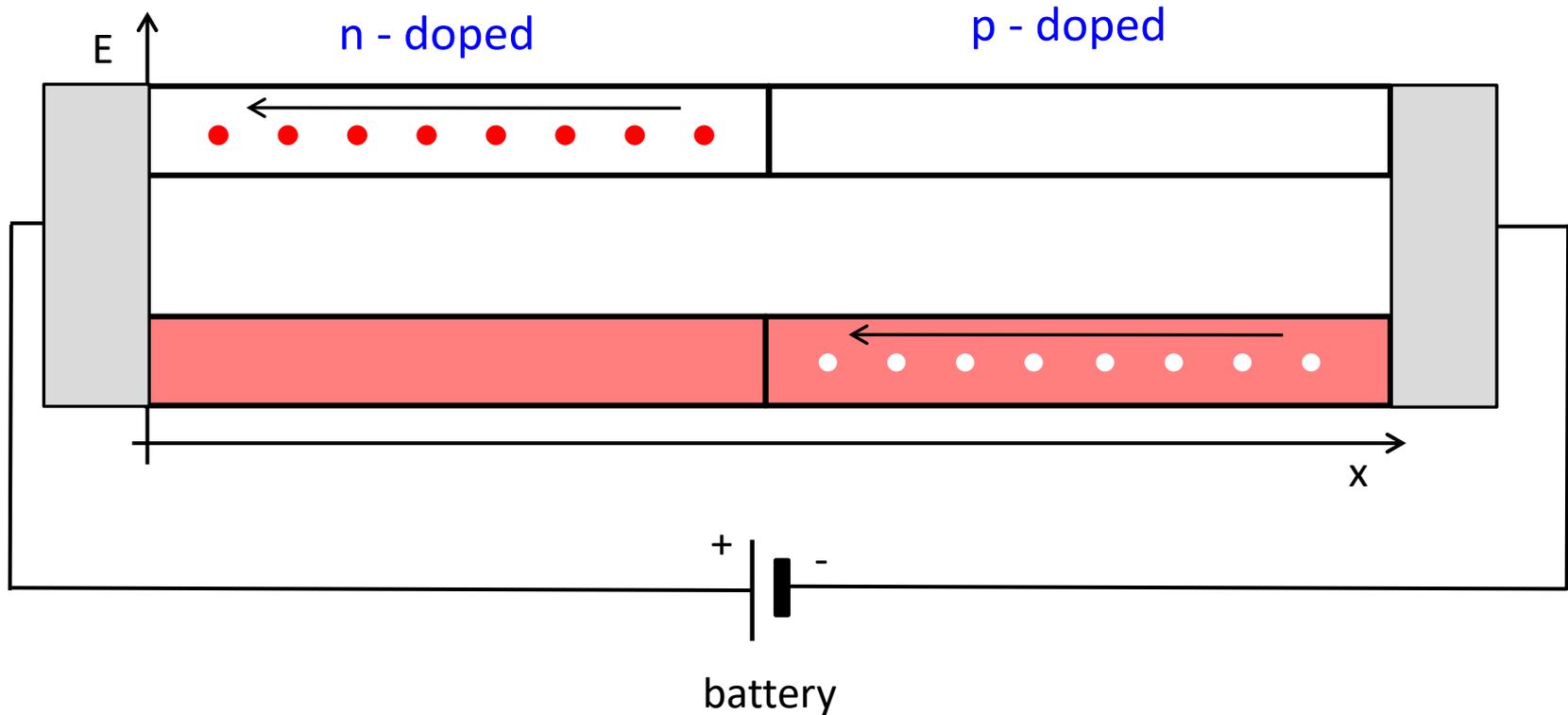
holes in valence band
carry current

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

→ diodes, transistors,... Basis of semiconductor industry.

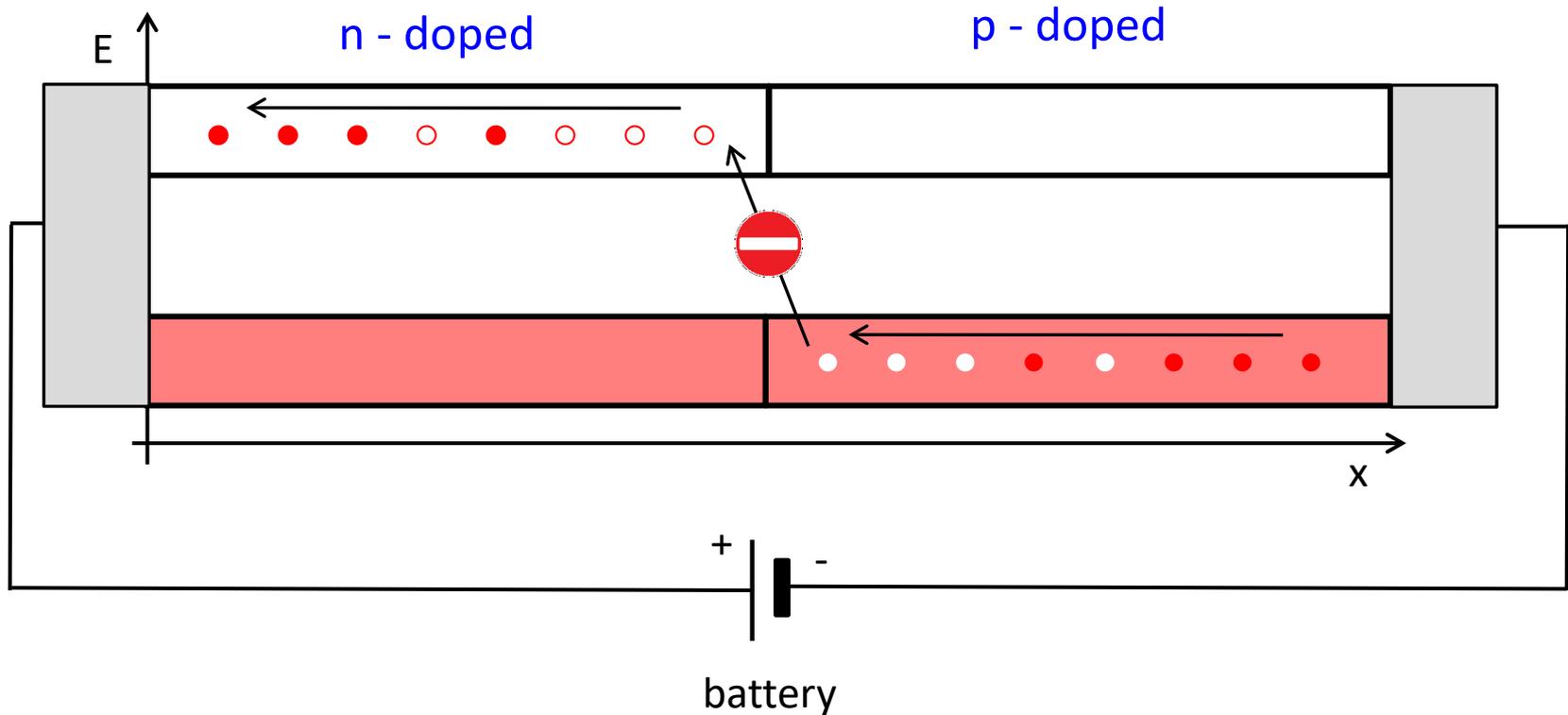
Light-emitting Diode (LED)

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)

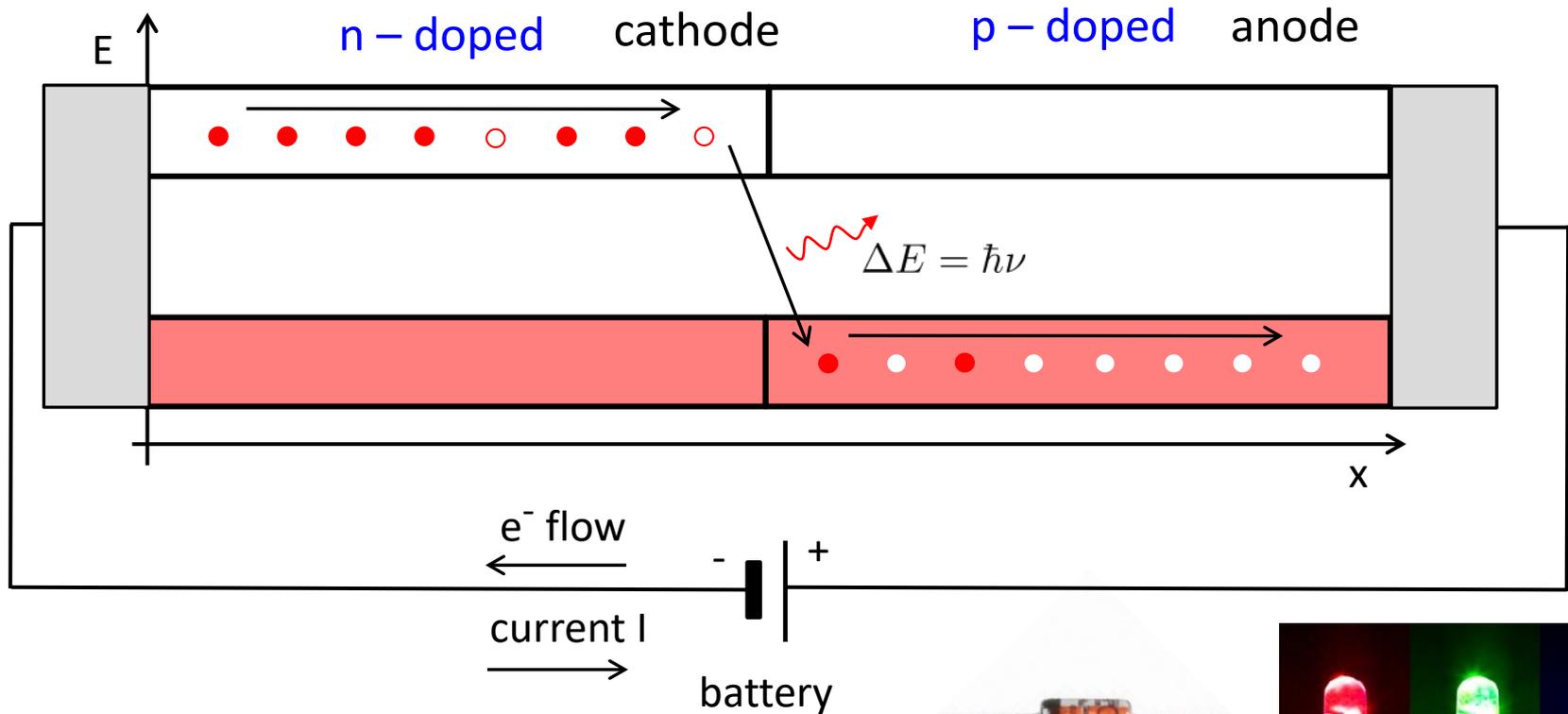
Placing n-doped and p-doped semiconductor next to each other leads to one-way conductor for current. Light can be emitted at interface.



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.



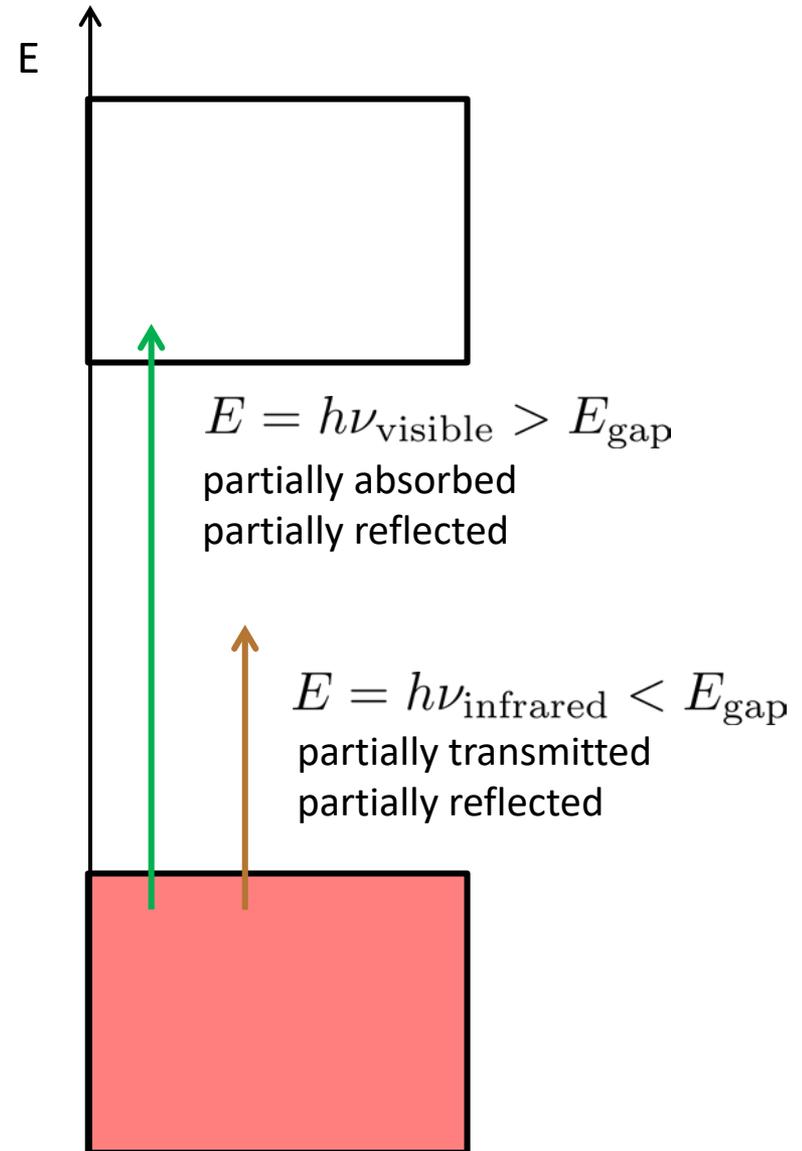
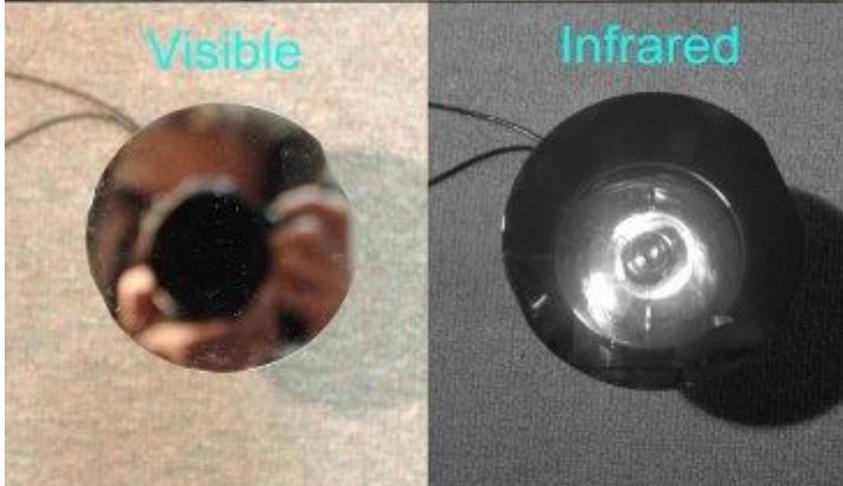
Current flows if voltage connected as shown.



In LEDs energy of electron combining with hole liberated as photon.

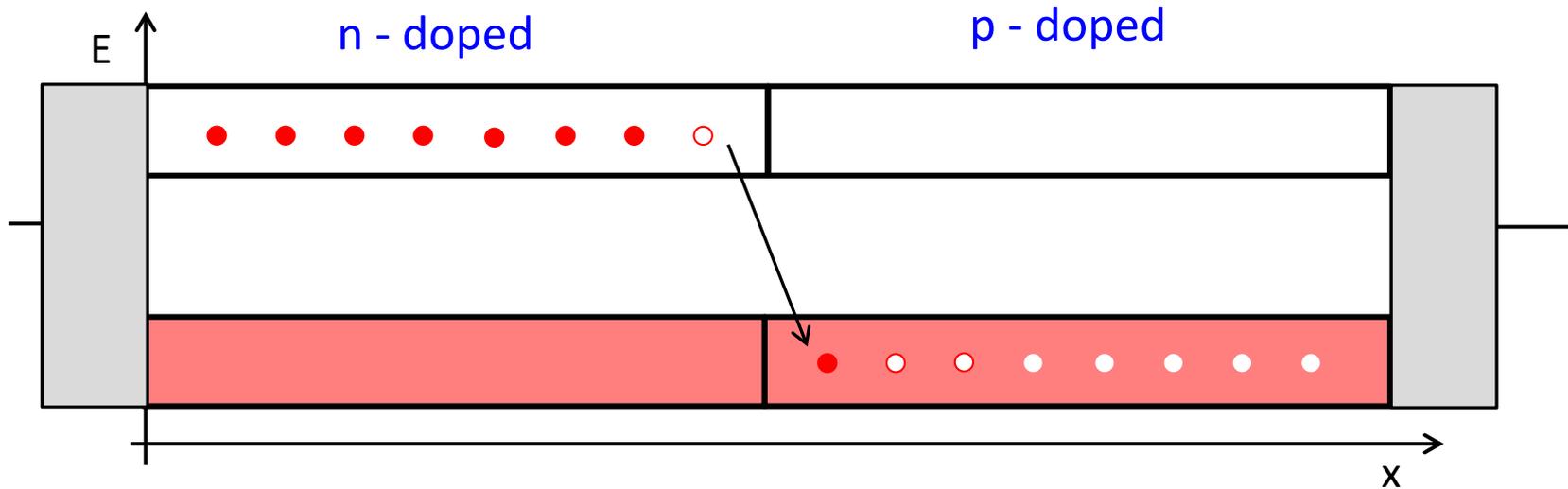


Infrared light transmission through silicon



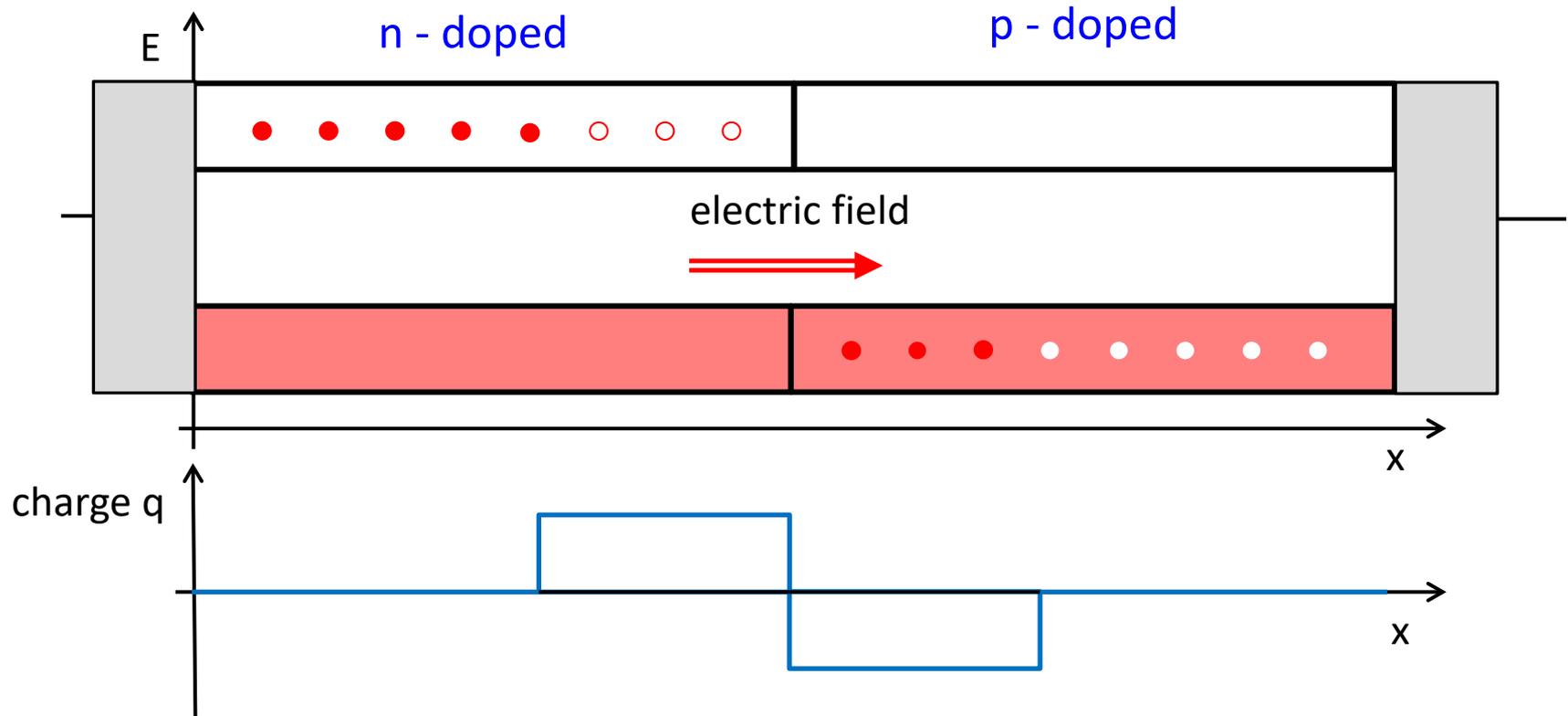
Photodiode / solar cell

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

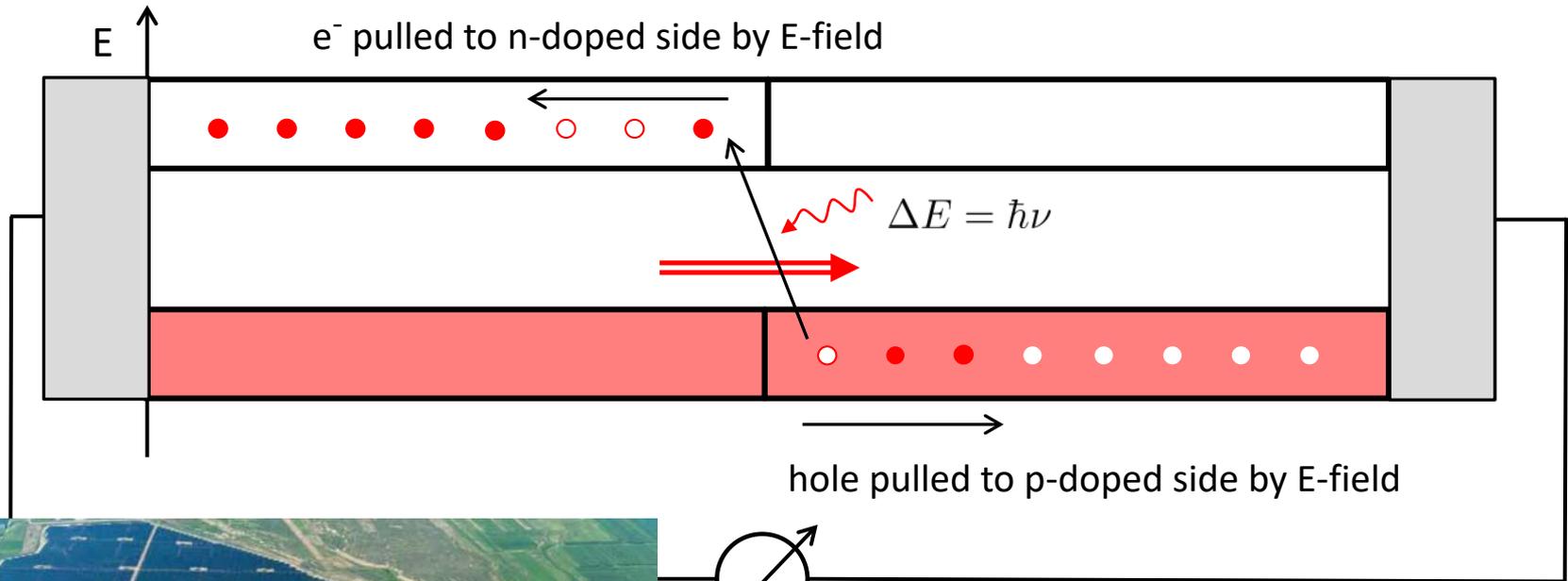


Photodiode / solar cell

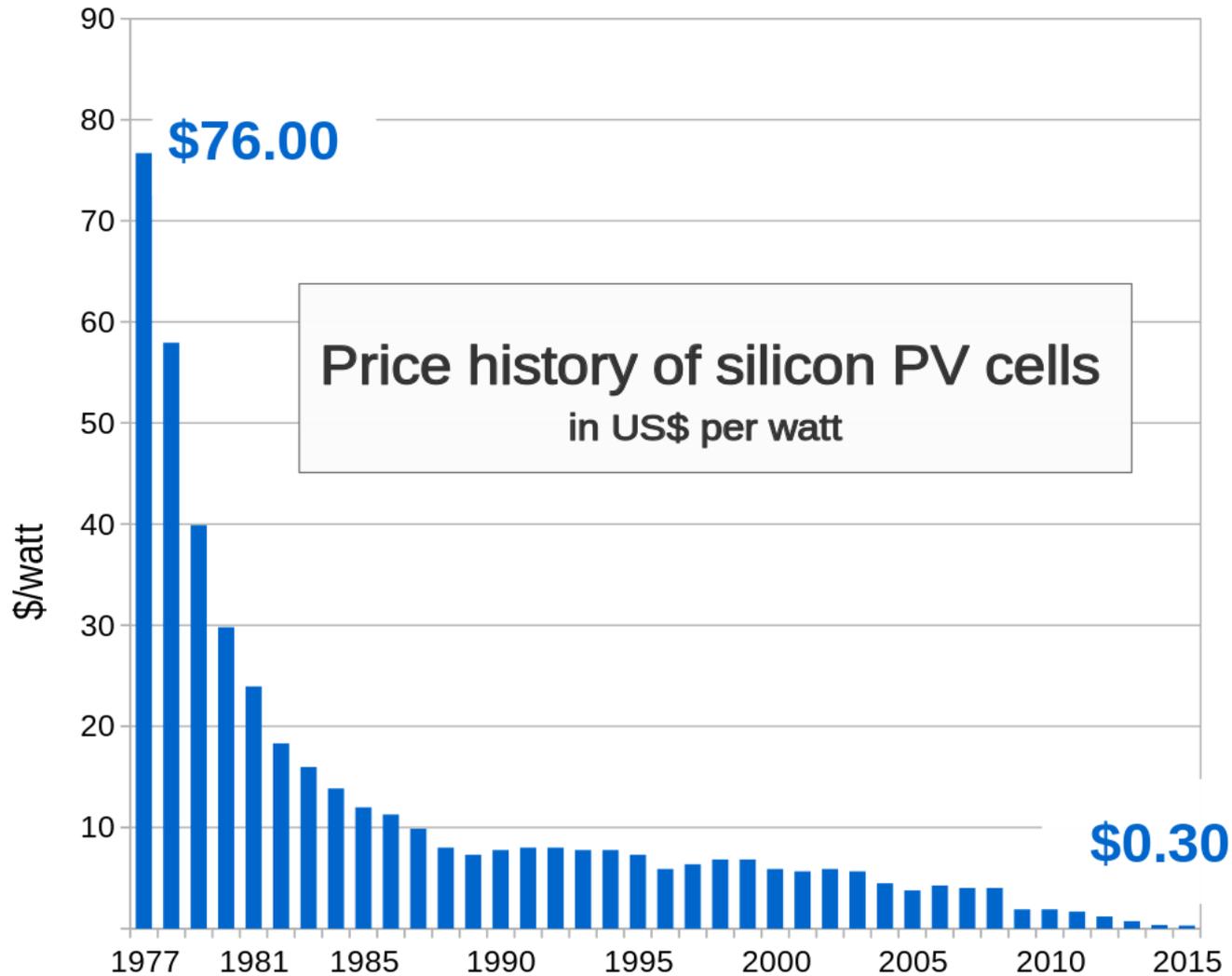
n-p junction at rest: e^- combine with holes, creating charge distribution and E-field

n - doped

p - doped



Solar cell cost

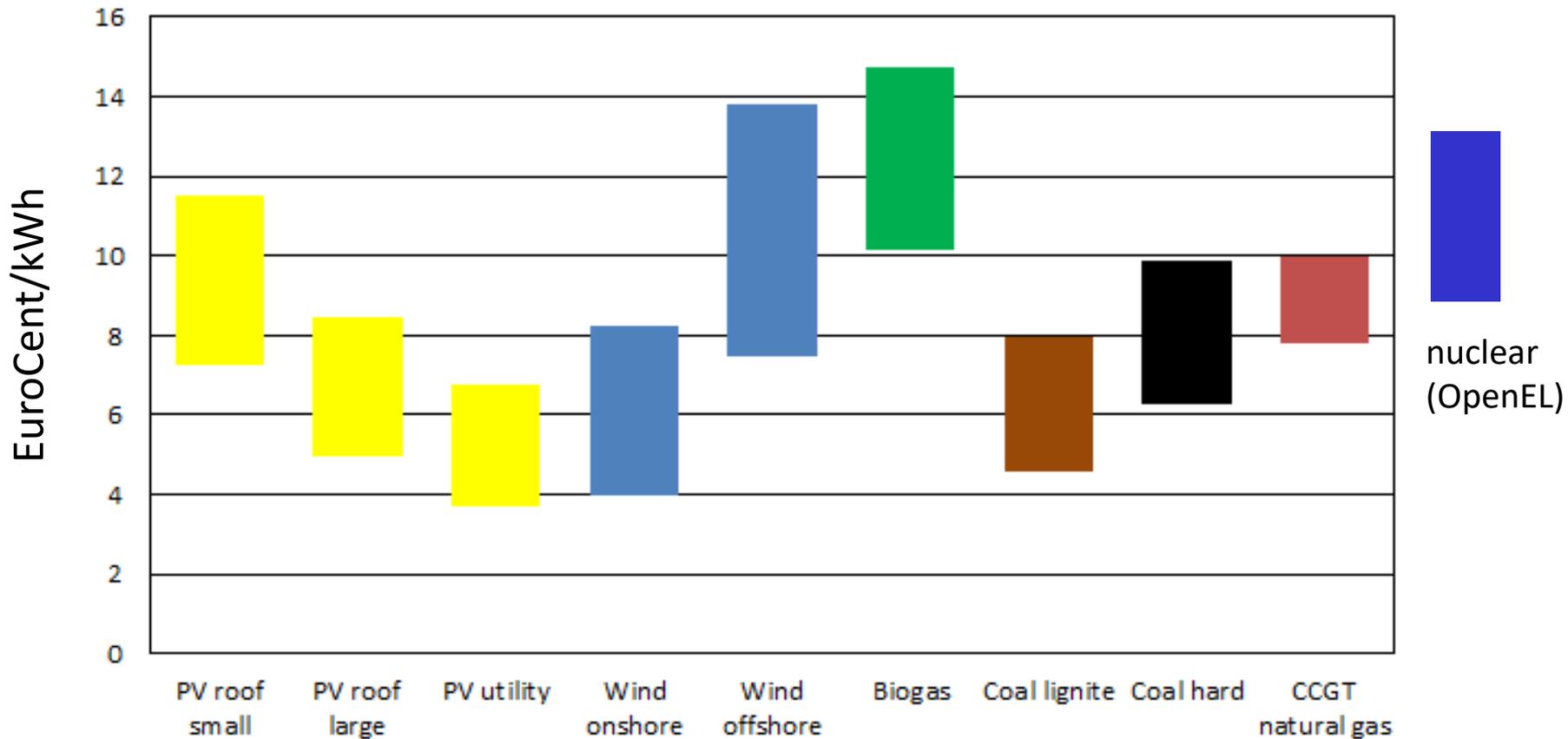


Source: Bloomberg New Energy Finance & pv.energytrend.com

Levelized cost of electricity

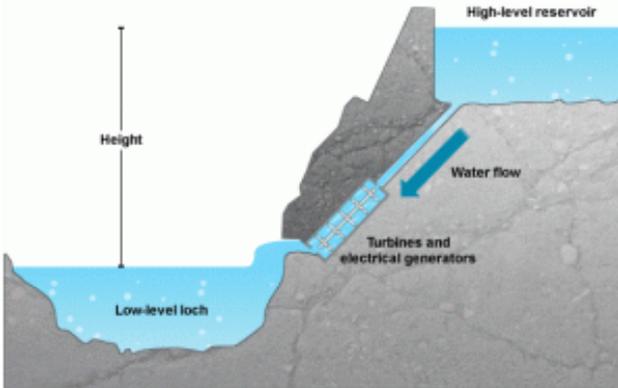
without storage

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

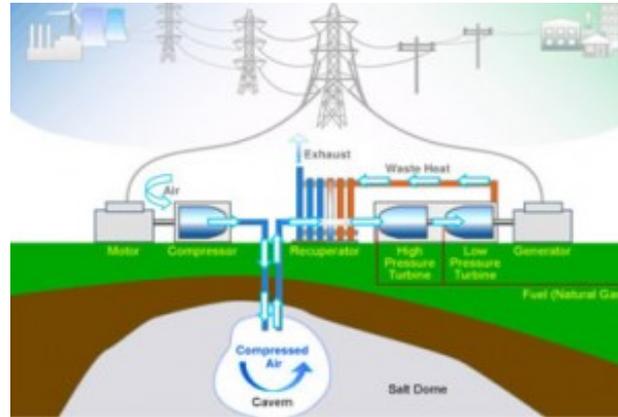


Energy storage

Pumped hydro



Compressed air

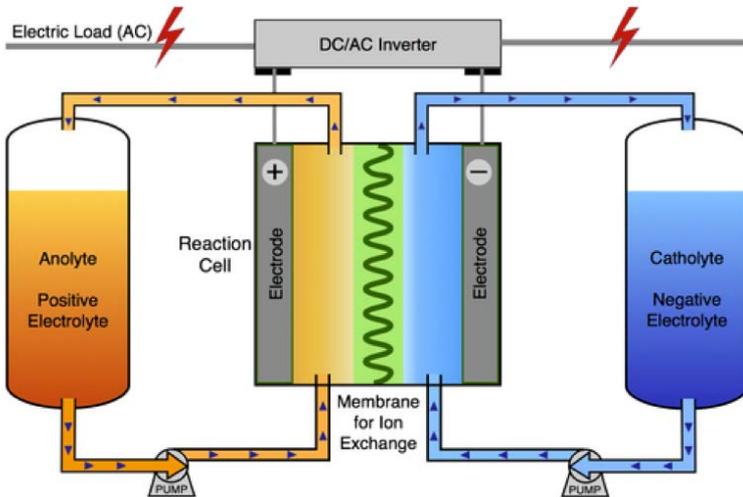


Cranes lifting concrete blocks



energyinformative.org

Flow battery



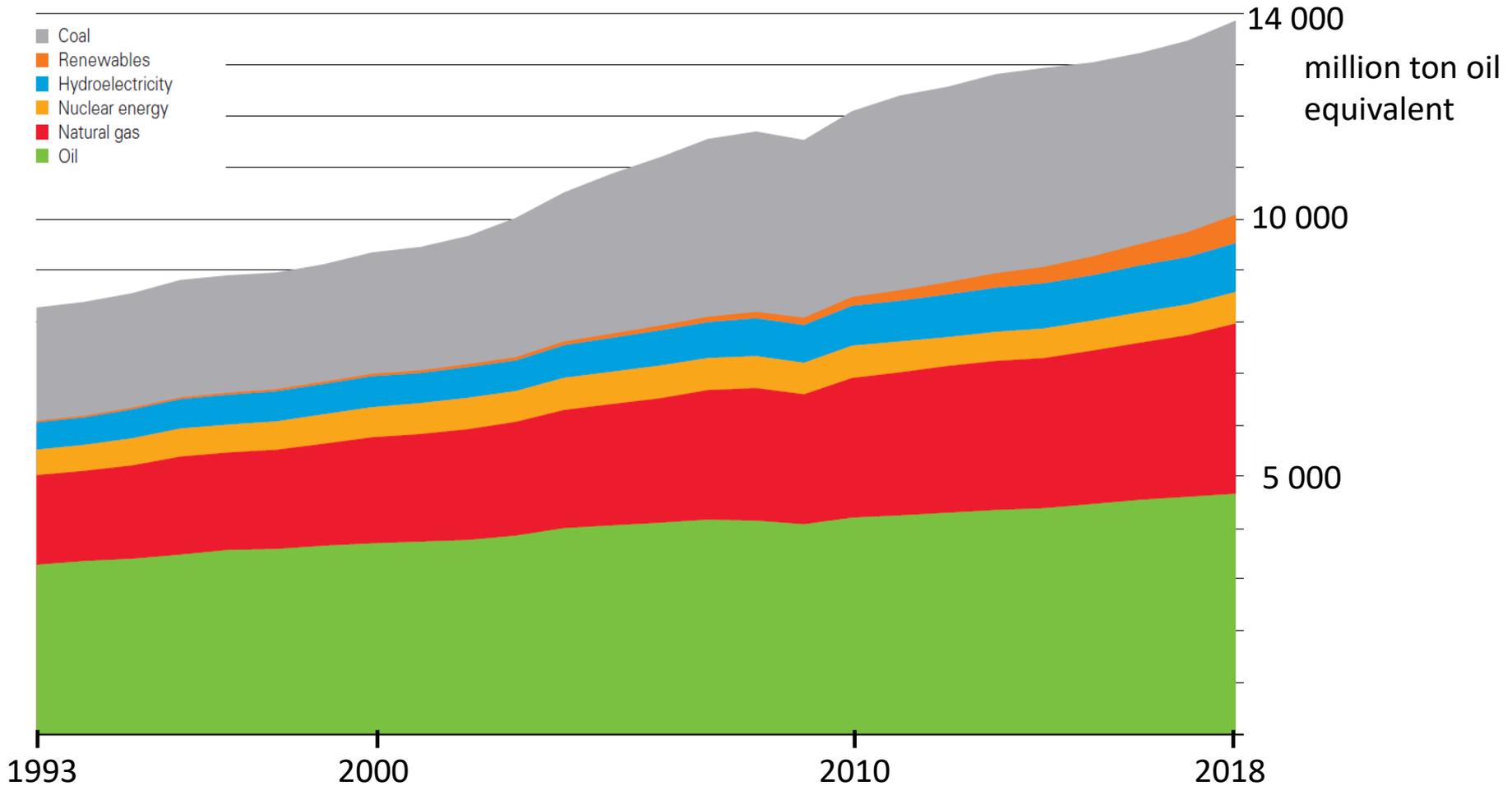
- batteries
- hydrogen
- fly wheel
- thermal storage
- ...

University of British Columbia

Energy Vault

World energy consumption

BP Statistical Review of World Energy 1019

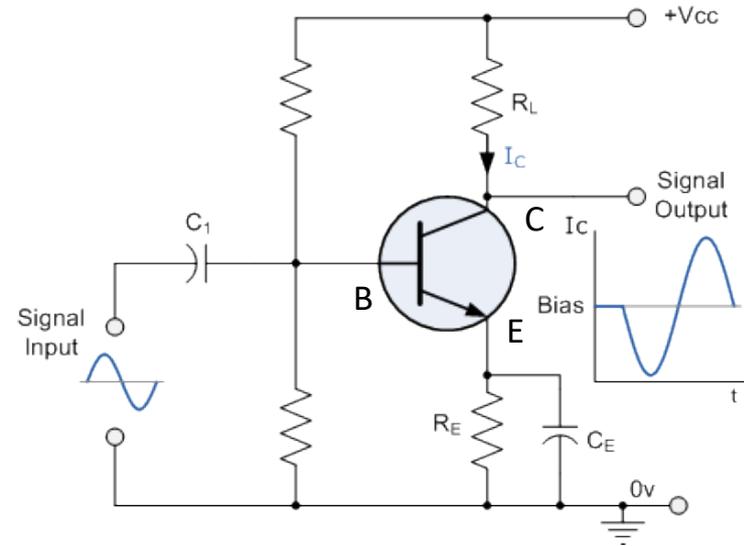
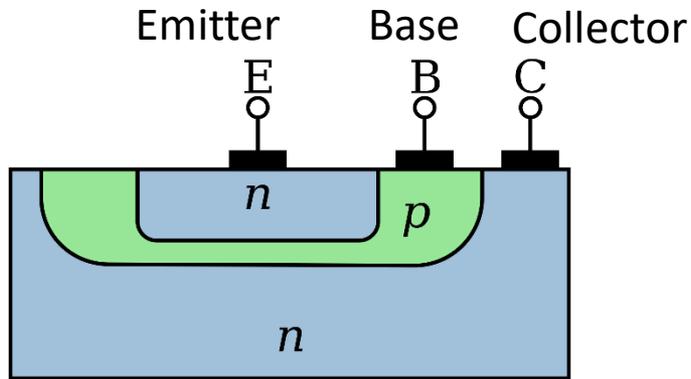


Solar increased by 30 million ton oil equivalent in 2018.
All renewables increased by 71 million ton oil equivalent.
Need 170 years to all renewable at this rate.
Need to ramp up efforts by ~ factor 10.

1 million ton oil equivalent
= 11.63 TWh

Bipolar transistor

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.

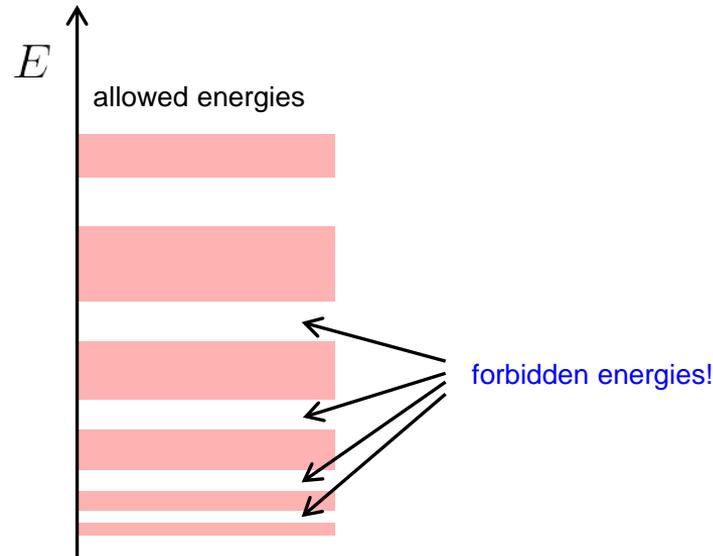
→ signal amplification



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
 - 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?



Overview of topic „Crystalline solids“

→ **Electrons in periodic potential**

Griffiths 3rd 5.3.2

simple model describing crystals

explains under which conditions a solid is a

- conductor
- semiconductor
- insulator

Applications

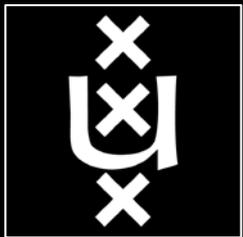
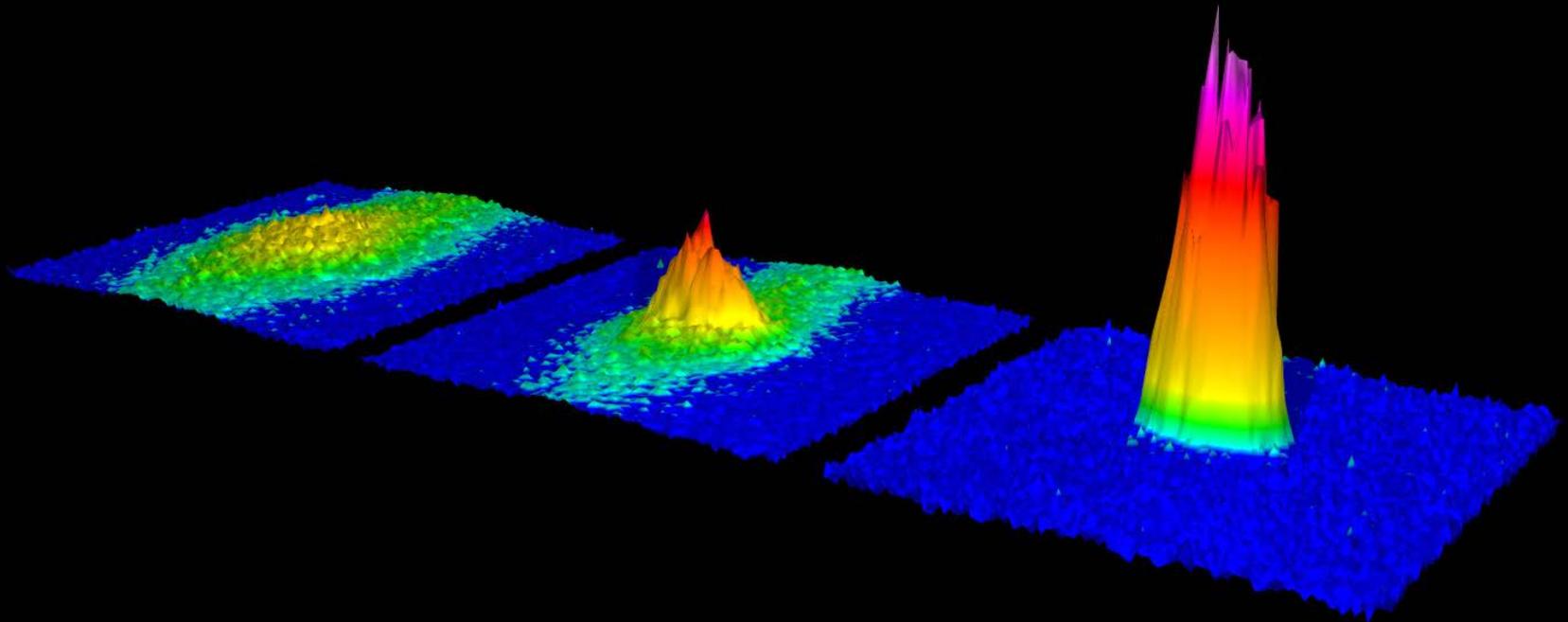
- LED
- solar cell
- transistor



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)

today {

Energy level structure of atoms & the periodic table	Griffiths 5.1, 5.2
Solids	5.3
Quantum statistics	5.4
Time-independent perturbation theory	6.1, 6.2
Structure of hydrogen	6.3 – 6.5
Variational principle	7.1 – 7.3

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

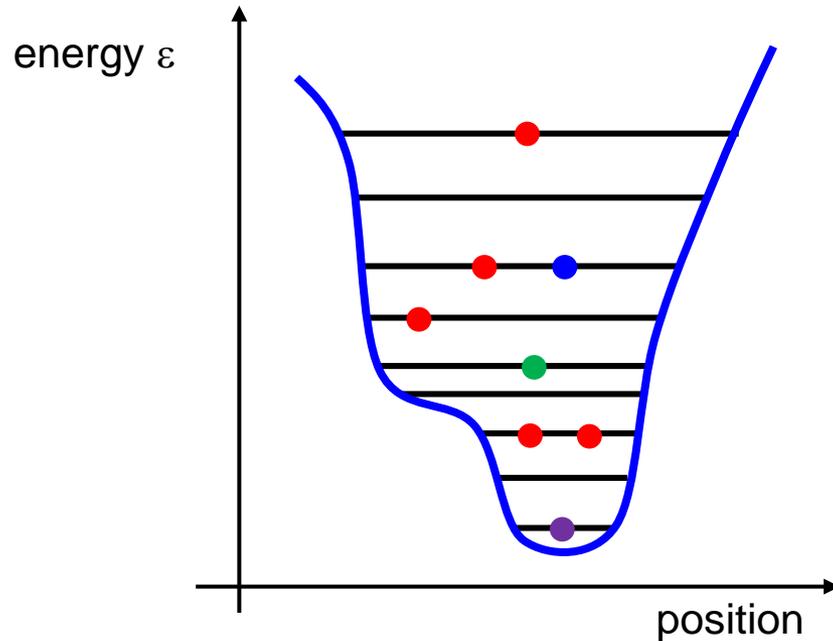
Application: spectrum of thermal electromagnetic radiation

Plan of this section

- 1) Introduction to the topic
- 2) Strategy to derive energy distributions Griffiths 5.4.1
- 3) Step 1 of strategy 5.4.2
- 4) Step 2 of strategy 5.4.3
- 5) Derivation of energy distribution functions 5.4.4
- 6) Application: blackbody spectrum 5.4.5

Quantum statistical mechanics

System: N weakly interacting particles with total energy E

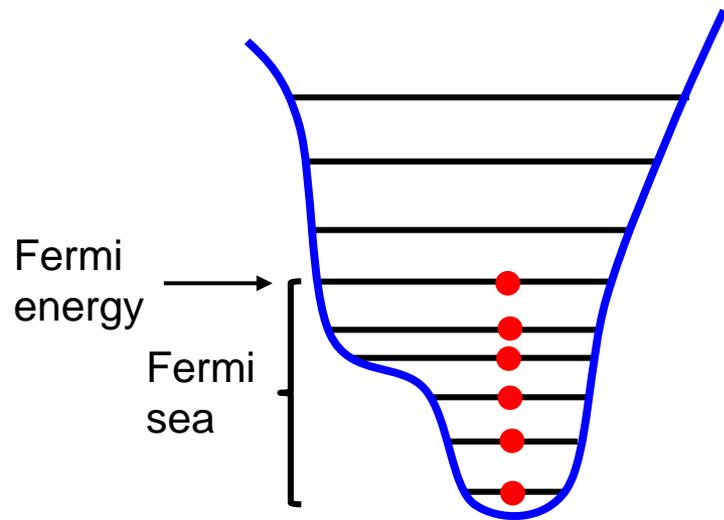


Question: What is most likely number of particles in state with energy ε ?

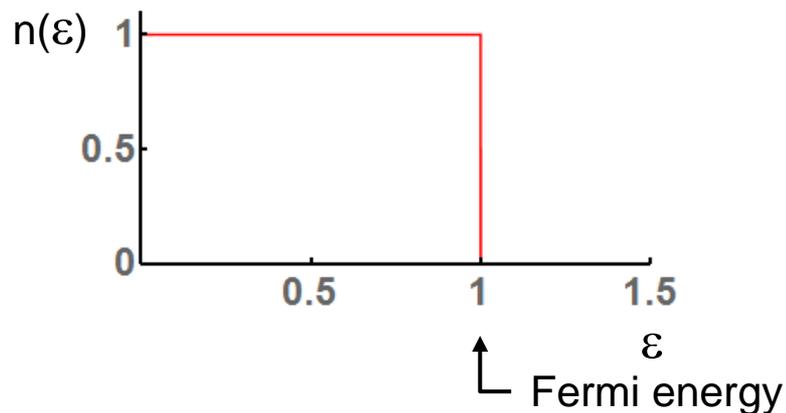
Example 1: identical fermions in 1D

Pauli exclusion \rightarrow at most 1 fermion per state

temperature $T = 0$



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



What are **identical fermions**?

Fermions have half-integer spin.

They always have two or more spin projections m_j .

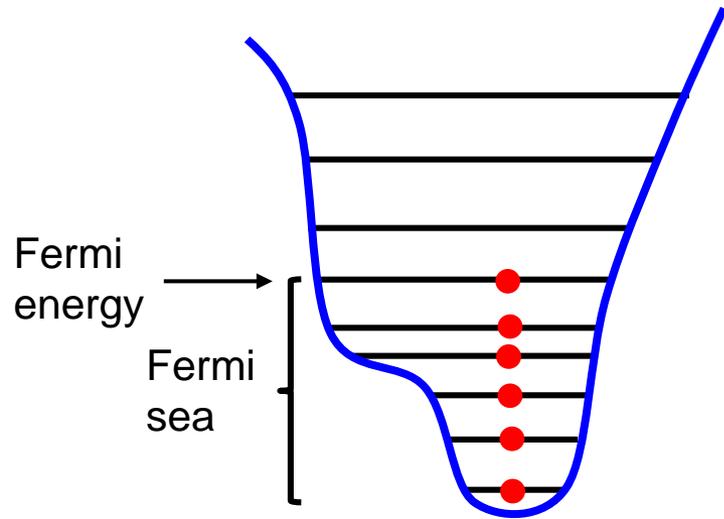
„identical fermions“ means that all fermions have somehow been put into the same m_j state and that they somehow can't leave that state.

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

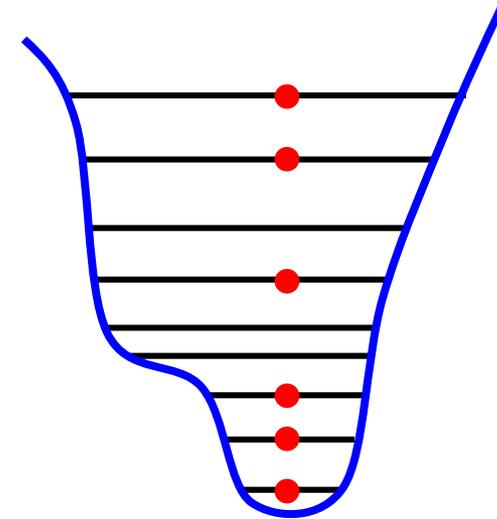
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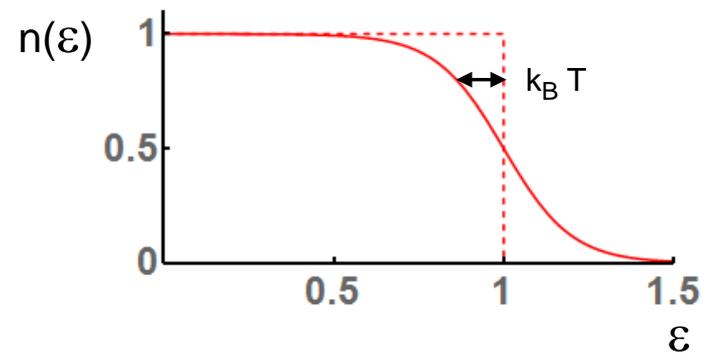
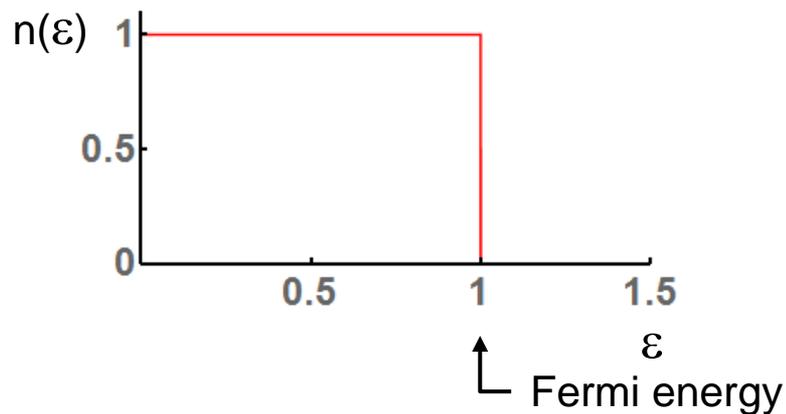
temperature $T = 0$



$T > 0$

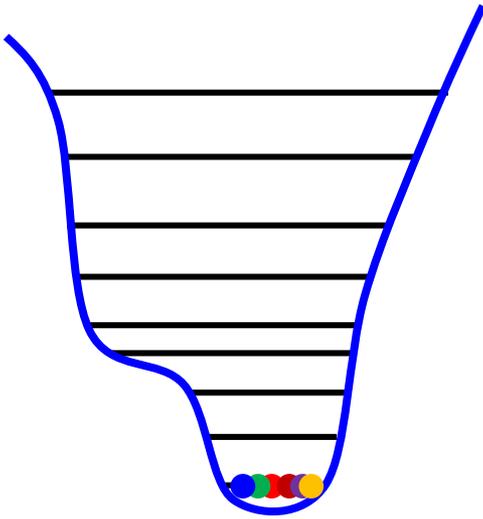


Energy distribution $n(\varepsilon)$: Fermi-Dirac distribution

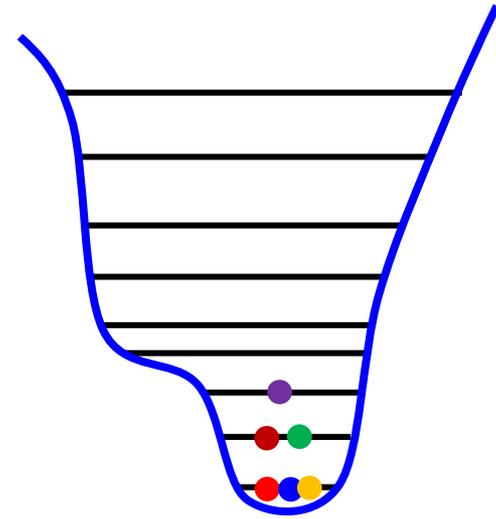


Example 2: distinguishable particles in 1D

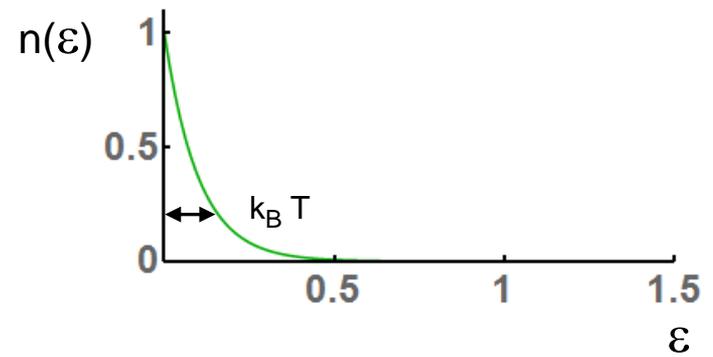
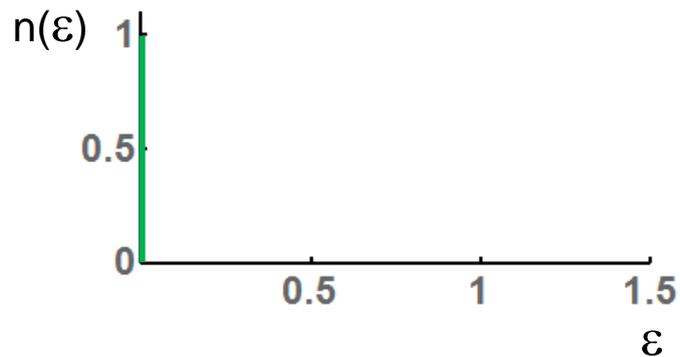
$T = 0$



$T > 0$

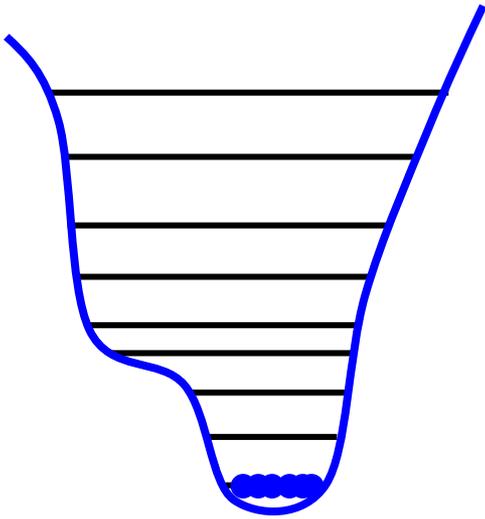


Energy distribution $n(\epsilon)$: Maxwell-Boltzmann distribution

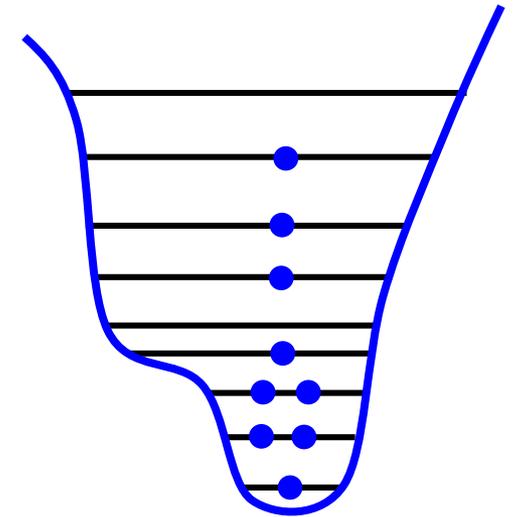


Example 3: identical bosons in 1D

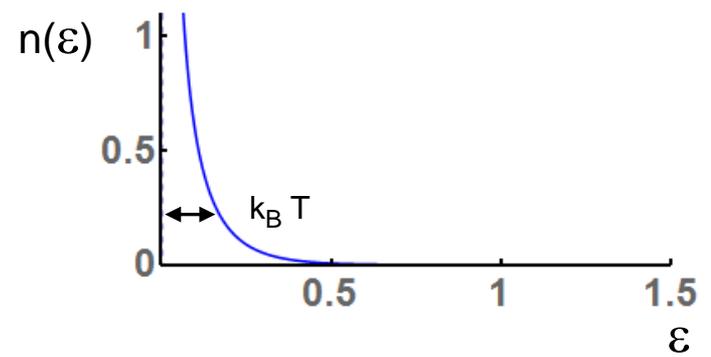
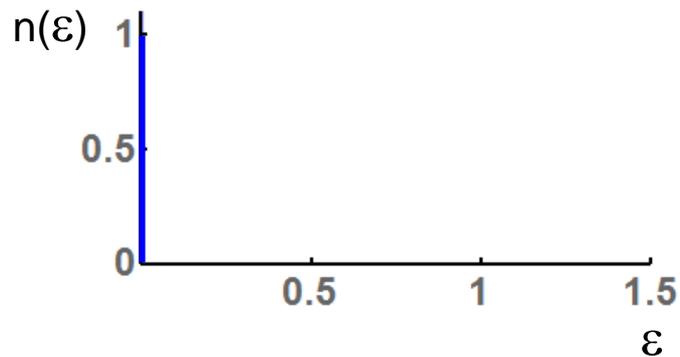
$T = 0$



$T > T_c$



Energy distribution $n(\epsilon)$: Bose-Einstein distribution

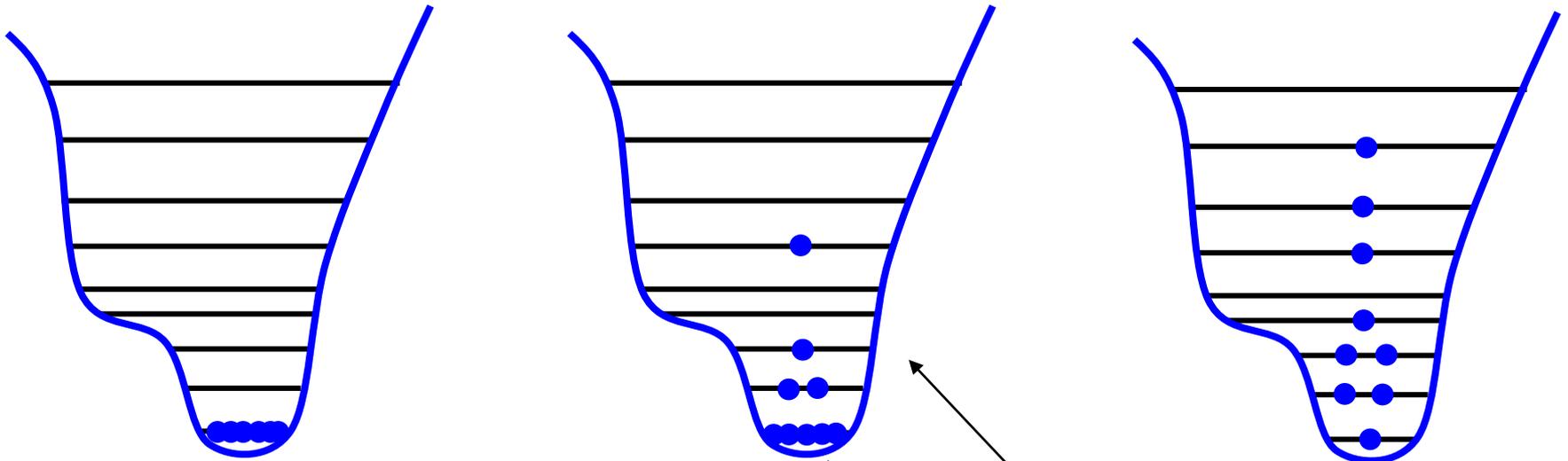


Example 3: identical bosons in 1D

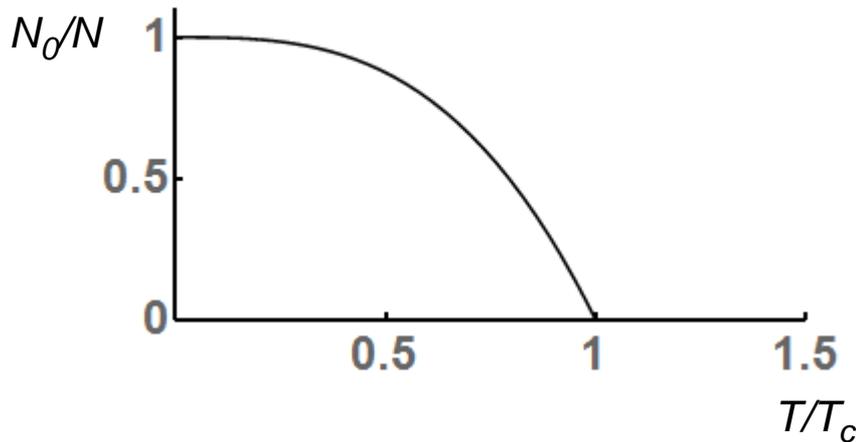
$T = 0$

$0 < T < T_c$

$T > T_c$



BEC atom number over total atom number:

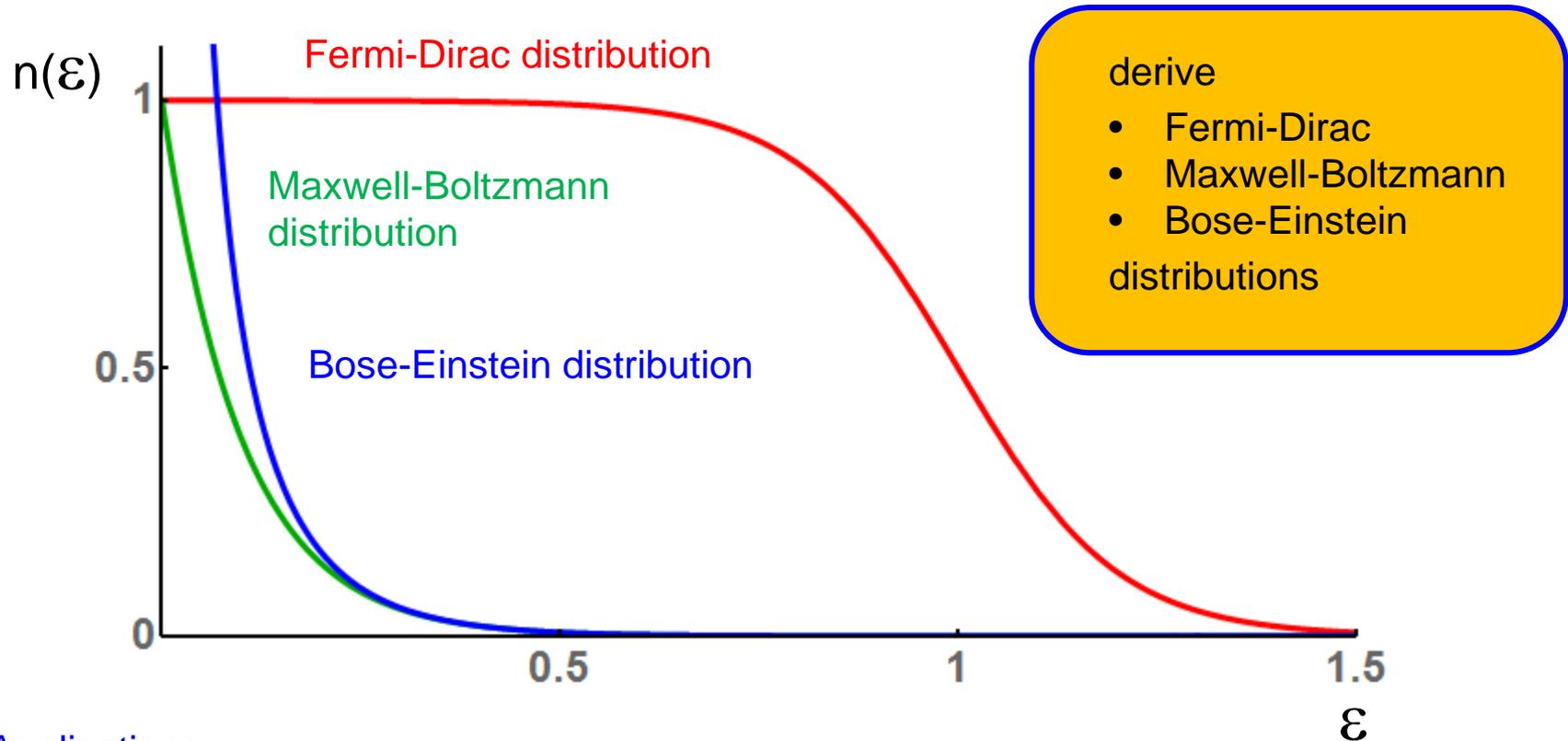


only limited number of bosons „fit“ in excited states

huge number of bosons N_0 „condense into“ ground state

They are Bose-Einstein condensate (BEC)

Goals of this lecture



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

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 Griffiths 5.4.1
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- 5) Derivation of energy distribution functions 5.4.4
- 6) Application: blackbody spectrum 5.4.5

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:

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

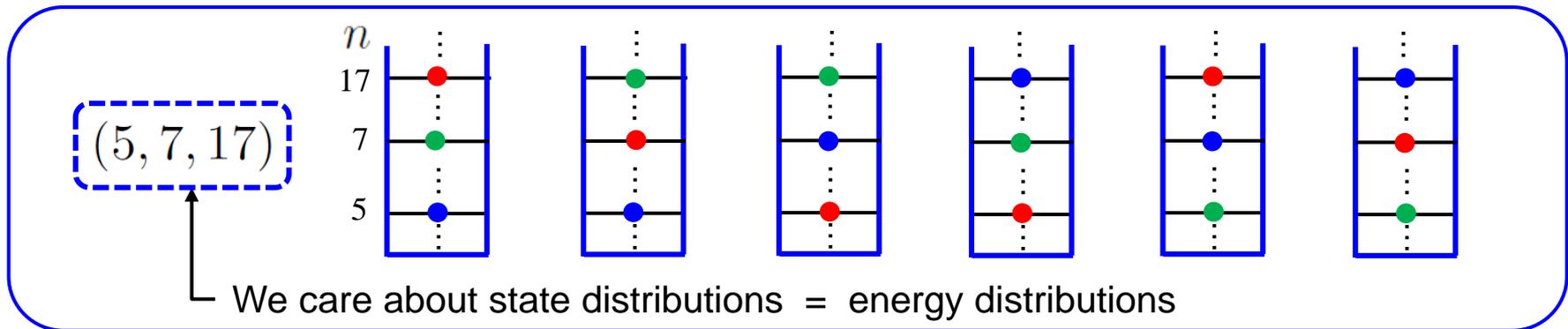
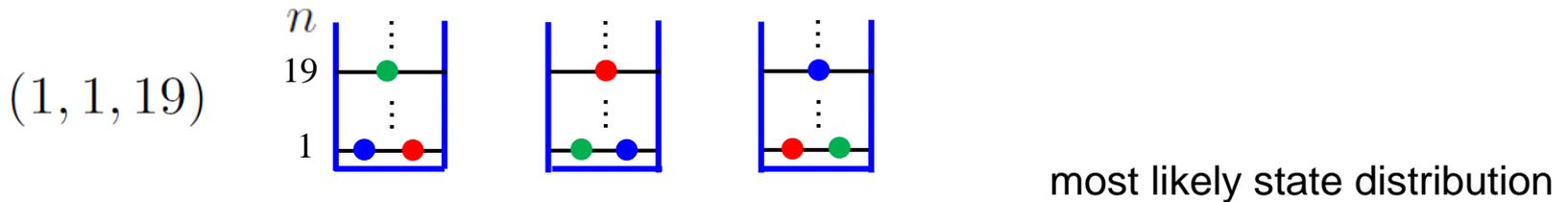
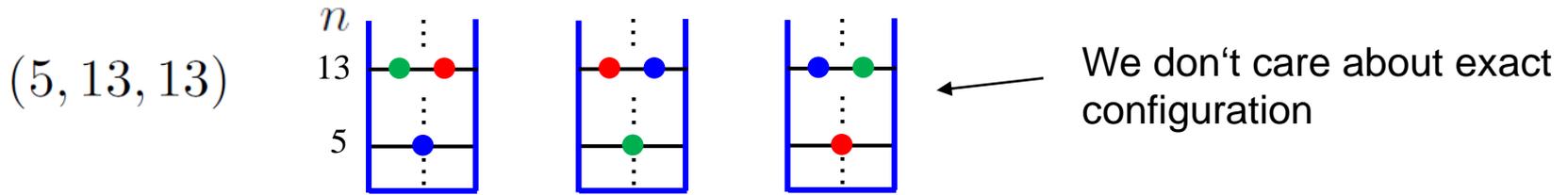
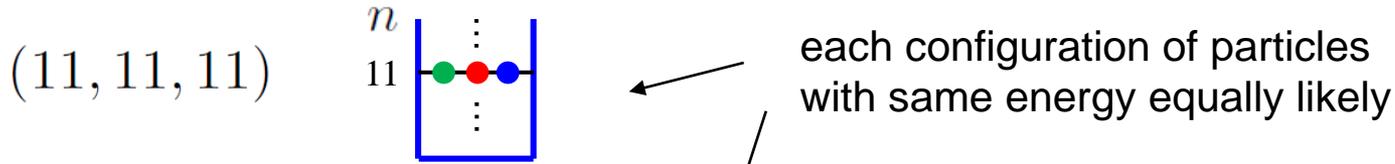
Energy of three particles:

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

What are the possible configurations of particles over energy levels for $E = \frac{\pi^2 \hbar^2}{2ma^2} * 363$?

3 distinguishable particles in square well

(n_A, n_B, n_C) example: $n_A^2 + n_B^2 + n_C^2 = 363$



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 ϵ ,
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

Step 1) Calculate number of configurations for given energy distribution

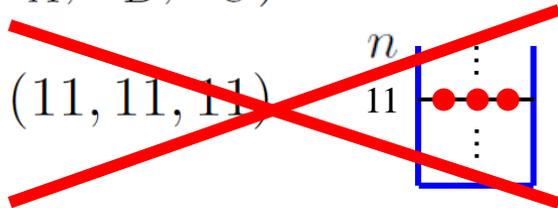
Step 2) Determine most probable energy distribution

Why does particle nature play a role?

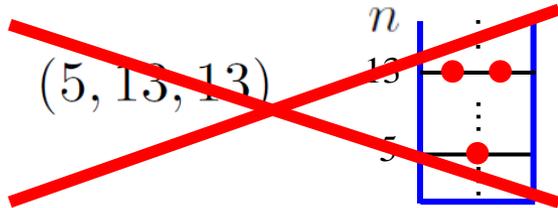
Same example, but for **identical fermions**:

(n_A, n_B, n_C)

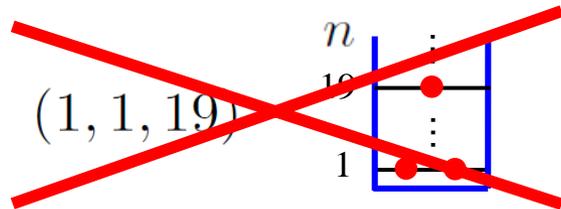
„fermionic statistics“



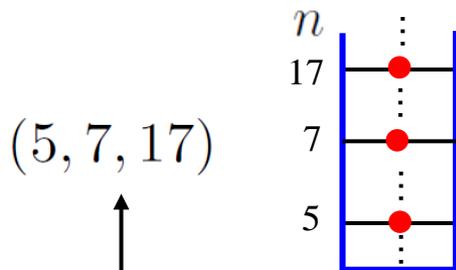
not allowed by Pauli exclusion



not allowed



not allowed



only one allowed configuration

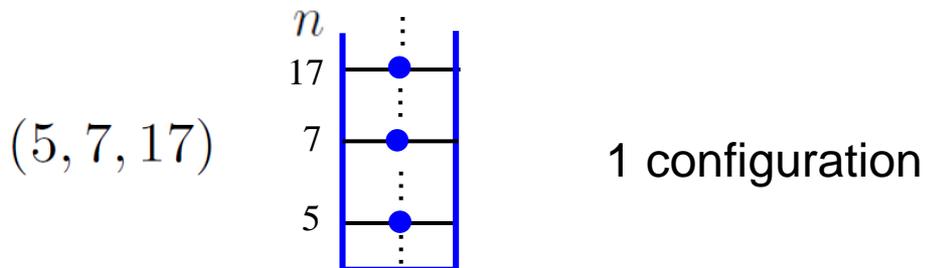
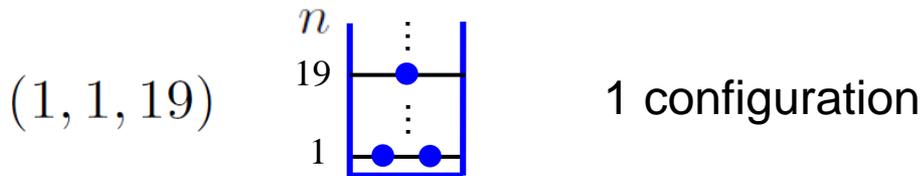
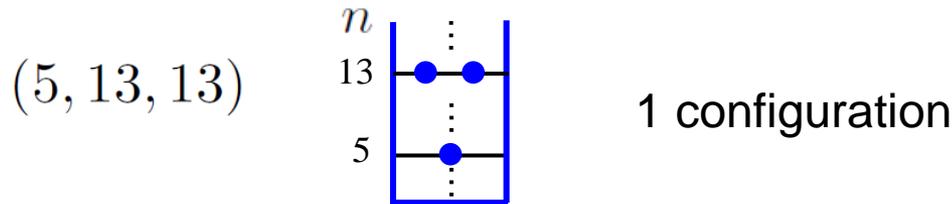
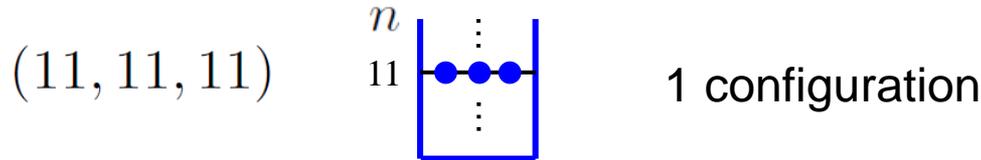
↑
(artefact of simple example: same energy distribution as for distinguishable particles)

Why does particle nature play a role?

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

(n_A, n_B, n_C)

„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

Griffiths 5.4.1

→ 3) Step 1 of strategy : calc. # of configurations for given energy distribution 5.4.2

4) Step 2 of strategy : determine most probable energy distribution 5.4.3

5) Derivation of energy distribution functions 5.4.4

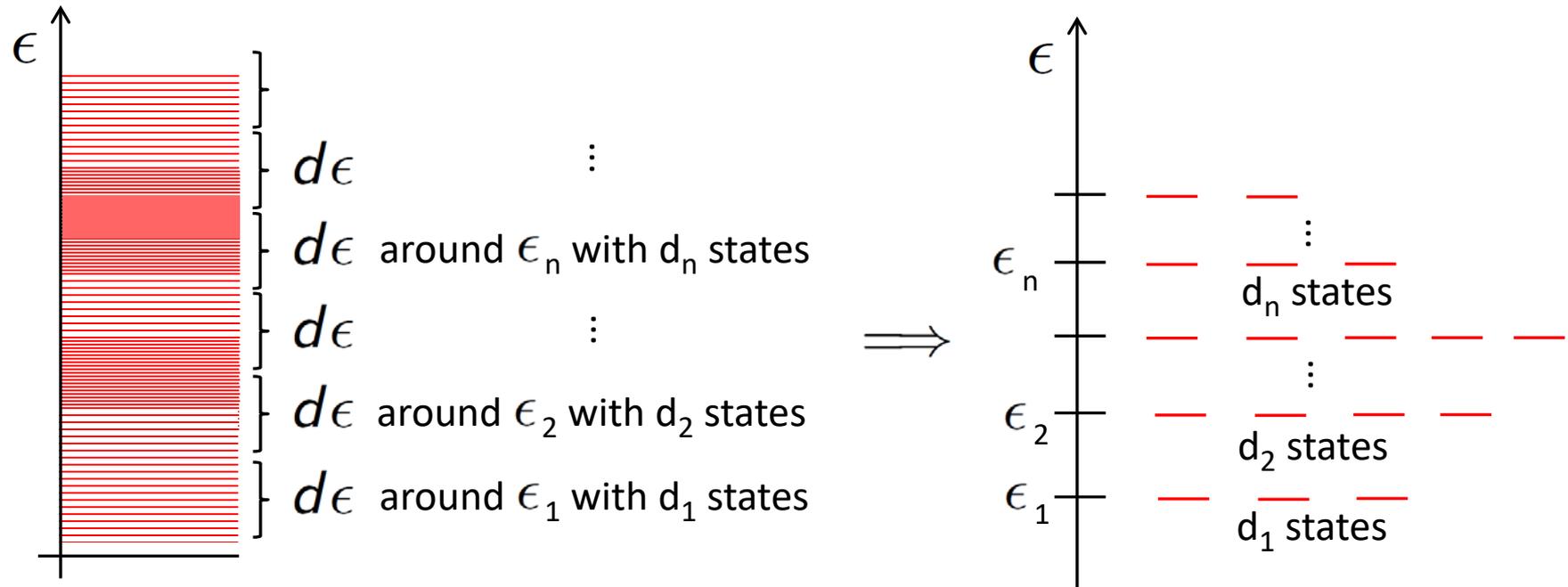
6) Application: blackbody spectrum 5.4.5

Step 1

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 ϵ as degenerate.

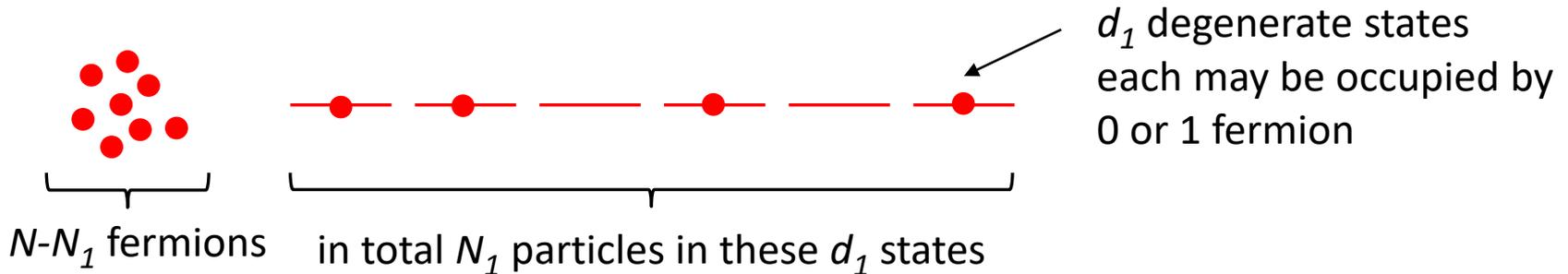


Alternative argument: think of system directly as having degenerate states with energy ϵ_n with degeneracy d_n

Step 1 for identical fermions

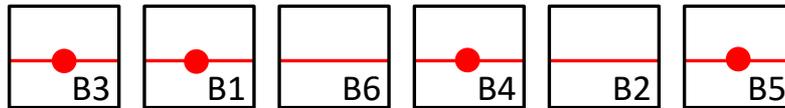
Step 1) Calculate number of configurations for given energy distribution $\{N_n\}$

Filling d_1 states with energy ϵ_1 with N_1 of our N fermions:



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 ($/N_1!$) or which  is where ($/(d_1 - N_1)!$).

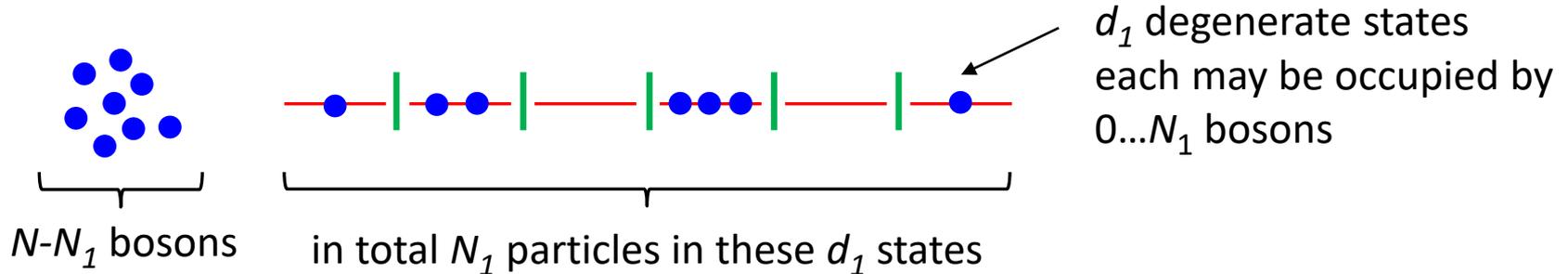
$\frac{d_1!}{N_1!(d_1 - N_1)!}$ configurations for level 1.

#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 ϵ_1 with N_1 of our N bosons:



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“ $|$:



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

We don't care which \bullet is where ($/N_1!$) or which $|$ is where ($/(d_1 - 1)!$).

$$\frac{(N_1 + d_1 - 1)!}{N_1! (d_1 - 1)!} \text{ configurations for level 1.}$$

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

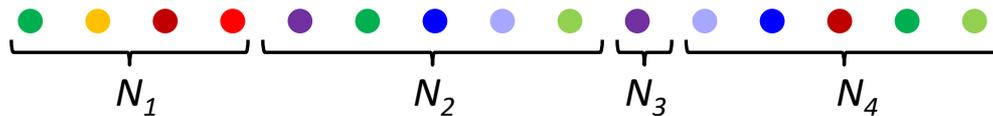
Step 1 for distinguishable particles

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

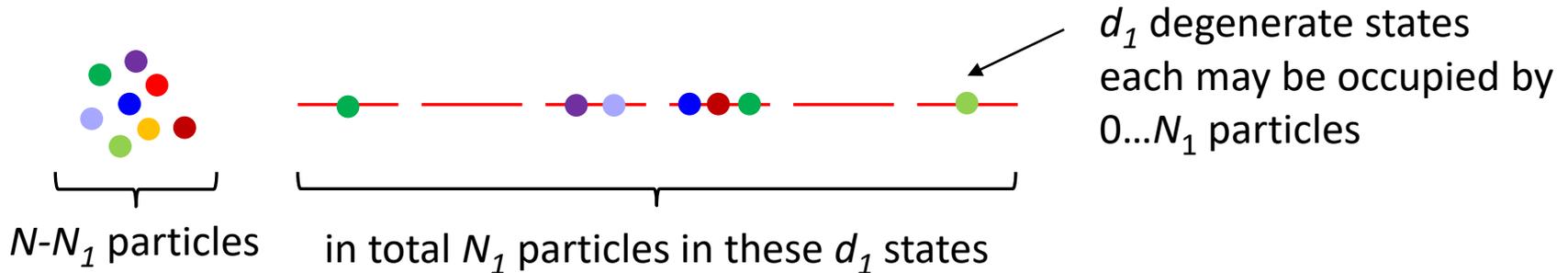
How many choices lead to the same distribution $\{N_n\}$?

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 ($/ \prod_{n=1}^{\infty} N_n!$).



Filling d_1 states with energy ϵ_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... $\longrightarrow d_1^{N_1}$ conf.

#configurations for all levels:
$$Q(N_n) = \frac{N!}{\prod_{n=1}^{\infty} N_n!} \prod_{n=1}^{\infty} d_n^{N_n} = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}$$

Overview of „Quantum stat. mech.“

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

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Griffiths 5.4.1

3) Step 1 of strategy : calc. # of configurations for given energy distribution

5.4.2



4) Step 2 of strategy : determine most probable energy distribution

5.4.3

5) Derivation of energy distribution functions

5.4.4

6) Application: blackbody spectrum

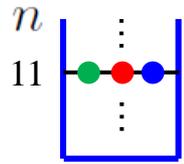
5.4.5

3 distinguishable particles in square well

Reminder

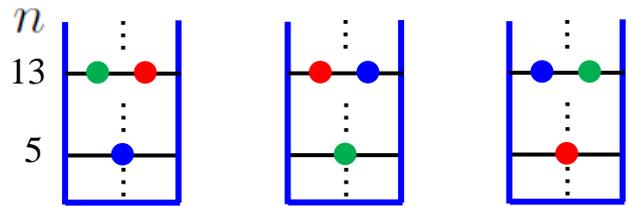
(n_A, n_B, n_C) example: $n_A^2 + n_B^2 + n_C^2 = 363$

$(11, 11, 11)$



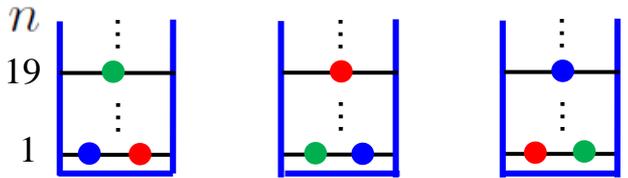
each configuration of particles with same energy equally likely

$(5, 13, 13)$



We don't care about exact configuration

$(1, 1, 19)$



most likely state distribution

$(5, 7, 17)$

We care about state distributions = energy distributions

Step 2

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

$$f_N(N_n) = N - \sum_{n=1}^{\infty} N_n \stackrel{!}{=} 0 \quad (*)$$

$$f_E(N_n) = E - \sum_{n=1}^{\infty} N_n E_n \stackrel{!}{=} 0 \quad (**)$$

Most probable energy distribution: $\frac{\partial Q}{\partial N_n} \stackrel{!}{=} 0$ or, simpler, $\frac{\partial}{\partial N_n} \ln Q \stackrel{!}{=} 0$

under constraints (*) and (**).

Use Lagrange multipliers! (here: α and β)

Minimize

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

$$\frac{\partial G}{\partial \alpha} \stackrel{!}{=} 0 \quad \text{imposes } (*) \quad ; \quad \frac{\partial G}{\partial \beta} \stackrel{!}{=} 0 \quad \text{imposes } (**)$$

$$\frac{\partial G}{\partial N_n} \stackrel{!}{=} 0 \quad \text{will find extremum of } \ln Q \text{ under constraints } (*) \text{ and } (**).$$

How do Lagrange multipliers work?

Example:

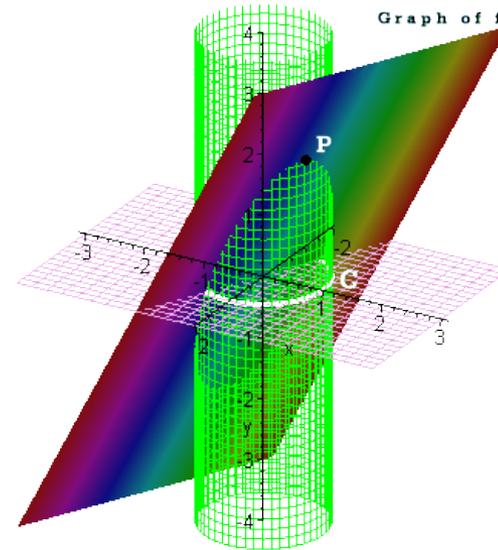
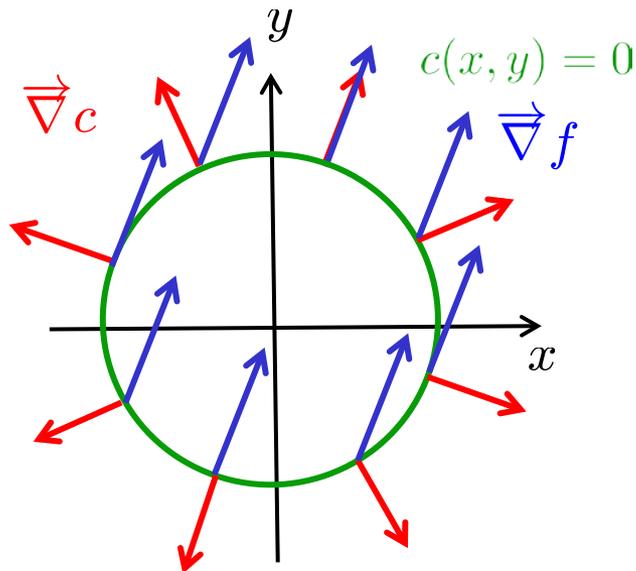
Find extremum of

$$f(x, y) = x + 2y$$

under constraint

$$c(x, y) = x^2 + y^2 - 1 = 0$$

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



If $\vec{\nabla} f \not\parallel \vec{\nabla} c$, the projection of $\vec{\nabla} f$ 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 $\vec{\nabla} f \parallel \vec{\nabla} c$, we have found an extremum.

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

\Rightarrow Find extrema of $f - \lambda c$.
Adjust λ such that constraint fulfilled.

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$$\frac{\partial G}{\partial N_n} \stackrel{!}{=} 0 \quad \text{will find extremum of } \ln Q \text{ under constraints } (*) \text{ and } (**).$$

Step 2 for identical bosons

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

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

Reminder

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

Use Stirling's approximation:

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

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

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

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

$$N_n = \frac{d_n - 1}{e^{(\alpha + \beta E_n)} - 1} \sim \frac{d_n}{e^{(\alpha + \beta E_n)} - 1} \quad (I)$$

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

$$\rightarrow N_n = \frac{d_n}{e^{(\alpha + \beta E_n)} + 1} \quad (\text{II})$$

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

$$\rightarrow N_n = d_n e^{-(\alpha + \beta E_n)} \quad (\text{III})$$

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

Griffiths 5.4.1

3) Step 1 of strategy : calc. # of configurations for given energy distribution

5.4.2

4) Step 2 of strategy : determine most probable energy distribution

5.4.3

→ 5) Derivation of energy distribution functions

5.4.4

6) Application: blackbody spectrum

5.4.5

Physical significance of α and β

Determining α and β : plug N_n from (I), (II) or (III) into (*) and (***) and solve.

Step 2

Reminder

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Physical significance of α and β

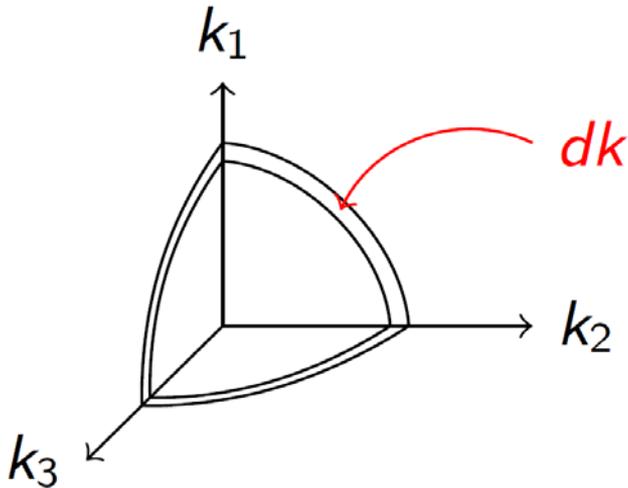
Determining α and β : plug N_n from (I), (II) or (III) into (*) and (**) and solve.

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:

$$E_k = \frac{\hbar^2 k^2}{2m} \quad ; \quad \vec{k} = \frac{\pi}{l} \vec{n} \quad ; \quad \vec{n} = (n_x, n_y, n_z)$$
$$n_i \in \{1, 2, \dots\}$$



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 α and β

Plug (III) into (*):

$$N = \sum_{n=1}^{\infty} N_n = \sum_{n=1}^{\infty} d_n e^{-(\alpha + \beta E_n)} = \int dk \frac{V}{2\pi^2} k^2 e^{-(\alpha + \beta E_k)} \quad \text{with } E_k = \frac{\hbar^2 k^2}{2m}$$
$$= V e^{-\alpha} \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2} \rightarrow e^{-\alpha} = \frac{N}{V} \left(\frac{2\pi\beta\hbar^2}{m} \right)^{3/2} \quad d_k = \frac{V}{2\pi^2} k^2 dk$$

Plug (III) into (**):

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

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:

$$\mu \equiv -\alpha k_b T \quad \rightarrow \quad \alpha = -\frac{\mu}{k_b T} \quad \mu \text{ is called „chemical potential“}$$

Energy distribution functions

$n(\epsilon)$ = most probable # of particles in a state with energy ϵ

Divide (I), (II), (III) by d_n , plug in α and β :

$$n(\epsilon) = \begin{cases} \frac{1}{e^{(\epsilon-\mu)/k_b T} - 1} & \text{Bose-Einstein} & \text{ident. bosons} \\ \frac{1}{e^{(\epsilon-\mu)/k_b T} + 1} & \text{Fermi-Dirac} & \text{ident. fermions} \\ e^{-(\epsilon-\mu)/k_b T} & \text{Maxwell-Boltzmann} & \text{distinguishable} \\ & & \text{particles} \end{cases}$$

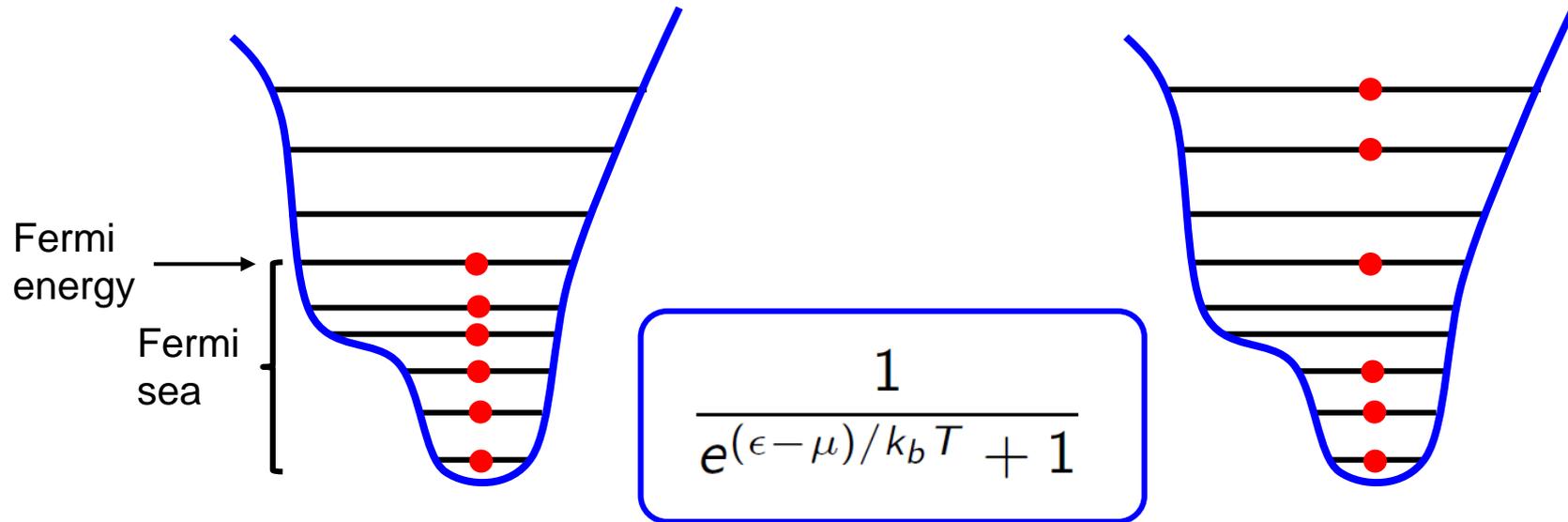
distribution

Example 1: identical fermions in 1D

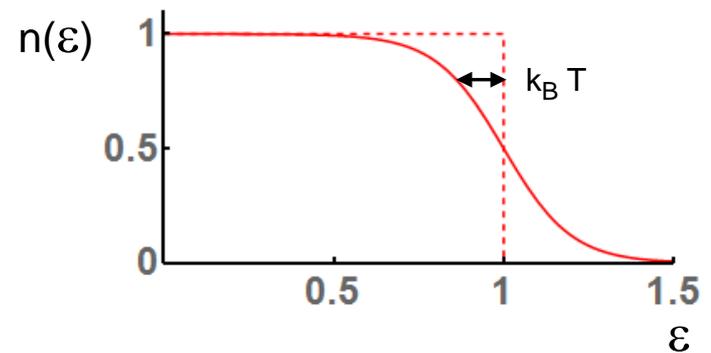
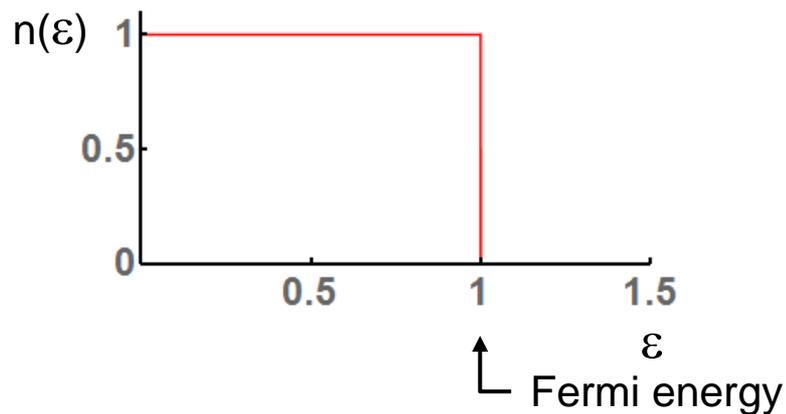
Pauli exclusion \rightarrow at most 1 fermion per state

temperature $T = 0$

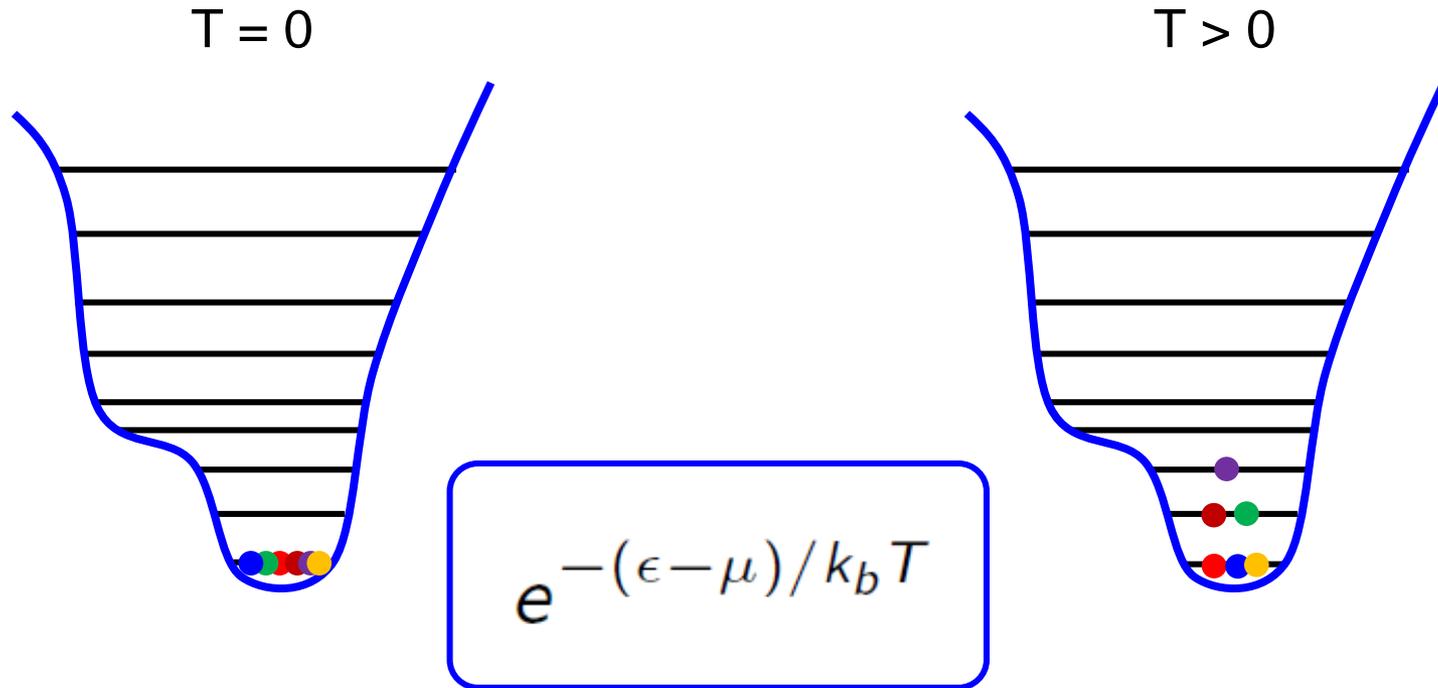
$T > 0$



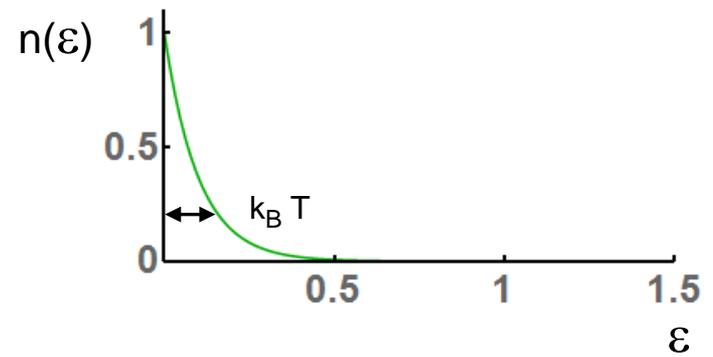
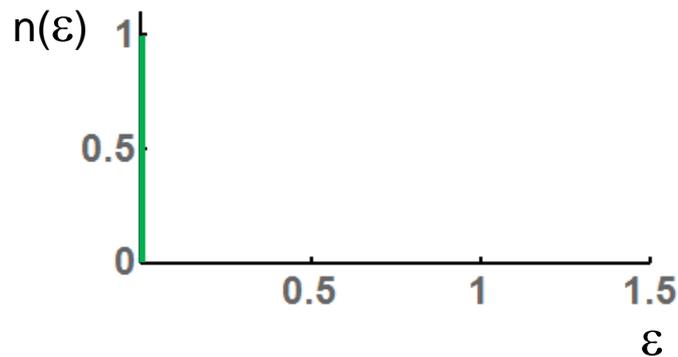
Energy distribution $n(\epsilon)$: **Fermi-Dirac distribution**



Example 2: distinguishable particles in 1D

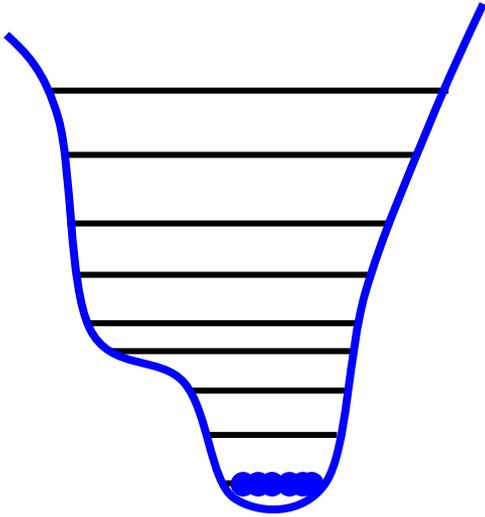


Energy distribution $n(\epsilon)$: Maxwell-Boltzmann distribution

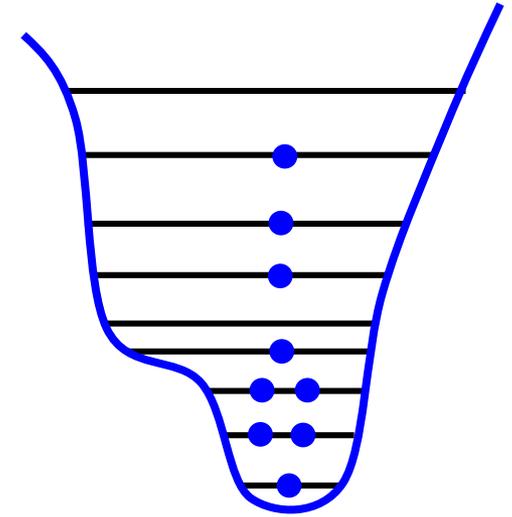


Example 3: identical bosons in 1D

$T = 0$

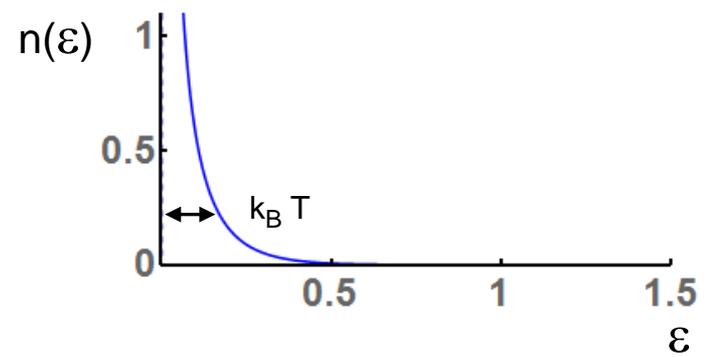
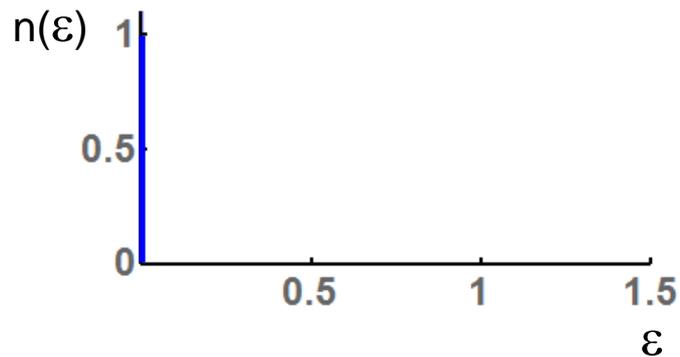


$T > T_c$



$$\frac{1}{e^{(\epsilon - \mu)/k_b T} - 1}$$

Energy distribution $n(\epsilon)$: Bose-Einstein distribution

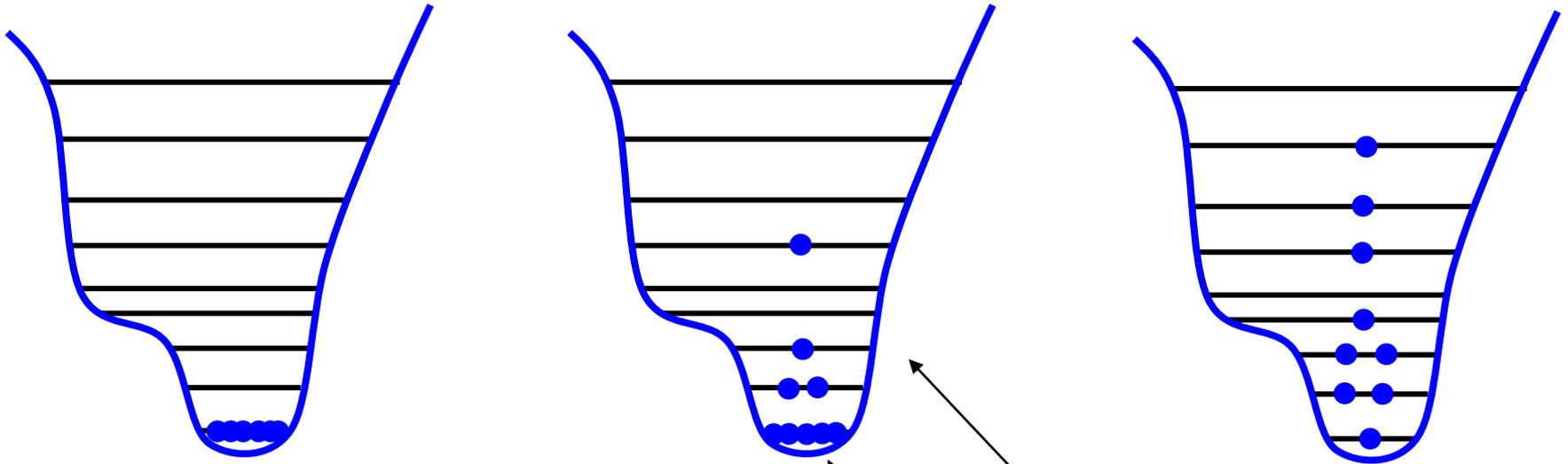


Example 3: identical bosons in 1D

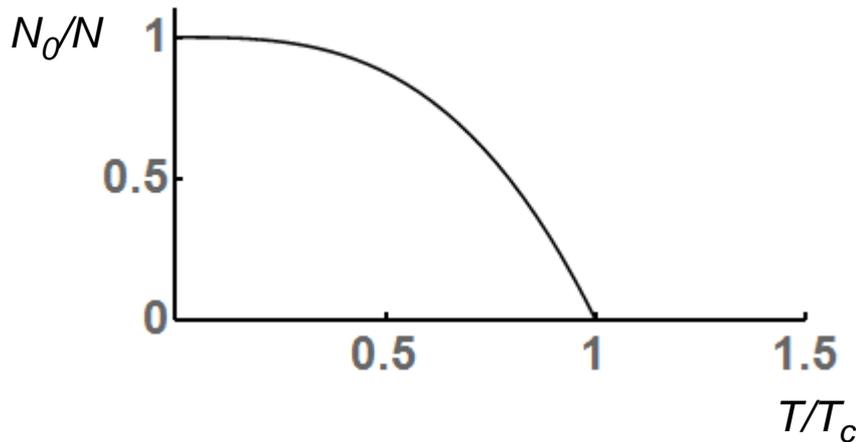
$T = 0$

$0 < T < T_c$

$T > T_c$



BEC atom number over total atom number:

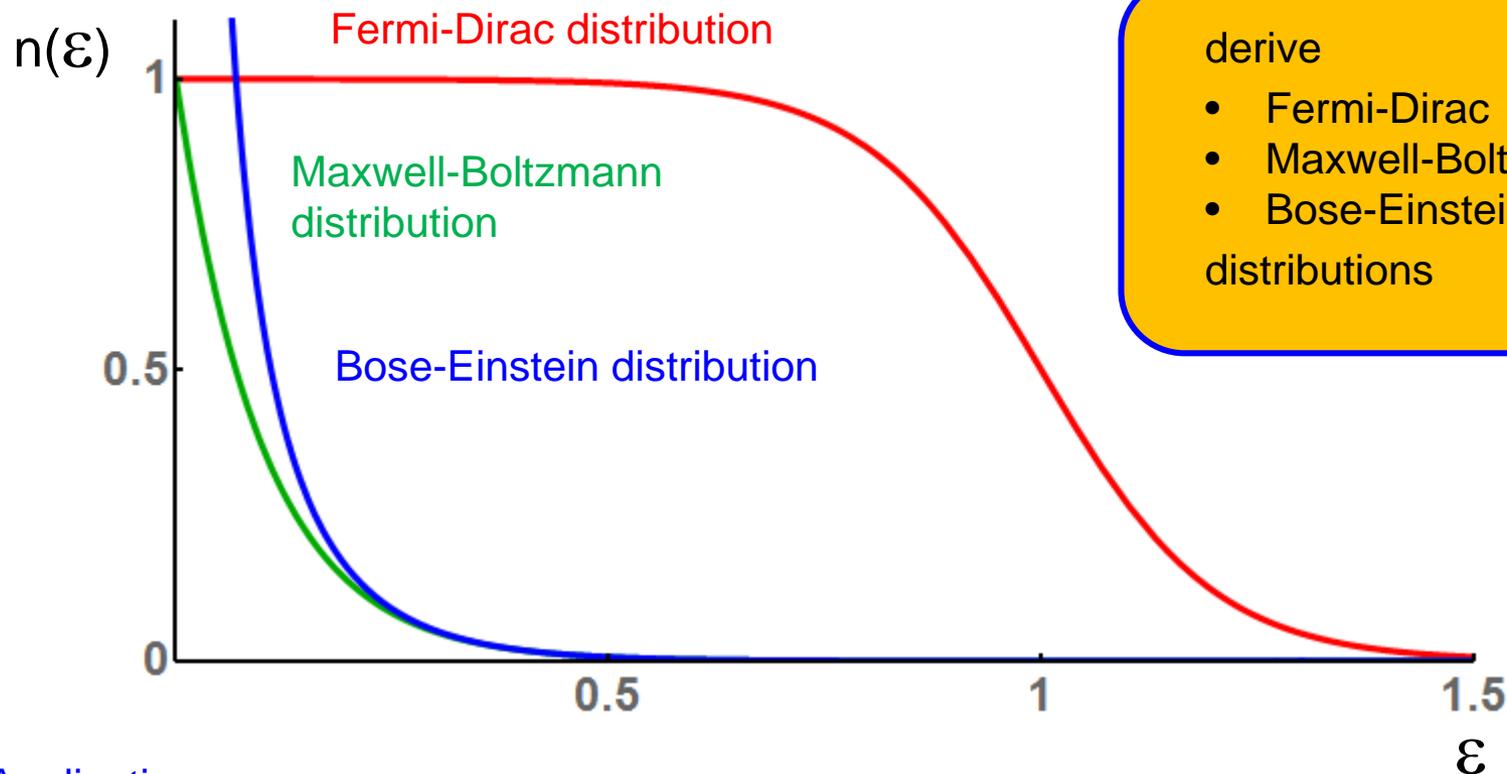


only limited number of bosons „fit“ in excited states

huge number of bosons N_0 „condense into“ ground state

They are Bose-Einstein condensate (BEC)

Goals of this lecture



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.“

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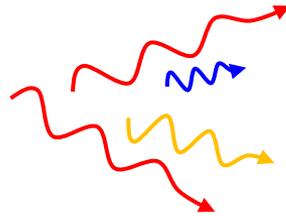
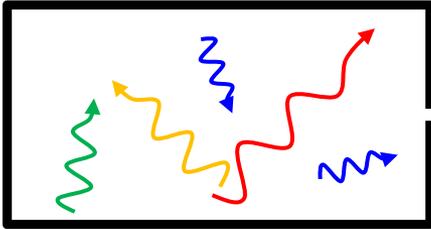
5.4.4

→ 6) Application: blackbody spectrum

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 (*) doesn't apply

Step 2

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Minimize

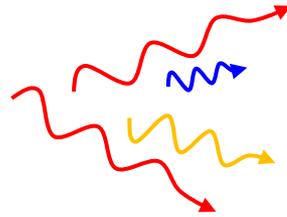
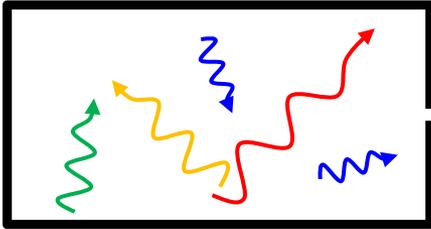
$$G(N_n, \alpha, \beta) = \ln Q(N_n) + \alpha f_N(N_n) + \beta f_E(N_n)$$

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(5) Photon number N not conserved \longrightarrow (*) doesn't apply $\longrightarrow \alpha = 0$

$$\mu \equiv -\alpha k_b T = 0$$

The blackbody spectrum

From (1) and (2):

$$N_\omega = \frac{d_k}{e^{\hbar\omega/k_b T} - 1}$$

reminder

$$\frac{1}{e^{(\epsilon - \mu)/k_b T} - 1} \quad \text{Bose-Einstein}$$

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

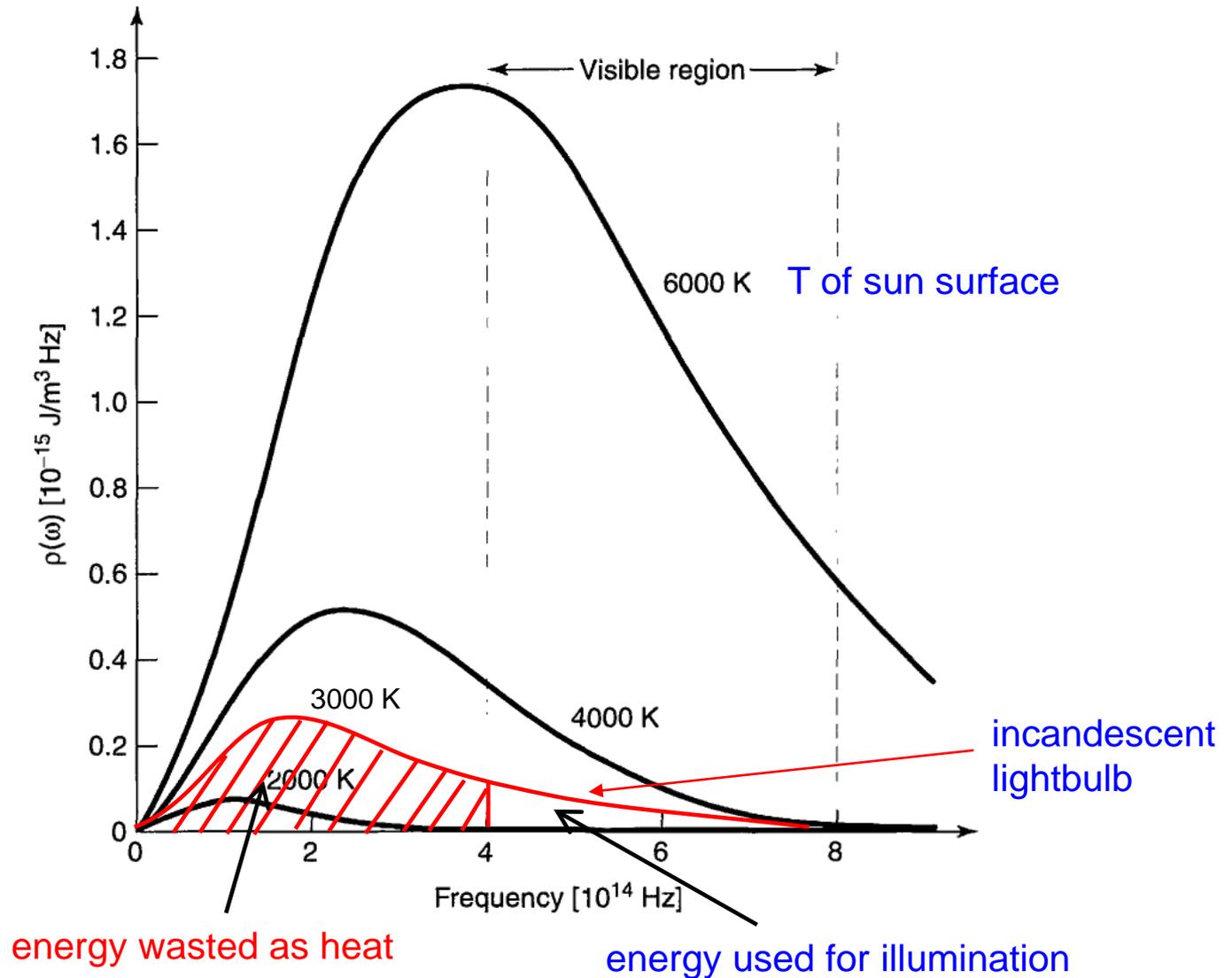
$$d_k = \frac{V}{\pi^2 c^3} \omega^2 d\omega$$

Energy density $N_\omega \hbar\omega / V$ in $d\omega$:

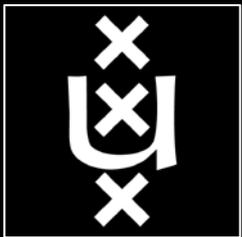
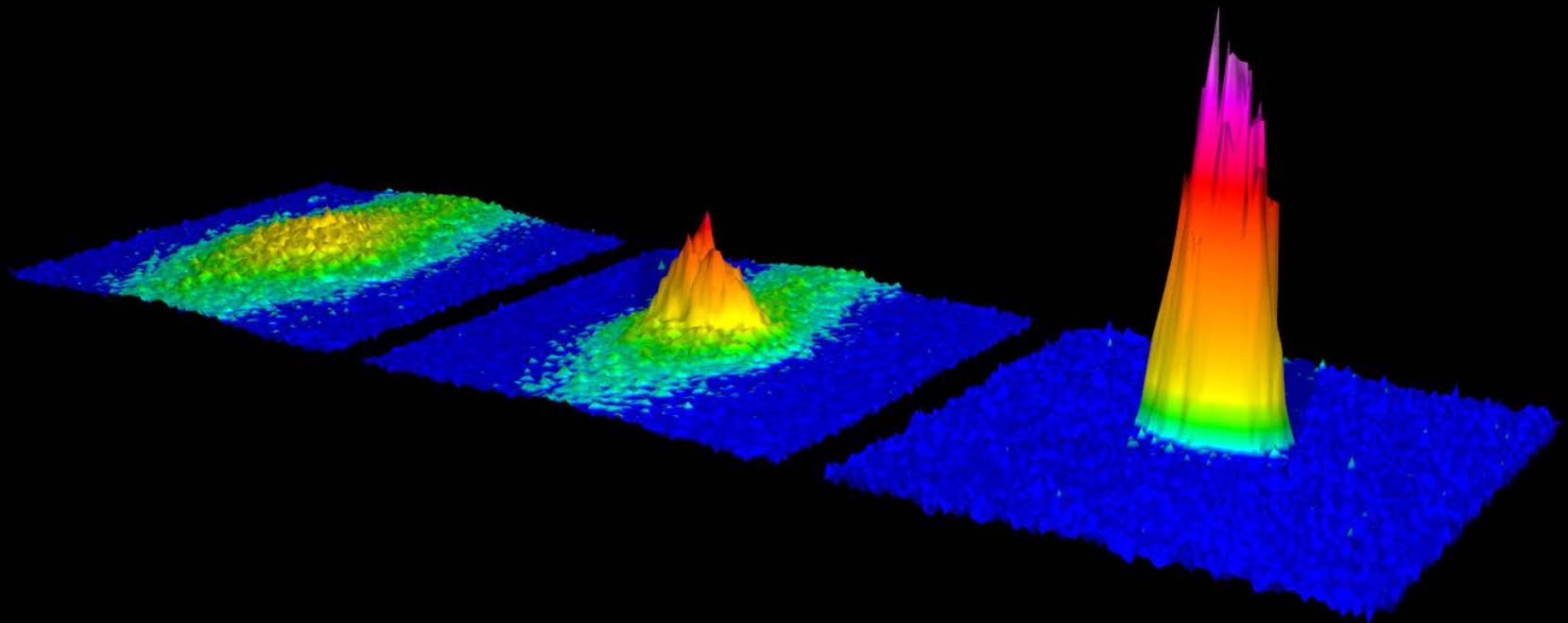
$$\rho(\omega) = \frac{N_\omega \hbar\omega}{V d\omega} = \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/k_b T} - 1)}$$

Planck's blackbody spectrum

Blackbody spectrum

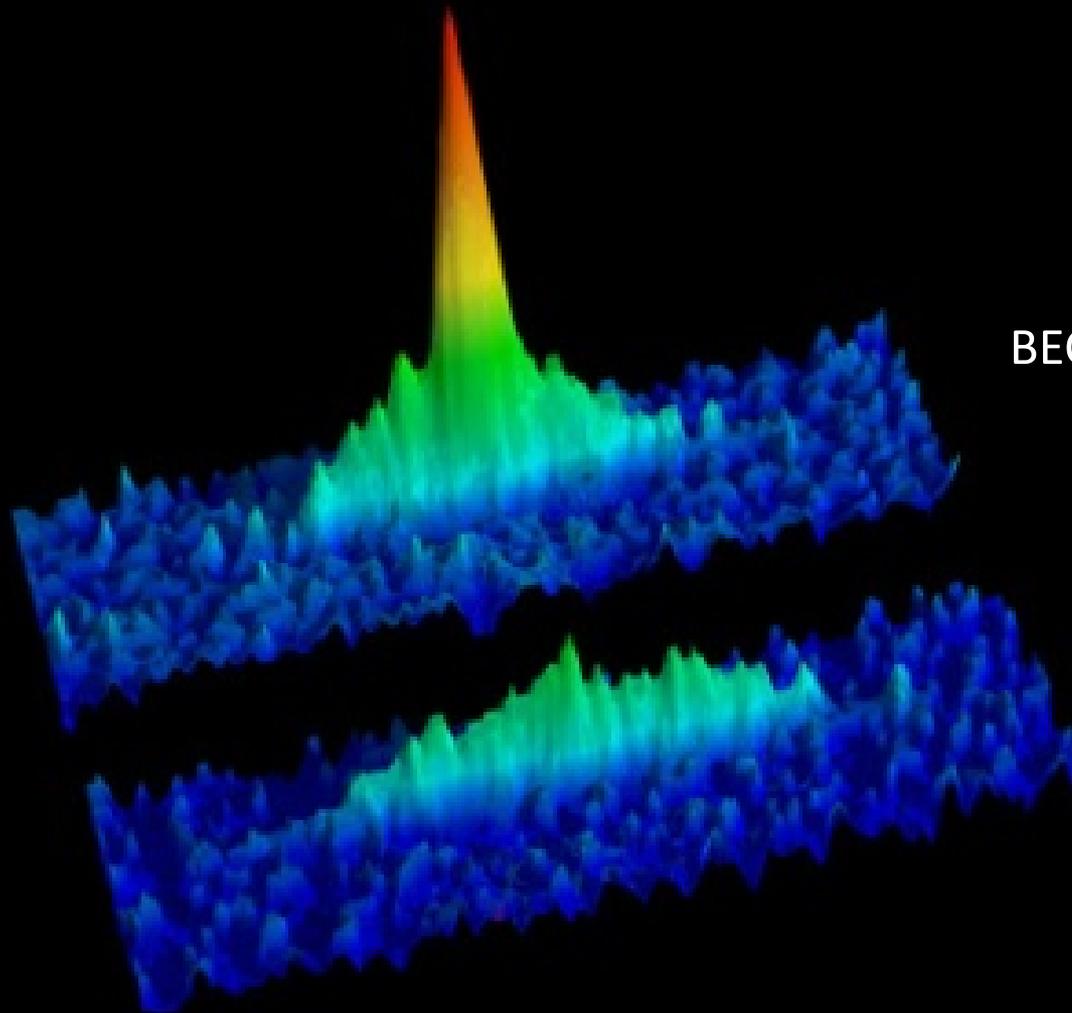


Bose-Einstein condensate of strontium



Schreck group
University of Amsterdam

BEC and Fermi gas



BEC of ^7Li

Fermi sea of ^6Li

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

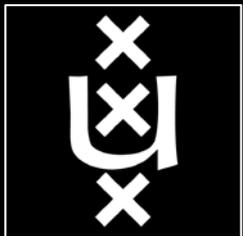
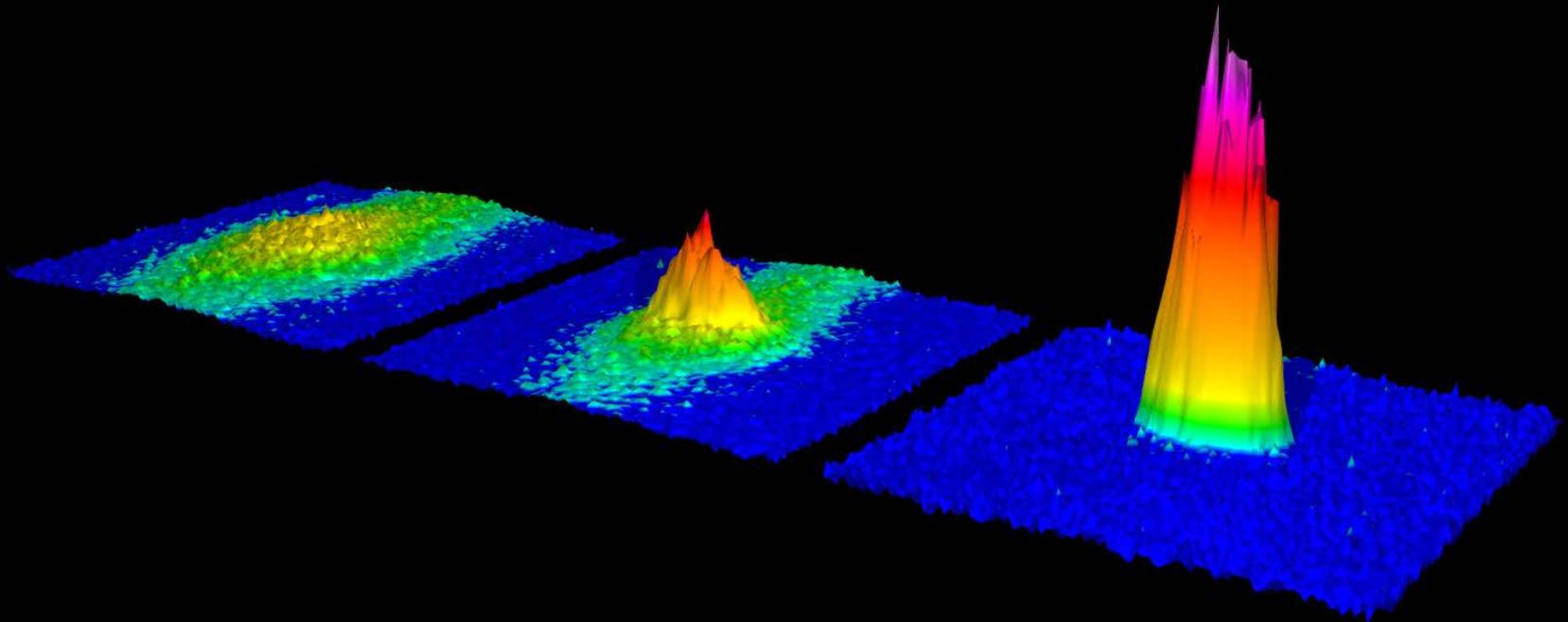
- 1) Introduction to the topic
- 2) Strategy to derive energy distributions Griffiths 5.4.1
- 3) Step 1 of strategy : calc. # of configurations for given energy distribution 5.4.2
- 4) Step 2 of strategy : determine most probable energy distribution 5.4.3
- 5) Derivation of energy distribution functions 5.4.4
- 6) Application: blackbody spectrum 5.4.5



Quantum mechanics 3

Structure of matter

Lecture 10



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	Griffiths 3 rd 5.1, 5.2
	Crystalline solids	5.3.2
today →	Time-independent perturbation theory	7.1, 7.2
	Structure of hydrogen	7.3 – 7.5
	Variational principle	8.1 – 8.3
	Time-dependent perturbation theory, atom-light interaction	11.1 – 11.4

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 | Griffiths 3 rd 7.1.1 |
| | 2) non-degenerate perturbation theory | 7.1.2 – 7.1.3 |
| | 3) 2-fold degenerate perturbation theory | 7.2.1 – 7.2.2 |
| | 4) n -fold degenerate perturbation theory | 7.2.3 |
| | 5) general perturbation theory | |

Time-independent perturbation theory

Starting point:

system with known eigenstates Ψ_n^0 and energies E_n^0

Modification:

system is exposed to a small, time-independent perturbation

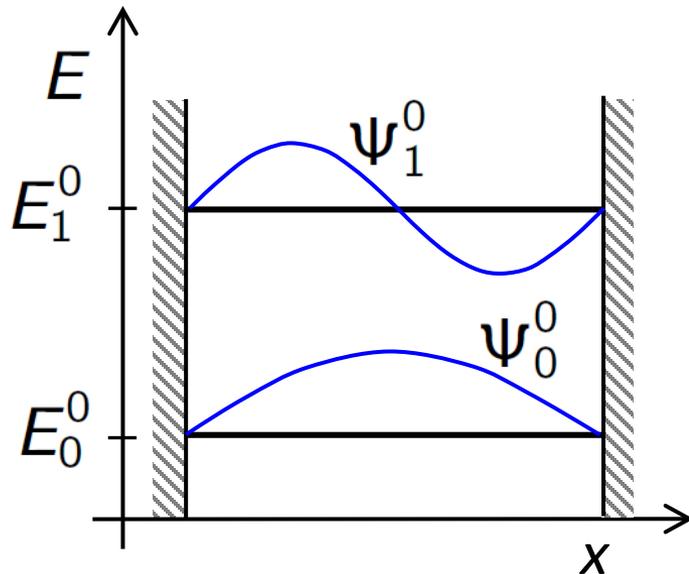
Question:

What are, approximately, the new eigenstates Ψ_n of the system and their energies E_n ?

Example: Particle in nearly square box

Starting point

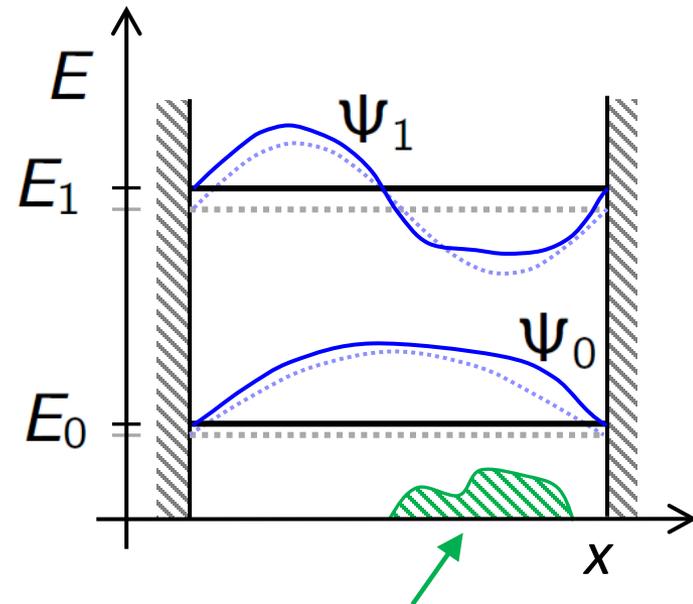
unperturbed system



We know $E_0^0, \psi_0^0, E_1^0, \psi_1^0, \dots$

Modification

perturbed system



Small perturbation
potential slightly altered

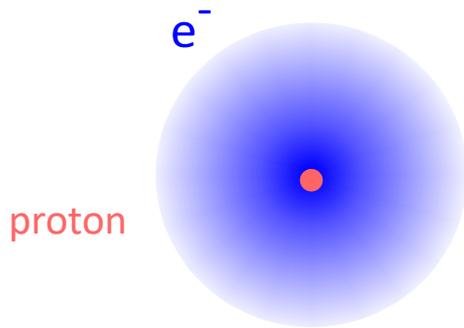
Question

What are, approximately,
 $E_0, \psi_0, E_1, \psi_1, \dots$?

Example: Atom in magnetic field

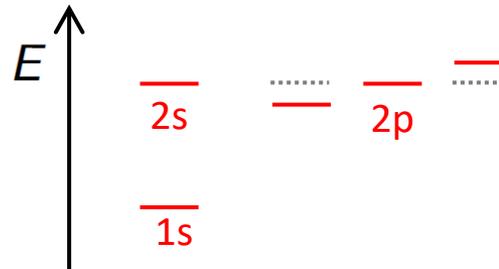
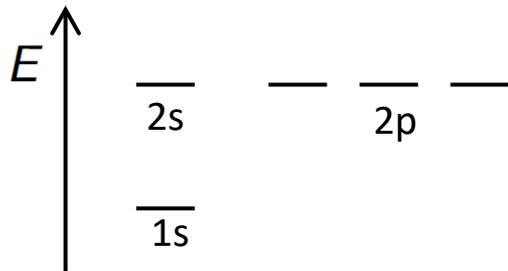
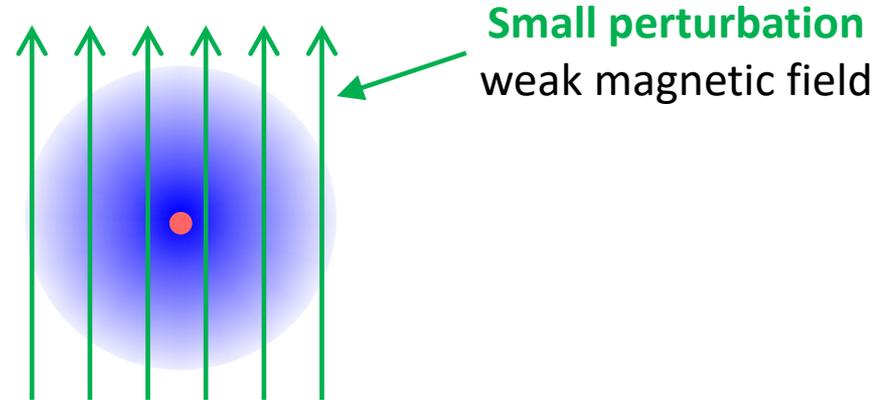
Starting point

unperturbed system



Modification

perturbed system



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

Griffiths 3rd 7.1.1

→ 2) non-degenerate perturbation theory

7.1.2 – 7.1.3

3) 2-fold degenerate perturbation theory

7.2.1 – 7.2.2

4) n -fold degenerate perturbation theory

7.2.3

5) general perturbation theory

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
 (will define later what „small“ means)
 Hamiltonian of unperturbed system

Unperturbed system has orthonormal eigenstates $\{\Psi_n^0\}$ with energies $\{E_n^0\}$:

$$H^0 |\Psi_n^0\rangle = E_n^0 |\Psi_n^0\rangle \quad ; \quad \langle \Psi_n^0 | \Psi_m^0 \rangle = \delta_{nm} \quad ; \quad E_n^0 \neq E_m^0 \text{ for } n \neq m$$

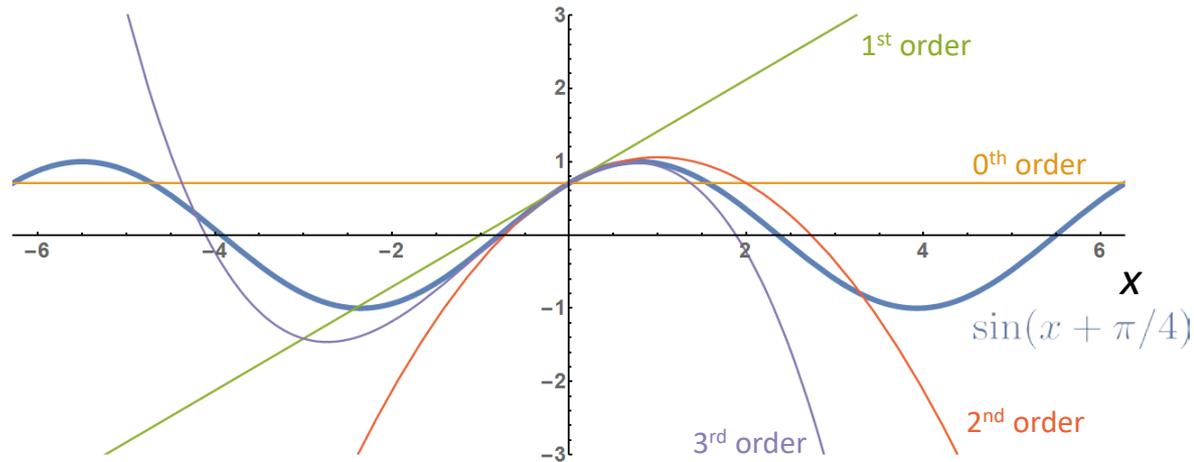
Perturbed system has eigenstates $|\Psi_n^{\text{ex}}\rangle$ with energy E_n^{ex} , i.e. $H |\Psi_n^{\text{ex}}\rangle = E_n^{\text{ex}} |\Psi_n^{\text{ex}}\rangle$
 („ex“ for „exact solution“)

These can be written as expansion in small parameter λ :

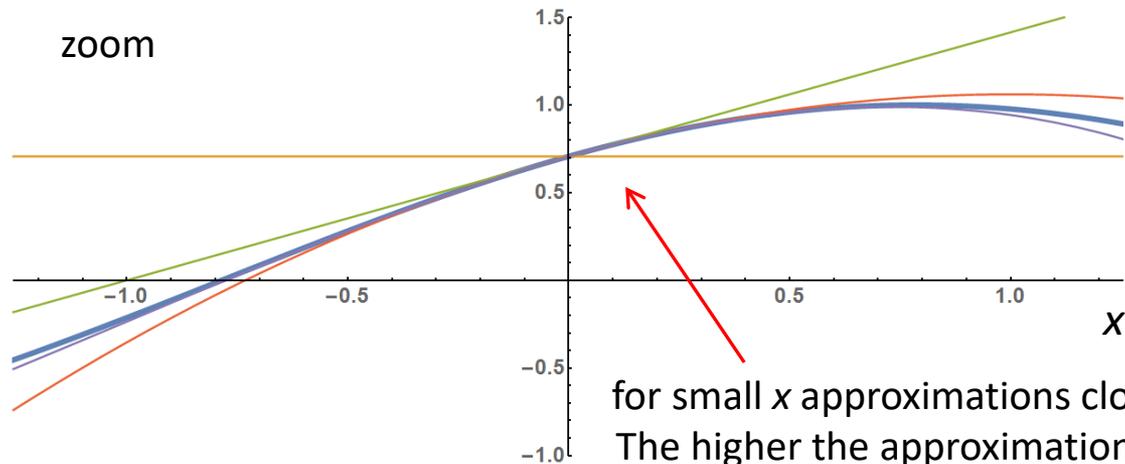
	0 th order	1 st order	2 nd order	3 rd and higher orders in λ
$ \Psi_n^{\text{ex}}\rangle =$	$ \Psi_n^0\rangle$	$+ \lambda \underbrace{ \tilde{\Psi}_n^1\rangle}_{\equiv \Psi_n^1\rangle}$	$+ \lambda^2 \underbrace{ \tilde{\Psi}_n^2\rangle}_{\equiv \Psi_n^2\rangle}$	$+ \dots$
$E_n^{\text{ex}} =$	E_n^0	$+ \lambda \underbrace{\tilde{E}_n^1}_{\equiv E_n^1}$	$+ \lambda^2 \underbrace{\tilde{E}_n^2}_{\equiv E_n^2}$	$+ \dots$

For comparison: Taylor expansion

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



zoom



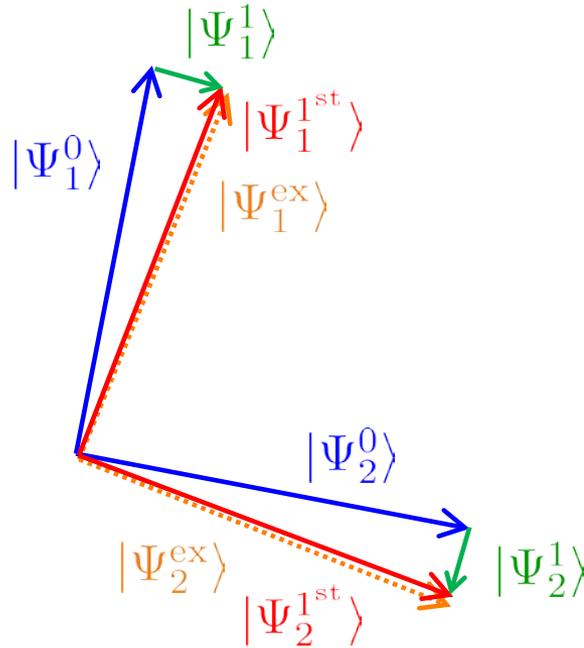
for small x approximations close to desired function
The higher the approximation order,
the better the result

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

Intuitive picture

Eigenstates

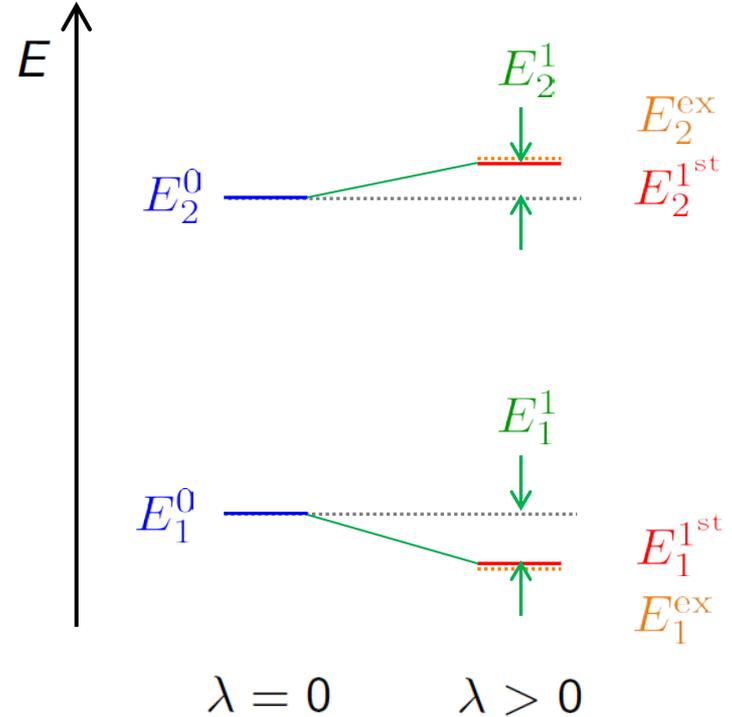
symbolize Hilbert space by 2D vector space



- 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)
- } $\lambda > 0$

Notice: $|\Psi_1^1\rangle$ and $|\Psi_1^0\rangle$ nearly orthogonal because correction small

Energies



Our goals

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

Details of $|\Psi_n\rangle$

$$\begin{array}{cccc}
 \text{0}^{\text{th}} \text{ order} & \text{1}^{\text{st}} \text{ order} & \text{2}^{\text{nd}} \text{ order} & \text{3}^{\text{rd}} \text{ and higher orders in } \lambda \\
 |\Psi_n^{\text{ex}}\rangle = & |\Psi_n^0\rangle & + \lambda \underbrace{|\tilde{\Psi}_n^1\rangle}_{\equiv |\Psi_n^1\rangle} & + \lambda^2 \underbrace{|\tilde{\Psi}_n^2\rangle}_{\equiv |\Psi_n^2\rangle} + \dots
 \end{array}$$

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 λ^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 $\{|\Psi_n^{\text{ex}}\rangle\}$.

To simplify upcoming calculation, we will choose phase of $|\Psi_n^{\text{ex}}\rangle$ such that $\langle \Psi_n^0 | \Psi_n^{\text{ex}} \rangle$ 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.

Our goals

0 th order	1 st order	2 nd order	3 rd and higher orders in λ
$ \Psi_n^{\text{ex}}\rangle = \Psi_n^0\rangle$	$+ \lambda \tilde{\Psi}_n^1\rangle$ $\equiv \Psi_n^1\rangle$	$+ \lambda^2 \tilde{\Psi}_n^2\rangle$ $\equiv \Psi_n^2\rangle$	$+ \dots$
$E_n^{\text{ex}} = E_n^0$	$+ \lambda \tilde{E}_n^1$ $\equiv E_n^1$	$+ \lambda^2 \tilde{E}_n^2$ $\equiv E_n^2$	$+ \dots$

Our goal is **not** to find $|\Psi_n^{\text{ex}}\rangle$ and E_n^{ex} , solving $H |\Psi_n^{\text{ex}}\rangle = E_n |\Psi_n^{\text{ex}}\rangle$, since this is (too) complicated.

We want to find **approximations**, the energy to 2nd order in λ and the state to first order in λ :

$$|\Psi_n^{1^{\text{st}}}\rangle = |\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle = |\Psi_n^{\text{ex}}\rangle + \mathcal{O}(\lambda^2) \neq |\Psi_n^{\text{ex}}\rangle$$

$$E_n^{2^{\text{nd}}} = E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 = E_n^{\text{ex}} + \mathcal{O}(\lambda^3) \neq E_n^{\text{ex}}$$

$H |\Psi_n^{1^{\text{st}}}\rangle \neq E_n^{2^{\text{nd}}} |\Psi_n^{1^{\text{st}}}\rangle$, but the error is of order λ^2 and therefore small

We need $|\langle \Psi_n^{1^{\text{st}}} | \Psi_n^{1^{\text{st}}} \rangle|^2 = 1$ to first order in λ . If we wouldn't, e.g. particle number not be conserved.

For simplicity we often write $|\Psi_n^{1^{\text{st}}}\rangle$ as $|\Psi_n\rangle$ and $E_n^{2^{\text{nd}}}$ as E_n

Schrödinger equn. of perturbed system

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

$$\begin{aligned} & (H^0 + \lambda \tilde{H}) \left[|\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots \right] \\ = & \left[E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \dots \right] \left[|\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots \right] \end{aligned}$$

reminder

$$H^0 + \lambda \tilde{H}$$

$$|\Psi_n^{\text{ex}}\rangle = |\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots$$

$$E_n^{\text{ex}} = E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \dots$$

Collect like powers of λ :

$$\begin{aligned} & \underline{H^0 |\Psi_n^0\rangle} + \lambda \left(\underline{H^0 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{H} |\Psi_n^0\rangle} \right) + \lambda^2 \left(\underline{H^0 |\tilde{\Psi}_n^2\rangle} + \underline{\tilde{H} |\tilde{\Psi}_n^1\rangle} \right) + \dots \\ = & \underline{E_n^0 |\Psi_n^0\rangle} + \lambda \left(\underline{E_n^0 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{E}_n^1 |\Psi_n^0\rangle} \right) + \lambda^2 \left(\underline{E_n^0 |\tilde{\Psi}_n^2\rangle} + \underline{\tilde{E}_n^1 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{E}_n^2 |\Psi_n^0\rangle} \right) + \dots \end{aligned}$$

0th order (λ^0):

$$H^0 |\Psi_n^0\rangle = E_n |\Psi_n^0\rangle$$

1st order (λ^1):

$$H^0 |\tilde{\Psi}_n^1\rangle + \tilde{H} |\Psi_n^0\rangle = E_n^0 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^1 |\Psi_n^0\rangle \quad (\text{I})$$

2nd order (λ^2):

$$H^0 |\tilde{\Psi}_n^2\rangle + \tilde{H} |\tilde{\Psi}_n^1\rangle = E_n^0 |\tilde{\Psi}_n^2\rangle + \tilde{E}_n^1 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^2 |\Psi_n^0\rangle \quad (\text{II})$$

First order correction to energy

$$(I) \quad H^0 |\tilde{\Psi}_n^1\rangle + \tilde{H} |\Psi_n^0\rangle = E_n^0 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^1 |\Psi_n^0\rangle$$

$\langle \Psi_n^0 | \cdot (I) :$

$$\underbrace{\langle \Psi_n^0 | H^0 | \tilde{\Psi}_n^1 \rangle}_{= \langle H^0 \Psi_n^0 | \tilde{\Psi}_n^1 \rangle} + \langle \Psi_n^0 | \tilde{H} | \Psi_n^0 \rangle = E_n^0 \underbrace{\langle \Psi_n^0 | \tilde{\Psi}_n^1 \rangle}_{= 0} + \tilde{E}_n^1 \underbrace{\langle \Psi_n^0 | \Psi_n^0 \rangle}_1$$

$$\tilde{E}_n^1 = \langle \Psi_n^0 | \tilde{H} | \Psi_n^0 \rangle$$

reminder

$$E_n^1 = \tilde{E}_n^1 / \lambda$$

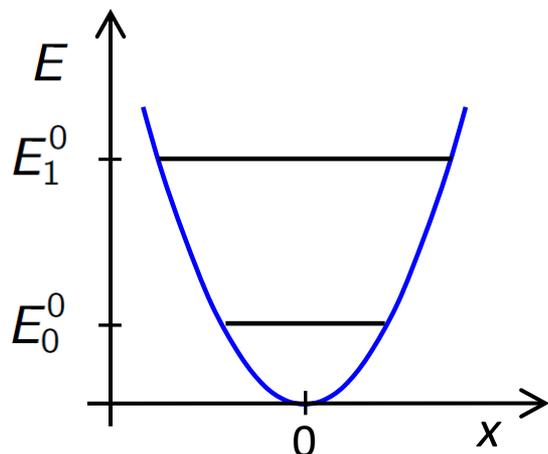
$$H' = \tilde{H} / \lambda$$

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

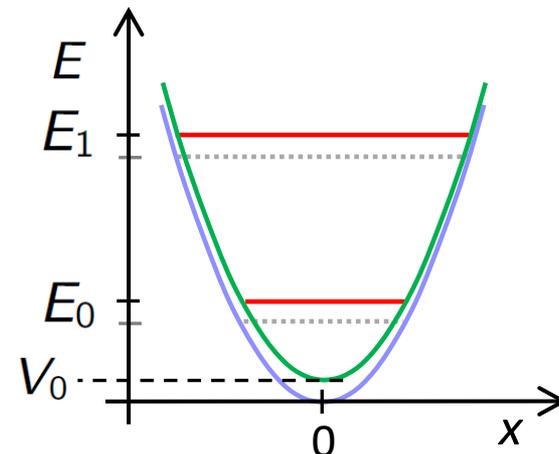
$$E_n = E_n^0 + E_n^1$$

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

Example 1: shifted potential



Perturbation:
shift in energy



$$H = H^0 + H'$$

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

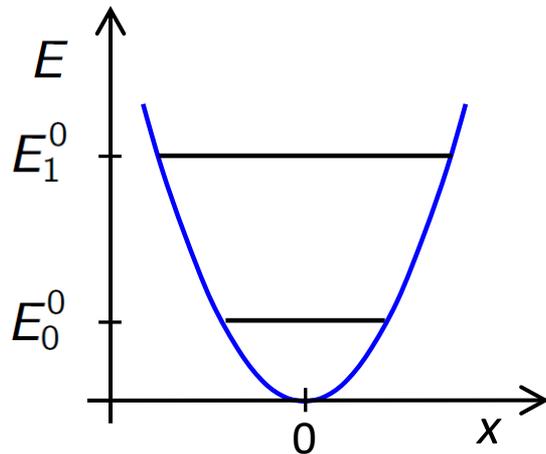
$$H' = V_0$$

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

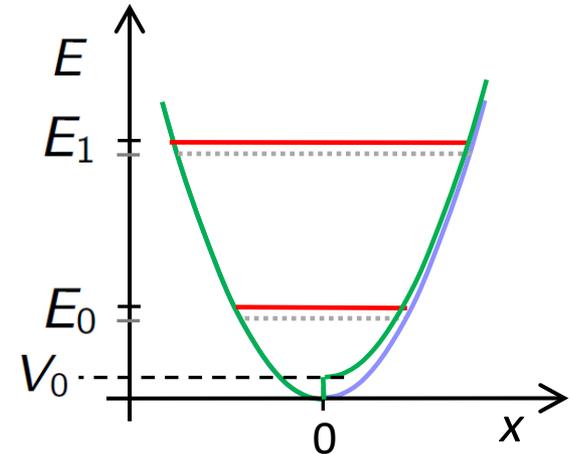
$$E_n = E_n^0 + E_n^1$$

All states simply shifted by potential shift.

Example 2: half-shifted symmetric potential



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



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

$$E_n^1 = \langle \Psi_n^0 | H' | \Psi_n^0 \rangle = \int_0^{\infty} V_0 |\Psi(x)|^2 dx = V_0 \underbrace{\int_0^{\infty} |\Psi(x)|^2 dx}_{=1/2} = \frac{V_0}{2}$$

$$1 = \langle \Psi_n^0 | \Psi_n^0 \rangle = \int_{-\infty}^{\infty} |\Psi_n(x)|^2 dx = 2 \int_0^{\infty} |\Psi_n(x)|^2 dx$$

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

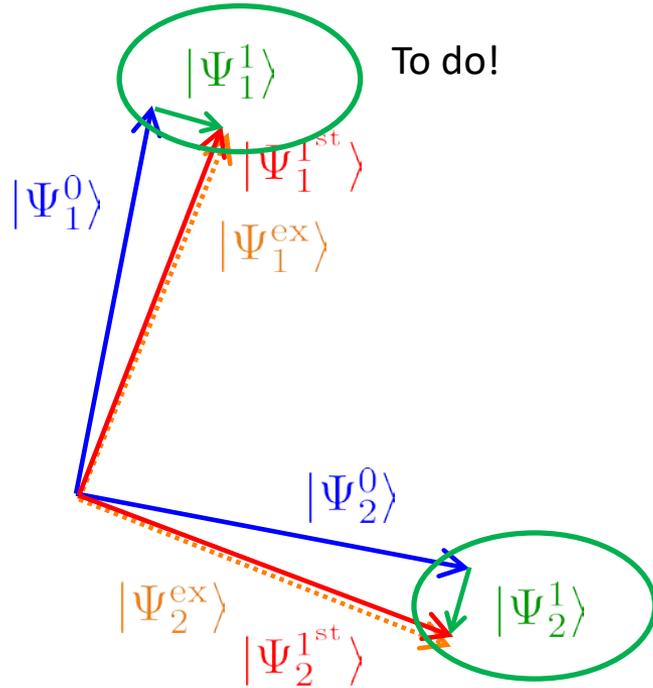
All states shifted by half of potential shift.

Intuitive picture

Reminder

Eigenstates

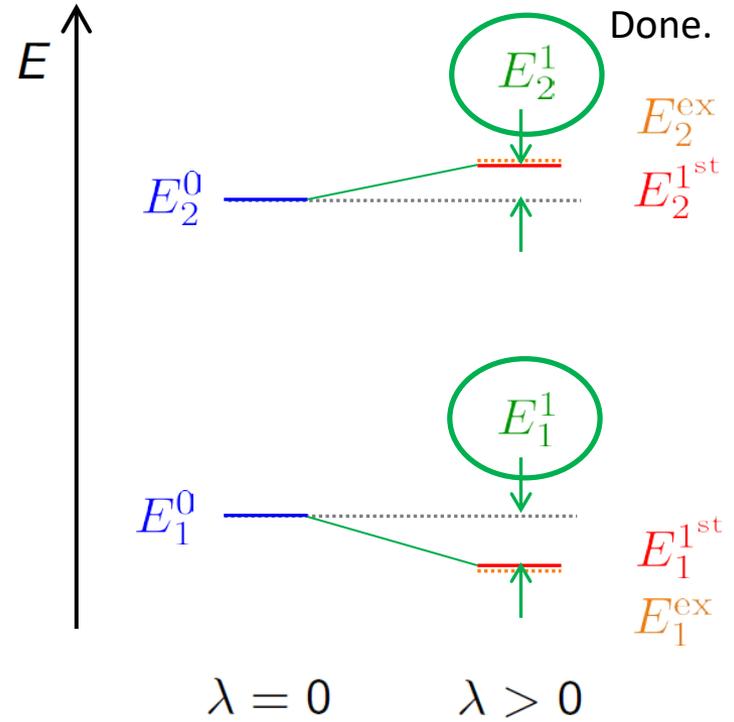
symbolize Hilbert space by 2D vector space



- 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)
- } $\lambda > 0$

Notice: $|\Psi_1^1\rangle$ and $|\Psi_1^0\rangle$ nearly orthogonal because correction small

Energies



Our goals

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

First order correction to eigenstate

Perturbed eigenstates can be expressed in unperturbed basis

$$|\Psi_n\rangle = |\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle = |\Psi_n^0\rangle + \lambda \underbrace{\sum_m c_m^{(n)} |\Psi_m^0\rangle}_{= |\tilde{\Psi}_n^1\rangle} \quad \text{with} \quad c_m^{(n)} = \langle \Psi_m^0 | \tilde{\Psi}_n^1 \rangle$$

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

Normalization:

$$= \underbrace{\langle \Psi_n^0 | \Psi_n^0 \rangle}_{= 1} + \lambda \left(\underbrace{\langle \Psi_n^0 | \tilde{\Psi}_n^1 \rangle}_{\stackrel{!}{=} 0} + c.c. \right) + \underbrace{\lambda^2(\dots)}_{\substack{\text{neglected} \\ \text{in first order}}}$$

$\Rightarrow c_n^{(n)} = 0$
since $\langle \Psi_n^0 | \tilde{\Psi}_n^1 \rangle$ is real

Details of $|\Psi_n\rangle$

Reminder

$$|\Psi_n^{\text{ex}}\rangle = \begin{array}{l} \text{0th order} \\ |\Psi_n^0\rangle \\ \text{1st order} \\ + \lambda \underbrace{|\tilde{\Psi}_n^1\rangle}_{\equiv |\Psi_n^1\rangle} \\ \text{2nd order} \\ + \lambda^2 \underbrace{|\tilde{\Psi}_n^2\rangle}_{\equiv |\Psi_n^2\rangle} \\ \text{3rd and higher orders in } \lambda \\ + \dots \end{array}$$

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 λ .

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 $\{|\Psi_n^{\text{ex}}\rangle\}$.

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

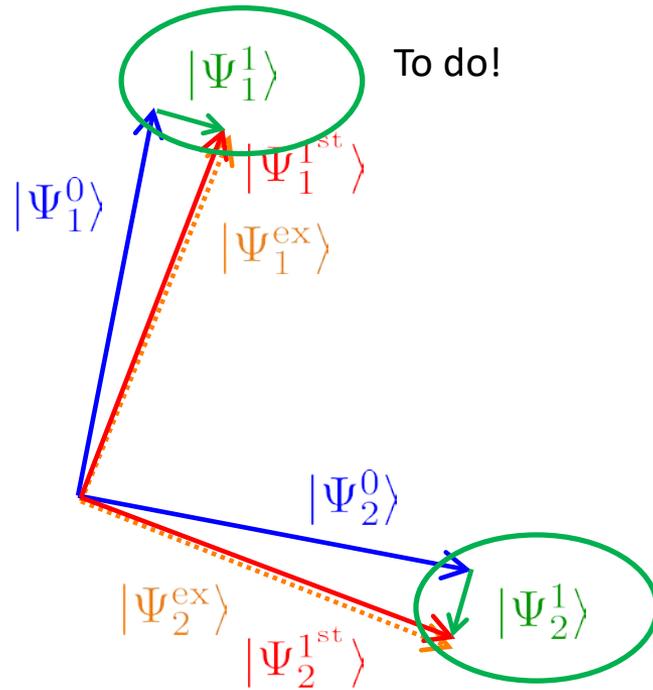
This implies that $\langle \Psi_n^0 | \tilde{\Psi}_n^i \rangle$ is real for any order i , since orders can't compensate each other.

Intuitive picture

Reminder

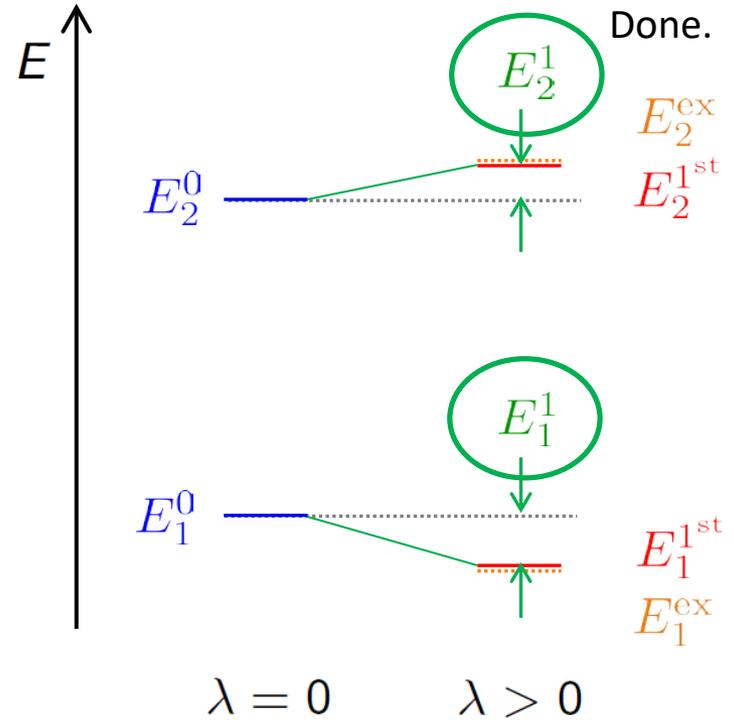
Eigenstates

symbolize Hilbert space by 2D vector space



To do!

Energies



Done.

- 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)
- } $\lambda > 0$

Notice: $|\Psi_1^1\rangle$ and $|\Psi_1^0\rangle$ nearly orthogonal because correction small

Our goals

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

First order correction to eigenstate

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

Normalization:

$$= \underbrace{\langle \Psi_n^0 | \Psi_n^0 \rangle}_{= 1} + \lambda \left(\underbrace{\langle \Psi_n^0 | \tilde{\Psi}_n^1 \rangle + c.c.}_{\neq 0} \right) + \underbrace{\lambda^2(\dots)}_{\text{neglected in first order}} \Rightarrow c_n^{(n)} = 0$$

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

Reminder

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

$$\begin{aligned} & (H^0 + \lambda \tilde{H}) \left[|\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots \right] \\ = & \left[E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \dots \right] \left[|\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots \right] \end{aligned}$$

reminder

$$H^0 + \lambda \tilde{H}$$

$$|\Psi_n^{\text{ex}}\rangle = |\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots$$

$$E_n^{\text{ex}} = E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \dots$$

Collect like powers of λ :

$$\begin{aligned} & \underline{H^0 |\Psi_n^0\rangle} + \lambda \left(\underline{H^0 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{H} |\Psi_n^0\rangle} \right) + \lambda^2 \left(\underline{H^0 |\tilde{\Psi}_n^2\rangle} + \underline{\tilde{H} |\tilde{\Psi}_n^1\rangle} \right) + \dots \\ = & \underline{E_n^0 |\Psi_n^0\rangle} + \lambda \left(\underline{E_n^0 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{E}_n^1 |\Psi_n^0\rangle} \right) + \lambda^2 \left(\underline{E_n^0 |\tilde{\Psi}_n^2\rangle} + \underline{\tilde{E}_n^1 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{E}_n^2 |\Psi_n^0\rangle} \right) + \dots \end{aligned}$$

0th order (λ^0):

$$H^0 |\Psi_n^0\rangle = E_n |\Psi_n^0\rangle$$

1st order (λ^1):

$$H^0 |\tilde{\Psi}_n^1\rangle + \tilde{H} |\Psi_n^0\rangle = E_n^0 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^1 |\Psi_n^0\rangle \quad (\text{I})$$

2nd order (λ^2):

$$H^0 |\tilde{\Psi}_n^2\rangle + \tilde{H} |\tilde{\Psi}_n^1\rangle = E_n^0 |\tilde{\Psi}_n^2\rangle + \tilde{E}_n^1 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^2 |\Psi_n^0\rangle \quad (\text{II})$$

First order correction to eigenstate

Perturbed eigenstates can be expressed in unperturbed basis

$$|\Psi_n\rangle = |\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle = |\Psi_n^0\rangle + \lambda \underbrace{\sum_m c_m^{(n)} |\Psi_m^0\rangle}_{= |\tilde{\Psi}_n^1\rangle} \quad \text{with} \quad c_m^{(n)} = \langle \Psi_m^0 | \tilde{\Psi}_n^1 \rangle$$

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

Normalization:

$$= \underbrace{\langle \Psi_n^0 | \Psi_n^0 \rangle}_{= 1} + \lambda \left(\underbrace{\langle \Psi_n^0 | \tilde{\Psi}_n^1 \rangle + c.c.}_{\stackrel{!}{=} 0} \Rightarrow c_n^{(n)} = 0 \right) + \underbrace{\lambda^2(\dots)}_{\text{neglected in first order}}$$

reminder: eqn. (I)

$$H^0 |\tilde{\Psi}_n^1\rangle + \tilde{H} |\Psi_n^0\rangle = E_n^0 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^1 |\Psi_n^0\rangle$$

$$(I): \quad (H^0 - E_n^0) |\tilde{\Psi}_n^1\rangle = -(\tilde{H} - \tilde{E}_n^1) |\Psi_n^0\rangle$$

$$\text{Insert (*)}: \quad \sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} |\Psi_m^0\rangle = -(\tilde{H} - \tilde{E}_n^1) |\Psi_n^0\rangle$$

$$\langle \Psi_l^0 | \cdot :$$

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \underbrace{\langle \Psi_l^0 | \Psi_m^0 \rangle}_{\delta_{lm}} = - \langle \Psi_l^0 | \tilde{H} | \Psi_n^0 \rangle + \tilde{E}_n^1 \underbrace{\langle \Psi_l^0 | \Psi_n^0 \rangle}_{\delta_{ln}}$$

For $l = n$ left-hand side (LHS) is zero \implies again we find $E_n^1 = \langle \Psi_n^0 | H' | \Psi_n^0 \rangle$

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 $c_m^{(n)}$:

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

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 $\left(\propto \frac{1}{E_n^0 - E_m^0} \right)$.

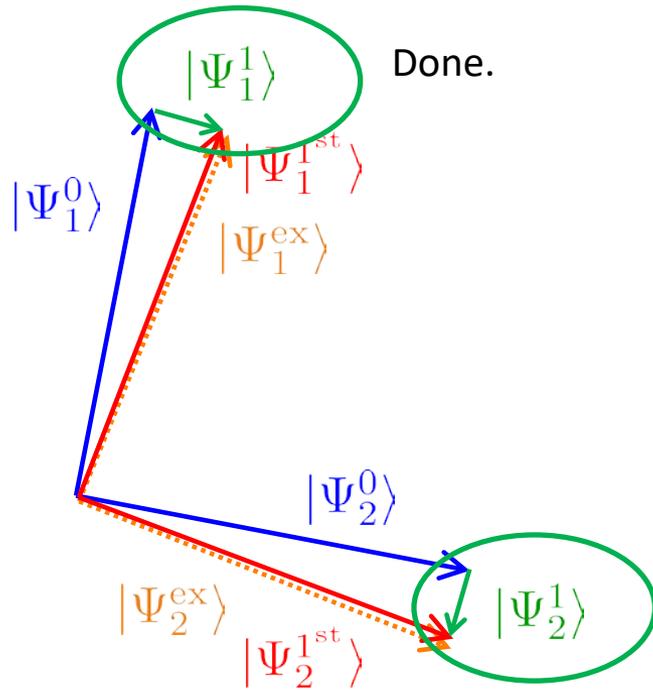
Trouble if $E_n^0 = E_m^0$. That's why we required non-degenerate spectrum.

Intuitive picture

Reminder

Eigenstates

symbolize Hilbert space by 2D vector space

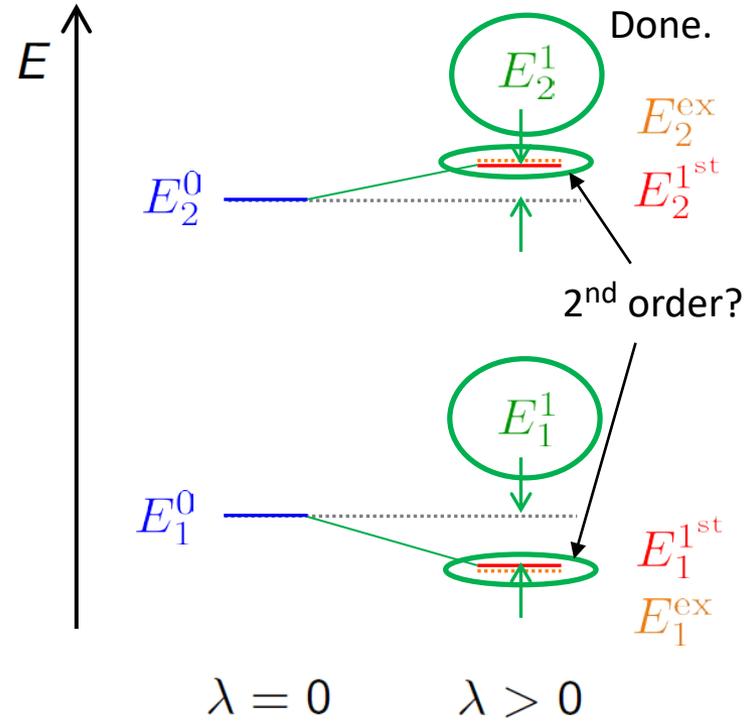


Done.

- 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)
- } $\lambda > 0$

Notice: $|\Psi_1^1\rangle$ and $|\Psi_1^0\rangle$ nearly orthogonal because correction small

Energies



Done.

Our goals

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

Schrödinger equn. of perturbed system

Reminder

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

$$\begin{aligned} & (H^0 + \lambda \tilde{H}) \left[|\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots \right] \\ = & \left[E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \dots \right] \left[|\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots \right] \end{aligned}$$

reminder

$$H^0 + \lambda \tilde{H}$$

$$|\Psi_n^{\text{ex}}\rangle = |\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots$$

$$E_n^{\text{ex}} = E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \dots$$

Collect like powers of λ :

$$\begin{aligned} & \underline{H^0 |\Psi_n^0\rangle} + \lambda \left(\underline{H^0 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{H} |\Psi_n^0\rangle} \right) + \lambda^2 \left(\underline{H^0 |\tilde{\Psi}_n^2\rangle} + \underline{\tilde{H} |\tilde{\Psi}_n^1\rangle} \right) + \dots \\ = & \underline{E_n^0 |\Psi_n^0\rangle} + \lambda \left(\underline{E_n^0 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{E}_n^1 |\Psi_n^0\rangle} \right) + \lambda^2 \left(\underline{E_n^0 |\tilde{\Psi}_n^2\rangle} + \underline{\tilde{E}_n^1 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{E}_n^2 |\Psi_n^0\rangle} \right) + \dots \end{aligned}$$

0th order (λ^0):

$$H^0 |\Psi_n^0\rangle = E_n |\Psi_n^0\rangle$$

1st order (λ^1):

$$H^0 |\tilde{\Psi}_n^1\rangle + \tilde{H} |\Psi_n^0\rangle = E_n^0 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^1 |\Psi_n^0\rangle \quad (I)$$

2nd order (λ^2):

$$H^0 |\tilde{\Psi}_n^2\rangle + \tilde{H} |\tilde{\Psi}_n^1\rangle = E_n^0 |\tilde{\Psi}_n^2\rangle + \tilde{E}_n^1 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^2 |\Psi_n^0\rangle \quad (II)$$

Second order correction to energy

reminder: eqn. (II)

$$H^0 |\tilde{\Psi}_n^2\rangle + \tilde{H} |\tilde{\Psi}_n^1\rangle = E_n^0 |\tilde{\Psi}_n^2\rangle + \tilde{E}_n^1 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^2 |\Psi_n^0\rangle$$

$\langle \Psi_n^0 | \cdot \rangle$ (II) :

$$\underbrace{\langle \Psi_n^0 | H^0 | \tilde{\Psi}_n^2 \rangle}_{= \langle H^0 \Psi_n^0 | \tilde{\Psi}_n^2 \rangle} + \langle \Psi_n^0 | \tilde{H} | \tilde{\Psi}_n^1 \rangle = E_n^0 \underbrace{\langle \Psi_n^0 | \tilde{\Psi}_n^2 \rangle}_{=0} + \tilde{E}_n^1 \underbrace{\langle \Psi_n^0 | \tilde{\Psi}_n^1 \rangle}_{=0} + \tilde{E}_n^2 \underbrace{\langle \Psi_n^0 | \Psi_n^0 \rangle}_{=1}$$

$$= \langle H^0 \Psi_n^0 | \tilde{\Psi}_n^2 \rangle = E_n^0 \langle \Psi_n^0 | \tilde{\Psi}_n^2 \rangle$$

reminder:

$$|\Psi_n^1\rangle = \sum_{m \neq n} \frac{\langle \Psi_m^0 | H' | \Psi_n^0 \rangle}{E_n^0 - E_m^0} |\Psi_m^0\rangle$$

$$E_n^2 = \lambda^2 \tilde{E}_n^2 = \langle \Psi_n^0 | \lambda \tilde{H} | \Psi_n^1 \rangle = \sum_{m \neq n} \frac{\langle \Psi_m^0 | H' | \Psi_n^0 \rangle}{E_n^0 - E_m^0} \langle \Psi_n^0 | H' | \Psi_m^0 \rangle$$

Second order correction to energy

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

Observations

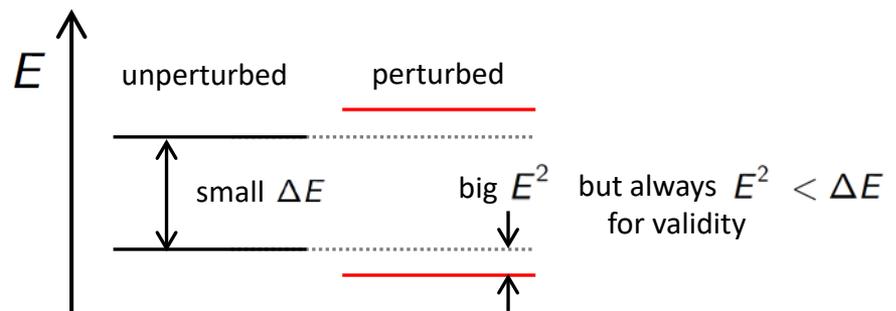
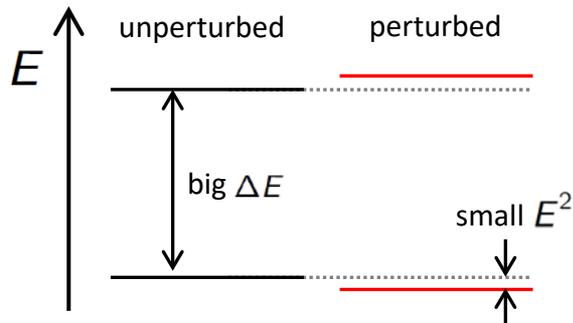
$$|\langle \Psi_m^0 | H' | \Psi_m^0 \rangle|^2 > 0$$

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 $\left(\frac{1}{E_n^0 - E_m^0}\right)$



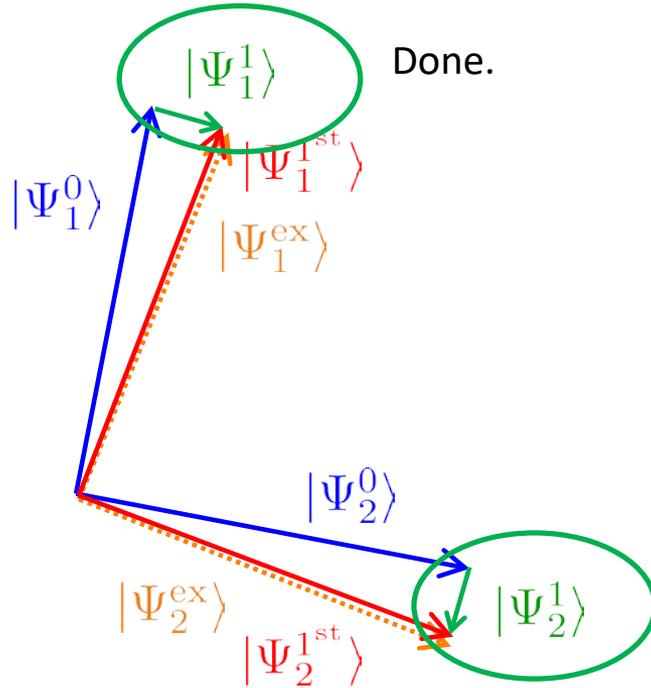
If first order correction to energy is zero, ground state is shifted down.

Intuitive picture

Reminder

Eigenstates

symbolize Hilbert space by 2D vector space

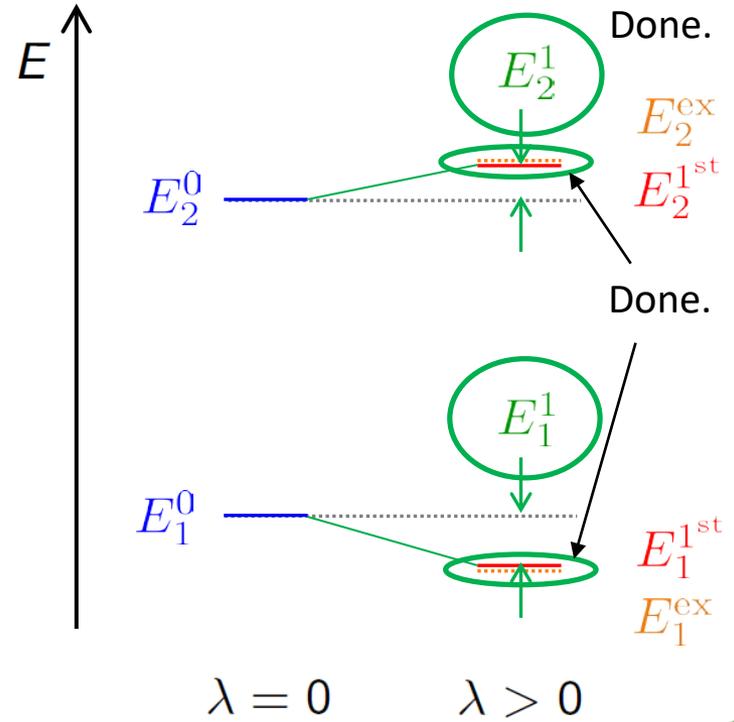


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Energies



$\lambda = 0$

$\lambda > 0$

Our goals

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Notice: $|\Psi_1^1\rangle$ and $|\Psi_1^0\rangle$ nearly orthogonal because correction small

Summary

Compact notation: $W_{mn} \equiv \langle \Psi_m^0 | H' | \Psi_n^0 \rangle$; $\Delta_{mn} \equiv E_m^0 - E_n^0$

Energy

$$E_n = E_n^0 + E_n^1 + E_n^2 + E_n^3 + \dots$$

$$E_n^3 = \sum_{l, m \neq n} \frac{W_{nl} W_{lm} W_{mn}}{\Delta_{nl} \Delta_{nm}} - W_{nn} \sum_{m \neq n} \frac{W_{nm}^2}{\Delta_{nm}^2}$$

State

$$|\Psi_n\rangle = |\Psi_n^0\rangle + |\Psi_n^1\rangle + \dots$$

$$|\Psi_n^1\rangle = \sum_{m \neq n} \frac{W_{mn}}{\Delta_{nm}} |\Psi_m^0\rangle$$

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.

Atoms, molecules, condensed-matter,...

Plan of this section

- | | | | |
|---|---|--|---------------------------------|
| | 1) intro, examples |  | Griffiths 3 rd 7.1.1 |
| → | 2) non-degenerate perturbation theory | | 7.1.2 – 7.1.3 |
| → | 3) 2-fold degenerate perturbation theory | | 7.2.1 – 7.2.2 |
| | 4) n -fold degenerate perturbation theory | | 7.2.3 |
| | 5) general perturbation theory | | |

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 $W_{nm} = 0$.

└ hint towards solution of challenge

$$W_{mn} \equiv \langle \Psi_m^0 | H' | \Psi_n^0 \rangle ; \Delta_{mn} \equiv E_m^0 - E_n^0$$

For simplicity consider system of only two degenerate states

$$H^0 | \Psi_a^0 \rangle = E^0 | \Psi_a^0 \rangle ; H^0 | \Psi_b^0 \rangle = E^0 | \Psi_b^0 \rangle$$

Notice: all superpositions of these states still eigenstates of H^0

$$\text{e.g. } | \Psi^0 \rangle = \alpha^0 | \Psi_a^0 \rangle + \beta^0 | \Psi_b^0 \rangle ; |\alpha^0|^2 + |\beta^0|^2 = 1$$

$$H^0 | \Psi^0 \rangle = E^0 | \Psi^0 \rangle$$

This makes perturbative expansion more complicated

$$| \Psi_n^{\text{ex}} \rangle = | \Psi_n^0 \rangle + \lambda | \tilde{\Psi}_n^1 \rangle + \dots$$

└ We don't know which superposition to use.

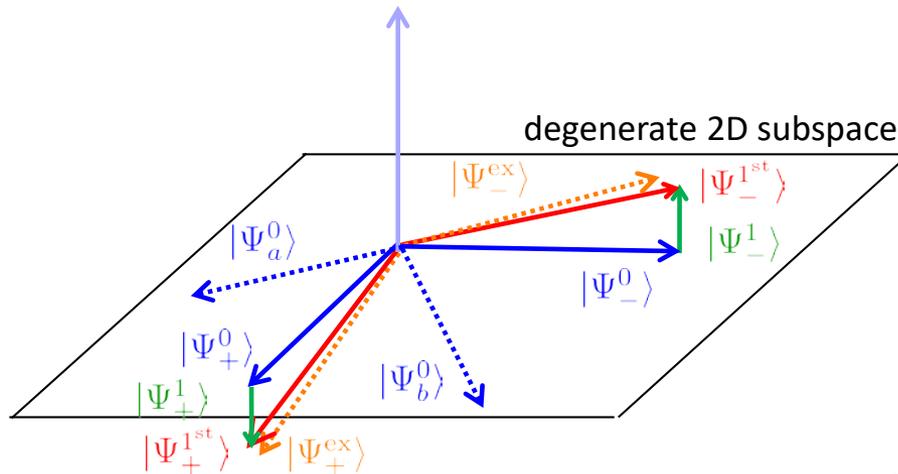
Task: find good $| \Psi_n^0 \rangle$

For 2-fold degeneracy, there will be two good $| \Psi_n^0 \rangle$, which we'll label $| \Psi_+^0 \rangle$ and $| \Psi_-^0 \rangle$. (Often we will skip index n entirely.)

Intuitive picture

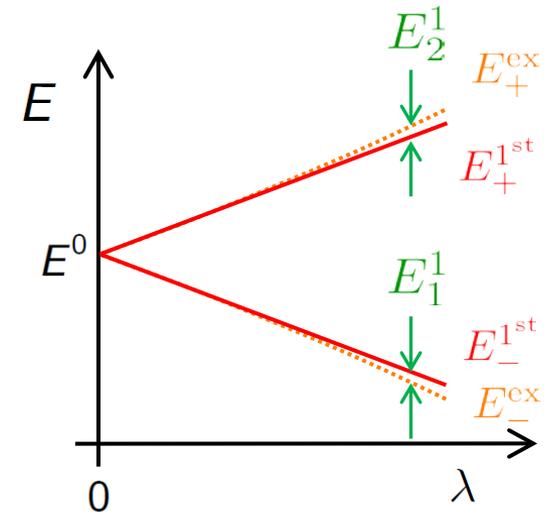
Eigenstates

symbolize Hilbert space by 3D vector space



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Energies



Our goals

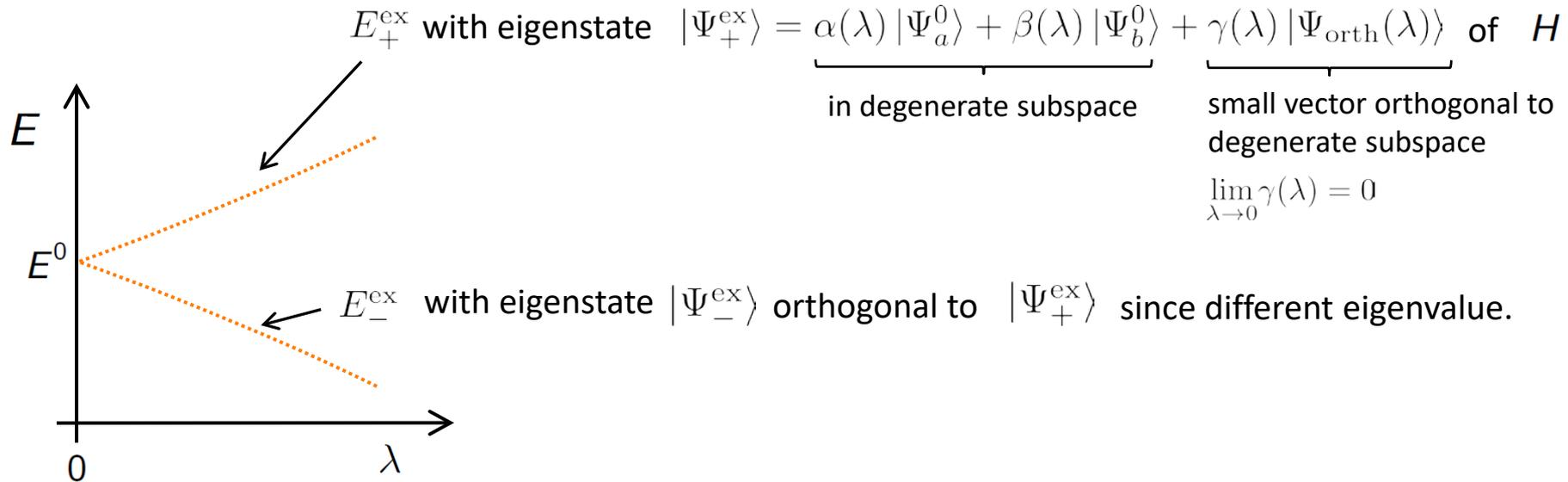
- change in energy to 1st order
- „good“ eigenstates (= „states to 0th order“)

„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: $H = H^0 + H' = H^0 + \lambda \tilde{H}$



We can guess that

$$|\Psi_{\pm}^0\rangle = \lim_{\lambda \rightarrow 0} |\Psi_{\pm}^{\text{ex}}\rangle$$

$$(\alpha^0 = \lim_{\lambda \rightarrow 0} \alpha(\lambda) ; \beta^0 = \lim_{\lambda \rightarrow 0} \beta(\lambda))$$

First order correction of energy

Solve $H|\Psi\rangle = E|\Psi\rangle$; $H = H^0 + H' = H^0 + \lambda\tilde{H}$

with $E^{\text{ex}} = E^0 + \lambda\tilde{E}^1 + \dots$

$$|\Psi^{\text{ex}}\rangle = |\Psi^0\rangle + \lambda|\tilde{\Psi}^1\rangle + \dots$$

Here we skip index $n = +/-$ for clarity.
Calculation applies for both states.

Insert, expand, collect 1st order in λ

$$\implies \text{eqn. (I) exactly as before: } H^0|\tilde{\Psi}^1\rangle + \tilde{H}|\Psi^0\rangle = E^0|\tilde{\Psi}^1\rangle + \tilde{E}^1|\Psi^0\rangle$$

Schrödinger equn. of perturbed system

Reminder

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

$$\begin{aligned} & (H^0 + \lambda \tilde{H}) \left[|\psi_n^0\rangle + \lambda |\tilde{\psi}_n^1\rangle + \lambda^2 |\tilde{\psi}_n^2\rangle + \dots \right] \\ = & \left[E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \dots \right] \left[|\psi_n^0\rangle + \lambda |\tilde{\psi}_n^1\rangle + \lambda^2 |\tilde{\psi}_n^2\rangle + \dots \right] \end{aligned}$$

reminder

$$H^0 + \lambda \tilde{H}$$

$$|\Psi_n^{\text{ex}}\rangle = |\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots$$

$$E_n^{\text{ex}} = E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \dots$$

Collect like powers of λ :

$$\begin{aligned} & \underline{H^0 |\Psi_n^0\rangle} + \lambda \left(\underline{H^0 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{H} |\Psi_n^0\rangle} \right) + \lambda^2 \left(\underline{H^0 |\tilde{\Psi}_n^2\rangle} + \underline{\tilde{H} |\tilde{\Psi}_n^1\rangle} \right) + \dots \\ = & \underline{E_0 |\Psi_n^0\rangle} + \lambda \left(\underline{E_n^0 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{E}_n^1 |\Psi_n^0\rangle} \right) + \lambda^2 \left(\underline{E_n^0 |\tilde{\Psi}_n^2\rangle} + \underline{\tilde{E}_n^1 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{E}_n^2 |\Psi_n^0\rangle} \right) + \dots \end{aligned}$$

0th order (λ^0):

$$H^0 |\Psi_n^0\rangle = E_n |\Psi_n^0\rangle$$

1st order (λ^1):

$$H^0 |\tilde{\Psi}_n^1\rangle + \tilde{H} |\Psi_n^0\rangle = E_n^0 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^1 |\Psi_n^0\rangle \quad (I)$$

2nd order (λ^2):

$$H^0 |\tilde{\Psi}_n^2\rangle + \tilde{H} |\tilde{\Psi}_n^1\rangle = E_n^0 |\tilde{\Psi}_n^2\rangle + \tilde{E}_n^1 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^2 |\Psi_n^0\rangle \quad (II)$$

First order correction of energy

Solve $H|\Psi\rangle = E|\Psi\rangle$; $H = H^0 + H' = H^0 + \lambda\tilde{H}$

with $E^{\text{ex}} = E^0 + \lambda\tilde{E}^1 + \dots$

Here we skip index $n = +/-$ for clarity.
Calculation applies for both states.

$|\Psi^{\text{ex}}\rangle = |\Psi^0\rangle + \lambda|\tilde{\Psi}^1\rangle + \dots$

Insert, expand, collect 1st order in λ

\implies eqn. (I) exactly as before: $H^0|\tilde{\Psi}^1\rangle + \tilde{H}|\Psi^0\rangle = E^0|\tilde{\Psi}^1\rangle + \tilde{E}^1|\Psi^0\rangle$

$\langle \Psi_a^0 | \cdot (I)$:

$$\underbrace{\langle \Psi_a^0 | H^0 | \tilde{\Psi}^1 \rangle + \langle \Psi_a^0 | \tilde{H} | \Psi^0 \rangle}_{= \langle H^0 \Psi_a^0 | \tilde{\Psi}^1 \rangle} = E^0 \langle \Psi_a^0 | \tilde{\Psi}^1 \rangle + \tilde{E}^1 \langle \Psi_a^0 | \Psi^0 \rangle$$

$$= \langle H^0 \Psi_a^0 | \tilde{\Psi}^1 \rangle = E^0 \langle \Psi_a^0 | \tilde{\Psi}^1 \rangle$$

insert $|\Psi^0\rangle = \alpha^0|\Psi_a^0\rangle + \beta^0|\Psi_b^0\rangle$:

$$\alpha^0 \langle \Psi_a^0 | \tilde{H} | \Psi_a^0 \rangle + \beta^0 \langle \Psi_a^0 | \tilde{H} | \Psi_b^0 \rangle = \alpha^0 \tilde{E}^1$$

$\cdot \lambda$ and compact notation:

$$\alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1$$

$$W_{ij} \equiv \langle \Psi_i^0 | H' | \Psi_j^0 \rangle ; \quad i, j \in \{a, b\}$$

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 α^0, β^0, E^1

Together with $|\alpha^0|^2 + |\beta^0|^2 = 1$, $|\Psi^0\rangle = \alpha^0 |\Psi_a^0\rangle + \beta^0 |\Psi_b^0\rangle$ and e.g. $\alpha^0 \in \mathbb{R}$

\implies good eigenstates and first order energy shifts $|\Psi^0\rangle, E^1$

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 α^0, β^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 $|\Psi_a^0\rangle$ and $|\Psi_b^0\rangle$ were already the desired zero order states $|\Psi_{\pm}^0\rangle$.

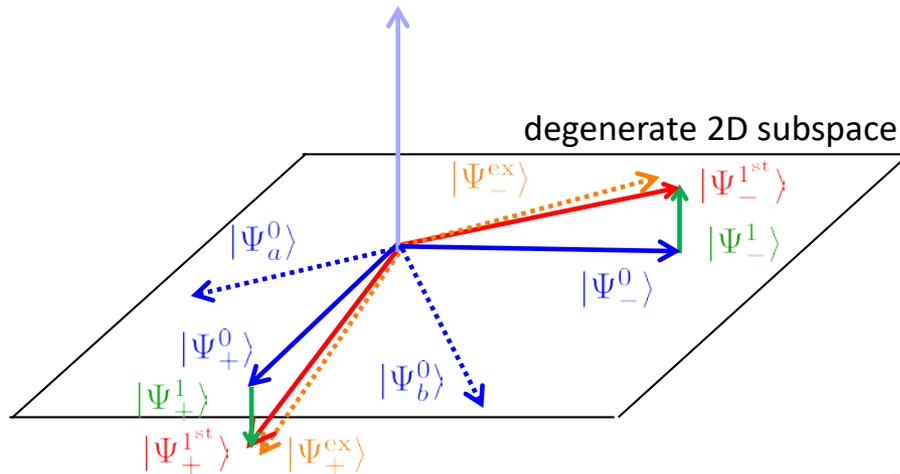
In that case energy correction expectation values of perturbation, as in non-degenerate case.

Intuitive picture

Reminder

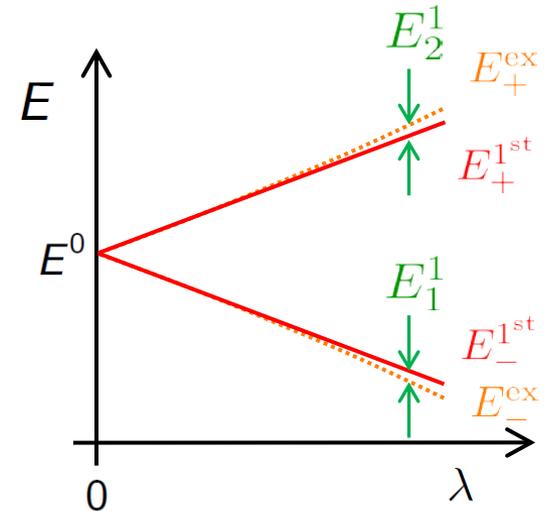
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„good choice“ of eigenstates: eigenstates that lead to first order correction orthogonal to degen. subspace

First order correction to eigenstate

Reminder

(Assume degeneracy infinitesimally 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 $c_m^{(n)}$:

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

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

Insert (*):

$$|\Psi_n^1\rangle = \lambda |\tilde{\Psi}_n^1\rangle = \lambda \sum_{m \neq n} \frac{\langle \Psi_m^0 | \tilde{H} | \Psi_n^0 \rangle}{E_n^0 - E_m^0} |\Psi_m^0\rangle$$

$$|\Psi_n^1\rangle = \sum_{m \neq n} \frac{\langle \Psi_m^0 | H' | \Psi_n^0 \rangle}{E_n^0 - E_m^0} |\Psi_m^0\rangle \quad \begin{array}{l} \text{Here: } W_{ab} = 0 \\ \rightarrow \text{No contamination} \end{array}$$

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

repeat
Griffith's style

$$(III) \quad \alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1$$

$$W_{ij} \equiv \langle \Psi_i^0 | H' | \Psi_j^0 \rangle$$

$$(IV) \quad \alpha^0 W_{ba} + \beta^0 W_{bb} = \beta^0 E^1$$

Solve equation system by hand.

First solve for E^1 :

$$(III): \quad \beta^0 W_{ab} = \alpha^0 (E^1 - W_{aa})$$

$W_{ab} \cdot (IV)$, insert \nearrow 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 $\alpha^0 \neq 0$:

$$(E^1)^2 - E^1 \underbrace{(W_{bb} + W_{aa})}_{-p} + \underbrace{(W_{aa} W_{bb} - \overbrace{W_{ab} W_{ba}}^{|W_{ab}|^2})}_{q} = 0$$

$$\text{Solution: } E_{\pm}^1 = \frac{1}{2} (-p \pm \sqrt{p^2 - 4q})$$

First order correction of energy

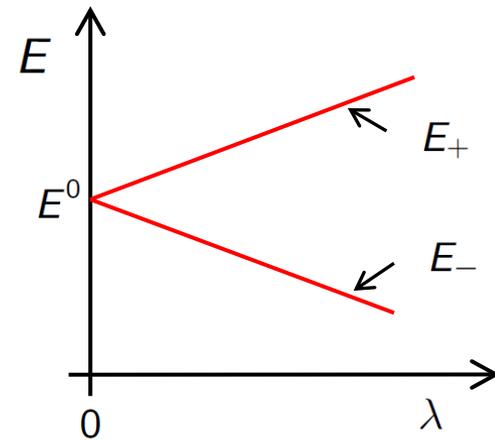
repeat
Griffith's style

If $\alpha^0 \neq 0$:

$$E_{\pm}^1 = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right]$$

Energy of the two perturbed states to first order:

$$E_{\pm} = E^0 + E_{\pm}^1$$



Find good eigenstates (0 order eigenstates):

Inserting E_{\pm}^1 into (III) $\beta^0 W_{ab} = \alpha^0 (E^1 - W_{aa})$ for $W_{ab} \neq 0$:

$$\frac{\beta_{\pm}^0}{\alpha_{\pm}^0} = (E_{\pm}^1 - W_{aa})/W_{ab}$$

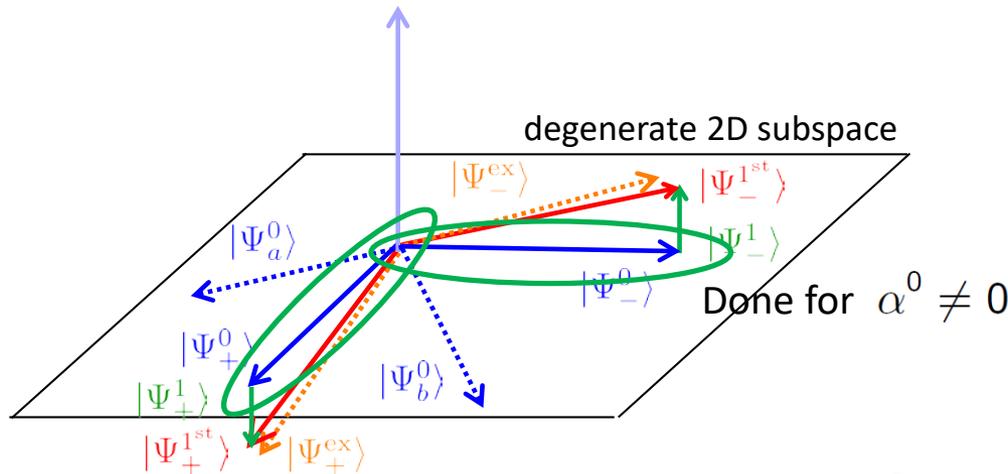
with $|\alpha_{\pm}^0|^2 + |\beta_{\pm}^0|^2 = 1$ and e.g. requiring $\alpha_{\pm}^0 \in \mathbb{R}$ gives $|\Psi_{\pm}^0\rangle$

Intuitive picture

Reminder

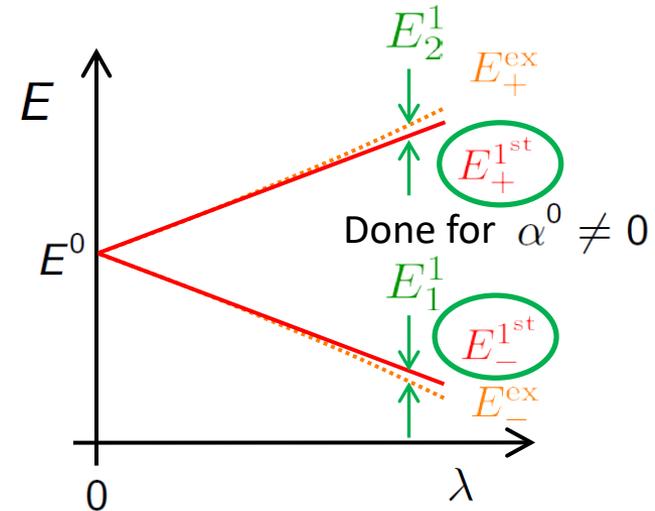
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First order correction of energy

repeat
Griffith's style

$$\text{If } \alpha^0 = 0 : \quad |\alpha^0|^2 + |\beta^0|^2 = 1 \quad \rightarrow \quad \beta^0 = e^{i\Phi_b}$$

$$\text{Using (III) } \alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1:$$

$$\beta^0 W_{ab} = 0 \quad \Rightarrow \quad W_{ab} = 0$$

$$\text{Using (IV) } \alpha^0 W_{ba} + \beta^0 W_{bb} = \beta^0 E^1:$$

$$E_b^1 = W_{bb} = \langle \Psi_b^0 | H' | \Psi_b^0 \rangle$$

$$\text{If } W_{ab} = 0 \text{ second solution: } \alpha^0 = e^{i\Phi_a} \rightarrow \beta^0 = 0$$

$$\rightarrow E_a^1 = W_{aa} = \langle \Psi_a^0 | H' | \Psi_a^0 \rangle$$

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 $|\Psi_a^0\rangle$ and $|\Psi_b^0\rangle$ were already the desired zero order states $|\Psi_{\pm}^0\rangle$.

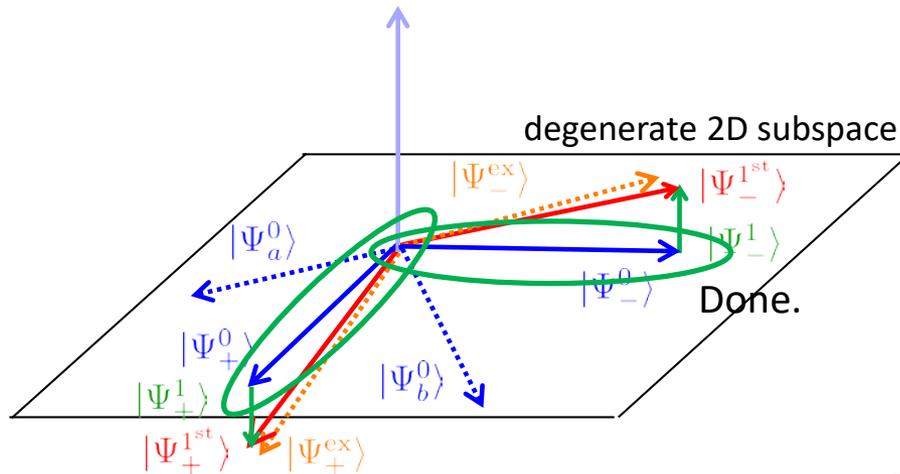
In that case energy correction expectation values of perturbation, as in non-degenerate case.

Intuitive picture

Reminder

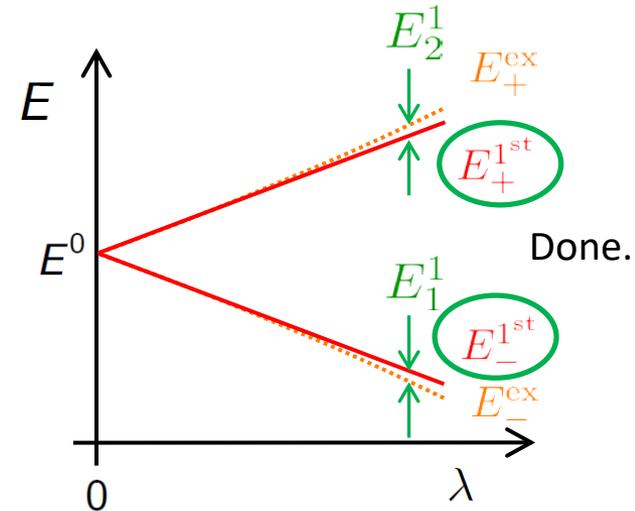
Eigenstates

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)
- } $\lambda = 0$
- } $\lambda > 0$

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

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

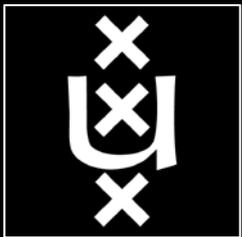
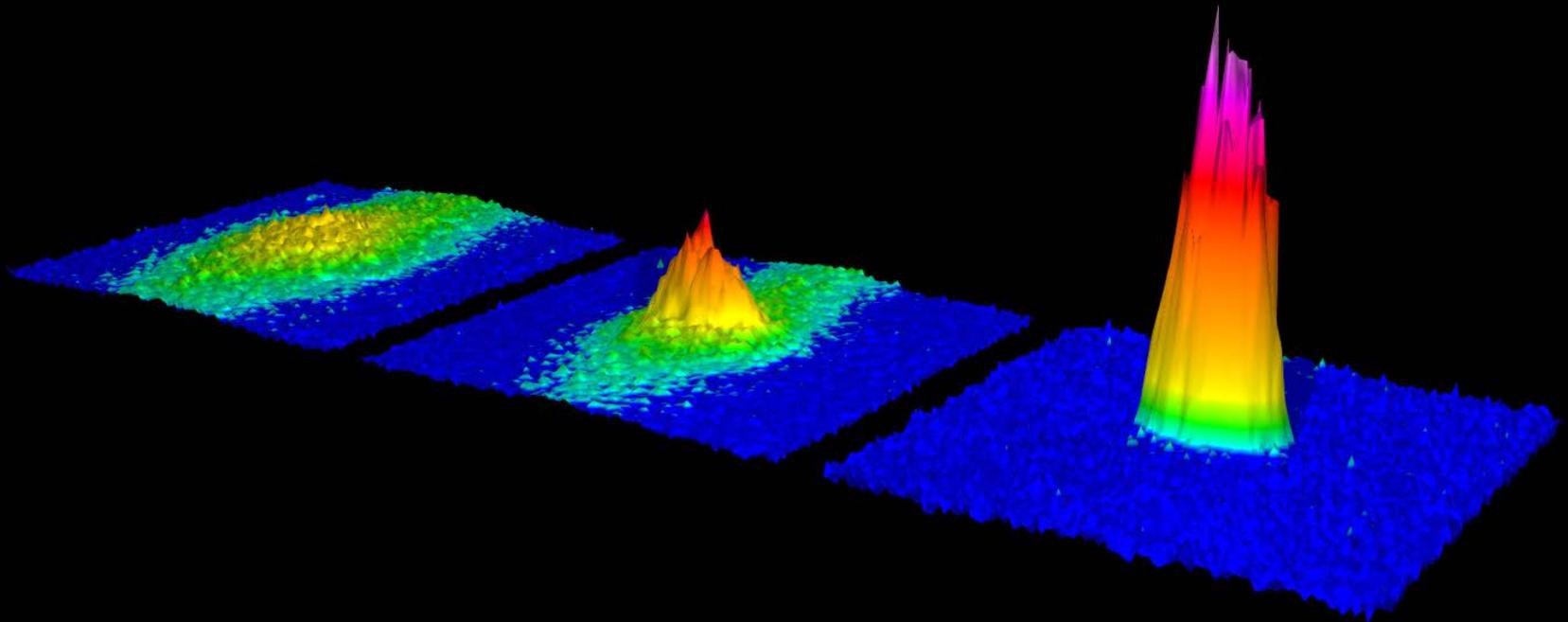
7.2.1 – 7.2.2

7.2.3

Quantum mechanics 3

Structure of matter

Lecture 11



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

Griffiths 3rd 5.1, 5.2

Crystalline solids

5.3.2

today { Time-independent perturbation theory

7.1, 7.2

Structure of hydrogen

7.3 – 7.5

Variational principle

8.1 – 8.3

Time-dependent perturbation theory, atom-light interaction

11.1 – 11.4

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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Atoms, molecules, condensed-matter,...

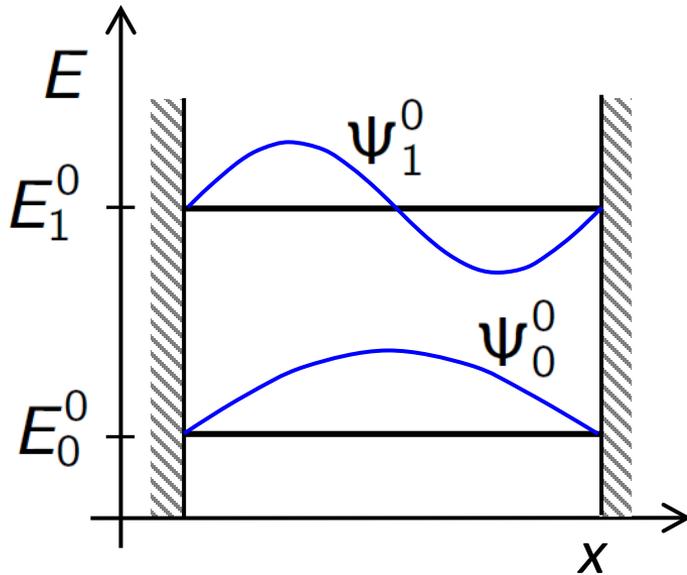
Plan of this section

- | | |
|---|---------------------------------|
| 1) intro, examples | Griffiths 3 rd 7.1.1 |
| 2) non-degenerate perturbation theory | 7.1.2 – 7.1.3 |
| 3) 2-fold degenerate perturbation theory | 7.2.1 – 7.2.2 |
| 4) n -fold degenerate perturbation theory | 7.2.3 |
| 5) general perturbation theory | |

Example: Particle in nearly square box

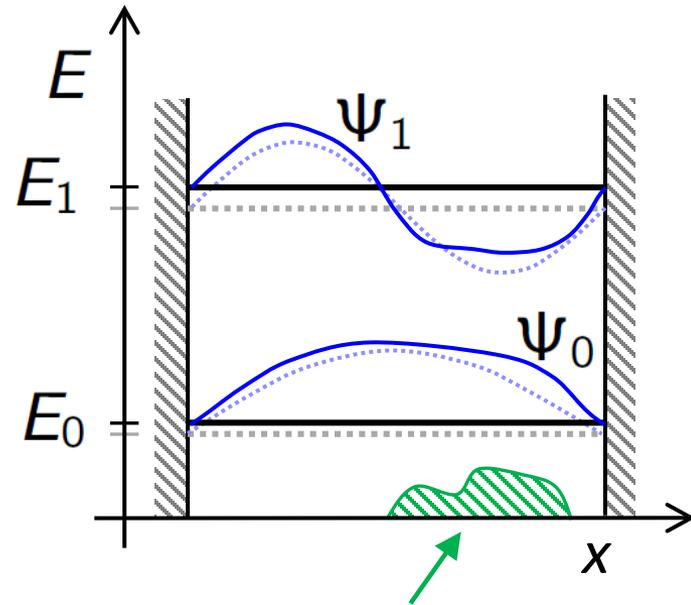
Reminder

Starting point
unperturbed system



We know $E_0^0, \psi_0^0, E_1^0, \psi_1^0, \dots$

Modification
perturbed system



Small perturbation
potential slightly altered

Question

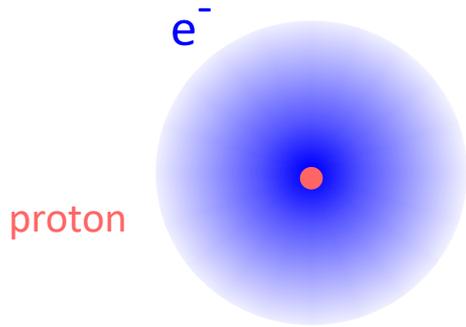
What are, approximately,
 $E_0, \psi_0, E_1, \psi_1, \dots$?

Example: Atom in magnetic field

Reminder

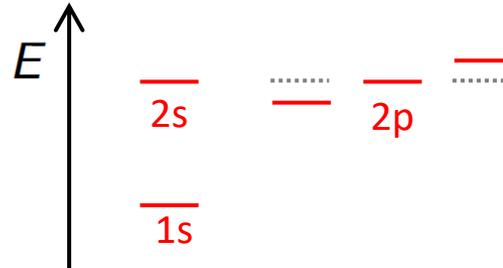
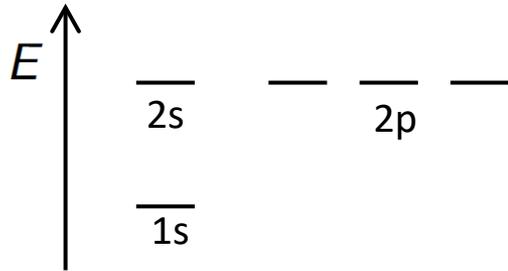
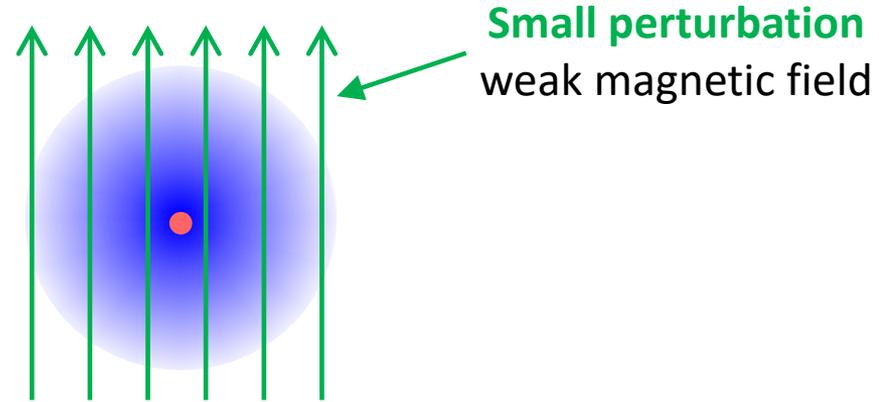
Starting point

unperturbed system



Modification

perturbed system



Question

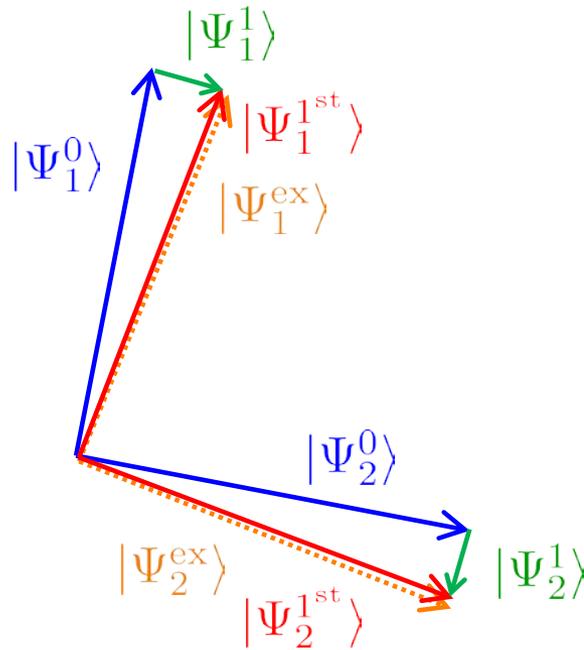
What are, approximately, perturbed eigenstates and energies?

Intuitive picture

Reminder

Eigenstates

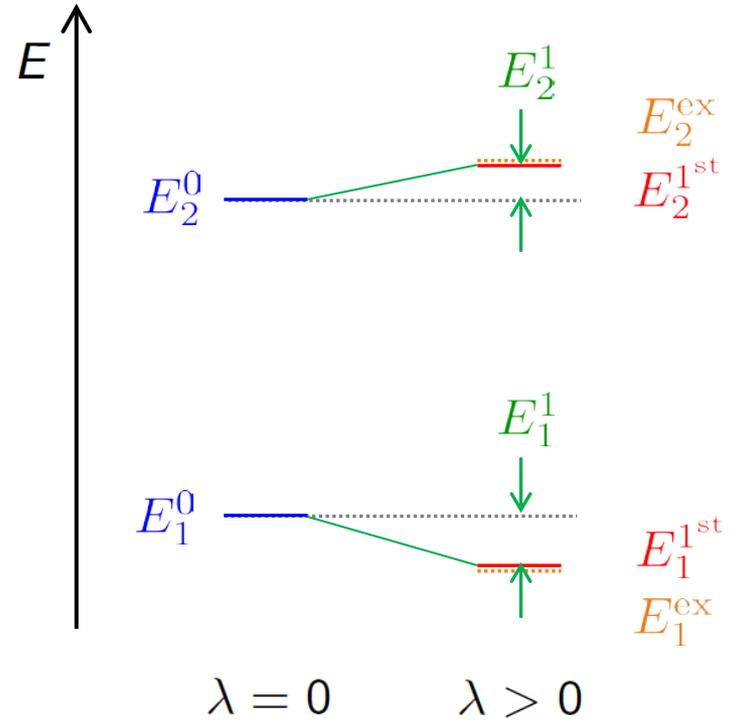
symbolize Hilbert space by 2D vector space



- 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)
- } $\lambda > 0$

Notice: $|\Psi_1^1\rangle$ and $|\Psi_1^0\rangle$ nearly orthogonal because correction small

Energies



Our goals

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

Non-degenerate perturbation theory

Reminder

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
 (will define later what „small“ means)
 Hamiltonian of unperturbed system

Unperturbed system has orthonormal eigenstates $\{\Psi_n^0\}$ with energies $\{E_n^0\}$:

$$H^0 |\Psi_n^0\rangle = E_n^0 |\Psi_n^0\rangle \quad ; \quad \langle \Psi_n^0 | \Psi_m^0 \rangle = \delta_{nm} \quad ; \quad E_n^0 \neq E_m^0 \text{ for } n \neq m$$

Perturbed system has eigenstates $|\Psi_n^{\text{ex}}\rangle$ with energy E_n^{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 λ :

	0 th order	1 st order	2 nd order	3 rd and higher orders in λ
$ \Psi_n^{\text{ex}}\rangle =$	$ \Psi_n^0\rangle$	$+\lambda \underbrace{ \tilde{\Psi}_n^1\rangle}_{\equiv \Psi_n^1\rangle}$	$+\lambda^2 \underbrace{ \tilde{\Psi}_n^2\rangle}_{\equiv \Psi_n^2\rangle}$	$+\dots$
$E_n^{\text{ex}} =$	E_n^0	$+\lambda \underbrace{\tilde{E}_n^1}_{\equiv E_n^1}$	$+\lambda^2 \underbrace{\tilde{E}_n^2}_{\equiv E_n^2}$	$+\dots$

Schrödinger equn. of perturbed system

Reminder

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

$$\begin{aligned} & (H^0 + \lambda \tilde{H}) \left[|\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots \right] \\ = & \left[E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \dots \right] \left[|\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots \right] \end{aligned}$$

reminder

$$H^0 + \lambda \tilde{H}$$

$$|\Psi_n^{\text{ex}}\rangle = |\Psi_n^0\rangle + \lambda |\tilde{\Psi}_n^1\rangle + \lambda^2 |\tilde{\Psi}_n^2\rangle + \dots$$

$$E_n^{\text{ex}} = E_n^0 + \lambda \tilde{E}_n^1 + \lambda^2 \tilde{E}_n^2 + \dots$$

Collect like powers of λ :

$$\begin{aligned} & \underline{H^0 |\Psi_n^0\rangle} + \lambda \left(\underline{H^0 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{H} |\Psi_n^0\rangle} \right) + \lambda^2 \left(\underline{H^0 |\tilde{\Psi}_n^2\rangle} + \underline{\tilde{H} |\tilde{\Psi}_n^1\rangle} \right) + \dots \\ = & \underline{E_n^0 |\Psi_n^0\rangle} + \lambda \left(\underline{E_n^0 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{E}_n^1 |\Psi_n^0\rangle} \right) + \lambda^2 \left(\underline{E_n^0 |\tilde{\Psi}_n^2\rangle} + \underline{\tilde{E}_n^1 |\tilde{\Psi}_n^1\rangle} + \underline{\tilde{E}_n^2 |\Psi_n^0\rangle} \right) + \dots \end{aligned}$$

0th order (λ^0):

$$H^0 |\Psi_n^0\rangle = E_n |\Psi_n^0\rangle$$

1st order (λ^1):

$$H^0 |\tilde{\Psi}_n^1\rangle + \tilde{H} |\Psi_n^0\rangle = E_n^0 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^1 |\Psi_n^0\rangle \quad (I)$$

2nd order (λ^2):

$$H^0 |\tilde{\Psi}_n^2\rangle + \tilde{H} |\tilde{\Psi}_n^1\rangle = E_n^0 |\tilde{\Psi}_n^2\rangle + \tilde{E}_n^1 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^2 |\Psi_n^0\rangle \quad (II)$$

First order correction to energy

Reminder

$$(I) \quad H^0 |\tilde{\Psi}_n^1\rangle + \tilde{H} |\Psi_n^0\rangle = E_n^0 |\tilde{\Psi}_n^1\rangle + \tilde{E}_n^1 |\Psi_n^0\rangle$$

$\langle \Psi_n^0 | \cdot (I) :$

$$\underbrace{\langle \Psi_n^0 | H^0 | \tilde{\Psi}_n^1 \rangle}_{=} + \langle \Psi_n^0 | \tilde{H} | \Psi_n^0 \rangle = E_n^0 \underbrace{\langle \Psi_n^0 | \tilde{\Psi}_n^1 \rangle}_{=} + \tilde{E}_n^1 \underbrace{\langle \Psi_n^0 | \Psi_n^0 \rangle}_1$$
$$= \langle H^0 \Psi_n^0 | \tilde{\Psi}_n^1 \rangle = E_n^0 \langle \Psi_n^0 | \tilde{\Psi}_n^1 \rangle$$

$$\tilde{E}_n^1 = \langle \Psi_n^0 | \tilde{H} | \Psi_n^0 \rangle$$

reminder

$$E_n^1 = \tilde{E}_n^1 / \lambda$$

$$H' = \tilde{H} / \lambda$$

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

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

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

First order correction to eigenstate

Reminder

$l \neq n$:

$$(E_l^0 - E_n^0)c_l^{(n)} = - \langle \Psi_l^0 | \tilde{H} | \Psi_n^0 \rangle$$

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

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

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

Reminder

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

Observations

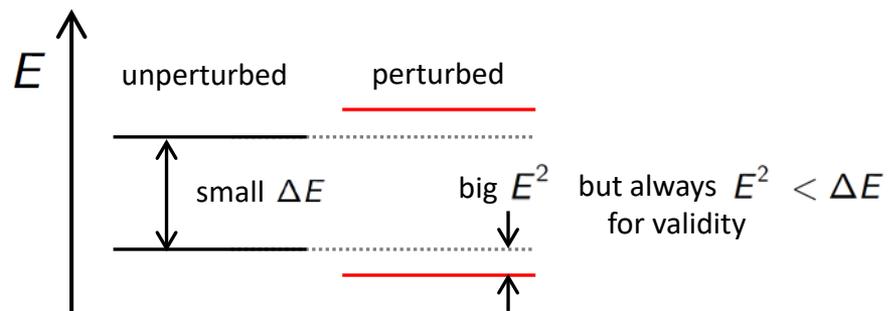
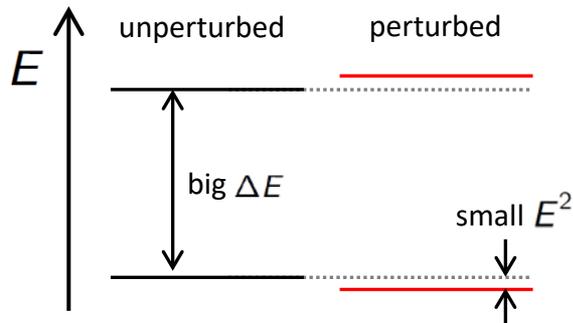
$$|\langle \Psi_m^0 | H' | \Psi_m^0 \rangle|^2 > 0$$

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

Reminder

Compact notation: $W_{mn} \equiv \langle \Psi_m^0 | H' | \Psi_n^0 \rangle$; $\Delta_{mn} \equiv E_m^0 - E_n^0$

Energy

$$E_n = E_n^0 + E_n^1 + E_n^2 + E_n^3 + \dots$$

$$E_n^3 = \sum_{l, m \neq n} \frac{W_{nl} W_{lm} W_{mn}}{\Delta_{nl} \Delta_{nm}} - W_{nn} \sum_{m \neq n} \frac{W_{nm}^2}{\Delta_{nm}^2}$$

State

$$|\Psi_n\rangle = |\Psi_n^0\rangle + |\Psi_n^1\rangle + \dots$$

$$|\Psi_n^1\rangle = \sum_{m \neq n} \frac{W_{mn}}{\Delta_{nm}} |\Psi_m^0\rangle$$

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“

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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,...

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

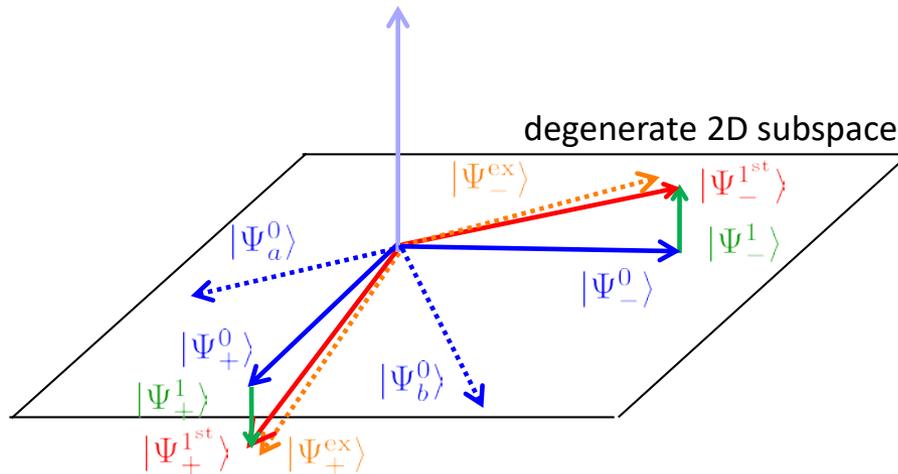
7.2.1 – 7.2.2

7.2.3

Intuitive picture

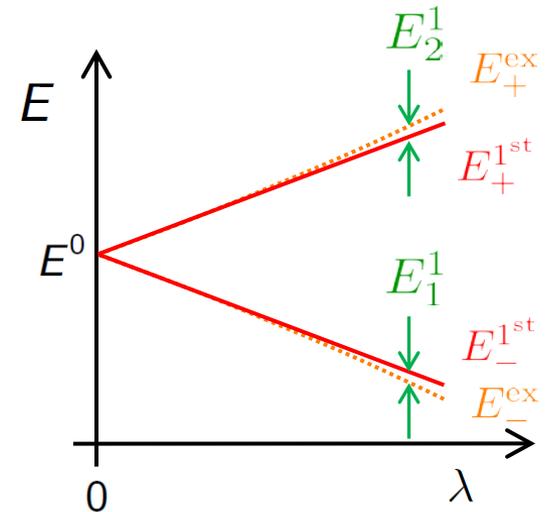
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symbolize Hilbert space by 3D vector space



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Energies



Our goals

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- „good“ eigenstates (= „states to 0th order“)

„good choice“ of eigenstates: eigenstates that lead to first order correction orthogonal to degen. subspace

Degenerate perturbation theory

Reminder

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 $W_{nm} = 0$.

└ hint towards solution of challenge

$$W_{mn} \equiv \langle \Psi_m^0 | H' | \Psi_n^0 \rangle ; \Delta_{mn} \equiv E_m^0 - E_n^0$$

For simplicity consider system of only two degenerate states

$$H^0 | \Psi_a^0 \rangle = E^0 | \Psi_a^0 \rangle ; H^0 | \Psi_b^0 \rangle = E^0 | \Psi_b^0 \rangle$$

Notice: all superpositions of these states still eigenstates of H^0

$$\text{e.g. } | \Psi^0 \rangle = \alpha^0 | \Psi_a^0 \rangle + \beta^0 | \Psi_b^0 \rangle ; |\alpha^0|^2 + |\beta^0|^2 = 1$$

$$H^0 | \Psi^0 \rangle = E^0 | \Psi^0 \rangle$$

This makes perturbative expansion more complicated

$$| \Psi_n^{\text{ex}} \rangle = | \Psi_n^0 \rangle + \lambda | \tilde{\Psi}_n^1 \rangle + \dots$$

└ We don't know which superposition to use.

Task: find good $| \Psi_n^0 \rangle$

For 2-fold degeneracy, there will be two good $| \Psi_n^0 \rangle$, which we'll label $| \Psi_+^0 \rangle$ and $| \Psi_-^0 \rangle$. (Often we will skip index n entirely.)

First order correction of energy

Reminder

$$\text{Solve } H|\Psi\rangle = E|\Psi\rangle \quad ; \quad H = H^0 + H' = H^0 + \lambda\tilde{H}$$

$$\text{with } E^{\text{ex}} = E^0 + \lambda\tilde{E}^1 + \dots$$

Here we skip index $n = +/-$ for clarity.
Calculation applies for both states.

$$|\Psi^{\text{ex}}\rangle = |\Psi^0\rangle + \lambda|\tilde{\Psi}^1\rangle + \dots$$

Insert, expand, collect 1st order in λ

$$\implies \text{eqn. (I) exactly as before: } H^0|\tilde{\Psi}^1\rangle + \tilde{H}|\Psi^0\rangle = E^0|\tilde{\Psi}^1\rangle + \tilde{E}^1|\Psi^0\rangle$$

$\langle \Psi_a^0 | \cdot (I)$:

$$\underbrace{\langle \Psi_a^0 | H^0 | \tilde{\Psi}^1 \rangle + \langle \Psi_a^0 | \tilde{H} | \Psi^0 \rangle}_{= \langle H^0 \Psi_a^0 | \tilde{\Psi}^1 \rangle} = E^0 \langle \Psi_a^0 | \tilde{\Psi}^1 \rangle + \tilde{E}^1 \langle \Psi_a^0 | \Psi^0 \rangle$$

use $|\Psi^0\rangle = \alpha^0|\Psi_a^0\rangle + \beta^0|\Psi_b^0\rangle$:

$$\alpha^0 \langle \Psi_a^0 | \tilde{H} | \Psi_a^0 \rangle + \beta^0 \langle \Psi_a^0 | \tilde{H} | \Psi_b^0 \rangle = \alpha^0 \tilde{E}^1$$

$\cdot \lambda$ and compact notation:

$$\alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1$$

$$W_{ij} \equiv \langle \Psi_i^0 | H' | \Psi_j^0 \rangle \quad ; \quad i, j \in \{a, b\}$$

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

Reminder

$$\alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1$$

$$W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle$$

$$\alpha^0 W_{ba} + \beta^0 W_{bb} = \beta^0 E^1$$

Two equations to help determine α^0, β^0, E^1

Together with $|\alpha^0|^2 + |\beta^0|^2 = 1$, $|\Psi^0\rangle = \alpha^0 |\psi_a^0\rangle + \beta^0 |\psi_b^0\rangle$ and e.g. $\alpha^0 \in \mathbb{R}$

\implies good eigenstates and first order energy shifts $|\Psi^0\rangle, E^1$

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 α^0, β^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 $|\psi_a^0\rangle$ and $|\psi_b^0\rangle$ were already the desired zero order states $|\psi_{\pm}^0\rangle$.

In that case energy correction expectation values of perturbation, as in non-degenerate case.

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| | 2) non-degenerate perturbation theory | | 7.1.2 – 7.1.3 |
| → | 3) 2-fold degenerate perturbation theory | | 7.2.1 – 7.2.2 |
| → | 4) n -fold degenerate perturbation theory | | 7.2.3 |
| | 5) general perturbation theory | | |

Generalization to n -fold degeneracy

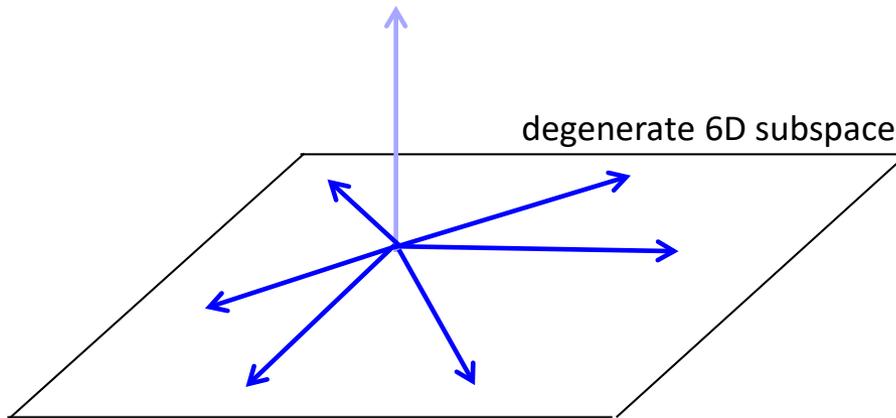
Manifold of eigenstates of unperturbed system with energy E^0 :

$$H^0 |\Psi_i^0\rangle = E^0 |\Psi_i^0\rangle \quad ; \quad i \in \{1, 2, \dots, n\}$$

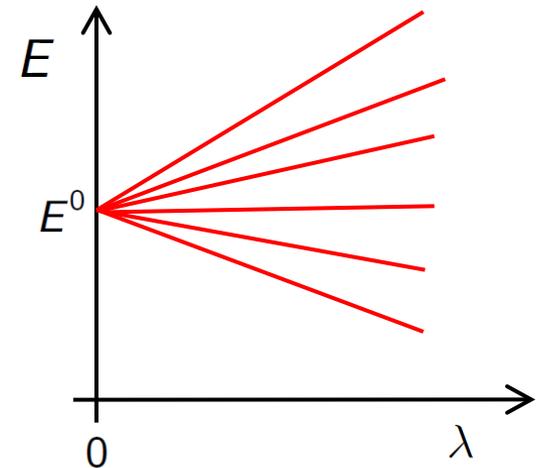
Intuitive picture

Eigenstates

symbolize Hilbert space by 3D vector space



Energies



- state with different energy
- „good“ choice of basisstates 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 :

$$H^0 |\Psi_i^0\rangle = E^0 |\Psi_i^0\rangle \quad ; \quad i \in \{1, 2, \dots, n\}$$

General eigenstate with that energy:

$$|\Psi^0\rangle = \sum_{i=1}^n \alpha_i^0 |\Psi_i^0\rangle$$

As before, $\langle \Psi_j^0 | \cdot \rangle$ (I) :

First order correction of energy

Reminder

$$\text{Solve } H|\Psi\rangle = E|\Psi\rangle \quad ; \quad H = H^0 + H' = H^0 + \lambda\tilde{H}$$

$$\text{with } E^{\text{ex}} = E^0 + \lambda\tilde{E}^1 + \dots$$

Here we skip index $n = +/-$ for clarity.
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Insert, expand, collect 1st order in λ

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$\langle \Psi_a^0 | \cdot (I)$:

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use $|\Psi^0\rangle = \alpha^0|\Psi_a^0\rangle + \beta^0|\Psi_b^0\rangle$:

$$\alpha^0 \langle \Psi_a^0 | \tilde{H} | \Psi_a^0 \rangle + \beta^0 \langle \Psi_a^0 | \tilde{H} | \Psi_b^0 \rangle = \alpha^0 \tilde{E}^1$$

$\cdot \lambda$ and compact notation:

$$\alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1$$

$$W_{ij} \equiv \langle \Psi_i^0 | H' | \Psi_j^0 \rangle \quad ; \quad i, j \in \{a, b\}$$

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

Reminder

$$\alpha^0 W_{aa} + \beta^0 W_{ab} = \alpha^0 E^1$$

$$W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle$$

$$\alpha^0 W_{ba} + \beta^0 W_{bb} = \beta^0 E^1$$

Two equations to help determine α^0, β^0, E^1

Together with $|\alpha^0|^2 + |\beta^0|^2 = 1$, $|\psi^0\rangle = \alpha^0 |\psi_a^0\rangle + \beta^0 |\psi_b^0\rangle$ and e.g. $\alpha^0 \in \mathbb{R}$

\implies good eigenstates and first order energy shifts $|\psi^0\rangle, E^1$

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 α^0, β^0, E^1 by e.g. diagonalizing matrix.

Generalization to n -fold degeneracy

Manifold of eigenstates of unperturbed system with energy E^0 :

$$H^0 |\Psi_i^0\rangle = E^0 |\Psi_i^0\rangle \quad ; \quad i \in \{1, 2, \dots, n\}$$

General eigenstate with that energy:

$$|\Psi^0\rangle = \sum_{i=1}^n \alpha_i^0 |\Psi_i^0\rangle$$

As before, $\langle \Psi_j^0 | \cdot \rangle$ (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

$$W \vec{\alpha} = E^1 \vec{\alpha}$$

$$W_{ij} = \langle \Psi_i^0 | H' | \Psi_j^0 \rangle$$

↑
 $n \times n$ matrix

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 $\{|\Psi_i^0\rangle\}$ in which W is diagonal:

Theorem: Let A be a hermitian operator with $[A, H^0] = [A, H'] = 0$

with $A|\Psi_i^0\rangle = \mu_i|\Psi_i^0\rangle$; $i, j \in \{1, \dots, n\}$

If $\mu_i \neq \mu_j$ for all $i \neq j$,

then $W_{ij} = 0$, i.e. $|\Psi_i^0\rangle$ have been chosen such that W is diagonal.

Proof: $[A, H'] = 0$

$$\langle \Psi_i^0 | [A, H'] | \Psi_j^0 \rangle = 0$$

$$0 = \langle \Psi_i^0 | A H' | \Psi_j^0 \rangle - \langle \Psi_i^0 | H' A | \Psi_j^0 \rangle$$

$$= \langle A \Psi_i^0 | H' \Psi_j^0 \rangle - \langle \Psi_i^0 | H' \mu_j | \Psi_j^0 \rangle$$

$$= (\mu_i - \mu_j) \langle \Psi_i^0 | H' | \Psi_j^0 \rangle = \underbrace{(\mu_i - \mu_j)}_{\neq 0} W_{ij}$$

$$\implies W_{ij} = 0 \quad \text{Q.E.D.}$$

Strategy: find A with $[A, H^0] = [A, H'] = 0$ (e.g. from symmetry considerations)

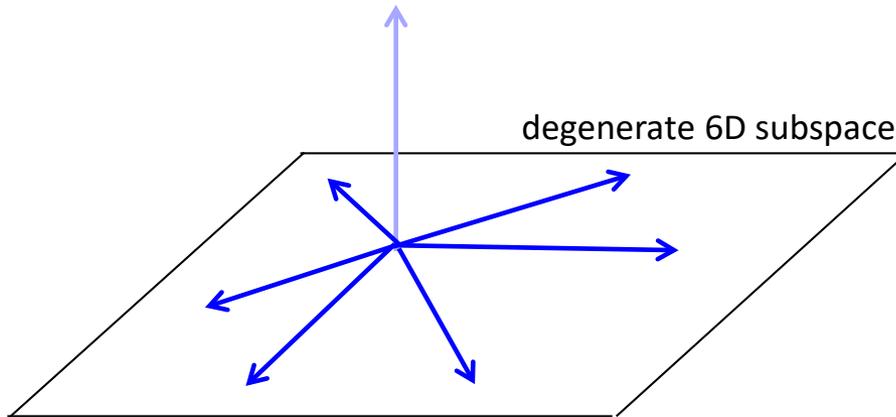
Use eigenstates of A (which are also eigenstates of H^0 and H') \rightarrow $E_i^1 = W_{ii}$

(If degeneracy not completely lifted, find several commuting observables A and their common eigenstates.)

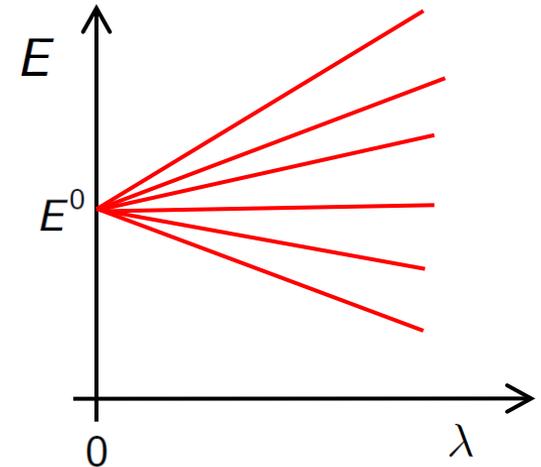
Intuitive picture

Eigenstates

symbolize Hilbert space by 3D vector space



Energies



- state with different energy
- „good“ choice of basisstates of degenerate manifold of unperturbed system

Our goals

- change in energy to 1st order
- „good“ eigenstates (= „states to 0th order“)

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

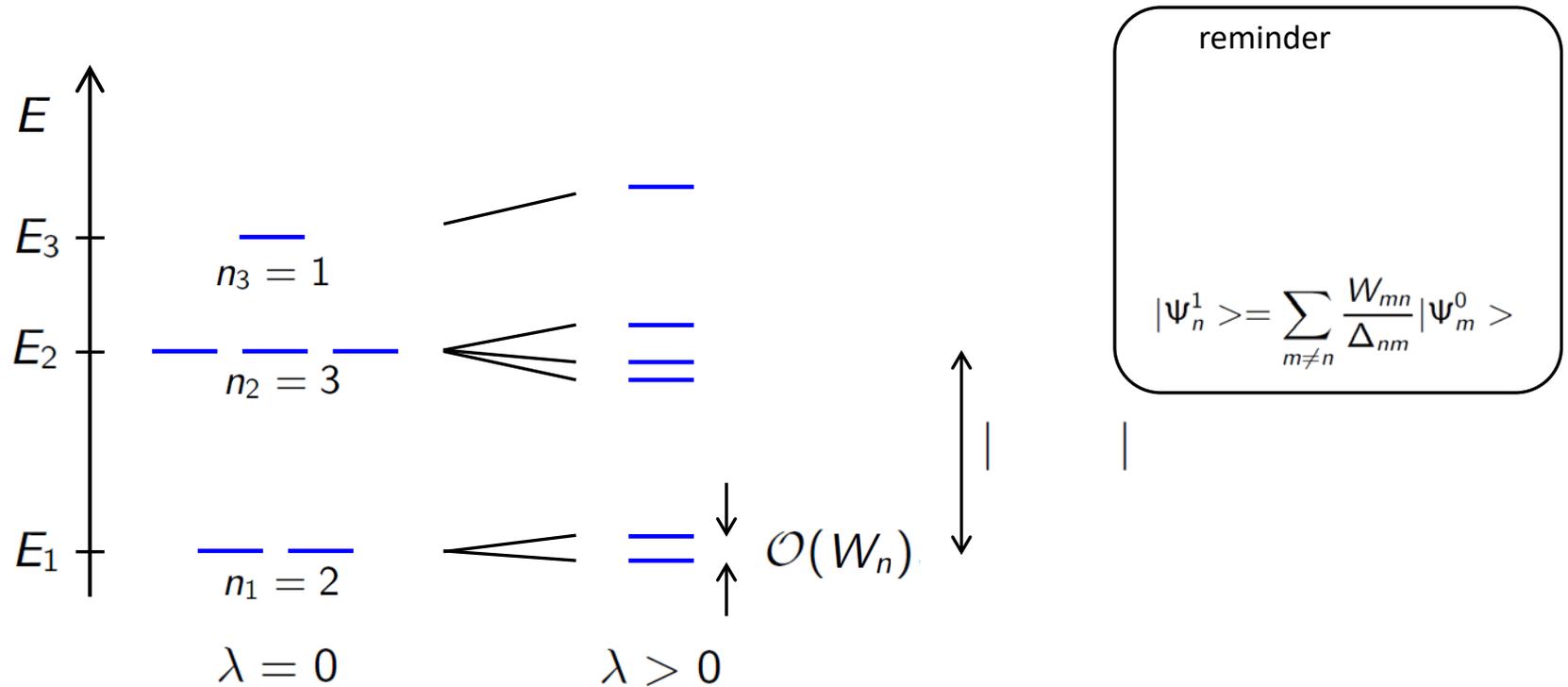
7.2.1 – 7.2.2

7.2.3

Generalization to 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 ; $i \in \{1, \dots, m\}$



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

$$E^1 = \langle H' \rangle = \langle H'_1 + H'_2 \rangle = \langle H'_1 \rangle + \langle H'_2 \rangle = E_1^1 + E_2^1$$

→ We can simply add up the first order energy shifts.

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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	Griffiths 3 rd 5.1, 5.2
	Crystalline solids	5.3.2
today {	Time-independent perturbation theory	7.1, 7.2
	Structure of hydrogen	7.3 – 7.5
	Variational principle	8.1 – 8.3
	Time-dependent perturbation theory, atom-light interaction	11.1 – 11.4



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

Questions: schreck@StrontiumBEC.com

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 Griffiths 3rd 7.3
- 3) Lamb shift 7.3
- 4) Hyperfine structure 7.5
- 5) Zeeman effect 7.4

The energy spectrum of hydrogen

So far, we considered only kinetic and potential energy

$$H^0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

⇒ Bohr energy levels.

Only correction taken into account:

Finite mass of nucleus → replace m 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	$\alpha^2 mc^2$	} effects intrinsic to atom
Fine structure	of order	$\alpha^4 mc^2$	
Lamb shift	of order	$\alpha^5 mc^2$	
Hyperfine structure	of order	$\left(\frac{m_{el}}{m_p}\right) \alpha^4 mc^2$	
Zeeman effect	typically in labs, same order as hyperfine, sometimes fine structure.		} effect by static, external B- respective E-field
DC Stark effect			

where

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137.036} \quad \text{„fine structure constant“}$$

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.

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Discuss effects in atoms beyond Coulomb interaction between nucleus and electron(s), using hydrogen as simplest possible example

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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 $\langle 1/r \rangle$ and $\langle 1/r^2 \rangle$
 - result
 - 2) spin-orbit coupling
- 3) Lamb shift
- 4) Hyperfine structure
- 5) Zeeman effect

Fine structure: 1) relativistic correction

Relativistic expression for kinetic energy:

$$E_{kin} = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \quad \text{with} \quad p = \frac{mv}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

$$E_{kin} = mc^2 \left[\sqrt{\left(\frac{p}{mc}\right)^2 + 1} - 1 \right] \stackrel{p \ll mc}{\downarrow} = mc^2 \left[\cancel{1} + \frac{1}{2} \left(\frac{p}{mc}\right)^2 - \frac{1}{8} \left(\frac{p}{mc}\right)^4 + \dots \cancel{-1} \right]$$

$$= \underbrace{\frac{p^2}{2m}}_{\text{non-relativistic, included in } H^0} - \underbrace{\frac{p^4}{8m^3 c^2}}_{= H'_r} + \dots$$

non-relativistic, included in H^0 = H'_r lowest order relativistic correction

Use first order perturbation theory. For eigenstates in which perturbation is diagonal:

$$E_r^1 = \langle H'_r \rangle = -\frac{1}{8m^3 c^2} \langle \psi^0 | p^4 | \psi^0 \rangle = -\frac{1}{8m^3 c^2} \langle p^2 \psi^0 | p^2 \psi^0 \rangle$$

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 :

$$L^2 \text{ and } L_z$$

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 1st order

$$E_r^1 = \langle H_r' \rangle = -\frac{1}{8m^3c^2} \langle p^2 \psi^0 | p^2 \psi^0 \rangle$$

To do: determine $p^2 |\Psi^0 \rangle$

Schrödinger equation for $|\Psi^0 \rangle$

$$\frac{p^2}{2m} |\psi^0 \rangle + V |\psi^0 \rangle = E |\psi^0 \rangle \longrightarrow p^2 |\psi^0 \rangle = 2m(E - V) |\psi^0 \rangle$$

$$E_r^1 = -\frac{1}{2mc^2} \langle (E - V)^2 \rangle = -\frac{1}{2mc^2} \left[E^2 - 2E \langle V \rangle + \langle V^2 \rangle \right]$$

For hydrogen $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$

$$E_{r,n}^1 = -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right]$$

To do: determine $\left\langle \frac{1}{r} \right\rangle$ and $\left\langle \frac{1}{r^2} \right\rangle$

Trick: use Feynman-Hellman theorem

Feynman-Hellman theorem

Given: a hamiltonian that depends on a parameter γ

$$H(\gamma) = H(\gamma^0 + \Delta\gamma) \simeq H(\gamma^0) + \Delta\gamma \frac{\partial H}{\partial \gamma} = H^0 + H'$$

The eigenenergies will also depend on γ

$$E(\gamma) = E(\gamma^0 + \Delta\gamma) \simeq E(\gamma^0) + \Delta\gamma \frac{\partial E}{\partial \gamma} = E^0 + E^1$$

First order perturbation theory:

$$\begin{array}{l} E^1 = \langle H' \rangle = \Delta\gamma \left\langle \frac{\partial H}{\partial \gamma} \right\rangle \\ \parallel \\ \Delta\gamma \frac{\partial E}{\partial \gamma} \end{array}$$

}

$$\frac{\partial E}{\partial \gamma} = \left\langle \frac{\partial H}{\partial \gamma} \right\rangle$$

Feynman-Hellman theorem

Determination of $\left\langle \frac{1}{r} \right\rangle$ and $\left\langle \frac{1}{r^2} \right\rangle$

To do: determine $\left\langle \frac{1}{r} \right\rangle$ and $\left\langle \frac{1}{r^2} \right\rangle$

Trick: use Feynman-Hellman theorem with

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

We know (Griffiths 3rd ed., Ch. 4, eqn. 4.70)

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2 \underbrace{(j_{\max} + l + 1)^2}_{= n}} \quad \begin{array}{l} \uparrow \\ \text{some integer} \end{array}$$

Use Feynman-Hellman theorem $\frac{\partial E}{\partial \gamma} = \left\langle \frac{\partial H}{\partial \gamma} \right\rangle$ with $\gamma = e$ exercise $\implies \left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a}$

Use Feynman-Hellman theorem $\frac{\partial E}{\partial \gamma} = \left\langle \frac{\partial H}{\partial \gamma} \right\rangle$ with $\gamma = l$ exercise $\implies \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{\left(l + \frac{1}{2}\right) n^3 a^2}$

Bohr radius $a = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.5 \times 10^{-10} \text{ m}$

Relativistic correction in 1st 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 $\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a}$ and $\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l + \frac{1}{2}) n^3 a^2}$, 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 α^2 times smaller than E_n .

Fine structure: 1) relativistic correction

Relativistic expression for kinetic energy:

$$E_{kin} = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \quad \text{with} \quad p = \frac{mv}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

$$E_{kin} = mc^2 \left[\sqrt{\left(\frac{p}{mc}\right)^2 + 1} - 1 \right] \stackrel{p \ll mc}{\downarrow} = mc^2 \left[\cancel{1} + \frac{1}{2} \left(\frac{p}{mc}\right)^2 - \frac{1}{8} \left(\frac{p}{mc}\right)^4 + \dots \cancel{-1} \right]$$

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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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Plan of this section

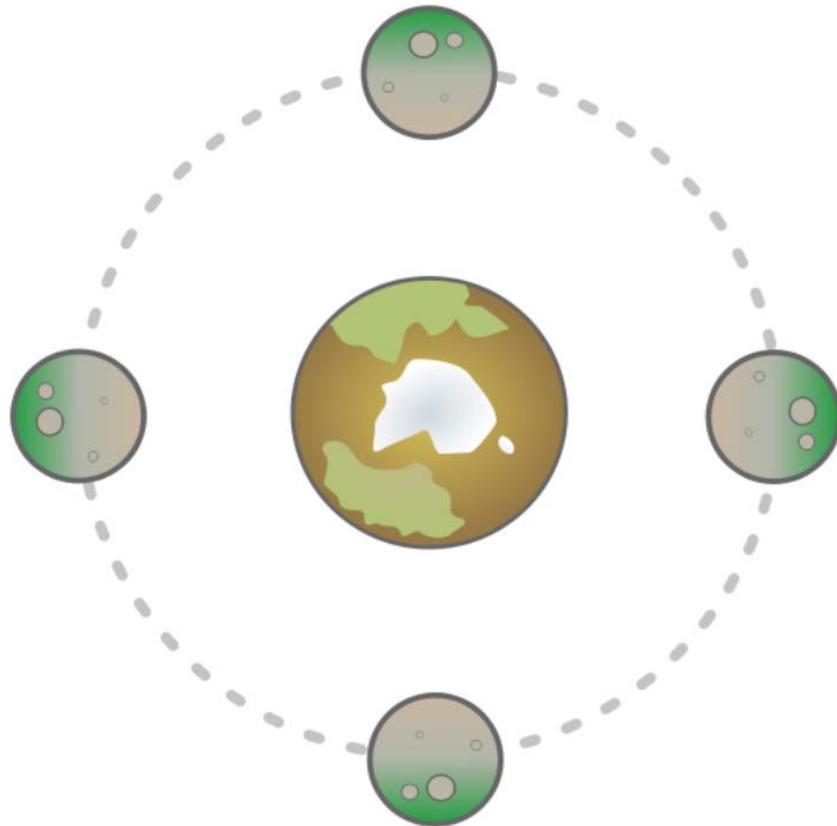
- 1) Intro
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Classical spin-orbit coupling

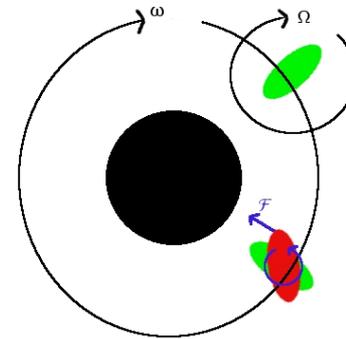
Bonus material

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.

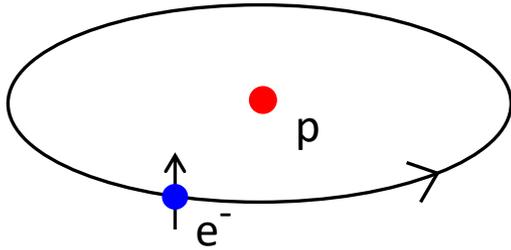
Fine structure: 2) Spin-orbit coupling

Correctly treated using relativistic quantum mechanics (Dirac equation).

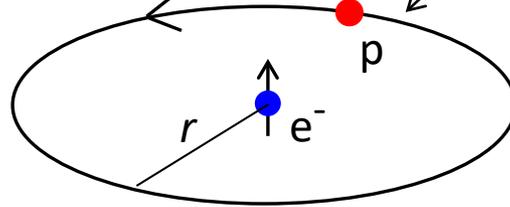
Here: rough, classical calculation

Consider hydrogen atom:

proton's
point of view



electron's
point of view



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 $B = \frac{\mu_0 I}{2r} = \frac{\mu_0}{2r} \frac{ev}{2\pi r}$

Magnetic moment μ of e^- experiences shift in that B-field

$$H = -\vec{\mu} \cdot \vec{B}$$

B-field of proton:

Angular momentum of e^- : $L = rmv$

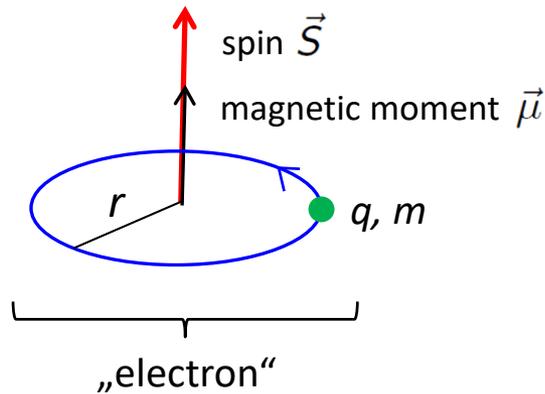
$$B = \frac{\mu_0}{2r} \frac{ev}{2\pi r} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} L$$

\uparrow
 $c = 1/\sqrt{\mu_0\epsilon_0}$

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.



magnetic dipole moment:

$$\mu = I \cdot A = \frac{q}{T} \pi r^2$$

angular momentum ("spin"):

$$S = mvr = m \frac{2\pi r}{T} \cdot r$$

Gyromagnetic ratio = ratio between magnetic moment and angular momentum

$$\frac{\mu}{S} = \frac{q}{2m} \quad \text{notice: independent of } r$$

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).

$$\vec{\mu} = g \frac{q}{2m} \vec{S} \quad g_{\text{classical}} = 1$$

Quantum mechanical calculation

(Special) relativistic quantum mechanics (Dirac equation) delivers

$$g_{el} = 2 \quad \text{where} \quad \vec{\mu} = g \frac{q}{2m} \vec{S} = -g \underbrace{\frac{|e|\hbar}{2m}}_{\mu_B \simeq 1.4 \frac{\text{MHz}}{\text{G}} h} \frac{\vec{S}}{\hbar}$$

„Bohr magneton“

Vacuum fluctuations of electromagnetic field give rise to a \textperthousand -level correction:

$$g_{el}^{\text{QED}} = 2.002319304361\dots$$

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:

$$H = -\vec{\mu} \cdot \vec{B}$$

$$\vec{\mu} = -g \frac{|e|\hbar}{2m} \frac{\vec{S}}{\hbar} \quad ; \quad \vec{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \vec{L}$$

Putting it all together: $(g_{el} = 2 \text{ for simplicity})$

$$H = \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L}$$

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:

$$H'_{SO} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} = \text{constant} \frac{1}{r^3} \vec{S} \cdot \vec{L}$$

To do: determine spin-orbit correction by first order perturbation theory

Basis for perturbation theory

We know solutions of unperturbed Hamiltonian H^0 :

$$E_n = \frac{E_1}{n^2} \qquad E_1 = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \simeq -13.6 \text{ eV}$$

$$|\Psi_{nlm_l m_s}^0\rangle = |\Psi_n^0(r)\rangle |\Psi_{lm_l m_s}^0\rangle$$

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

$$H'_{SO} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} = C_1 \frac{1}{r^3} \vec{S} \cdot \vec{L}$$

Perturbation matrix elements

$$\begin{aligned} \langle \Psi_{nlm_l m_s}^0 | H'_{SO} | \Psi_{n'l' m'_l s' m'_s}^0 \rangle &= C_1 \langle \Psi_n^0(r) | \frac{1}{r^3} | \Psi_n^0(r) \rangle \langle \Psi_{lm_l m_s}^0 | \vec{S} \cdot \vec{L} | \Psi_{l' m'_l s' m'_s}^0 \rangle \\ &= C_2 \langle \Psi_{lm_l m_s}^0 | \vec{S} \cdot \vec{L} | \Psi_{l' m'_l s' m'_s}^0 \rangle \end{aligned}$$

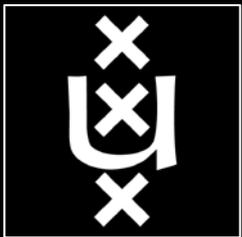
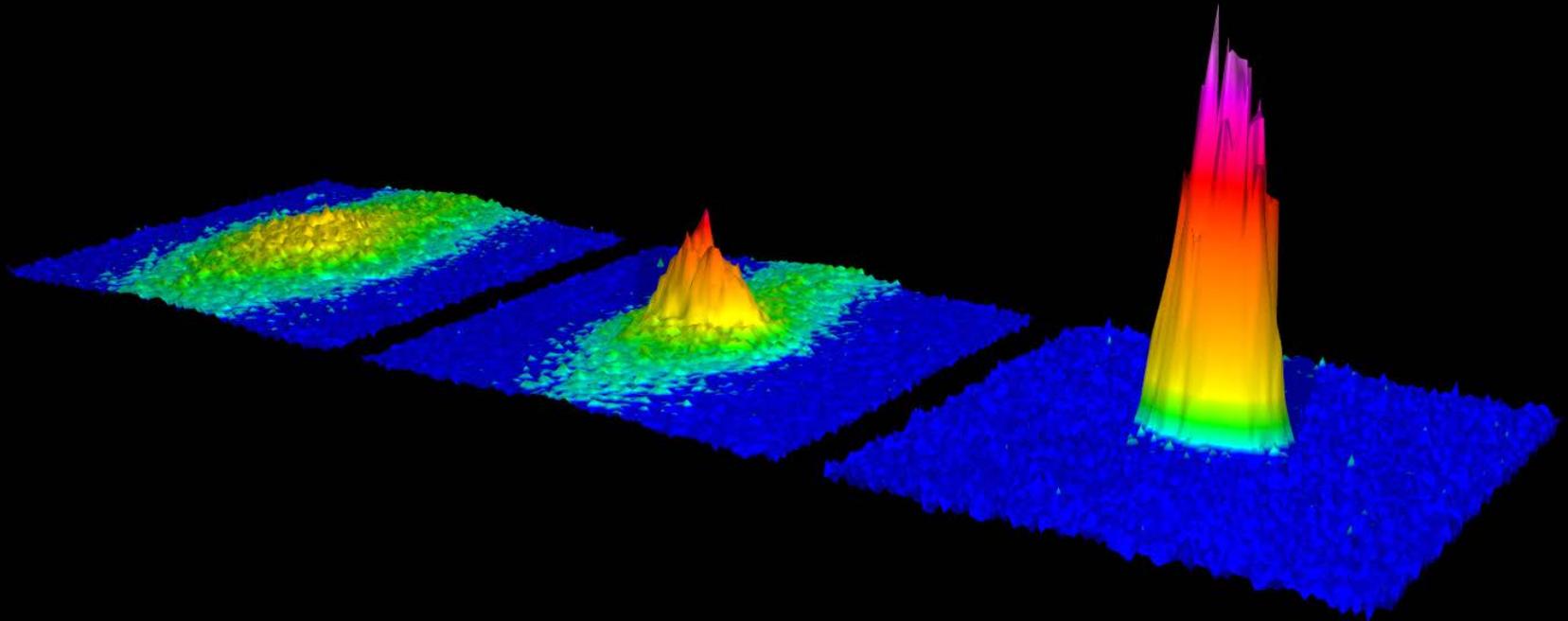
for chosen n

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	Griffiths 3 rd 5.1, 5.2
	Crystalline solids	5.3.2
	Time-independent perturbation theory	7.1, 7.2
today →	Structure of hydrogen	7.3 – 7.5
	Variational principle	8.1 – 8.3
	Time-dependent perturbation theory, atom-light interaction	11.1 – 11.4

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

Questions: schreck@StrontiumBEC.com

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 Griffiths 3rd 7.3
 - 1) relativistic correction 7.3.1
 - 2) spin-orbit coupling 7.3.2
 - origin
 - good basis for pert. theory
 - result
- 3) Lamb shift 7.3
- 4) Hyperfine structure 7.5
- 5) Zeeman effect 7.4

Fine structure: 1) relativistic correction

Reminder

Relativistic expression for kinetic energy:

$$E_{kin} = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \quad \text{with} \quad p = \frac{mv}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

$$E_{kin} = mc^2 \left[\sqrt{\left(\frac{p}{mc}\right)^2 + 1} - 1 \right] \stackrel{p \ll mc}{\downarrow} = mc^2 \left[\cancel{1} + \frac{1}{2} \left(\frac{p}{mc}\right)^2 - \frac{1}{8} \left(\frac{p}{mc}\right)^4 + \dots \cancel{-1} \right]$$

$$= \underbrace{\frac{p^2}{2m}}_{\text{non-relativistic, included in } H^0} - \underbrace{\frac{p^4}{8m^3 c^2}}_{= H'_r} + \dots$$

non-relativistic, included in H^0 $= H'_r$ lowest order relativistic correction

Use first order perturbation theory. For eigenstates in which perturbation is diagonal:

$$E_r^1 = \langle H'_r \rangle = -\frac{1}{8m^3 c^2} \langle \psi^0 | p^4 | \psi^0 \rangle \longrightarrow E_r^1 = -\frac{E_n^2}{2mc^2} \left[\frac{4n}{l + 1/2} - 3 \right]$$

Fine structure: 2) Spin-orbit coupling

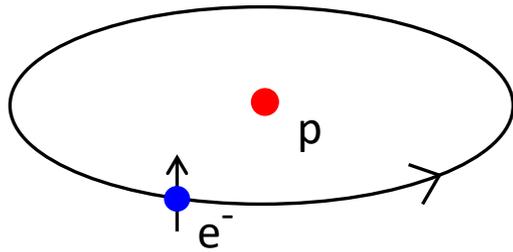
Reminder

Correctly treated using relativistic quantum mechanics (Dirac equation).

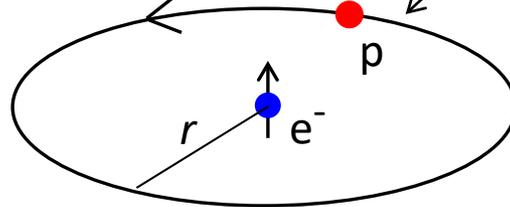
Here: rough, classical calculation

Consider hydrogen atom:

proton's
point of view



electron's
point of view



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 $B = \frac{\mu_0 I}{2r}$

Magnetic moment μ of e^- experiences shift in that B-field

$$H = -\vec{\mu} \cdot \vec{B}$$

B-field of proton:

Angular momentum of e^- : $L = rmv$

$$B = \frac{\mu_0 I}{2r} = \frac{\mu_0}{2r} \frac{ev}{2\pi r} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} L$$

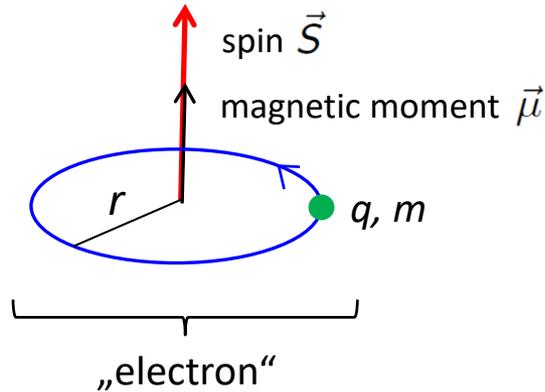
\uparrow
 $c = 1/\sqrt{\mu_0\epsilon_0}$

Magnetic moment of e^-

Reminder

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.



magnetic dipole moment:

$$\mu = I \cdot A = \frac{q}{T} \pi r^2$$

angular momentum ("spin"):

$$S = mvr = m \frac{2\pi r}{T} \cdot r$$

Gyromagnetic ratio = ratio between magnetic moment and angular momentum

$$\frac{\mu}{S} = \frac{q}{2m} \quad \text{notice: independent of } r$$

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).

$$\vec{\mu} = g \frac{q}{2m} \vec{S} \quad g_{\text{classical}} = 1$$

Quantum mechanical calculation

Reminder

(Special) relativistic quantum mechanics (Dirac equation) delivers

$$g_{el} = 2 \quad \text{where} \quad \vec{\mu} = g \frac{q}{2m} \vec{S} = -g \underbrace{\frac{|e|\hbar}{2m}}_{\mu_B \simeq 1.4 \frac{\text{MHz}}{\text{G}} h} \vec{S}$$

„Bohr magneton“

Vacuum fluctuations of electromagnetic field give rise to a \textperthousand -level correction:

$$g_{el}^{\text{QED}} = 2.002319304361\dots$$

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

Reminder

We know:

$$H = -\vec{\mu} \cdot \vec{B}$$

$$\vec{\mu} = -g \frac{|e|\hbar}{2m} \frac{\vec{S}}{\hbar} \quad ; \quad \vec{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \vec{L}$$

Putting it all together: $(g_{el} = 2 \text{ for simplicity})$

$$H = \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L}$$

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:

$$H'_{SO} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} = \text{constant} \frac{1}{r^3} \vec{S} \cdot \vec{L}$$

To do: determine spin-orbit correction by first order perturbation theory

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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

$$H' \propto \vec{S} \cdot \vec{L} = S_x L_x + S_y L_y + S_z L_z \quad \text{e.g.} \quad [L_y, L_z] = i\hbar L_x$$

Solution: good basis formed by eigenstates of complete set of commuting operators

$$H^0, L^2, S^2, J^2, J_z \quad \text{with} \quad \vec{J} = \vec{S} + \vec{L}$$

Proof: show that all commutators between these operators among each other and between these operators and H' are zero.

$$[L^2, J_z] = [L^2, S_z] + [L^2, L_z] = 0$$

$$[S^2, J_z] = [S^2, S_z] + [S^2, L_z] = 0$$

$$[J^2, J_z] = 0$$

Good basis states for perturbation theory

Proof: (continued)

$$[H'_{SO}, J_z] \propto [\vec{L} \cdot \vec{S}, J_z] \propto [J^2, J_z] - [L^2, J_z] - [S^2, J_z] = 0$$

Trick: use

$$J^2 = (\vec{L} + \vec{S}) \cdot (\vec{L} + \vec{S}) = L^2 + S^2 + 2\vec{L} \cdot \vec{S}$$

$$\longrightarrow \vec{L} \cdot \vec{S} = \frac{1}{2} (J^2 - L^2 - S^2)$$

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 :

$$|\psi^0_{l_s j m_j}\rangle = \sum_{m_l, m_s} c_{m_l, m_s} |\psi^0_{l m_l s m_s}\rangle$$

↑
Clebsch-Gordan coefficients (known, can e.g. be looked up in tables)

These are eigenstates of $\vec{L} \cdot \vec{S}$:

$$\begin{aligned} \vec{L} \cdot \vec{S} |\psi^0_{l_s j m_j}\rangle &= \frac{1}{2} (J^2 - L^2 - S^2) |\psi^0_{l_s j m_j}\rangle \\ &= \frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)] |\psi^0_{l_s j m_j}\rangle \end{aligned}$$

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

$$E_{SO}^1 = \langle \psi_{l s m_j}^0 | H'_{SO} | \psi_{l s m_j}^0 \rangle = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m c^2} \left\langle \frac{1}{r^3} \right\rangle \frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)]$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l+1/2)(l+1)n^3 a^3} \quad (\text{Griffiths})$$

Energy shift of hydrogen from spin-orbit coupling

$$E_{SO}^1 = \frac{(E_n)^2}{m c^2} \left[\frac{n [j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)} \right] \quad (\text{for } l \neq 0)$$

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)

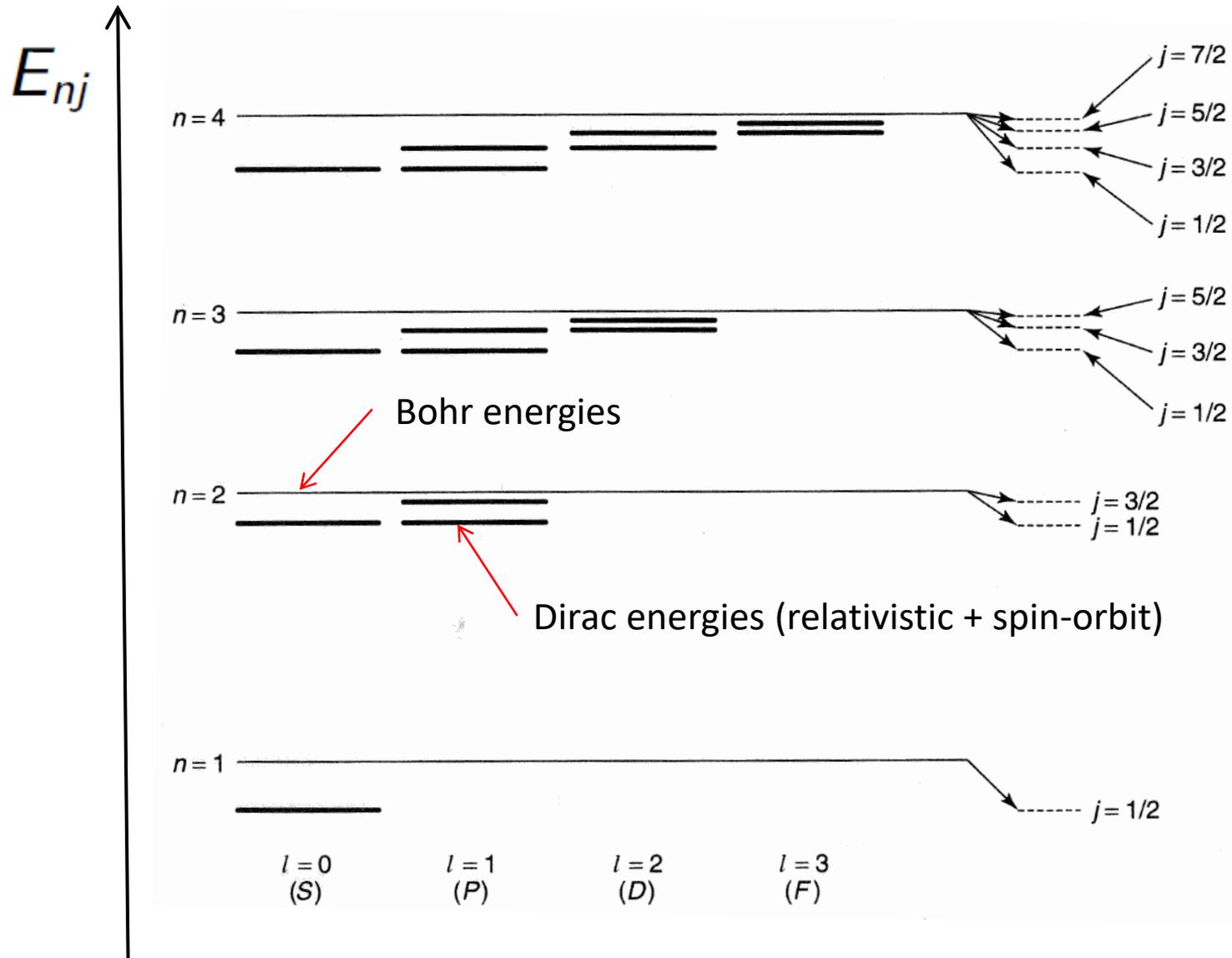
Energy of hydrogen levels with fine structure

$$E_{nj} = E_n + E_{fs}^1 = \frac{E_1}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j+1/2} - \frac{3}{4} \right) \right]$$

$$E_1 = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \simeq -13.6 \text{ eV}$$

$$j = l + s \quad ; \quad \alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137.036}$$

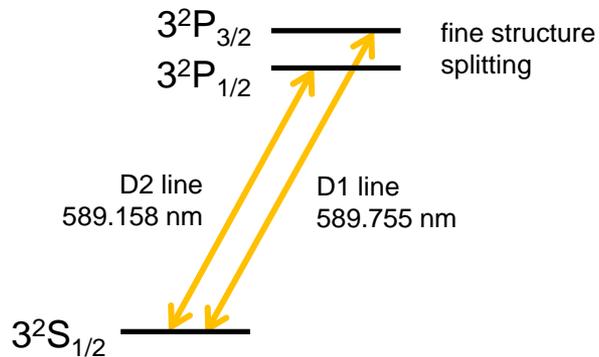
Hydrogen with fine-structure



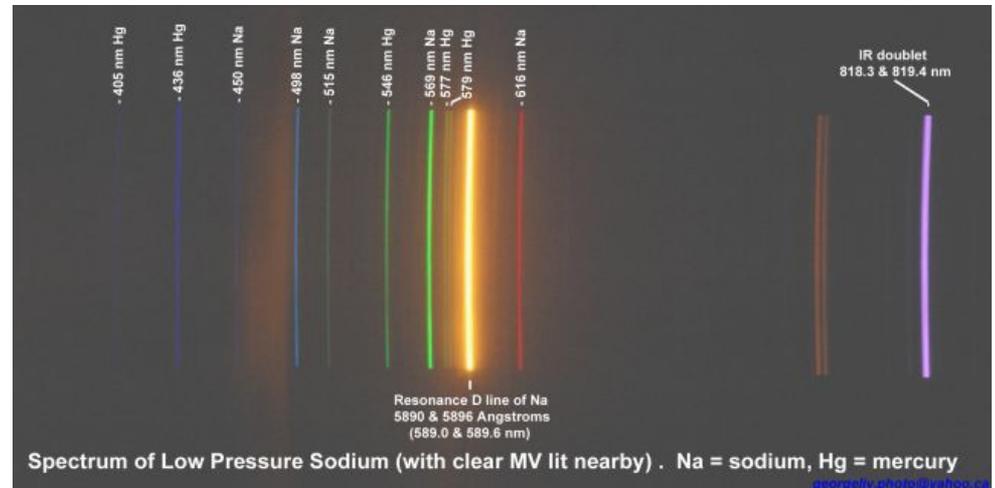
Na vapour lamp



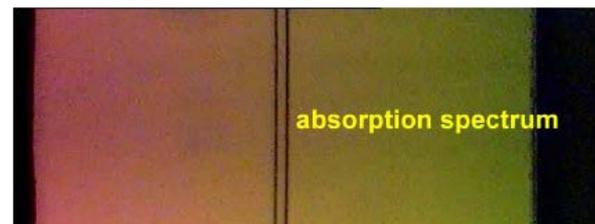
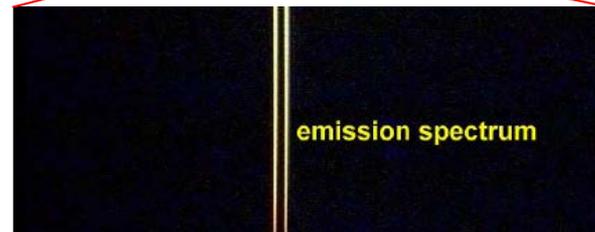
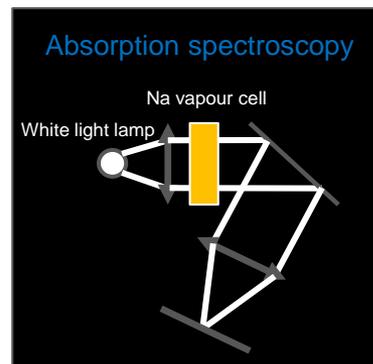
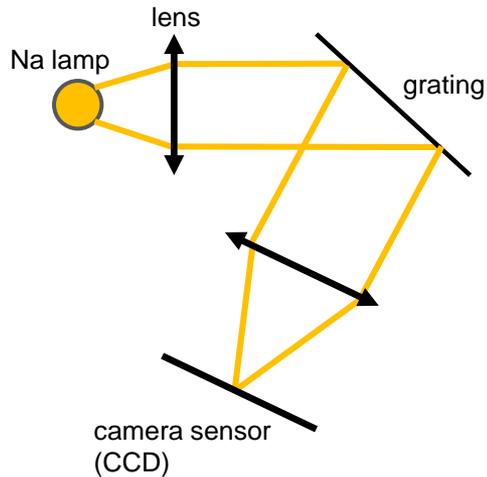
Fine structure in sodium spectrum



<https://www.lighting-gallery.net/gallery/displayimage.php?album=3248&pos=38&pid=110444>



Emission 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

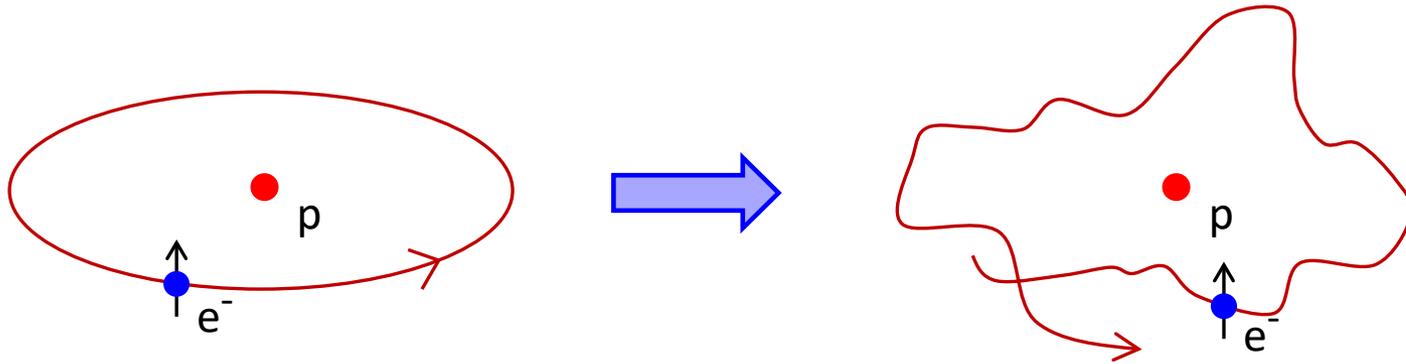
Plan of this section

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Lamb shift

The electromagnetic vacuum performs quantum fluctuations.

These fluctuating electromagnetic fields create forces on the e^- , changing its trajectory.

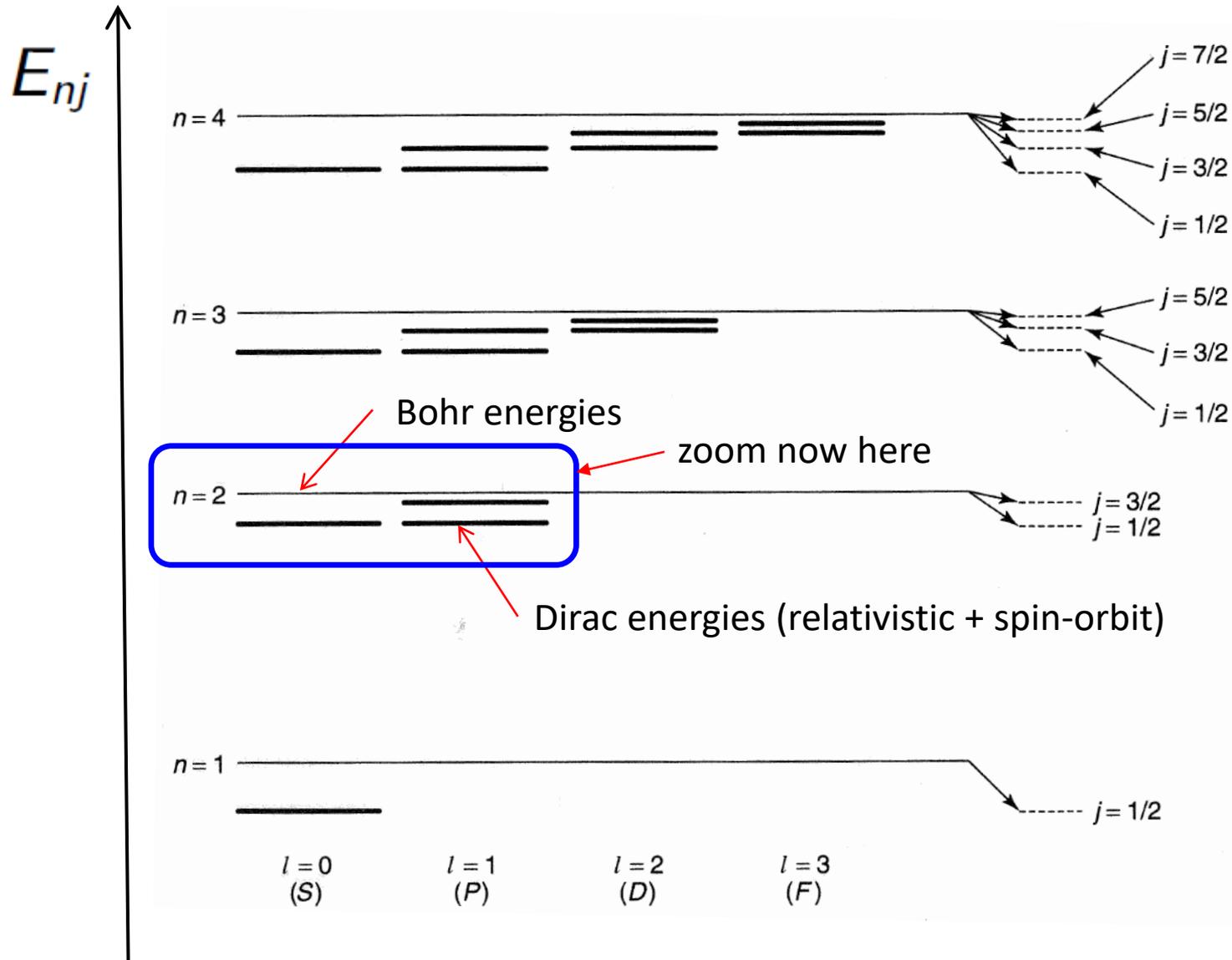


The e^- samples different regions of the Coulomb potential compared with what it would have sampled on its original trajectory.

\Rightarrow s states slightly shifted

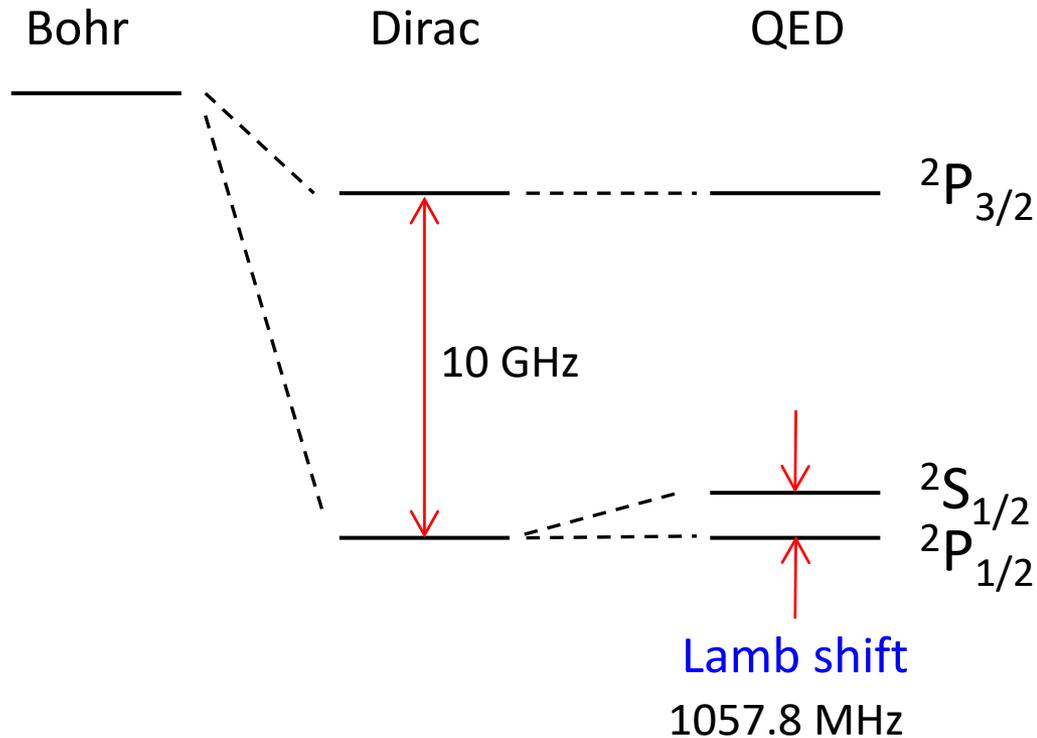
Hydrogen with fine-structure

Reminder



Lamb shift

n=2 levels of hydrogen



Lamb shift measured in 1947 by Lamb and Retherford.
Crucial in development of quantum electrodynamics (QED).

Overview of „*Structure of hydrogen*“

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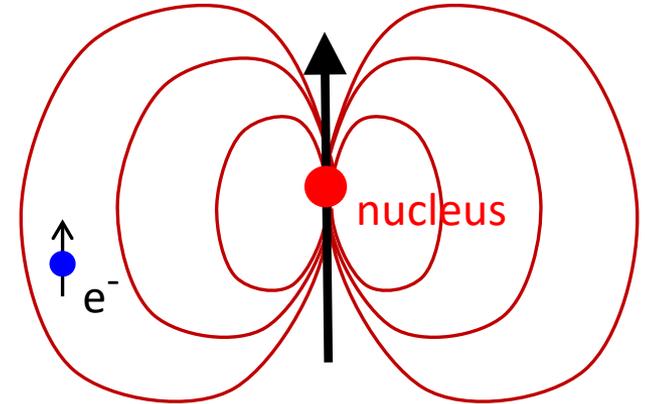
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origin
good basis for perturbation theory
result and discussion
- 5) Zeeman effect 7.4

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.



magnetic field of nucleus

Nuclear magnetic moment

$$\vec{\mu}_n = g_n \frac{|e|\hbar}{2m_p} \frac{\vec{I}}{\hbar}$$

compare to $\vec{\mu}_{el} = -g_{el} \frac{|e|\hbar}{2m_{el}} \frac{\vec{S}}{\hbar} = -g_{el} \mu_B \frac{\vec{S}}{\hbar}$

for proton $\vec{\mu}_n = \left(\frac{m_{el}}{m_p} \right) \mu_B \simeq h \cdot 0.762 \frac{\text{kHz}}{\text{G}}$

$g_n = g_p = 5.59$ $\simeq 1/1836$

\vec{I} : nuclear spin (operator) with eigenstates $|I, m_I\rangle$

as usual $I^2 |I, m_I\rangle = \hbar^2 I(I+1) |I, m_I\rangle$

$I_z |I, m_I\rangle = \hbar m_I |I, m_I\rangle$

Attention:

confusing fonts:

lower case l and upper case I look similar: l, I

Clearer in „hand writing“:

$$\mathcal{L}^2 |l, m_l\rangle = \hbar^2 l(l+1) |l, m_l\rangle$$

$$\mathcal{I}^2 |I, m_I\rangle = \hbar^2 I(I+1) |I, m_I\rangle$$

No problem here since lower case „l“ not used

Hyperfine structure

Interaction energy:

$$H'_{\text{hf}} = -\vec{\mu}_{\text{el}} \cdot \vec{B}_n \quad \text{with} \quad \vec{\mu}_{\text{el}} \simeq -\frac{|e|\hbar}{m_{\text{el}}} \vec{S} \quad (\text{for } g_{\text{el}} = 2)$$

Magnetic field created by nucleus (see e.g. Griffiths, Am. J. Phys. **50**, 698 (1982))

$$\vec{B}_n = \frac{\mu_0}{4\pi r^3} [3(\vec{\mu}_n \cdot \hat{r})\hat{r} - \vec{\mu}_n] + \frac{2\mu_0}{3} \vec{\mu}_n \delta^3(\vec{r}) \quad \text{with} \quad \vec{\mu}_n = g_p \frac{|e|\hbar}{2m_p} \vec{I}$$

\hat{r} : unit vector (operator) of electron position

Perturbation term:

$$H'_{\text{hf}} = \frac{\mu_0 g_p e^2}{8\pi m_p m_{\text{el}}} \frac{3(\vec{I} \cdot \hat{r})(\vec{S} \cdot \hat{r}) - \vec{I} \cdot \vec{S}}{r^3} + \frac{\mu_0 g_p e^2}{3m_p m_{\text{el}}} \vec{I} \cdot \vec{S} \delta^3(\vec{r})$$

First order perturbation theory (using good basis):

$$\langle H'_{\text{hf}} \rangle$$

Basis for perturbation theory

We know solutions of unperturbed Hamiltonian H^0 :

$$E_n = \frac{E_1}{n^2} \quad E_1 = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \simeq -13.6 \text{ eV}$$

$$|\Psi_{nlm_l m_s m_i}^0\rangle = |\Psi_n^0(r)\rangle |\Psi_{lm_l m_s m_i}^0\rangle$$

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

We can ignore l, m_l since we are only interested in ground state where $l = 0, m_l = 0$.

Perturbation matrix elements

$$\begin{aligned}
 \langle \Psi_n^0(r) | \langle \Psi_{nsm_s im_i}^0 | H'_{\text{hf}} | \Psi_n^0(r) \rangle | \Psi_{ns' m'_s i' m'_i}^0 \rangle &= \frac{\mu_0 g_p e^2}{8\pi m_p m_{\text{el}}} \underbrace{\left\langle \frac{3(\vec{l} \cdot \hat{r})(\vec{s} \cdot \hat{r}) - \vec{l} \cdot \vec{s}}{r^3} \right\rangle}_{= 0 \text{ for } l = 0 \text{ (exercise)}} + \\
 &+ \frac{\mu_0 g_p e^2}{3m_p m_{\text{el}}} \langle \Psi_{lm_l m_s im_i}^0 | \vec{l} \cdot \vec{s} | \Psi_{lm_l m_s im_i}^0 \rangle \underbrace{\langle \Psi_n^0(r) | \delta^3(\vec{r}) | \Psi_n^0(r) \rangle}_{= |\Psi_n^0(0)|^2}
 \end{aligned}$$

Hyperfine structure in hydrogen ground state

To do: first order perturbation theory with perturbation

$$H'_{\text{hf}} = \frac{\mu_0 g_p e^2}{3m_p m_{\text{el}}} \vec{I} \cdot \vec{S} |\psi(0)|^2$$

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 $l = 0$ state.

$$H^0, S^2, S_z, I^2, I_z \quad \text{as before do not lead to good basis, since } [S_z, \vec{I} \cdot \vec{S}] \neq 0$$

Suitable set of commuting observables for coupled S and I :

$$H^0, S^2, I^2, F^2, F_z \quad \text{with} \quad \vec{F} = \vec{I} + \vec{S}$$

Proof: as before, check commutators among those operators and among them and with coupling operator $\vec{I} \cdot \vec{S}$

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 :

$$|\psi_{sifm_f}^0\rangle = \sum_{m_s, m_i} c_{m_s, m_i} |\psi_{sm_s im_i}^0\rangle$$

↑ Clebsch-Gordan coefficients (known, can e.g. be looked up in tables)

These are eigenstates of $\vec{I} \cdot \vec{S}$:

$$\begin{aligned} \vec{I} \cdot \vec{S} |\psi_{sifm_f}^0\rangle &= \frac{1}{2} (F^2 - I^2 - S^2) |\psi_{sifm_f}^0\rangle \\ &= \frac{\hbar^2}{2} \underbrace{[f(f+1)]}_{2} \underbrace{[s(s+1) - i(i+1)]}_{-2\frac{3}{4}} |\psi_{sifm_f}^0\rangle \end{aligned}$$

since s and $i = 1/2$

{

2

S and I

parallel:

f=1

{

0

S and I anti-parallel:

f=0

$$\vec{I} \cdot \vec{S} |\psi_{sifm_f}^0\rangle = \begin{cases} +\frac{1}{4} \hbar^2 |\psi_{sifm_f}^0\rangle & \text{for } F = 1 & \text{(capital „F“ more common than „f“)} \\ -\frac{3}{4} \hbar^2 |\psi_{sifm_f}^0\rangle & \text{for } F = 0 \end{cases}$$

Hyperfine structure in hydrogen ground state

To do: first order perturbation theory with perturbation

$$\frac{\mu_0 g_p e^2}{3 m_p m_{e1}} \langle \vec{I} \cdot \vec{S} \rangle |\psi(0)|^2$$

For hydrogen ground state $|\psi_{100}(0)|^2 = \frac{1}{\pi a^3}$; $a = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$

with $\vec{I} \cdot \vec{S} |\psi_{sifm_f}^0\rangle = \begin{cases} +\frac{1}{4} \hbar^2 |\psi_{sifm_f}^0\rangle & \text{for } F = 1 \\ -\frac{3}{4} \hbar^2 |\psi_{sifm_f}^0\rangle & \text{for } F = 0 \end{cases}$

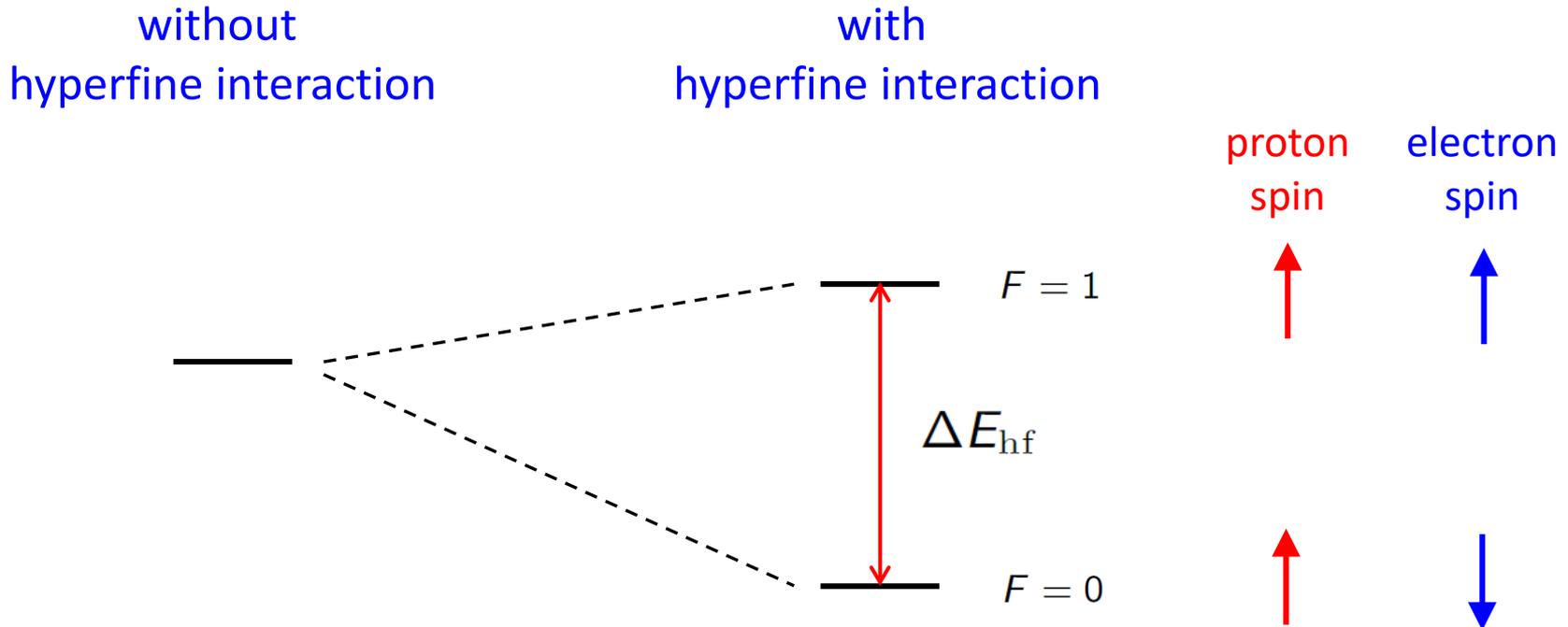
Hyperfine energy shift

$$E_{\text{hf}}^1 = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 a^4} \begin{cases} \cdot \frac{1}{4}, & \text{for } F = 1 \\ \cdot -\frac{3}{4}, & \text{for } F = 0 \end{cases}$$

Hyperfine splitting: energy difference the two states

$$\Delta E_{\text{hf}} = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 a^4} = h \cdot 1420 \text{MHz}$$

Energy level diagram of H ground state



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.

NGC 5457 (M 101)

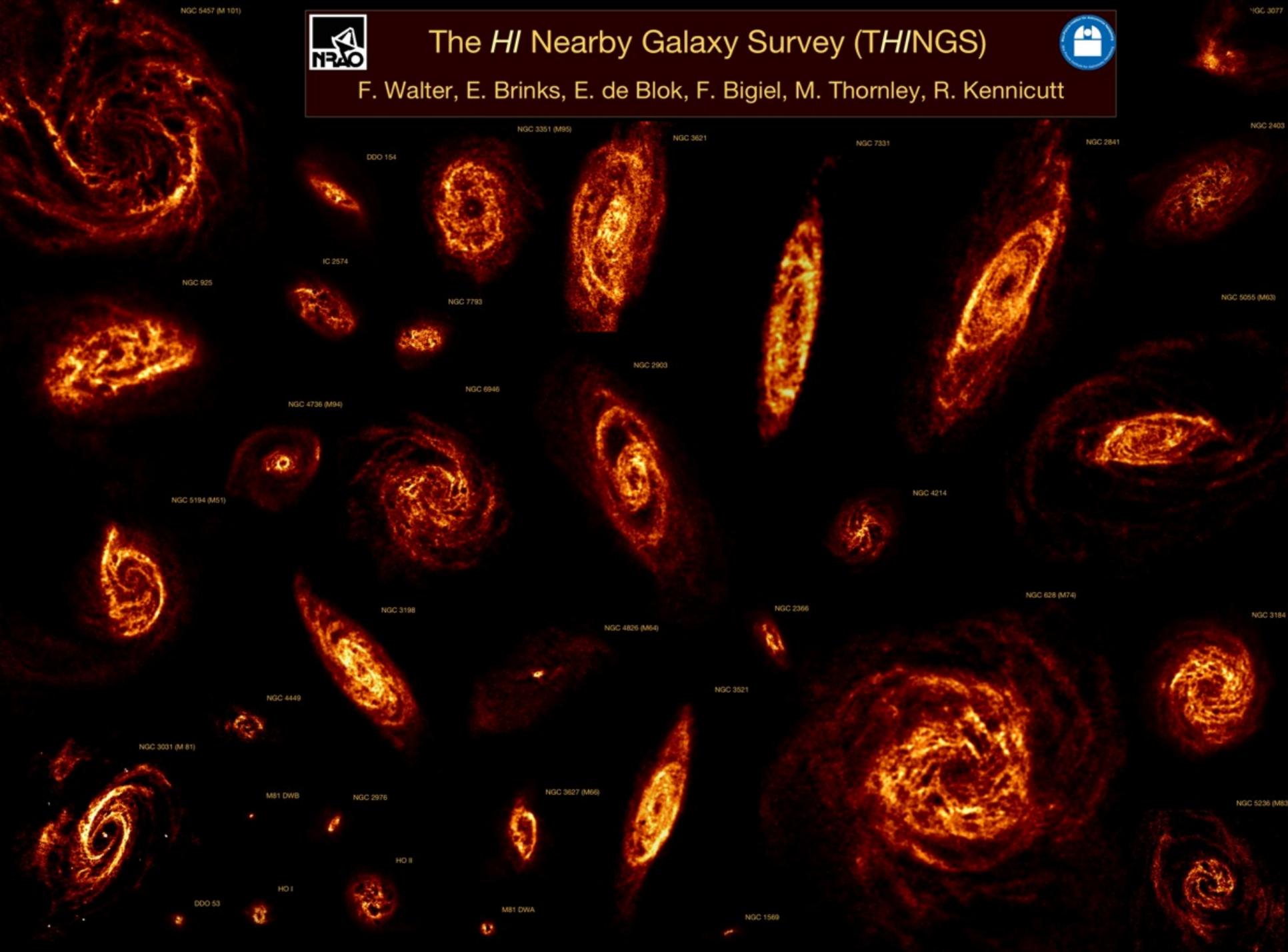


The *HI* Nearby Galaxy Survey (*THINGS*)



F. Walter, E. Brinks, E. de Blok, F. Bigiel, M. Thornley, R. Kennicutt

NGC 3077



NGC 2403

NGC 3351 (M95)

NGC 3621

NGC 7331

NGC 2841

DDO 154

IC 2574

NGC 7793

NGC 2903

NGC 5055 (M63)

NGC 925

NGC 6946

NGC 4738 (M94)

NGC 4214

NGC 5194 (M51)

NGC 3198

NGC 4826 (M64)

NGC 2366

NGC 628 (M74)

NGC 3184

NGC 4449

NGC 3521

NGC 3031 (M 81)

M81 DWB

NGC 2976

NGC 3627 (M96)

NGC 5236 (M83)

HO II

HO I

DDO 53

M81 DWA

NGC 1569

Radioastronomy of hydrogen

atomic hydrogen (blue)
8 microns (green)
24 microns (red)



Radioastronomy of hydrogen

Hydrogen gas (blue) in image of the post-merger pair of galaxies UGC 813 and UGC 816



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.

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

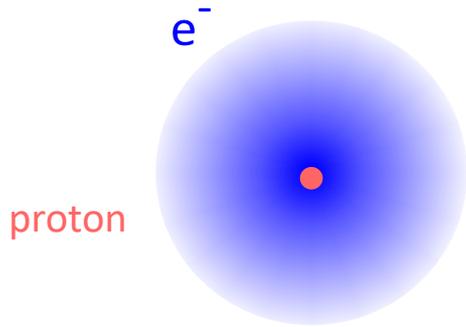
- 1) Intro
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 - strong B-field 7.4.2
 - all B-fields 7.4.3

Example: Atom in magnetic field

Reminder

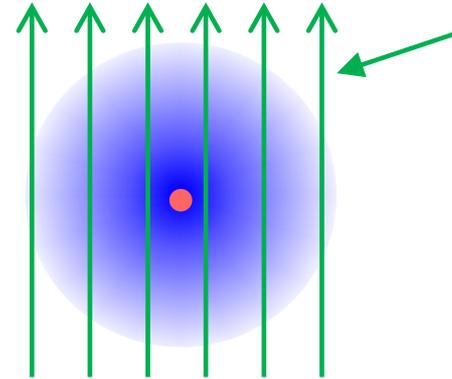
Starting point

unperturbed system

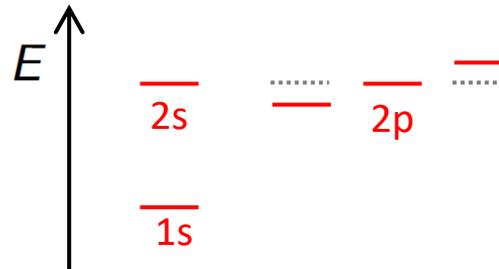
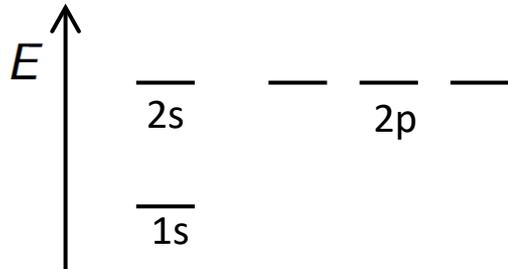


Modification

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

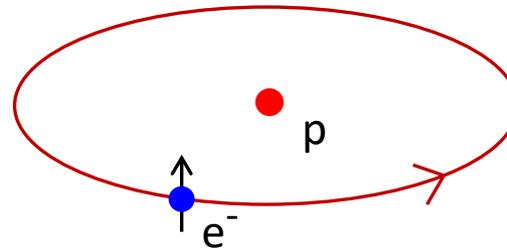
1) spin magnetic moment

$$\vec{\mu}_s = -g_{\text{el}}\mu_B \frac{\vec{S}}{\hbar}$$

2) orbital magnetic moment

e^- rotates around nucleus, giving rise to magnetic moment

$$\vec{\mu}_l = -\mu_B \frac{\vec{L}}{\hbar}$$



Atom in magnetic field: Zeeman effect

Total perturbation:

$$H'_z = -(\vec{\mu}_l + \vec{\mu}_s) \cdot \vec{B}_{\text{ext}} = \frac{\mu_B}{\hbar} (\vec{L} + 2\vec{S}) \cdot \vec{B}_{\text{ext}} \quad (g_{el} = 2 \text{ for simplicity})$$

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:

$$H^0 + H'_{\text{rel}} + H'_{\text{so}} + H'_z$$

↑ good quantum numbers: l, m_l, s, m_s
↑
∝ $\vec{L} \cdot \vec{S}$ → \vec{L} and \vec{S} coupled to \vec{J}
→ good quantum numbers: l, s, j, m_j

Two competing effects:

H'_{so} : internal B-field created by nucleus circling around e^- acts on e^- magnetic moment and locks \vec{L} and \vec{S} to \vec{J} .

Fine structure: 2) Spin-orbit coupling

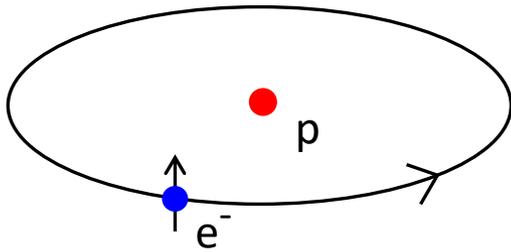
Reminder

Correctly treated using relativistic quantum mechanics (Dirac equation).

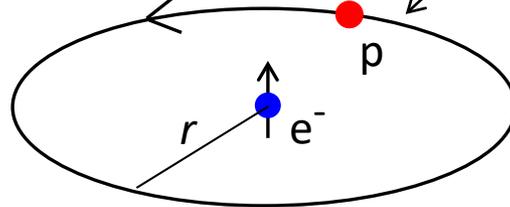
Here: rough, classical calculation

Consider hydrogen atom:

proton's
point of view



electron's
point of view



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 $B = \frac{\mu_0 I}{2r}$

Magnetic moment μ of e^- experiences shift in that B-field

$$H = -\vec{\mu} \cdot \vec{B}$$

B-field of proton:

Angular momentum of e^- : $L = rmv$

$$B = \frac{\mu_0 I}{2r} = \frac{\mu_0}{2r} \frac{ev}{2\pi r} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} L$$

\uparrow
 $c = 1/\sqrt{\mu_0\epsilon_0}$

Atom in magnetic field: Zeeman effect

Total perturbation:

$$H'_z = -(\vec{\mu}_l + \vec{\mu}_s) \cdot \vec{B}_{\text{ext}} = \frac{\mu_B}{\hbar} (\vec{L} + 2\vec{S}) \cdot \vec{B}_{\text{ext}} \quad (g_{el} = 2 \text{ for simplicity})$$

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:

$$H^0 + H'_{\text{rel}} + H'_{\text{so}} + H'_z$$

↑ ↑ good quantum numbers: l, m_l, s, m_s

↙ $\propto \vec{L} \cdot \vec{S}$ → \vec{L} and \vec{S} coupled to \vec{J}

→ good quantum numbers: l, s, j, m_j

Two competing effects:

H'_{so} : internal B-field created by nucleus circling around e^- acts on e^- magnetic moment and locks \vec{L} and \vec{S} to \vec{J} .

H'_z : external B-field acts on e^- spin and orbital magnetic moment and locks \vec{L} and \vec{S} to \vec{B} .

Atom in magnetic field: Zeeman effect

For $B_{\text{ext}} \ll B_{\text{int}}$: H'_{so} wins $\implies |\psi_{nlsjm_j}^0\rangle$ good states, perturbed by H'_z

$B_{\text{ext}} \gg B_{\text{int}}$: H'_z wins $\implies |\psi_{nls m_l m_s}^0\rangle$ good states, perturbed by H'_{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

Plan of this section

- | | |
|------------------------|-------------------------------|
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| - all B-fields | 7.4.3 |

Weak-field Zeeman effect $B_{ext} \ll B_{int}$

For $B_{ext} \ll B_{int}$: H'_{so} wins $\implies |\psi_{nlsjm_j}^0\rangle$ good states, perturbed by H'_z

$$= \frac{\mu_B}{\hbar} (L_z + 2S_z) B_{ext}$$

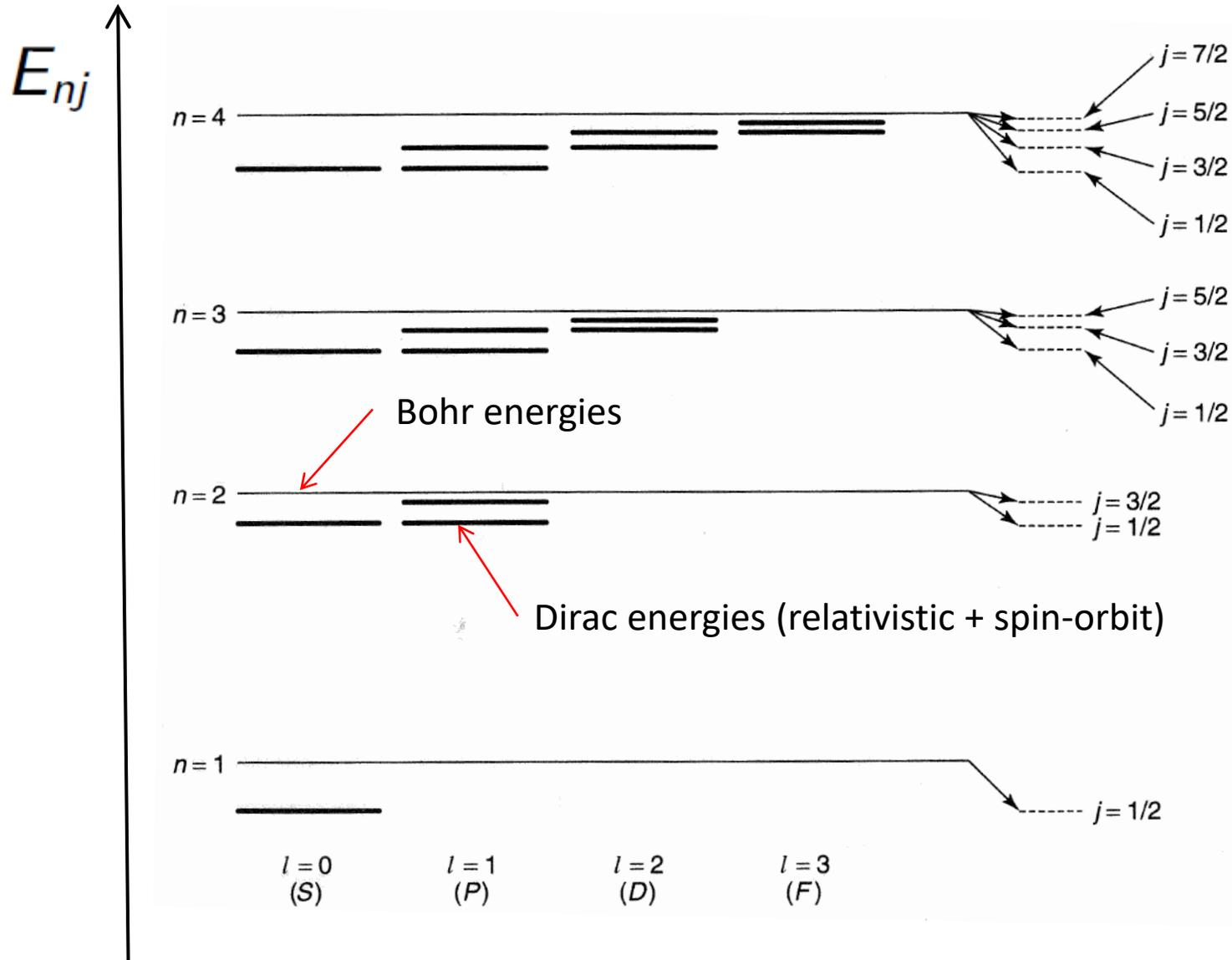
Need to determine matrix elements of H'_z with basis states $|\Psi_n^0(r)\rangle |\Psi_{lsjm_j}^0\rangle$

Simplifications

- independent of $r \implies$ spatial part of matrix element $\langle \Psi_n^0(r) | \Psi_n^0(r) \rangle = 1$
- Dirac energies + Lamb shift different for different n or different j .

Hydrogen with fine-structure

Reminder



Weak-field Zeeman effect $B_{ext} \ll B_{int}$

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- Dirac energies + Lamb shift different for different n or different j .

For weak fields perturbation always less than splitting between j - and n -manifolds.

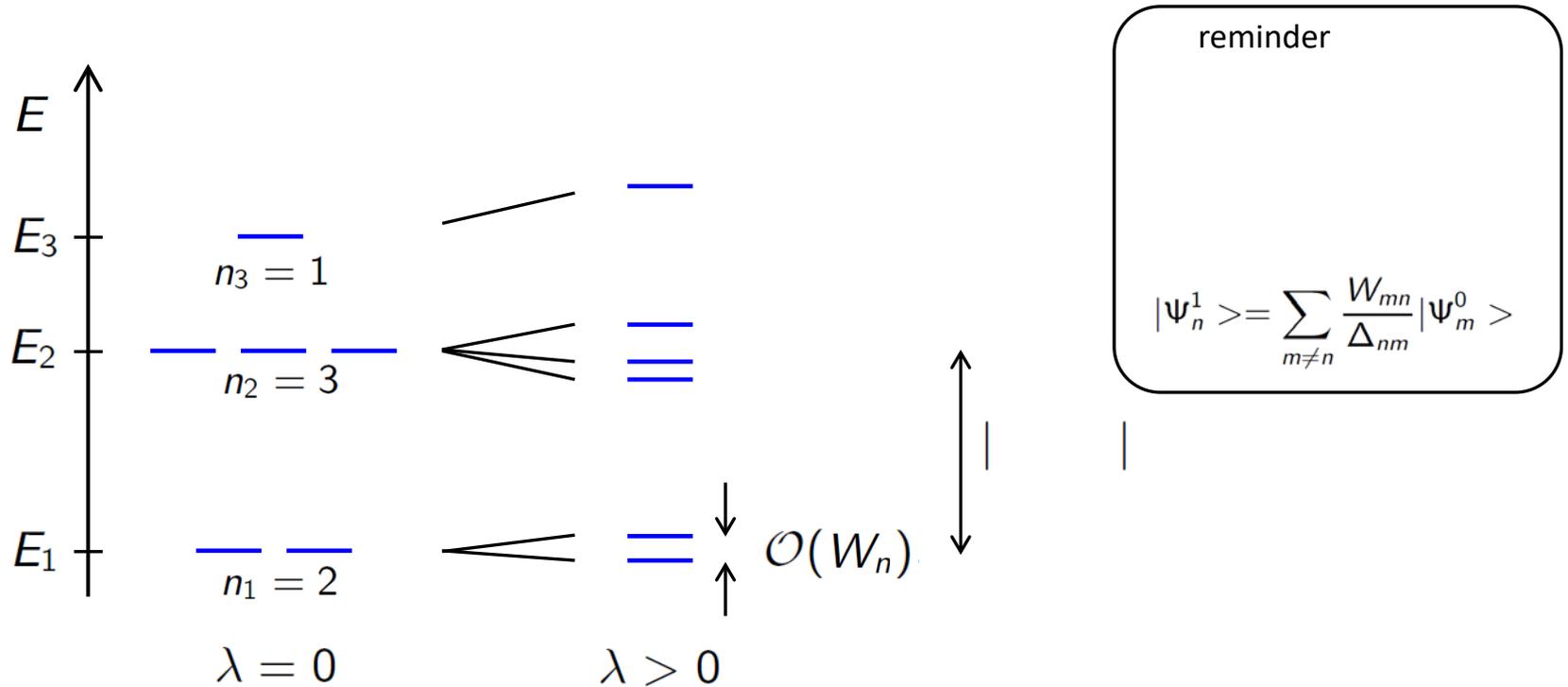
\implies no mixing of states with different j or n . Can consider (n,j) -manifolds individually.

Generalization to m manifolds

Reminder

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 ; $i \in \{1, \dots, m\}$



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 $B_{ext} \ll B_{int}$

For $B_{ext} \ll B_{int}$: H'_{so} wins $\implies |\psi_{nlsjm_j}^0\rangle$ good states, perturbed by H'_z

$$= \frac{\mu_B}{\hbar} (L_z + 2S_z) B_{ext}$$

Need to determine matrix elements of H'_z with basis states $|\Psi_n^0(r)\rangle |\Psi_{lsjm_j}^0\rangle$

Simplifications

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- 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:

$$|m_j\rangle \equiv |\Psi_{nlsjm_j}^0\rangle \quad \text{for chosen } n, l, s, j$$

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

$$W = \langle H'_z \rangle = \frac{\mu_B}{\hbar} (\langle J_z \rangle + \langle S_z \rangle) B_{\text{ext}}$$

$$\langle J_z \rangle = \langle \tilde{m}_j | J_z | m_j \rangle = \hbar m_j \delta_{\tilde{m}_j m_j}$$

What is $\langle S_z \rangle = \langle \tilde{m}_j | S_z | m_j \rangle$?

Expand: $|m_j\rangle = \sum_{m_l m_s} c_{m_l m_s}^{m_j} |m_l m_s\rangle$

$$\begin{aligned} \langle \tilde{m}_j | S_z | m_j \rangle &= \sum_{\tilde{m}_l \tilde{m}_s} \sum_{m_l m_s} c_{\tilde{m}_l \tilde{m}_s}^{\tilde{m}_j*} c_{m_l m_s}^{m_j} \underbrace{\langle \tilde{m}_l \tilde{m}_s | S_z | m_l m_s \rangle}_{= \delta_{\tilde{m}_l m_l} \delta_{\tilde{m}_s m_s} \hbar m_s} = \sum_{m_l m_s} c_{m_l m_s}^{\tilde{m}_j*} c_{m_l m_s}^{m_j} \hbar m_s \\ &= \delta_{\tilde{m}_l m_l} \delta_{\tilde{m}_s m_s} \hbar m_s \end{aligned}$$

$$W = \langle \tilde{m}_j | H'_z | m_j \rangle = \mu_B \left(\delta_{\tilde{m}_j m_j} m_j + \sum_{m_l m_s} c_{m_l m_s}^{\tilde{m}_j*} c_{m_l m_s}^{m_j} \hbar m_s \right) B_{\text{ext}}$$

One way to solve problem: look up $c_{m_l m_s}^{m_j}$, calculate matrix elements and diagonalize matrix

(Here: matrix is already diagonal because of Clebsch-Gordan property $c_{m_l m_s}^{m_j} = 0$ if $m_j \neq m_l + m_s$.)

Perturbation matrix

More elegant and powerful way to calculate $\langle S_z \rangle$ and then $W = \langle H'_z \rangle = \frac{\mu_B}{\hbar} (\langle J_z \rangle + \langle S_z \rangle) B_{\text{ext}}$

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: $L^2 = (J - S)^2 = J^2 + S^2 - 2\vec{J} \cdot \vec{S}$

$$\longrightarrow \vec{J} \cdot \vec{S} = -\frac{1}{2}(L^2 - J^2 - S^2)$$

Using $|\psi_{nlsm_j}^0\rangle$ 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:

$$E_z^1 = \frac{\mu_B}{\hbar} \langle J_z + S_z \rangle B = \left[1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right] m_j \mu_B B$$

$$E_z^1 = g_J m_j \mu_B B \quad ; \quad g_J = \left[1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right] \text{ Landé g-factor}$$

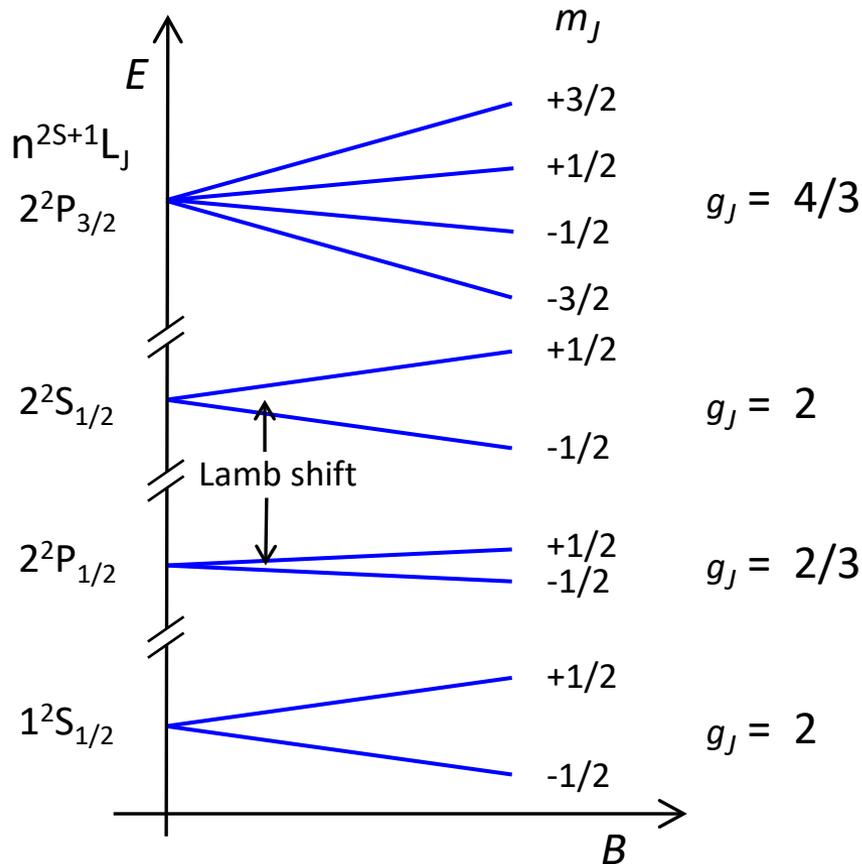
Weak-field Zeeman effect $B_{ext} \ll B_{int}$

Result

$$E_Z^1 = \underbrace{\mu_B g_j m_j}_{\text{magnetic moment of atom}} B_{ext}$$

magnetic moment of atom
not necessarily equal to e^- spin or orbital magnetic moment

Hydrogen



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:

$$E_z^1 = g_J m_j \mu_B B \quad ; \quad g_J = \left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right] \text{ Landé g-factor}$$

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Strong-field Zeeman effect $B_{\text{ext}} \gg B_{\text{int}}$

$|\psi_{nls m_l m_s}^0\rangle$ good states

Total Hamiltonian

$$H = \underbrace{H^0 + H'_z}_{\text{exactly solvable}} + \underbrace{H'_{\text{rel}} + H'_{\text{so}}}_{\text{two perturbations}}$$

Zeeman shifts:

$$H'_z = \frac{\mu_B}{\hbar} (L_z + g_e S_z) B_{\text{ext}} \longrightarrow E_z^1 = \mu_B (m_l + g_e m_s) B_{\text{ext}}$$

Calculate perturbation of H'_{rel} as before (same result since independent of spin).

Relativistic correction in 1st order

Reminder

$$E_{r,n}^1 = -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right]$$

Insert $\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a}$ and $\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l + \frac{1}{2}) n^3 a^2}$, 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 α^2 times smaller than E_n .

Strong-field Zeeman effect $B_{\text{ext}} \gg B_{\text{int}}$

$|\psi_{nls m_l m_s}^0\rangle$ good states

Total Hamiltonian

$$H = \underbrace{H^0 + H'_z}_{\text{exactly solvable}} + \underbrace{H'_{\text{rel}} + H'_{\text{so}}}_{\text{two perturbations}}$$

Zeeman shifts:

$$H'_z = \frac{\mu_B}{\hbar} (L_z + g_e S_z) B_{\text{ext}} \longrightarrow E_z^1 = \mu_B (m_l + g_e m_s) B_{\text{ext}}$$

Calculate perturbation of H'_{rel} as before (same result since independent of spin).

Calculate perturbation by H'_{so}

$$E_{\text{so}}^1 = \underbrace{\left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2} \left\langle \frac{1}{r^3} \right\rangle}_{\text{as before}} \langle \vec{S} \cdot \vec{L} \rangle$$

Spin-orbit coupling in first order

Reminder

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

$$E_{SO}^1 = \langle \psi_{lsm_j}^0 | H'_{SO} | \psi_{lsm_j}^0 \rangle = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{mc^2} \left\langle \frac{1}{r^3} \right\rangle \frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)]$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l+1/2)(l+1)n^3 a^3} \quad (\text{Griffiths})$$

Energy shift of hydrogen from spin-orbit coupling

$$E_{SO}^1 = \frac{(E_n)^2}{mc^2} \left[\frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)} \right] \quad (\text{for } l \neq 0)$$

Strong-field Zeeman effect $B_{\text{ext}} \gg B_{\text{int}}$

$|\psi_{nls m_l m_s}^0\rangle$ good states

Total Hamiltonian

$$H = \underbrace{H^0 + H'_z}_{\text{exactly solvable}} + \underbrace{H'_{\text{rel}} + H'_{\text{so}}}_{\text{two perturbations}}$$

Zeeman shifts:

$$H'_z = \frac{\mu_B}{\hbar} (L_z + g_e S_z) B_{\text{ext}} \longrightarrow E_z^1 = \mu_B (m_l + g_e m_s) B_{\text{ext}}$$

Calculate perturbation of H'_{rel} as before (same result since independent of spin).

Calculate perturbation by H'_{so}

$$E_{\text{so}}^1 = \underbrace{\left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2} \left\langle \frac{1}{r^3} \right\rangle}_{\text{as before}} \langle \vec{S} \cdot \vec{L} \rangle$$
$$\langle \vec{S} \cdot \vec{L} \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle = \hbar^2 m_l m_s$$

Sum up both perturbations ($H'_{\text{rel}} + H'_{\text{so}}$):

$$E_{\text{fs}}^1 = \frac{E_1}{n^3} \alpha^2 \left\{ \frac{3}{4n} - \left[\frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)} \right] \right\}$$

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Zeeman effect for all B_{ext}

Perturbation can not be separated in small and big contribution

$$\longrightarrow H' = H'_{\text{fs}} + H'_z$$

Degenerate perturbation theory: need to solve

$$W\vec{\alpha} = E^1\vec{\alpha} \quad ; \quad W_{pq} = \langle \psi_p^0 | H' | \psi_q^0 \rangle$$

i.e. we need to diagonalize W

We are free to choose basis states. W is simpler in basis $\{ |\Psi_{nlsjm_j}^0 \rangle \}$

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

$$E_{nj} = E_n + E_{fs}^1 = \frac{E_1}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j+1/2} - \frac{3}{4} \right) \right]$$

$$E_1 = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \simeq -13.6 \text{ eV}$$

$$j = l + s \quad ; \quad \alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137.036}$$

Zeeman effect for all B_{ext}

Perturbation can not be separated in small and big contribution

$$\longrightarrow H' = H'_{\text{fs}} + H'_z$$

Degenerate perturbation theory: need to solve

$$W\vec{\alpha} = E^1\vec{\alpha} \quad ; \quad W_{pq} = \langle \psi_p^0 | H' | \psi_q^0 \rangle$$

i.e. we need to diagonalize W

We are free to choose basis states. W is simpler in basis $\{ |\Psi_{nlsm_j}^0 \rangle \}$

We already calculated

$$(W_{\text{fs}})_{pq} = \langle H'_{\text{fs}} \rangle_{pq} = \frac{E_1}{n^4} \alpha^2 \left(\frac{n}{j + 1/2} - \frac{3}{4} \right)$$

We need

$$(W_z)_{pq} = \langle H'_z \rangle_{pq} = \frac{\mu_B}{\hbar} B_{\text{ext}} \langle L_z + 2S_z \rangle_{pq}$$

Zeeman effect for all B_{ext}

We need

$$(W_z)_{pq} = \langle H'_z \rangle_{pq} = \frac{\mu_B}{\hbar} B_{\text{ext}} \underbrace{\langle L_z + 2S_z \rangle_{pq}}_{= \hbar(m_l + 2m_s) \text{ in basis } \{ |\psi_{nlm_l m_s}^0 \rangle \}}$$

but we need it in basis $\{ |\Psi_{nlsjm_j}^0 \rangle \}$

Express $|\psi_{nlsjm_j}^0 \rangle$ in terms of $|\psi_{nlm_l m_s}^0 \rangle$

$$|\psi_{nlsjm_j}^0 \rangle = \sum_{m_l, m_s} c_{m_l m_s}^{jm_j} |\psi_{nlm_l m_s}^0 \rangle$$

calculate

look Clebsch-Gordan coefficients up e.g. in tables

$$\begin{aligned} \langle \psi_{nls\tilde{j}\tilde{m}_j} | L_z + 2S_z | \psi_{nlsjm_j} \rangle &= \sum_{\tilde{m}_l, \tilde{m}_s} \sum_{m_l, m_s} c_{\tilde{m}_l \tilde{m}_s}^{\tilde{j}\tilde{m}_j*} c_{m_l m_s}^{jm_j} \underbrace{\langle \psi_{nl\tilde{m}_l \tilde{m}_s}^0 | L_z + 2S_z | \psi_{nlm_l m_s}^0 \rangle}_{\hbar(m_l + 2m_s) \delta_{\tilde{m}_l m_l} \delta_{\tilde{m}_s m_s}} \\ &= \sum_{m_l, m_s} c_{\tilde{m}_l \tilde{m}_s}^{\tilde{j}\tilde{m}_j*} c_{m_l m_s}^{jm_j} \hbar(m_l + 2m_s) \end{aligned}$$

Which gives us

$$(W_z)_{pq} = \langle H'_z \rangle_{pq} = \frac{\mu_B}{\hbar} B_{\text{ext}} \langle L_z + 2S_z \rangle_{pq} \text{ in basis } \{ |\Psi_{nlsjm_j}^0 \rangle \}$$

Perturbation for all B_{ext}

Perturbation can not be separated in small and big contribution

$$\longrightarrow H' = H'_{\text{fs}} + H'_z$$

Degenerate perturbation theory: need to solve

$$W\vec{\alpha} = E^1\vec{\alpha} \quad ; \quad W_{pq} = \langle \psi_p^0 | H' | \psi_q^0 \rangle$$

i.e. we need to diagonalize W

We are free to choose basis states. W is simpler in basis $\{ |\Psi_{nlsjm_j}^0 \rangle \}$

We already calculated

$$(W_{\text{fs}})_{pq} = \langle H'_{\text{fs}} \rangle_{pq} = \frac{E_1}{n^4} \alpha^2 \left(\frac{n}{j + 1/2} - \frac{3}{4} \right)$$

And now we have

$$\begin{aligned} (W_z)_{pq} &= \langle H'_z \rangle_{pq} = \frac{\mu_B}{\hbar} B_{\text{ext}} \langle L_z + 2S_z \rangle_{pq} \quad \text{in basis } \{ |\Psi_{nlsjm_j}^0 \rangle \} \\ &= \sum_{m_l, m_s} c_{\tilde{m}_l \tilde{m}_s}^{\tilde{j} \tilde{m}_j^*} c_{m_l m_s}^{jm_j} \hbar (m_l + 2m_s) \end{aligned}$$

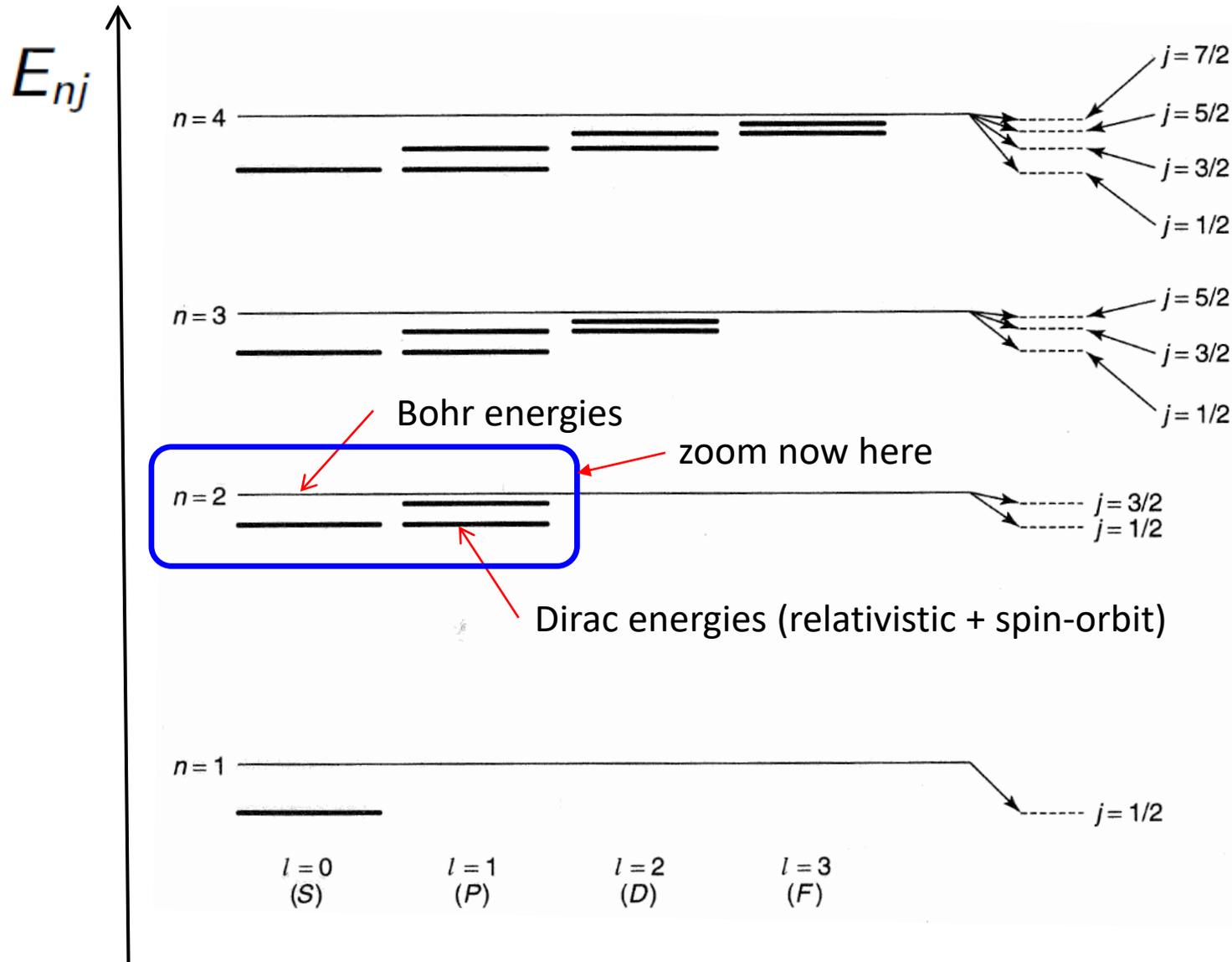
Zeeman effect for H $n = 2$ states

To note down matrix W , we need to specify order of basis states.

We limit ourselves to the $n=2$ states of hydrogen

Hydrogen with fine-structure

Reminder



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

exact eigenstates for zero field \rightarrow $|jm_j\rangle = \sum_{m_l, m_s} c_{m_l m_s} \underbrace{|lm_l\rangle |sm_s\rangle}_{\text{exact eigenstates for infinite field}}$

notice: $m_j = m_l + m_s$ for each component

With this rule you can find the components that can contribute

$$l = 0 \left\{ \begin{array}{l} \psi_1 \equiv |\frac{1}{2} \frac{1}{2}\rangle = |00\rangle |\frac{1}{2} \frac{1}{2}\rangle, \\ \psi_2 \equiv |\frac{1}{2} \frac{-1}{2}\rangle = |00\rangle |\frac{1}{2} \frac{-1}{2}\rangle, \end{array} \right.$$

$$l = 1 \left\{ \begin{array}{l} \psi_3 \equiv |\frac{3}{2} \frac{3}{2}\rangle = |11\rangle |\frac{1}{2} \frac{1}{2}\rangle, \\ \psi_4 \equiv |\frac{3}{2} \frac{-3}{2}\rangle = |1-1\rangle |\frac{1}{2} \frac{-1}{2}\rangle, \\ \psi_5 \equiv |\frac{3}{2} \frac{1}{2}\rangle = \sqrt{2/3}|10\rangle |\frac{1}{2} \frac{1}{2}\rangle + \sqrt{1/3}|11\rangle |\frac{1}{2} \frac{-1}{2}\rangle, \\ \psi_6 \equiv |\frac{1}{2} \frac{1}{2}\rangle = -\sqrt{1/3}|10\rangle |\frac{1}{2} \frac{1}{2}\rangle + \sqrt{2/3}|11\rangle |\frac{1}{2} \frac{-1}{2}\rangle, \\ \psi_7 \equiv |\frac{3}{2} \frac{-1}{2}\rangle = \sqrt{1/3}|1-1\rangle |\frac{1}{2} \frac{1}{2}\rangle + \sqrt{2/3}|10\rangle |\frac{1}{2} \frac{-1}{2}\rangle, \\ \psi_8 \equiv |\frac{1}{2} \frac{-1}{2}\rangle = -\sqrt{2/3}|1-1\rangle |\frac{1}{2} \frac{1}{2}\rangle + \sqrt{1/3}|10\rangle |\frac{1}{2} \frac{-1}{2}\rangle. \end{array} \right.$$

Perturbation for all B_{ext}



Perturbation can not be separated in small and big contribution

$$\longrightarrow H' = H'_{\text{fs}} + H'_z$$

Degenerate perturbation theory: need to solve

$$W\vec{\alpha} = E^1\vec{\alpha} \quad ; \quad W_{pq} = \langle \psi_p^0 | H' | \psi_q^0 \rangle$$

i.e. we need to diagonalize W

We are free to choose basis states. W is simpler in basis $\{ |\Psi_{nlsjm_j}^0 \rangle \}$

We already calculated

$$(W_{\text{fs}})_{pq} = \langle H'_{\text{fs}} \rangle_{pq} = \frac{E_1}{n^4} \alpha^2 \left(\frac{n}{j + 1/2} - \frac{3}{4} \right)$$

And now we have

$$\begin{aligned} (W_z)_{pq} &= \langle H'_z \rangle_{pq} = \frac{\mu_B}{\hbar} B_{\text{ext}} \langle L_z + 2S_z \rangle_{pq} \quad \text{in basis } \{ |\Psi_{nlsjm_j}^0 \rangle \} \\ &= \sum_{m_l, m_s} c_{\tilde{m}_l \tilde{m}_s}^{\tilde{j} \tilde{m}_j^*} c_{m_l m_s}^{jm_j} \hbar (m_l + 2m_s) \end{aligned}$$

First order perturbation theory

Perturbation matrix:

$$W = W_{fs} + W_z$$

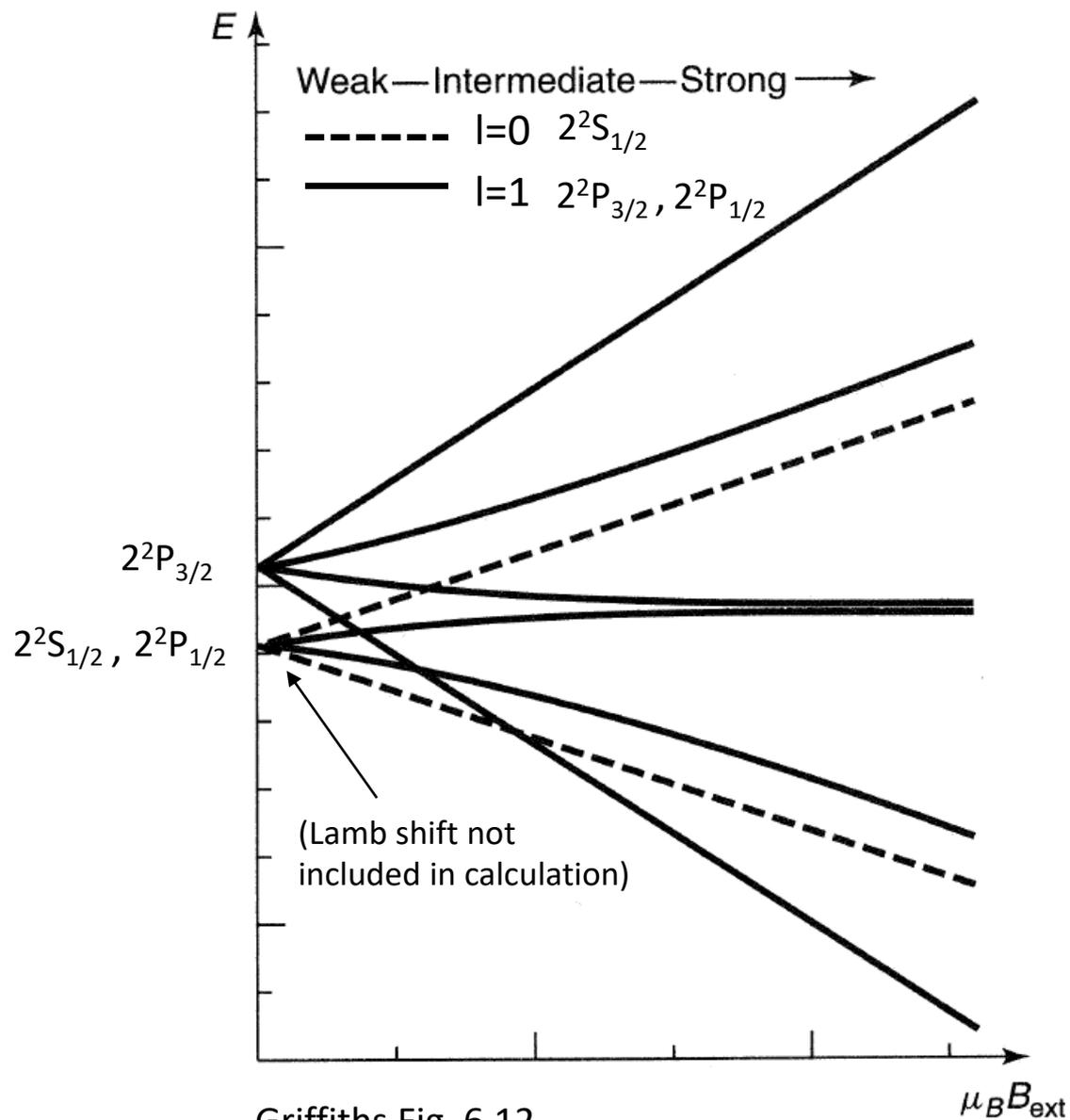
$$\langle \Psi_A | W | \Psi_B \rangle = \begin{matrix} \Psi_A = \Psi_1 & \Psi_2 & \Psi_3 & \Psi_4 & \Psi_5 & \Psi_6 & \Psi_7 & \Psi_8 & \Psi_B = \\ \left(\begin{array}{cccccccc} 5\gamma - \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5\gamma + \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \gamma - 2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma + 2\beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \gamma - \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma - \frac{1}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \gamma + \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma + \frac{1}{3}\beta \end{array} \right) & \begin{array}{l} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \\ \Psi_5 \\ \Psi_6 \\ \Psi_7 \\ \Psi_8 \end{array} \end{matrix}$$

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 $|\psi^0\rangle = \sum_{i=1}^n \alpha_i^0 |\psi_i^0\rangle$ solve

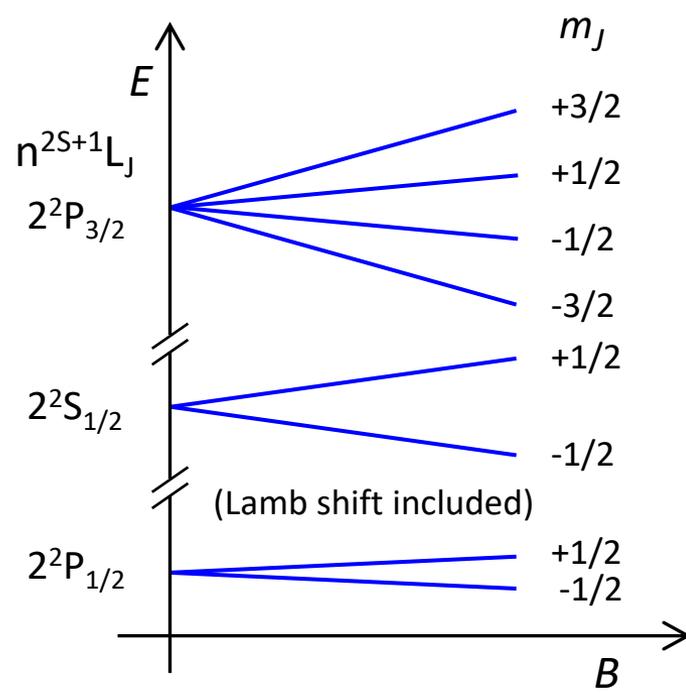
$$W\vec{\alpha} = E^1\vec{\alpha}$$

Zeeman effect for H $n = 2$ states



Griffiths Fig. 6.12

Compare to weak field result:



Interpretation in weak field

- L and S strongly coupled to J
- J states split in $2J+1$ m_J states

Zeeman effect for H $n = 2$ states

Interpretation in strong field

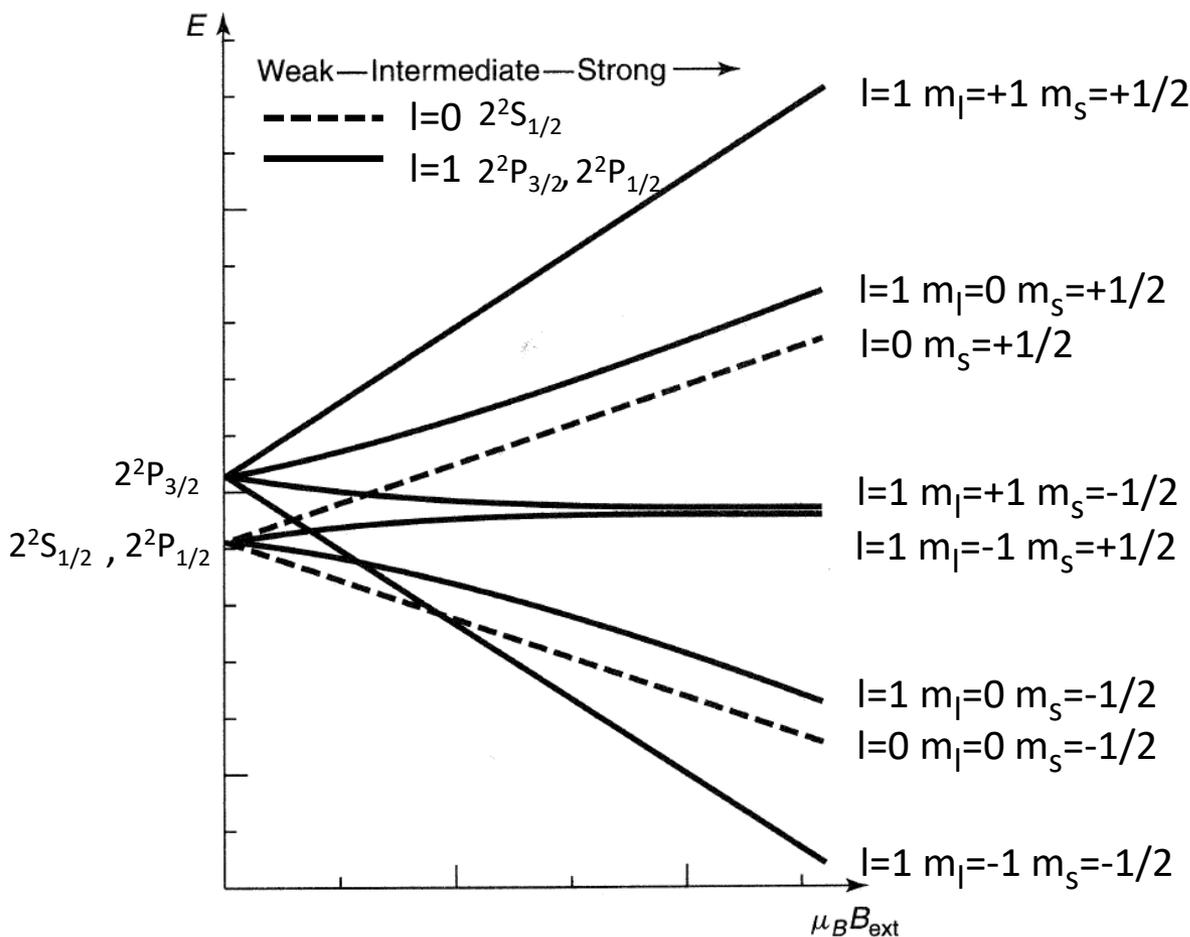
- L and S strongly coupled to B-field
- spin and orbital magnetic momenta just add up

- spin and orbital magnetic momenta here have same magnitude, 1 Bohr magneton:

$$E_z^1 = \mu_B (m_l + g_e m_s) B_{\text{ext}}$$

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.

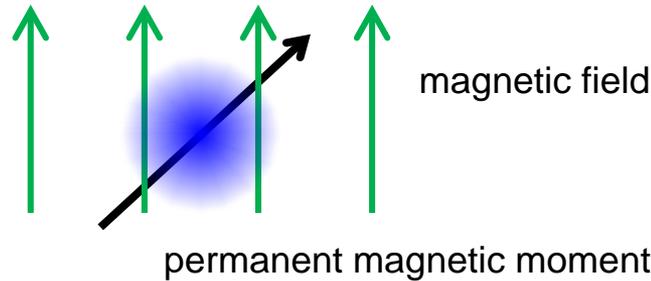
Hyperfine structure

- 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

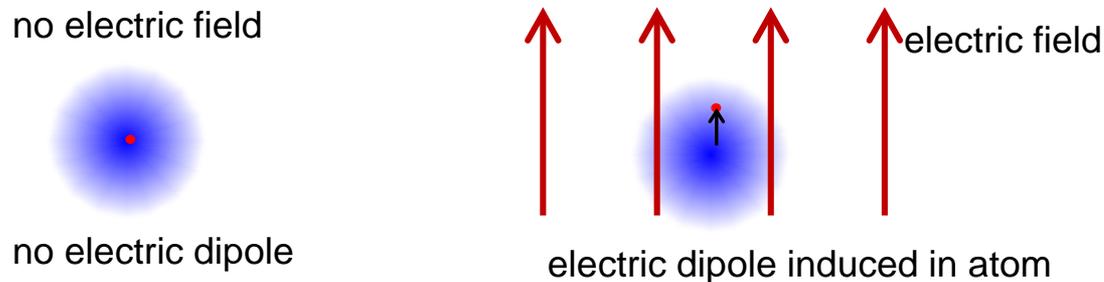
B-field couples to magnetic moment of atom



Stark effect

E-field induces electric dipole moment in atom

Polarized atom experiences energy shift in that field



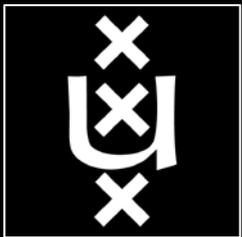
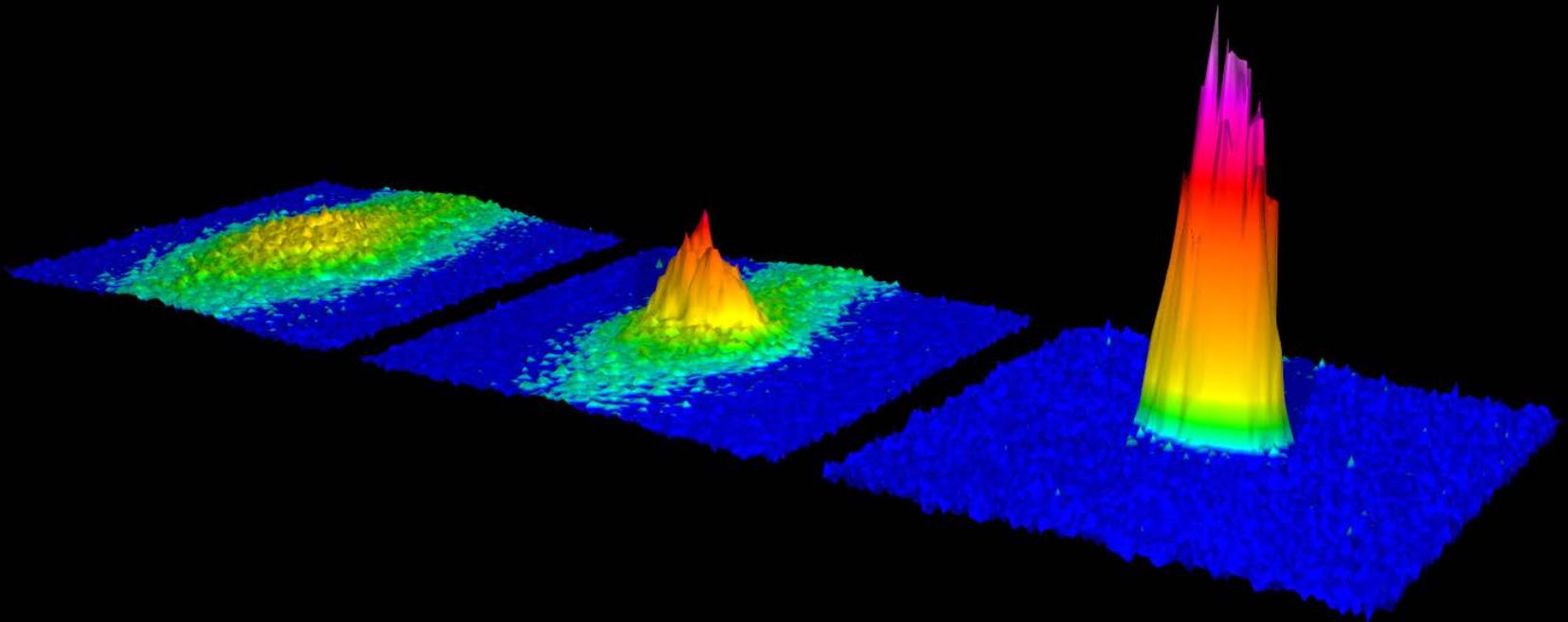
These are all static effects. In addition effects from time-dependent fields (AC-Stark effect, photon absorption and emission)

→ time-dependent perturbation theory (next lecture)

Quantum mechanics 3

Structure of matter

Lecture 13



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

Griffiths 3rd 5.1, 5.2

Crystalline solids

5.3.2

Time-independent perturbation theory

7.1, 7.2

Structure of hydrogen

7.3 – 7.5

Variational principle

8.1 – 8.3

Time-dependent perturbation theory, atom-light interaction

11.1 – 11.4

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 Griffiths 3rd 8.1
- 2) Examples
 - harmonic oscillator example 8.1
 - delta function potential example 8.2
- 3) Applications
 - helium atom 8.2
 - hydrogen molecule ion 8.3

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

be $\{|\psi_n\rangle\}$ a complete, orthonormal basis ; $H|\psi_n\rangle = E_n|\psi_n\rangle$

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle$$

Normalization:

$$1 = \langle \psi | \psi \rangle = \sum_{n,m} c_n^* c_m \underbrace{\langle \psi_n | \psi_m \rangle}_{\delta_{n,m}} = \sum_n |c_n|^2$$

Expectation value of H

$$\sum_{n,m} c_n^* c_m \langle \psi_n | H | \psi_m \rangle = \sum_{n,m} c_n^* c_m E_m \underbrace{\langle \psi_n | \psi_m \rangle}_{\delta_{n,m}} \geq E_{gs} \sum_n |c_n|^2 = E_{gs}$$

$E_{gs} \leq E_n$ 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 :

$$\psi(x) = A e^{-bx^2}$$

Normalization:

$$1 \stackrel{!}{=} A^2 \int e^{-2bx^2} dx = A^2 \sqrt{\frac{\pi}{2b}} \quad \Longrightarrow \quad A = \left(\frac{2b}{\pi} \right)^{1/4}$$

$\langle H \rangle$:

$$\langle T \rangle = -\frac{\hbar^2}{2m} A^2 \int e^{-bx^2} \frac{d^2}{dx^2} \left(e^{-bx^2} \right) dx = \frac{\hbar^2 b}{2m}$$

$$\langle V \rangle = \frac{1}{2} m \omega^2 A^2 \int e^{-2bx^2} x^2 dx = \frac{m \omega^2}{8b}$$

$$\Longrightarrow \quad \langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m \omega^2}{8b}$$

Example 1: the harmonic oscillator ground state

$$\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$$

Minimize $\langle H \rangle$:

$$\frac{d}{db} \langle H \rangle = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \quad \Longrightarrow \quad b = \frac{m\omega}{2\hbar}$$

$$\Longrightarrow \langle H \rangle_{min} = \frac{1}{2} \hbar\omega$$

$$\psi_{min}(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \exp \left(-\frac{m\omega}{2\hbar} x^2 \right)$$

Since we started with gaussian, we even were able to find true ground state.

Example 2: delta function potential

$$H = T + V \quad ; \quad T = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad ; \quad V(x) = -\alpha\delta(x)$$

Trial wave function: again gaussian

$$\langle V \rangle = -\alpha A^2 \int e^{-2bx^2} \delta(x) dx = -\alpha \sqrt{\frac{2b}{\pi}}$$

$$\implies \langle H \rangle = \frac{\hbar^2 b}{2m} - \alpha \sqrt{\frac{2b}{\pi}}$$

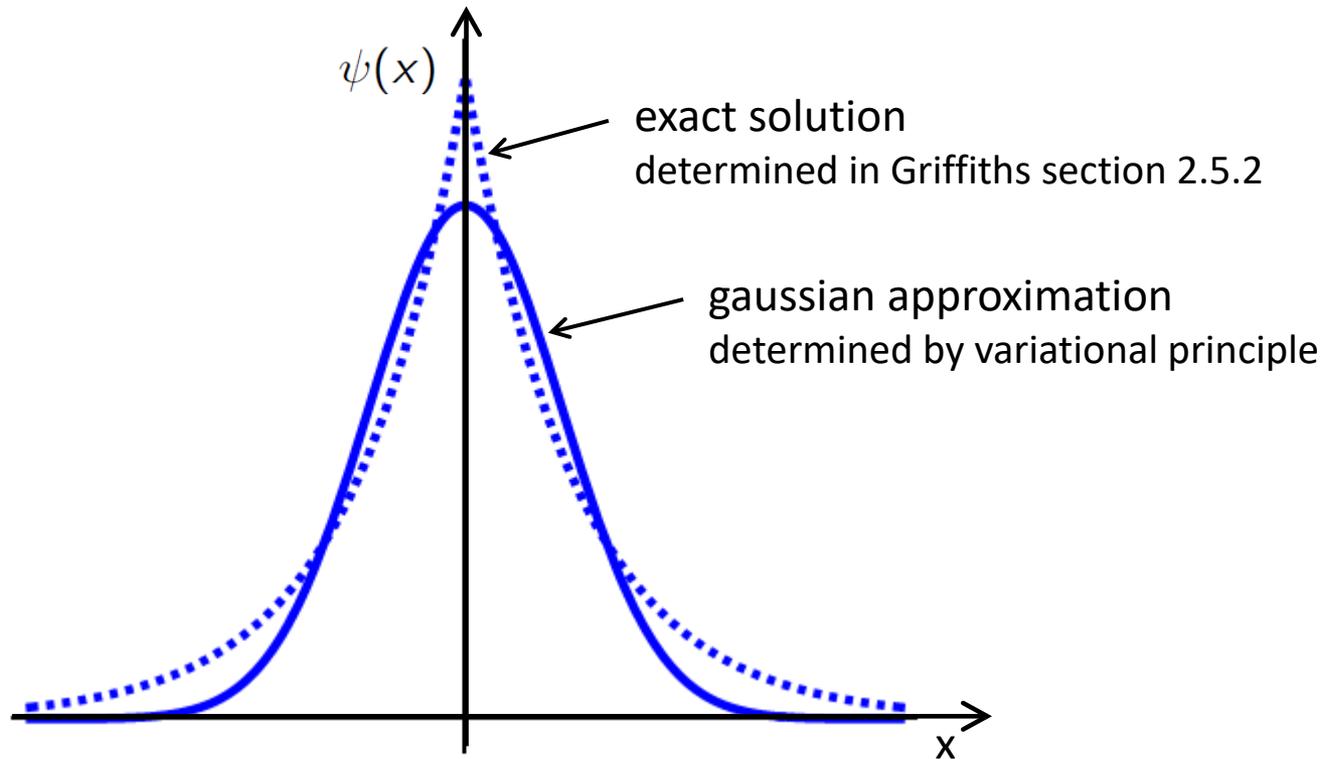
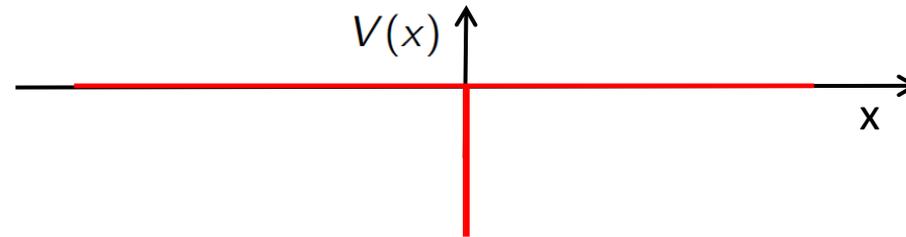
Minimize:

$$\frac{d}{db} \langle H \rangle = \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} = 0 \quad \implies \quad b = \frac{2m^2 \alpha^2}{\pi \hbar^4}$$

$$\implies \langle H \rangle_{min} = -\frac{m\alpha^2}{\pi \hbar^2}$$

Indeed higher than true ground-state energy $E_{gs} = -\frac{m\alpha^2}{2\hbar^2}$

Example 2: delta function potential



Overview of „*Variational principle*“

Goal of this section

Determine approximate solutions for ground-state wavefunction and energy

Plan of this section

1) General principle

Griffiths 3rd 8.1

2) Examples

- harmonic oscillator

example 8.1

- delta function potential

example 8.2

 3) Applications

- helium atom

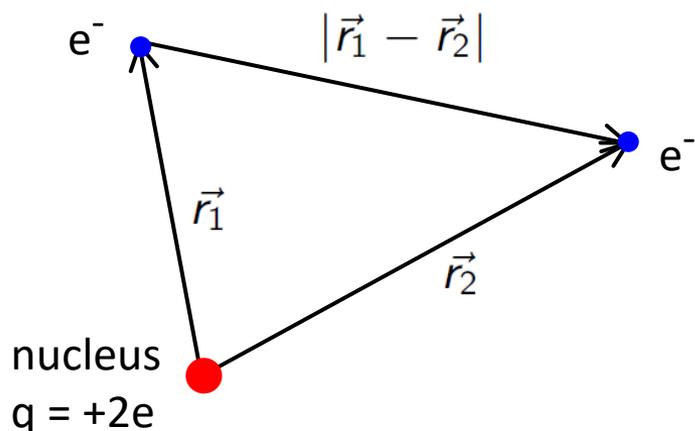
8.2

- hydrogen molecule ion

8.3

The ground state of Helium

$$H = -\frac{\hbar^2}{2m} (\vec{\nabla}_1^2 + \vec{\nabla}_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right)$$



measured ground-state
binding energy: $E_{gs} = -78.975 \text{ eV}$

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 $\Psi_0(\vec{r}_1, \vec{r}_2)$

$$H\Psi_0 = (8E_1 + V_{ee})\Psi_0$$

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle$$

$$\langle V_{ee} \rangle = \frac{e^2}{4\pi\epsilon_0} \left(\frac{8}{\pi a^3} \right)^2 \int \frac{e^{-4(r_1+r_2)/a}}{|\vec{r}_1 - \vec{r}_2|} d^3\vec{r}_1 d^3\vec{r}_2 = \frac{5}{4a} \frac{e^2}{4\pi\epsilon_0} = -\frac{5}{2}E_1$$

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.

Variational ansatz

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 :

$$\psi_0(\vec{r}_1) = \sqrt{\frac{Z^3}{\pi a^3}} e^{-Zr/a} \quad ; \quad E = Z^2 E_1$$

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

Minimization using variational principle

write Hamiltonian

$$H = \underbrace{-\frac{\hbar^2}{2m} (\vec{\nabla}_1^2 + \vec{\nabla}_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right)}_{\text{Hamiltonian of hydrogen-like atom with charge } Z \text{ for each electron}} + \underbrace{\frac{e^2}{4\pi\epsilon_0} \left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right)}_{\text{everything remaining for He Hamiltonian}}$$

Upper limit for ground state energy:

$$\langle H \rangle = 2Z^2 E_1 + 2(Z-2) \left(\frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a} \quad ; \quad \langle V_{ee} \rangle = -\frac{5Z}{4} E_1$$

$$\langle H \rangle = \left[2Z^2 - 4Z(Z-2) - \frac{5}{4}Z \right] E_1 = \left[-2Z^2 + \frac{27}{4}Z \right] E_1$$

Minimize

$$\frac{d}{dZ} \langle H \rangle = \left[-4Z + \frac{27}{4} \right] E_1 \stackrel{!}{=} 0 \quad \Longrightarrow \quad Z = \frac{27}{16} \simeq 1.69$$

$$\Longrightarrow \quad \langle H \rangle = \frac{1}{2} \left(\frac{3}{2} \right)^6 E_1 \simeq -77.5 \text{ eV} \quad \text{compare to measured value } E_{gs} = -79 \text{ eV} : 2\% \text{ off.}$$

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

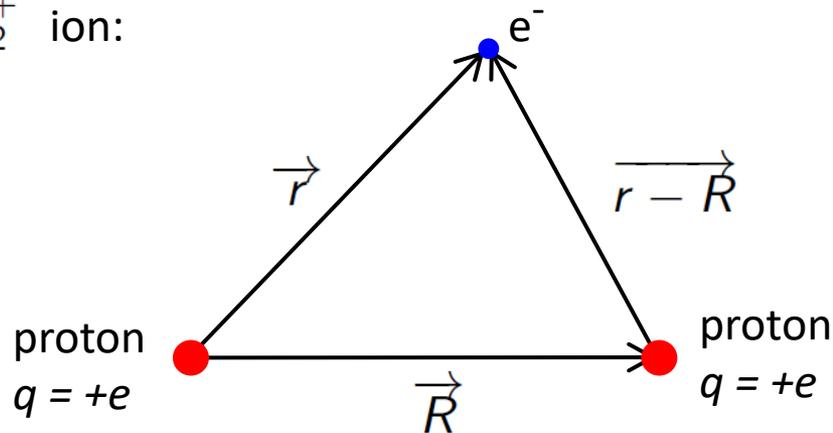
Plan of this section

- | | |
|----------------------------|-------------------------------|
| 1) General principle | Griffiths 3 rd 8.1 |
| 2) Examples | |
| - harmonic oscillator | example 8.1 |
| - delta function potential | example 8.2 |
| 3) Applications | |
| - helium atom | 8.2 |
| - hydrogen molecule ion | 8.3 |



The hydrogen molecule ion

H_2^+ ion:



Heisenberg uncertainty principle $\Delta x \Delta p \geq \hbar \longrightarrow \Delta v \geq \frac{\hbar}{m \Delta x}$

Mass of e^- 1836 times lighter than mass of proton

\longrightarrow e^- wave function adapts quickly to slow change of positions of nuclei

Born-Oppenheimer approximation

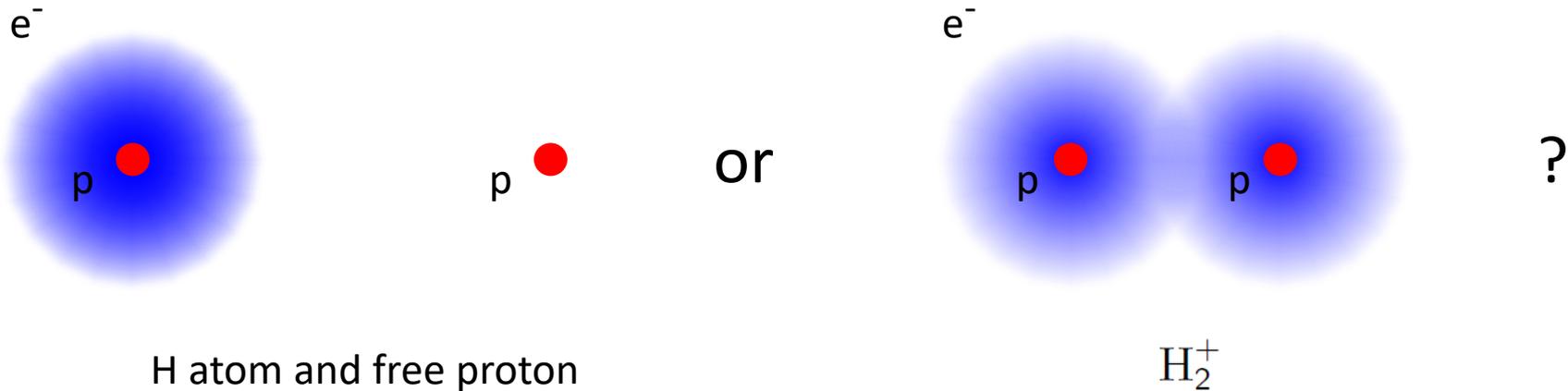
separate total molecular wavefunction into nuclear and e- wavefunction:

$$\Psi_{\text{tot}} = \Psi_{\text{el}} \Psi_{\text{nuc}}$$

Our goal: approximate Ψ_{el} , determine energy of e^- and then of ion

Can H_2^+ ion exist?

i.e. what is energetically favorable



Strategy to find answer

For each R :

- chose trial wavefunction Ψ_{trial} for Ψ_{el}
- calculate upper limit of e^- energy using variational principle: $E_{\text{gs}} \leq \langle \Psi_{\text{trial}} | H_{\text{el}} | \Psi_{\text{trial}} \rangle$
- determine total energy: electron energy + proton-proton repulsion

$$E_{\text{tot}}(R) = E_{\text{el}}(R) + E_{\text{p-p}}(R)$$

If $E_{\text{tot}} < E_1$ for some value of R , then H_2^+ has chance of existing.

Trial wavefunction

Electron Hamiltonian (consider R fixed)

$$H_{\text{el}} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{|\vec{r}|} + \frac{1}{|\vec{r} - \vec{R}|} \right)$$

Trial wavefunction

Hydrogen ground-state $\Psi_0(\vec{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$; $a = \text{Bohr radius}$

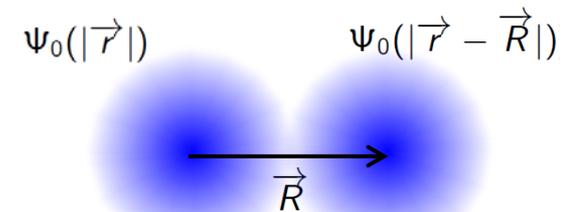
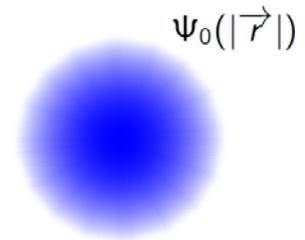
Good approximation for e- around one proton and the other at huge distance R .

But don't know which proton \longrightarrow try superposition state

$$\Psi_{\text{trial}} = A[\Psi_0(|\vec{r}|) + \Psi_0(|\vec{r} - \vec{R}|)]$$

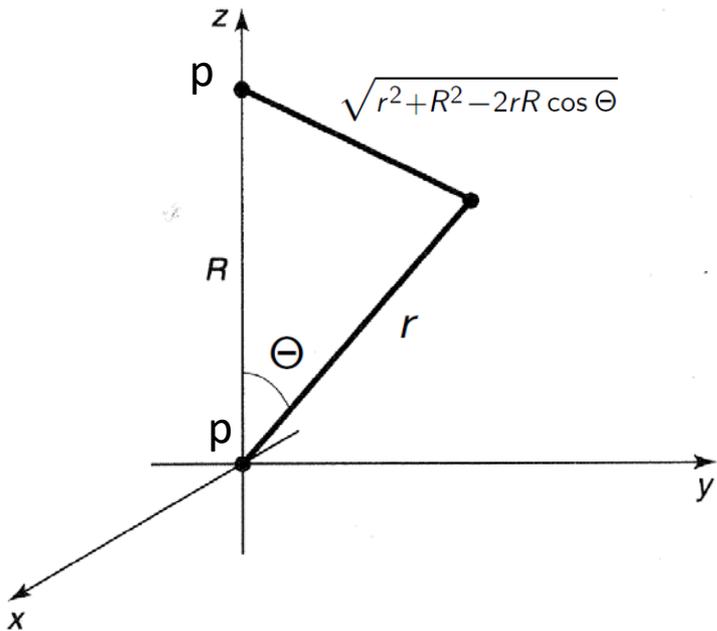
At least if R big, this should be a good wavefunction, since second proton doesn't disturb too much.

This approach is called „Linear Combination of Atomic Orbitals“ (LCAO)



Normalization

$$1 = \int |\Psi_{\text{trial}}|^2 d^3\vec{r} = A^2 \left[\underbrace{\int |\Psi_0(|\vec{r}|)|^2 d^3\vec{r}}_{=1} + \underbrace{\int |\Psi_0(|\vec{r} - \vec{R}|)|^2 d^3\vec{r}}_{=1} + 2 \underbrace{\int \Psi_0(|\vec{r}|)\Psi_0(|\vec{r} - \vec{R}|) d^3\vec{r}}_{\equiv I \text{ overlap integral}} \right]$$



$$\begin{aligned} I &= \frac{1}{\pi a^3} \int e^{-|\vec{r}|/a} e^{-|\vec{r} - \vec{R}|/a} d^3\vec{r} \\ &= \frac{1}{\pi a^3} \int e^{-r/a} e^{-\sqrt{r^2 + R^2 - 2rR \cos \Theta}} r^2 \sin \Theta dr d\Theta d\phi \\ &= \dots = e^{-R/a} \left[1 + \left(\frac{R}{a}\right) + \frac{1}{3} \left(\frac{R}{a}\right)^2 \right] \end{aligned}$$

Notice: $I \xrightarrow{R \rightarrow 0} 1$ and $I \xrightarrow{R \rightarrow \infty} 0$

$$\Rightarrow A^2 = \frac{1}{2(1 + I)}$$

Electron ground-state energy

Variational principle

$$E_{\text{gs}} \leq \langle \Psi_{\text{trial}} | H_{\text{el}} | \Psi_{\text{trial}} \rangle$$

reminder

$$\Psi_{\text{trial}} = A[\psi_0(|\vec{r}|) + \psi_0(|\vec{r} - \vec{R}|)]$$

with (from hydrogen):

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi_0(r) = E_1 \psi_0(r)$$

First step:

$$\begin{aligned} H_{\text{el}} \Psi_{\text{trial}} &= \left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{|\vec{r}|} + \frac{1}{|\vec{r} - \vec{R}|} \right) \right] A [\psi_0(|\vec{r}|) + \psi_0(|\vec{r} - \vec{R}|)] \\ &= \underbrace{\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}|} \right] A \psi_0(|\vec{r}|)}_{= E_1 A \psi_0(|\vec{r}|)} + \underbrace{\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r} - \vec{R}|} \right] A \psi_0(|\vec{r} - \vec{R}|)}_{= E_1 A \psi_0(|\vec{r} - \vec{R}|) \text{ shifted Hydrogen Schrödinger equation}} \\ &\quad - A \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|\vec{r} - \vec{R}|} \psi_0(|\vec{r}|) + \frac{1}{|\vec{r}|} \psi_0(|\vec{r} - \vec{R}|) \right] \end{aligned}$$

$$H_{\text{el}} \Psi_{\text{trial}} = E_1 \Psi_{\text{trial}} - A \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|\vec{r} - \vec{R}|} \psi_0(|\vec{r}|) + \frac{1}{|\vec{r}|} \psi_0(|\vec{r} - \vec{R}|) \right]$$

Electron ground-state energy

$$H_{\text{el}}\Psi_{\text{trial}} = E_1\Psi_{\text{trial}} - |A|^2 \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|\vec{r} - \vec{R}|} \Psi_0(|\vec{r}|) + \frac{1}{|\vec{r}|} \Psi_0(|\vec{r} - \vec{R}|) \right]$$

$$\langle \Psi_{\text{trial}} | H_{\text{el}} | \Psi_{\text{trial}} \rangle = E_1 - 2|A|^2 \frac{e^2}{4\pi\epsilon_0} \left[\underbrace{\left\langle \Psi_0(|\vec{r}|) \left| \frac{1}{|\vec{r} - \vec{R}|} \right| \Psi_0(|\vec{r}|) \right\rangle}_{\equiv D/a} + \underbrace{\left\langle \Psi_0(|\vec{r}|) \left| \frac{1}{|\vec{r}|} \right| \Psi_0(|\vec{r} - \vec{R}|) \right\rangle}_{\equiv X/a} \right]$$

Integrals like D and X appear 2 times each.

To make equal to D and X, change coordinates by exploiting mirror symmetry of molecule.

direct integral

exchange integral

$$D = \frac{a}{R} - \left(1 + \frac{a}{R}\right) e^{-2R/a}$$

$$X = \left(1 + \frac{R}{a}\right) e^{-R/a}$$

$$\langle \Psi_{\text{trial}} | H_{\text{el}} | \Psi_{\text{trial}} \rangle = \left[1 + 2 \frac{D + X}{1 + I} \right] E_1$$

In addition: energy from proton-proton repulsion

$$V_{\text{P-P}} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} = -\frac{2a}{R} E_1$$

Result: upper limit for ground-state energy

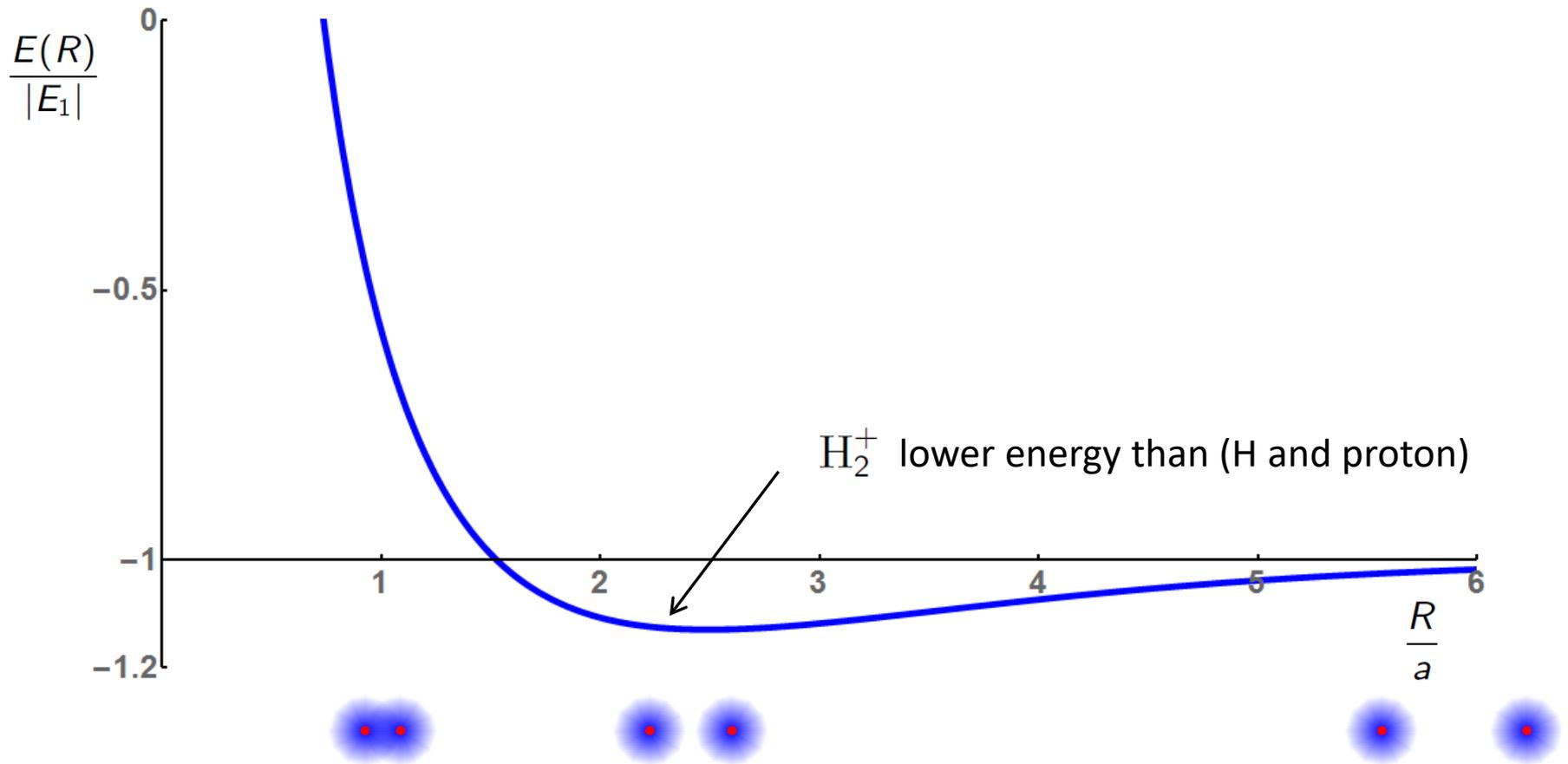
$$E(x) = -E_1 \left[-1 + \frac{2}{x} \left\{ \frac{(1 - (2/3)x^2)e^{-x} + (1+x)e^{-2x}}{1 + (1+x + (1/3)x^2)e^{-x}} \right\} \right] ; \quad x \equiv \frac{R}{a}$$

reminder

$$\Psi_{\text{trial}} = A[\Psi_0(|\vec{r}|) + \Psi_0(|\vec{r} - \vec{R}|)]$$

$$E_1 = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2a}$$

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 H₂⁺ are held together by the electron.

Overview of „*Variational principle*“

Goal of this section

Determine approximate solutions for ground-state wavefunction and energy

Plan of this section

- | | |
|----------------------------|-------------------------------|
| 1) General principle | Griffiths 3 rd 8.1 |
| 2) Examples | |
| - harmonic oscillator | example 8.1 |
| - delta function potential | example 8.2 |
| 3) Applications | |
| - helium atom | 8.2 |
| - hydrogen molecule ion | 8.3 |



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

Griffiths 3rd 5.1, 5.2

Crystalline solids

5.3.2

Time-independent perturbation theory

7.1, 7.2

Structure of hydrogen

7.3 – 7.5

Variational principle

8.1 – 8.3

today → Time-dependent perturbation theory, atom-light interaction 11.1 – 11.4

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 Griffiths 3rd 11.0
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 - sinusoidal perturbation
- 3) Emission and absorption of radiation 11.2 - 3
 - 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

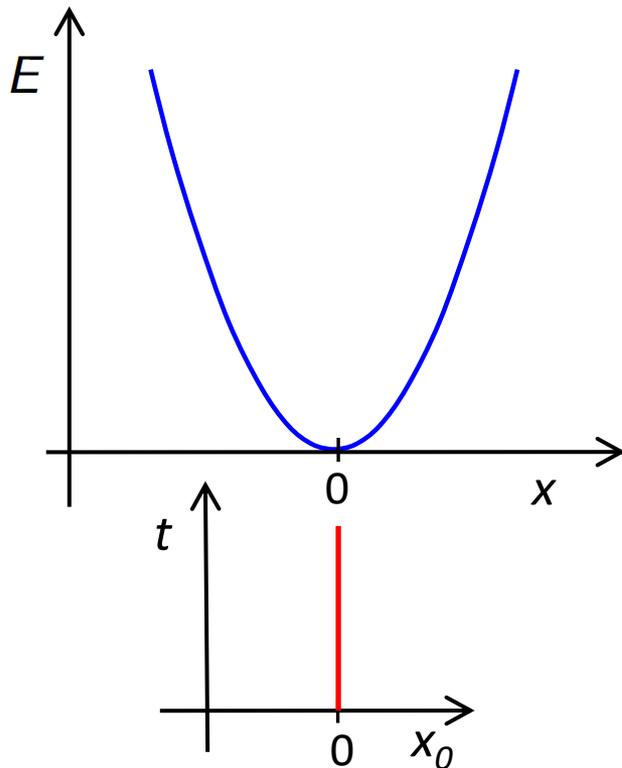
Introduction

So far: „quantum statics“

Hamiltonian **independent** of time

i.e. potential $V(\vec{r}, t) = V(\vec{r})$

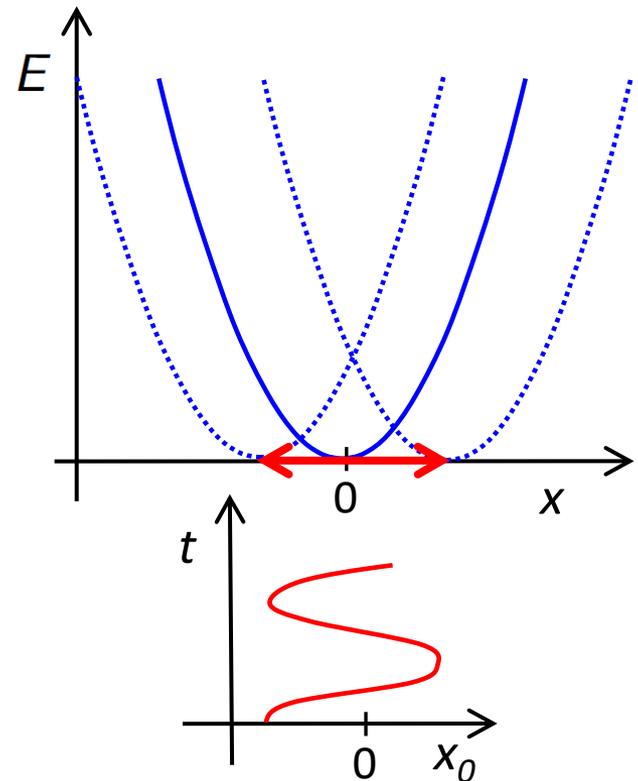
Example: **static** harmonic oscillator



Now: „quantum dynamics“

Hamiltonian **dependent** of time

Example: **driven** harmonic oscillator



Time evolution for time-independent H

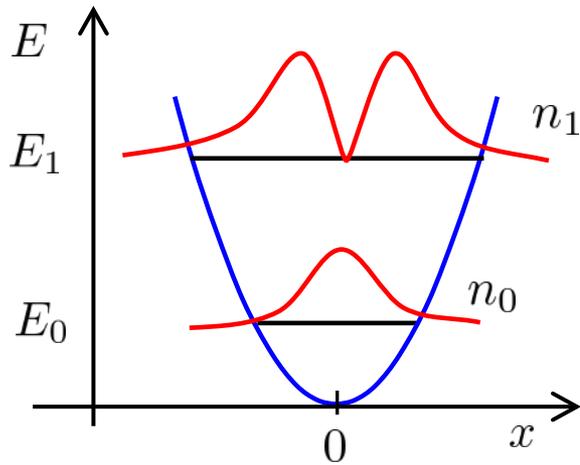
Even if Hamiltonian time-independent, quantum system evolves over time.

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad \text{has solutions} \quad \Psi_n(\vec{r}, t) = \Psi_n(\vec{r}) e^{-iE_n t/\hbar}$$

$$\text{with } \Psi_n(\vec{r}), E_n \text{ satisfying } H\Psi_n(\vec{r}) = E_n \Psi_n(\vec{r})$$

$$\text{and general solution } \Psi(\vec{r}, t) = \sum_n c_n \Psi_n(\vec{r}) e^{-iE_n t/\hbar}$$

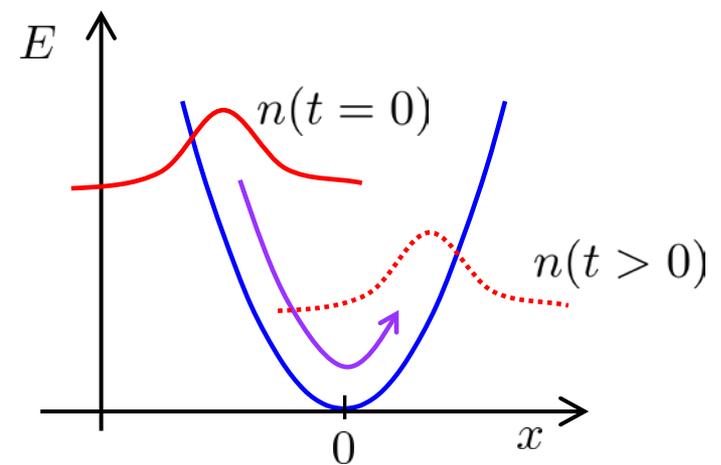
Eigenstates



density distributions & energy don't evolve

$$n_n(\vec{r}) = |\Psi_n(\vec{r}, t)|^2 = |\Psi_n(\vec{r})|^2$$

Superposition states



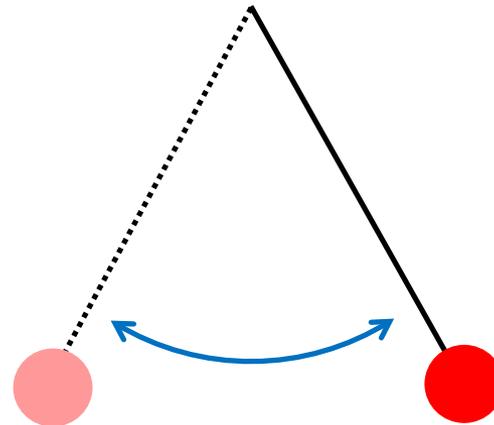
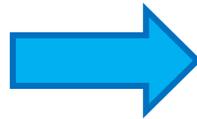
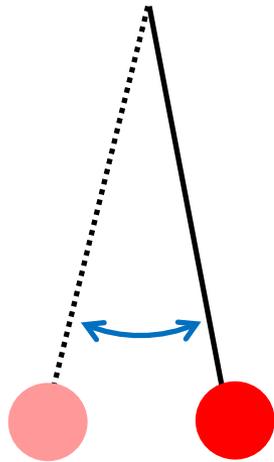
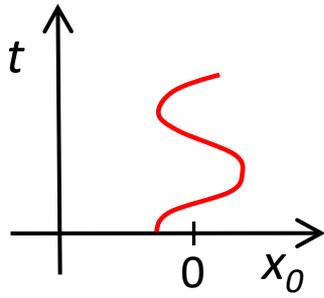
density distribution can evolve
energy doesn't evolve

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*“

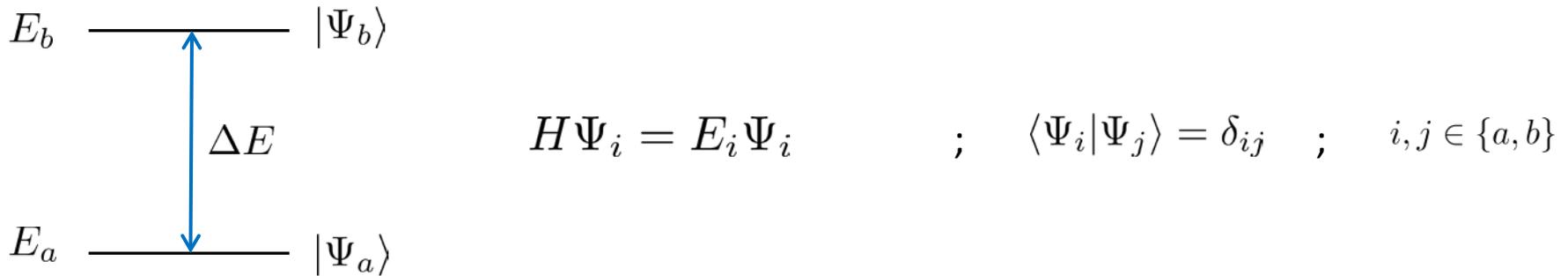
Goal of this section

Describe the reaction of a system to a time-dependent perturbation, especially absorption and emission of photons by atoms.

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- 4) Fermi's golden rule

Two level system with time-dependent H



Initial state: $\Psi(t=0) = c_a(0)\Psi_a + c_b(0)\Psi_b$ $|c_a(0)|^2 + |c_b(0)|^2 = 1$

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 $H = H^0 + H'(t)$

$$\Psi(t) = c_a(t)e^{-iE_a t/\hbar}\Psi_a + c_b(t)e^{-iE_b t/\hbar}\Psi_b$$
 $|c_a(t)|^2 + |c_b(t)|^2 = 1$

Task: (approximately) find $c_a(t)$ and $c_b(t)$

Two level system with time-dependent H

$$H = H^0 + H'(t)$$

$\left\{ \begin{array}{l} \text{time-dependent part of Hamiltonian (not necessarily small)} \\ \text{static} \end{array} \right.$

Solve $H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$ with ansatz $\Psi(t) = c_a(t)e^{-iE_a t/\hbar}\Psi_a + c_b(t)e^{-iE_b t/\hbar}\Psi_b$

~~$$c_a[H^0\Psi_a]e^{-iE_a t/\hbar} + c_b[H^0\Psi_b]e^{-iE_b t/\hbar} + c_a[H'\Psi_a]e^{-iE_a t/\hbar} + c_b[H'\Psi_b]e^{-iE_b t/\hbar}$$~~

~~$$= i\hbar \left[\dot{c}_a\Psi_a e^{-iE_a t/\hbar} + \dot{c}_b\Psi_b e^{-iE_b t/\hbar} + c_a\Psi_a \left(\frac{-iE_a}{\hbar}\right) e^{-iE_a t/\hbar} + c_b\Psi_b \left(\frac{-iE_b}{\hbar}\right) e^{-iE_b t/\hbar} \right]$$~~

$$c_a[H'\Psi_a]e^{-iE_a t/\hbar} + c_b[H'\Psi_b]e^{-iE_b t/\hbar} = i\hbar \left[\dot{c}_a\Psi_a e^{-iE_a t/\hbar} + \dot{c}_b\Psi_b e^{-iE_b t/\hbar} \right]$$

$\langle \Psi_a | \cdot :$

$$c_a \langle \Psi_a | H' | \Psi_a \rangle e^{-iE_a t/\hbar} + c_b \langle \Psi_a | H' | \Psi_b \rangle e^{-iE_b t/\hbar} = i\hbar \dot{c}_a e^{-iE_a t/\hbar}$$

$$H'_{ij} \equiv \langle \Psi_i | H' | \Psi_j \rangle : \quad \dot{c}_a = -\frac{i}{\hbar} \left[c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar} \right]$$

$$\langle \Psi_b | \cdot : \quad \dot{c}_b = -\frac{i}{\hbar} \left[c_a H'_{ba} e^{i(E_b - E_a)t/\hbar} + c_b H'_{bb} \right]$$

Matrix notation:
$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = \begin{pmatrix} H'_{aa} & H'_{ab} e^{-i(E_b - E_a)t/\hbar} \\ H'_{ba} e^{i(E_b - E_a)t/\hbar} & H'_{bb} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix}$$

Two level system with time-dependent H

$$H = H^0 + H'(t)$$

└── static
└── time-dependent part of Hamiltonian (not necessarily small)

Solve $H\Psi = i\hbar \frac{\partial\Psi}{\partial t}$ with ansatz $\Psi(t) = c_a(t)e^{-iE_a t/\hbar}\Psi_a + c_b(t)e^{-iE_b t/\hbar}\Psi_b$

$$\dot{c}_a = -\frac{i}{\hbar} [c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar}]$$

$$\dot{c}_b = -\frac{i}{\hbar} [c_a H'_{ba} e^{i(E_b - E_a)t/\hbar} + c_b H'_{bb}]$$

Often $H'_{aa} = H'_{bb} = 0$:

$$\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b$$

$$\dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a$$

with $\omega_0 \equiv \frac{E_b - E_a}{\hbar}$

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.

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Time-dependent perturbation theory

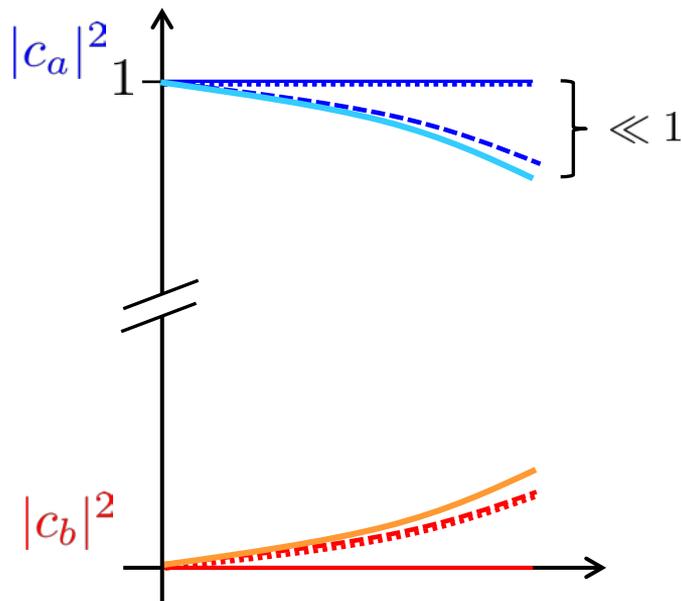
$$H = H^0 + H'(t)$$

static \perp \perp small time-dependent perturbation

Initial condition: system in ground state $c_a(0) = 1$, $c_b(0) = 0$

Iteratively solve $\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b$; $\omega_0 \equiv \frac{E_b - E_a}{\hbar}$

$$\dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a$$



— true solution

would be nice to have, but too complicated to calculate

— — zeroth order: $c_a(t) = 1$, $c_b(t) = 0$

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: $c_a^{(1)}(t)$, $c_b^{(1)}(t)$

less far away from true solution

Idea: iterate this process

should lead to ever better solution

- - - - - - second order: $c_a^{(2)}(t)$, $c_b^{(2)}(t)$

even less far away from true solution

Note: there is no need to add up $c_a^{(0)}(t) + c_a^{(1)}(t) + \dots$. $c_a^{(n)}(t)$ is already the full n^{th} order solution.

Time-dependent perturbation theory

$$H = H^0 + H'(t)$$

static \perp \perp small time-dependent perturbation

Initial condition: system in ground state $c_a(0) = 1$, $c_b(0) = 0$

Iteratively solve $\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b$; $\omega_0 \equiv \frac{E_b - E_a}{\hbar}$

$$\dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a$$

Zeroth Order: $(H' = 0)$

$$c_a^{(0)}(t) = 1 , \quad c_b^{(0)}(t) = 0$$

First Order:

Note: $|c_a^{(1)}(t)|^2 + |c_b^{(1)}(t)|^2 = 1 + \mathcal{O}(H'_{ab}{}^2) \neq 1$

$$\dot{c}_a^{(1)} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b^{(0)} = 0 \quad \Rightarrow \quad c_a^{(1)}(t) = 1$$

$$\dot{c}_b^{(1)} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a^{(0)} \quad \Rightarrow \quad c_b^{(1)}(t) = -\frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt'$$

Second Order:

$$\dot{c}_a^{(2)} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} \left(-\frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \right)$$

$$\Rightarrow c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2} \int_0^t H'_{ab}(t') e^{-i\omega_0 t'} \left[\int_0^{t'} H'_{ba}(t'') e^{i\omega_0 t''} dt'' \right] dt'$$

$$\dot{c}_b^{(2)} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a^{(1)} \Rightarrow c_b^{(2)}(t) = c_b^{(1)}(t)$$

etc.

Interpretation

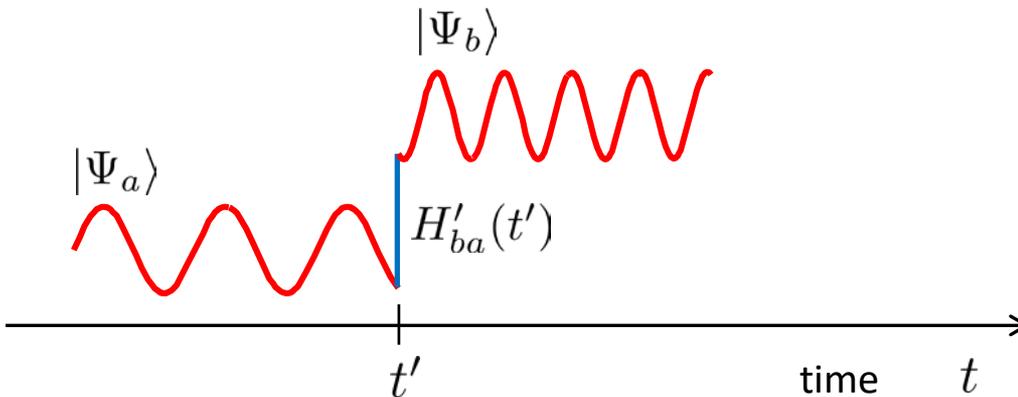
Probability amplitude to find system in $|\Psi_b\rangle$ after time t in second order:

$$c_b^{(1)}(t) = -\frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \quad \text{with} \quad \omega_0 = \frac{E_b - E_a}{\hbar}$$

rewrite:

$$c_b^{(1)}(t) e^{-iE_b t/\hbar} = -\frac{i}{\hbar} \int_0^t e^{-iE_b(t-t')/\hbar} H'_{ba}(t') e^{-iE_a t'/\hbar} dt' \quad (\text{read from right to left})$$

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:

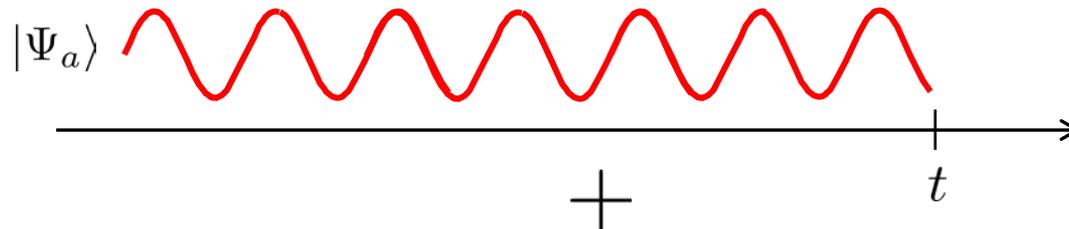
$$c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2} \int_0^t H'_{ab}(t') e^{-i\omega_0 t'} \left[\int_0^{t'} H'_{ba}(t'') e^{i\omega_0 t''} dt'' \right] dt' \quad \text{with} \quad \omega_0 = \frac{E_b - E_a}{\hbar}$$

rewrite:

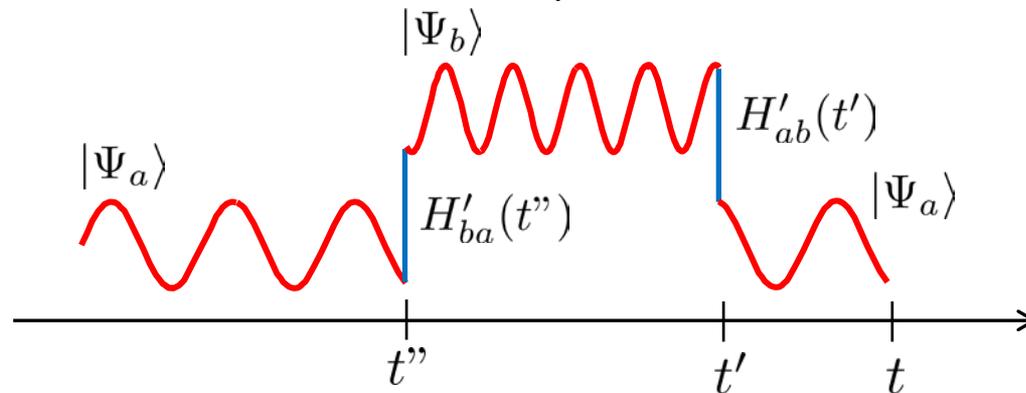
$$c_a^{(2)}(t) e^{-iE_a t/\hbar} = e^{-iE_a t/\hbar} + \left(\frac{i}{\hbar}\right)^2 \int_0^t \int_0^{t'} e^{-iE_a(t-t')/\hbar} H'_{ab}(t') e^{-iE_b(t'-t'')/\hbar} H'_{ba}(t'') e^{-iE_a t''/\hbar} dt'' dt'$$

Interpretation: probability amplitude to transition from $|\Psi_a\rangle$ to $|\Psi_b\rangle$ to $|\Psi_a\rangle$ is sum over all possibilities

Zeroth Order:



Second Order:

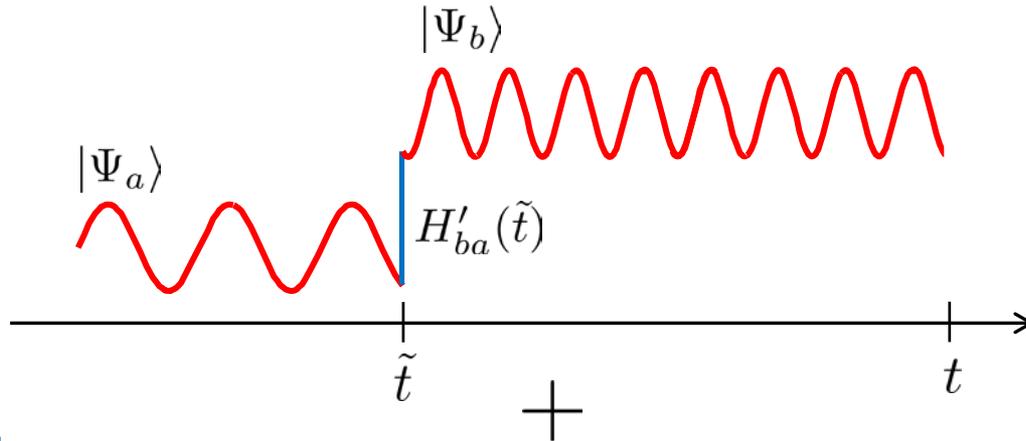


Total transition amplitude = sum over all possibilities.

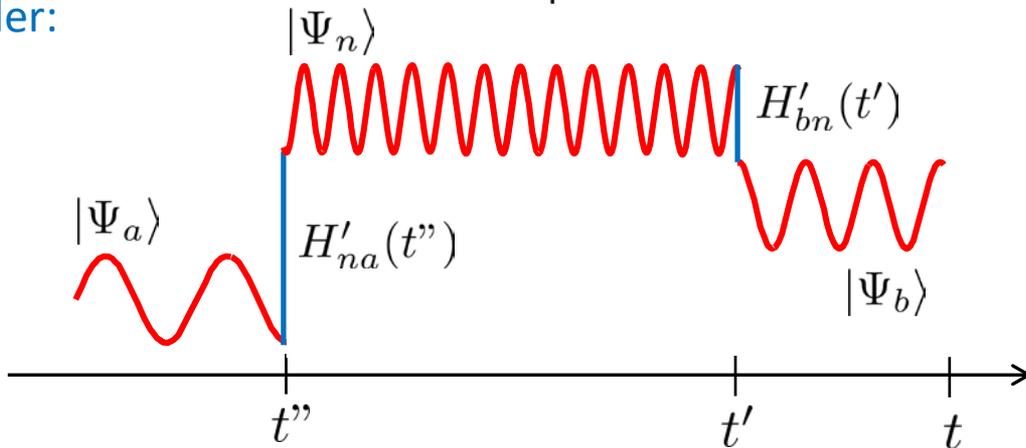
N-level system

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:



$$c_b^{(2)}(t)e^{-iE_b t/\hbar} = + \left(-\frac{i}{\hbar}\right) \int_0^t e^{-iE_b(t-\tilde{t})/\hbar} H'_{ba}(\tilde{t}) e^{-iE_a \tilde{t}/\hbar} d\tilde{t} \\ + \sum_n \left(-\frac{i}{\hbar}\right)^2 \int_0^t \int_0^{t'} e^{-iE_b(t-t')/\hbar} H'_{bn}(t') e^{-iE_n(t'-t'')/\hbar} H'_{na}(t'') e^{-iE_a t''/\hbar} dt'' dt'$$

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Sinusoidal perturbation

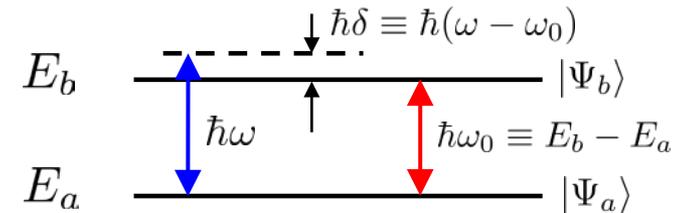
$$H = H^0 + H'(t)$$

static $\left\{ \begin{array}{l} \text{small time-dependent perturbation} \\ H'(t) = V \cos(\omega t) \end{array} \right.$

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: $H'_{ij}(t) \equiv V_{ij} \cos(\omega t)$

$$c_a(t) \cong 1$$

$$c_b(t) \cong -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t') e^{i\omega_0 t'} dt' = -\frac{iV_{ba}}{2\hbar} \int_0^t \left[e^{i(\omega_0 + \omega)t'} + e^{i(\omega_0 - \omega)t'} \right] dt'$$

$$= -\frac{V_{ba}}{2\hbar} \left[\frac{e^{i(\omega_0 + \omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0 - \omega)t} - 1}{\omega_0 - \omega} \right]$$

Simplifying assumption: $\omega_0 + \omega \gg |\omega_0 - \omega| = |\delta|$, i.e. detuning small compared to transition frequency

$$c_b(t) \cong -\frac{V_{ba}}{2\hbar} \frac{e^{i(\omega_0 - \omega)t/2}}{\omega_0 - \omega} \left[e^{i(\omega_0 - \omega)t/2} - e^{-i(\omega_0 - \omega)t/2} \right]$$

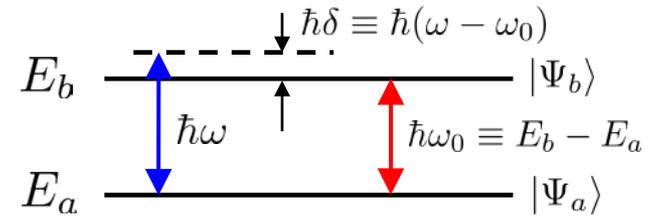
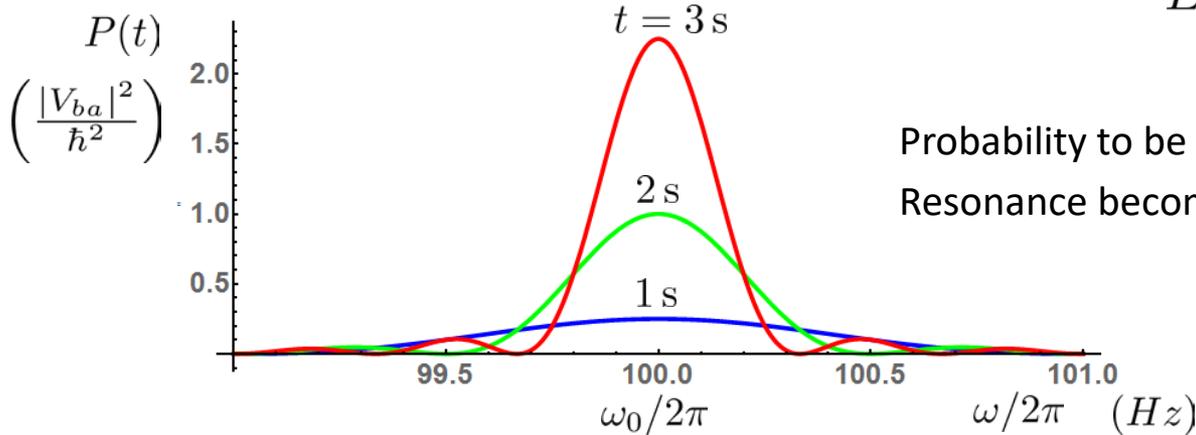
$$= -i \frac{V_{ba}}{\hbar} \frac{\sin[(\omega_0 - \omega)t/2]}{\omega_0 - \omega} e^{i(\omega_0 - \omega)t/2}$$

Transition probability

$$P_{a \rightarrow b}(t) = |c_b(t)|^2 \cong \frac{|V_{ba}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}$$

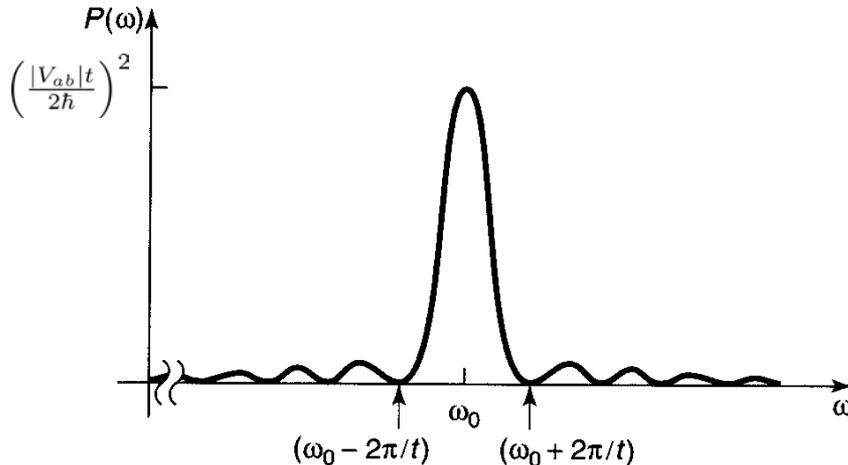
$$\frac{|V_{ba}|^2}{\hbar^2} \ll 1 \text{ for perturbation theory to be valid}$$

Spectrum:



Probability to be in $|\Psi_b\rangle$ higher if detuning δ small.
Resonance becomes narrower and higher over time.

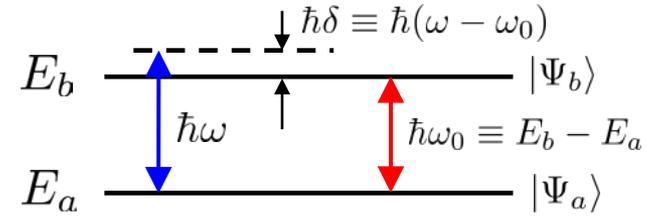
Rescaling collapses resonances for all times on one graph:



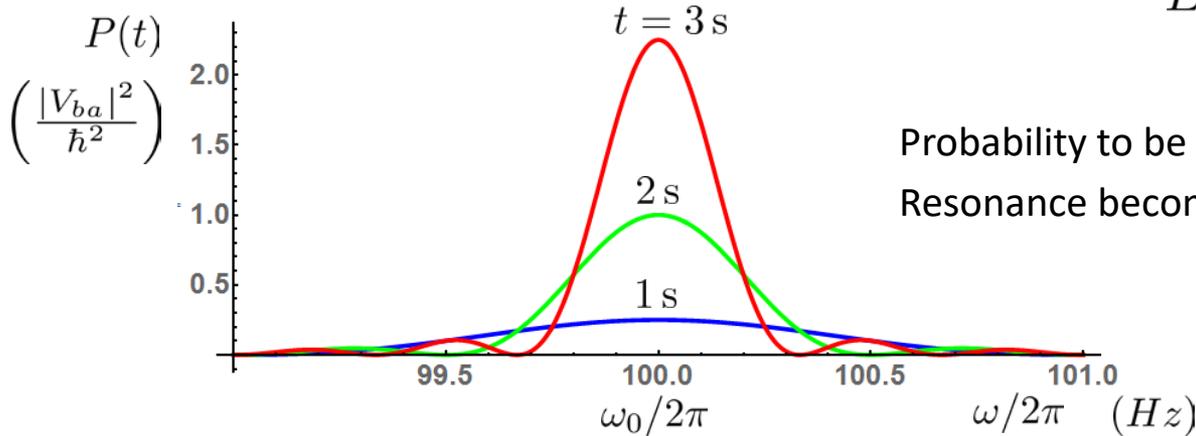
Transition probability

$$P_{a \rightarrow b}(t) = |c_b(t)|^2 \cong \frac{|V_{ba}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}$$

$$\frac{|V_{ba}|^2}{\hbar^2} \ll 1 \text{ for perturbation theory to be valid}$$

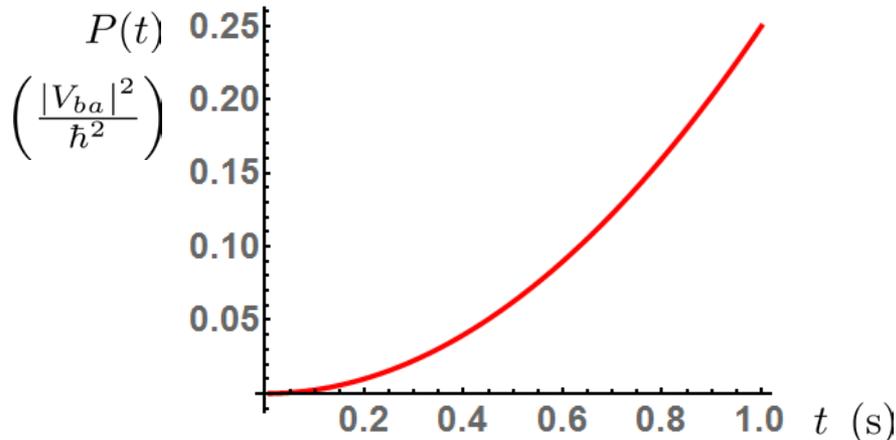


Spectrum:



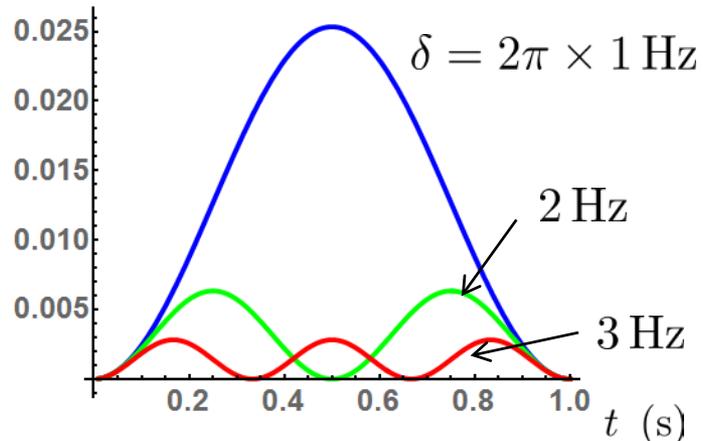
Probability to be in $|\Psi_b\rangle$ higher if detuning δ small.
Resonance becomes narrower and higher over time.

On resonance ($\delta = 0$):



Probability to be in $|\Psi_b\rangle$ increases with t^2 .

Off resonance:



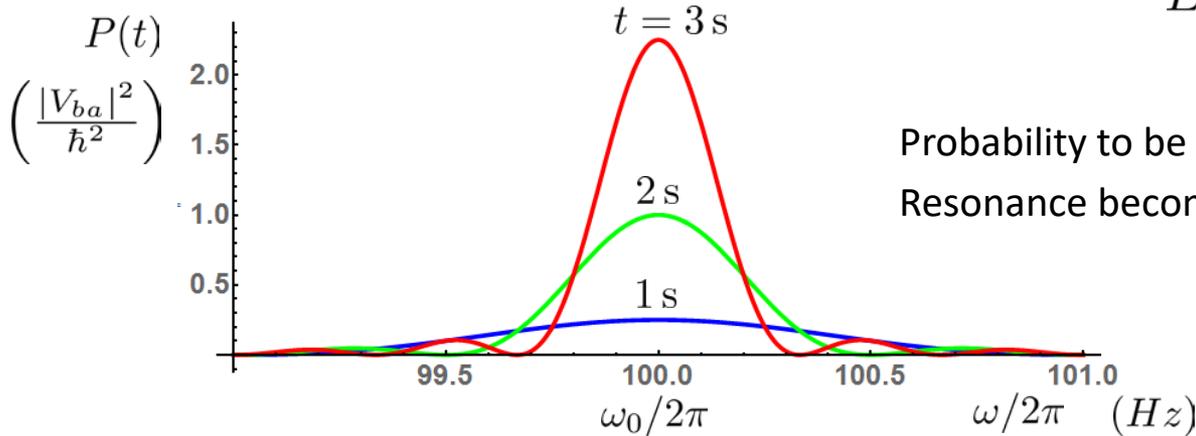
Probability to be in $|\Psi_b\rangle$ oscillates.

Transition probability

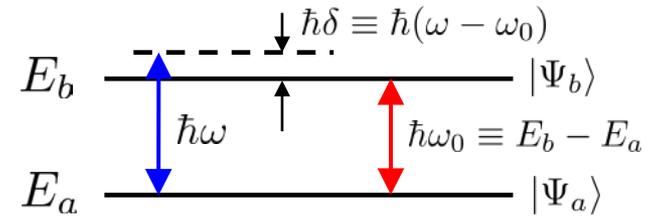
$$P_{a \rightarrow b}(t) = |c_b(t)|^2 \cong \frac{|V_{ba}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}$$

$$\frac{|V_{ba}|^2}{\hbar^2} \ll 1 \text{ for perturbation theory to be valid}$$

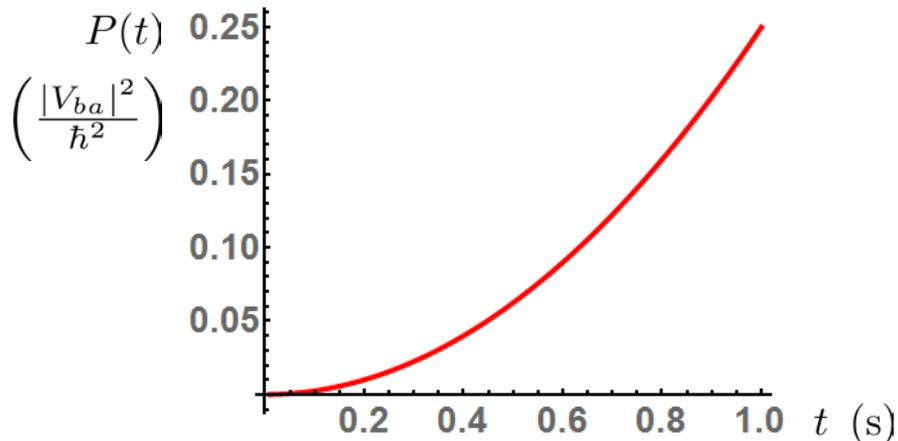
Spectrum:



Probability to be in $|\Psi_b\rangle$ higher if detuning δ small.
Resonance becomes narrower and higher over time.



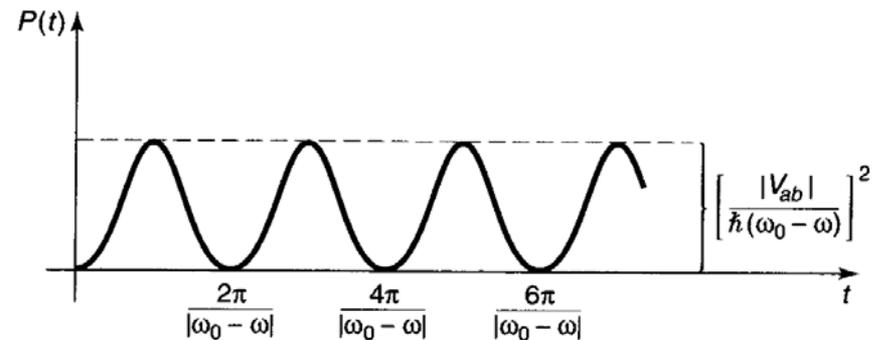
On resonance ($\delta = 0$):



Probability to be in $|\Psi_b\rangle$ increases with t^2 .

Off resonance:

Rescaling collapses graph:



Probability to be in $|\Psi_b\rangle$ oscillates.

Overview of „*Time-dependent perturbation theory*“

Goal of this section

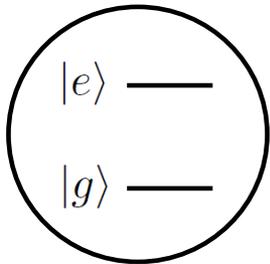
Describe the reaction of a system to a time-dependent perturbation, especially absorption and emission of photons by atoms.

Plan of this section

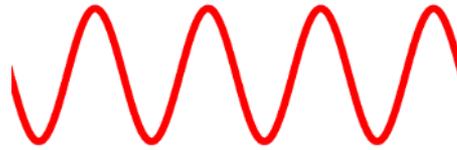
- 1) Introduction Griffiths 3rd 11.0
- 2) Two-level system with time-dependent H 11.1
 - time-dependent perturbation theory
 - sinusoidal perturbation
-  3) Emission and absorption of radiation 11.2 - 3
 - absorption, stimulated emission, spontaneous emission
 - spontaneous emission
 - incoherent perturbation
 - Einstein's A and B coefficients
 - lifetime of excited state
 - selection rules
- 4) Fermi's golden rule

Meet the players

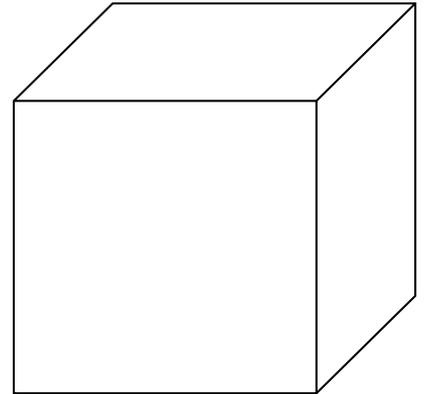
Atom



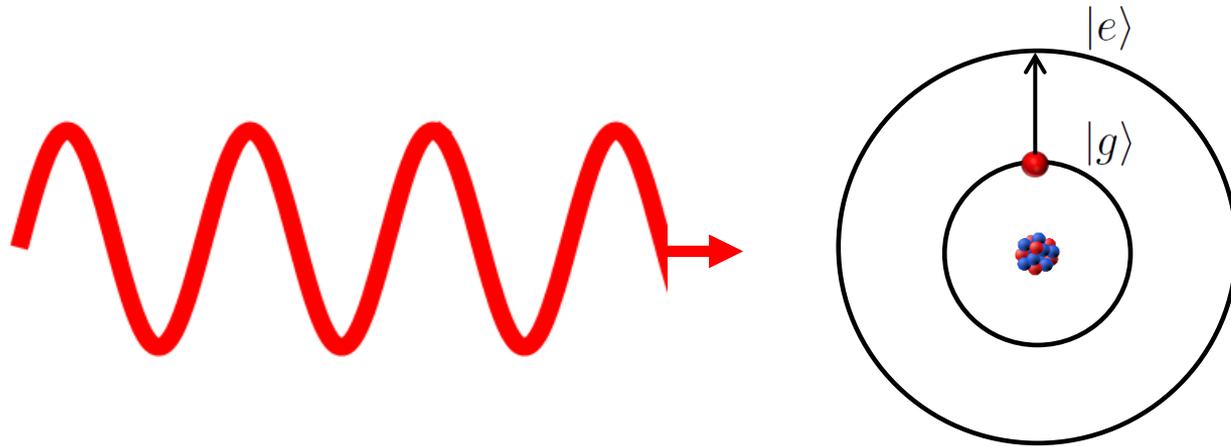
Laser beam



EM field modes

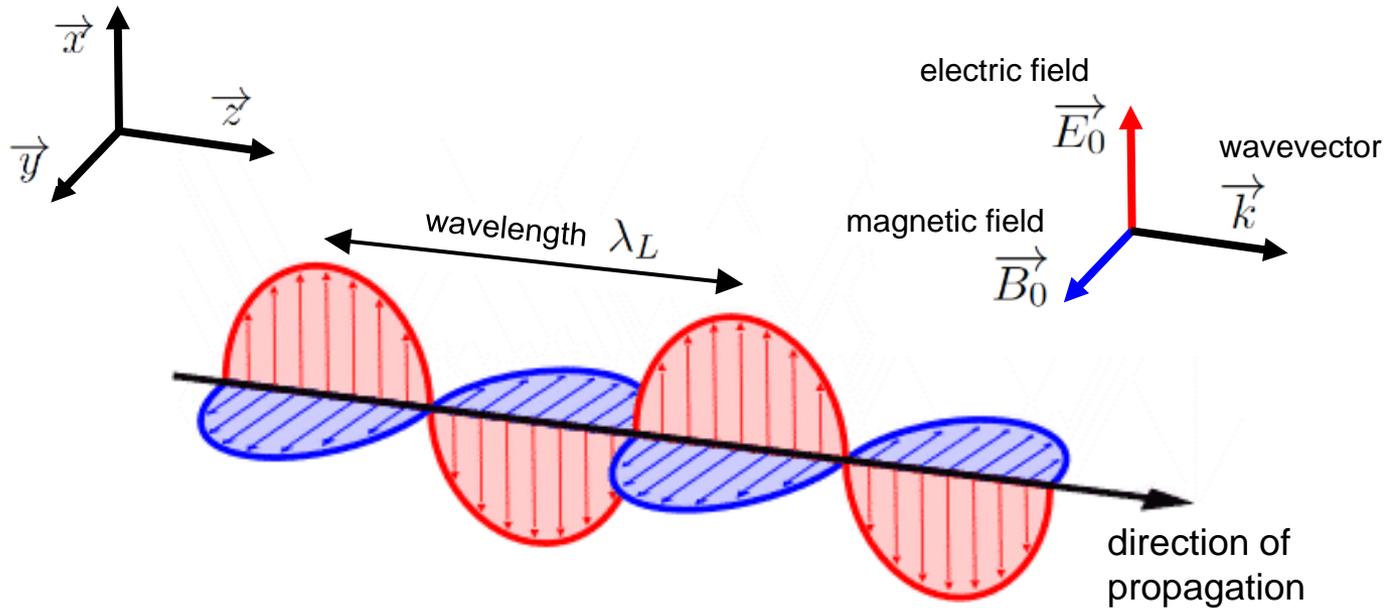


Atom-light interaction



Electromagnetic waves

Linearly polarized plane wave



frequency: $f_L = c/\lambda_L$

angular frequency: $\omega_L = 2\pi \times f_L$

intensity: $I = E_0^2/2\mu_0 c$

energy of photon: $E_L = hf_L$

momentum of photon: $\vec{p} = \hbar \vec{k}$

wavevector: $\vec{k} = \frac{2\pi}{\lambda_L} \vec{e}_L$

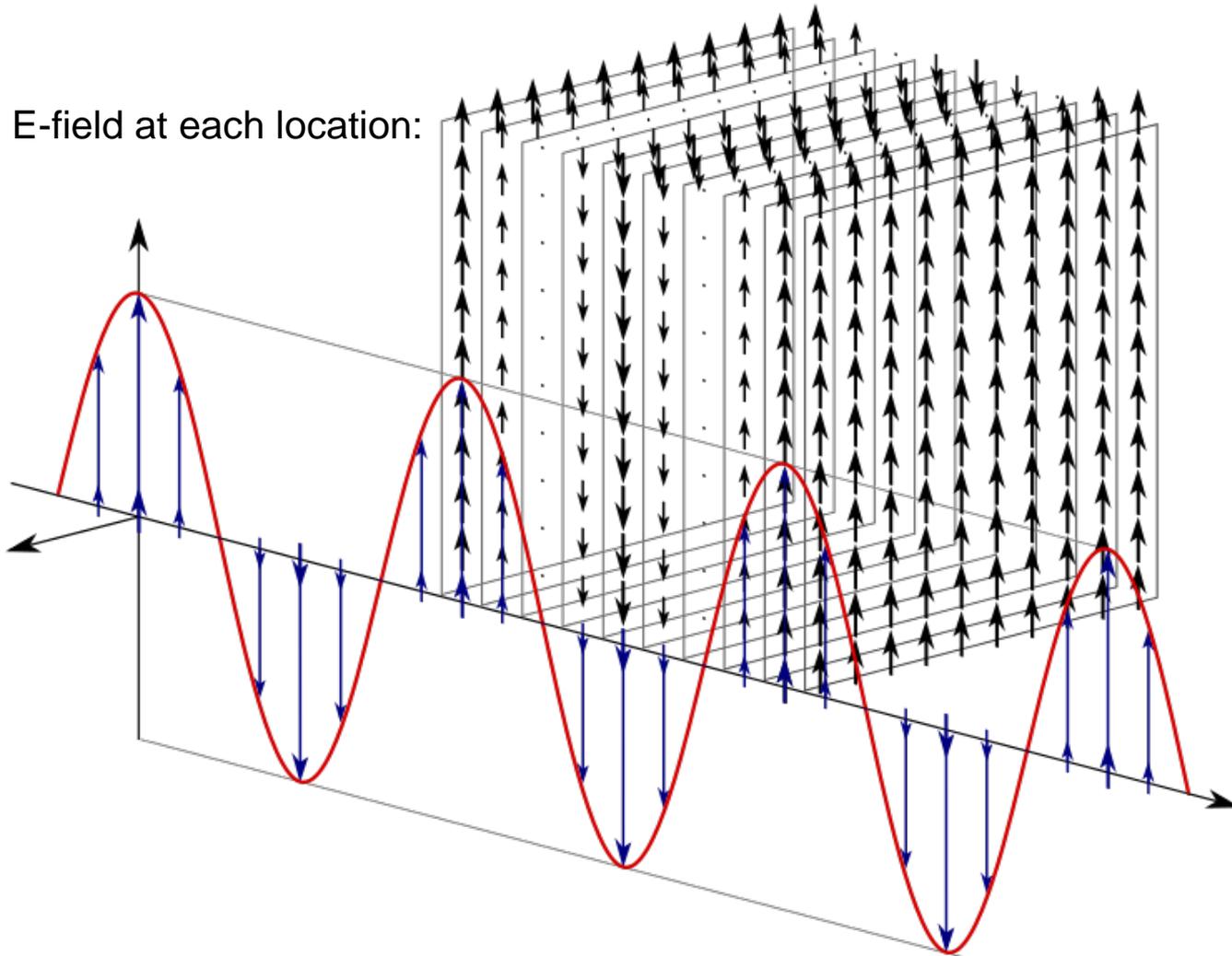
↑ unit vector pointing in direction of propagation

electric field: $\vec{E} = \vec{E}_0 \cos(\vec{k} \cdot \vec{r} - \omega_L t + \varphi_L)$

magnetic field: magnitude $B_0 = E_0/c$

Plane waves

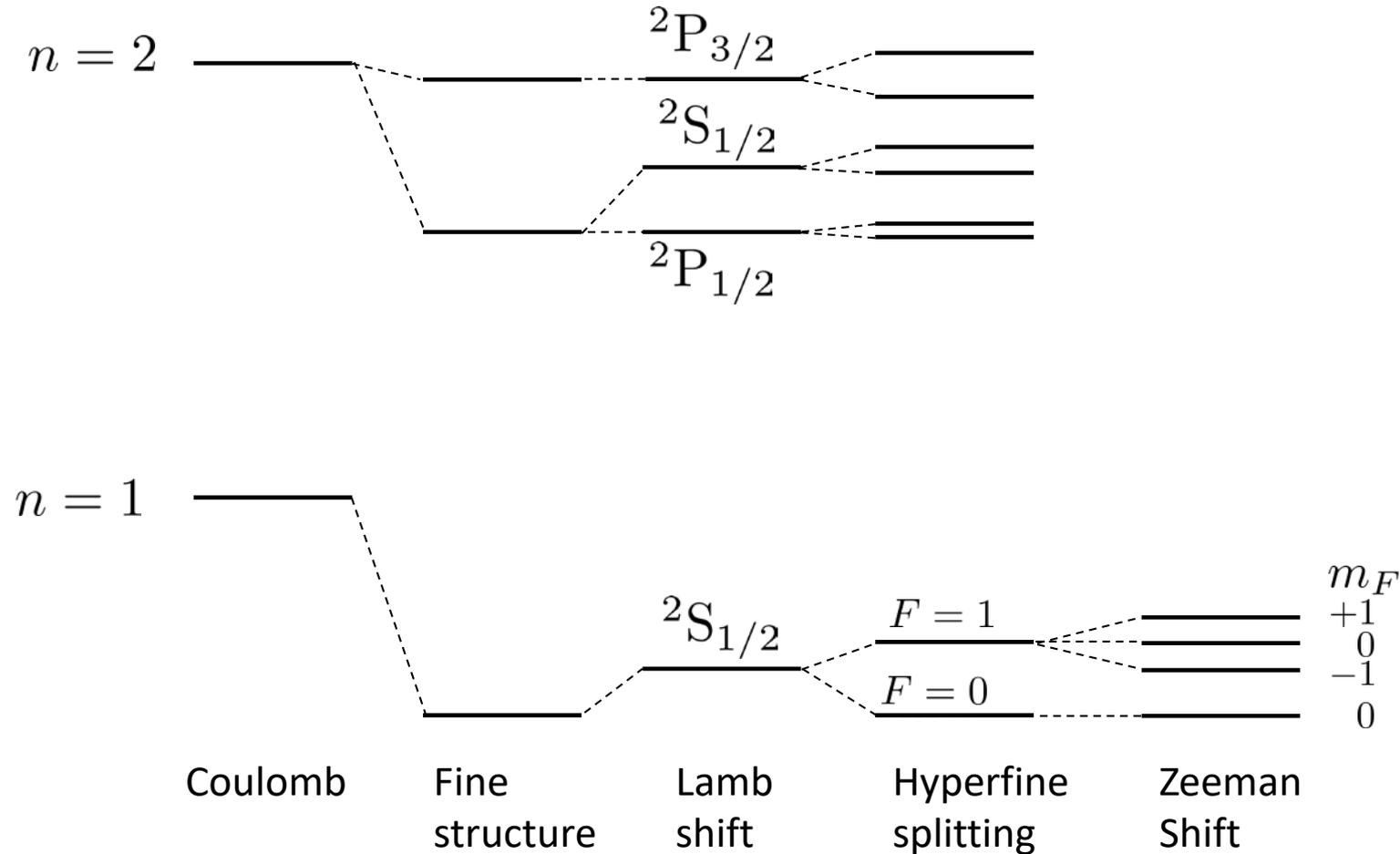
A plane wave fills all of space.



Atomic transitions

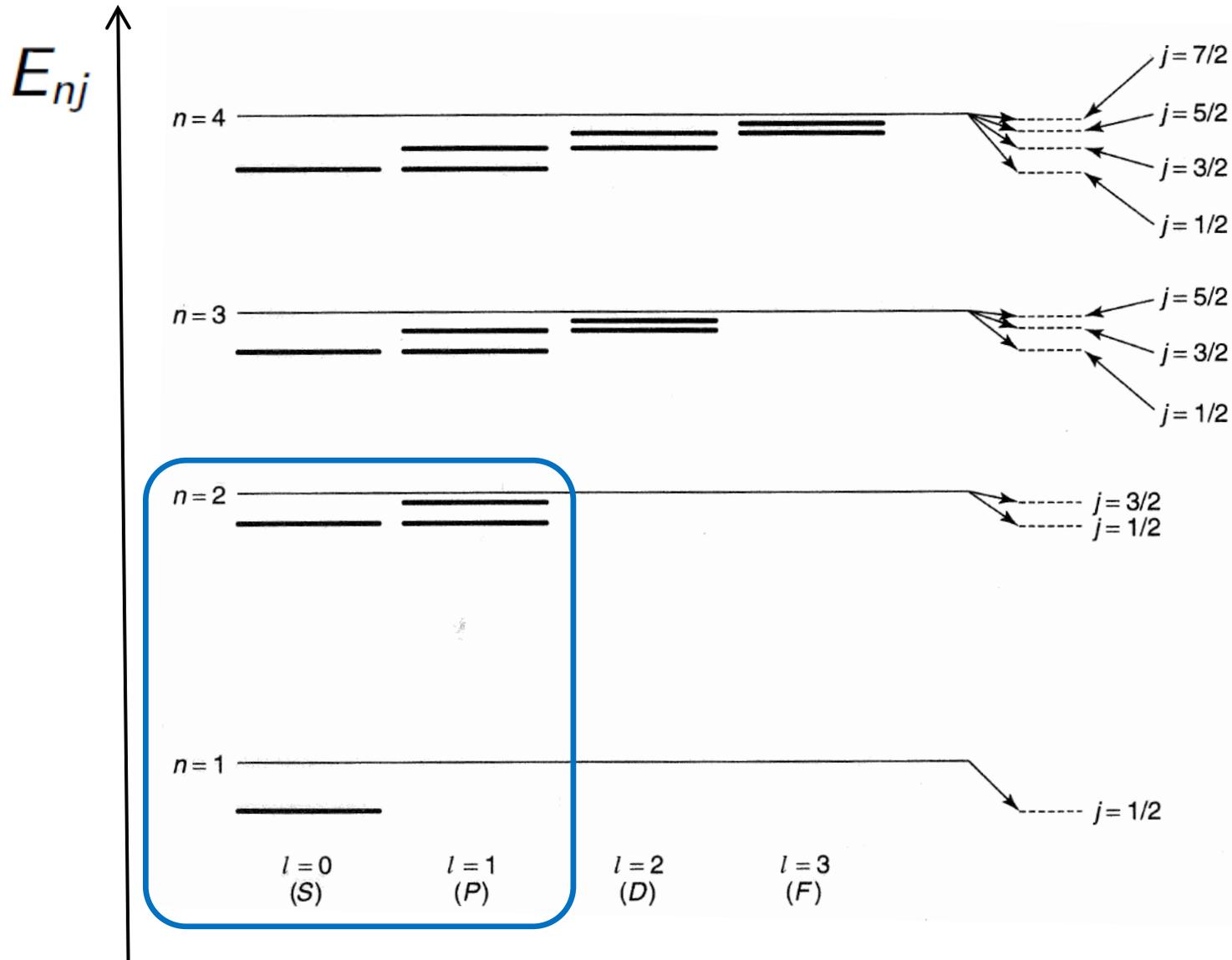
Electromagnetic radiation can drive different types of transitions in atoms:

Example: hydrogen



Hydrogen with fine-structure

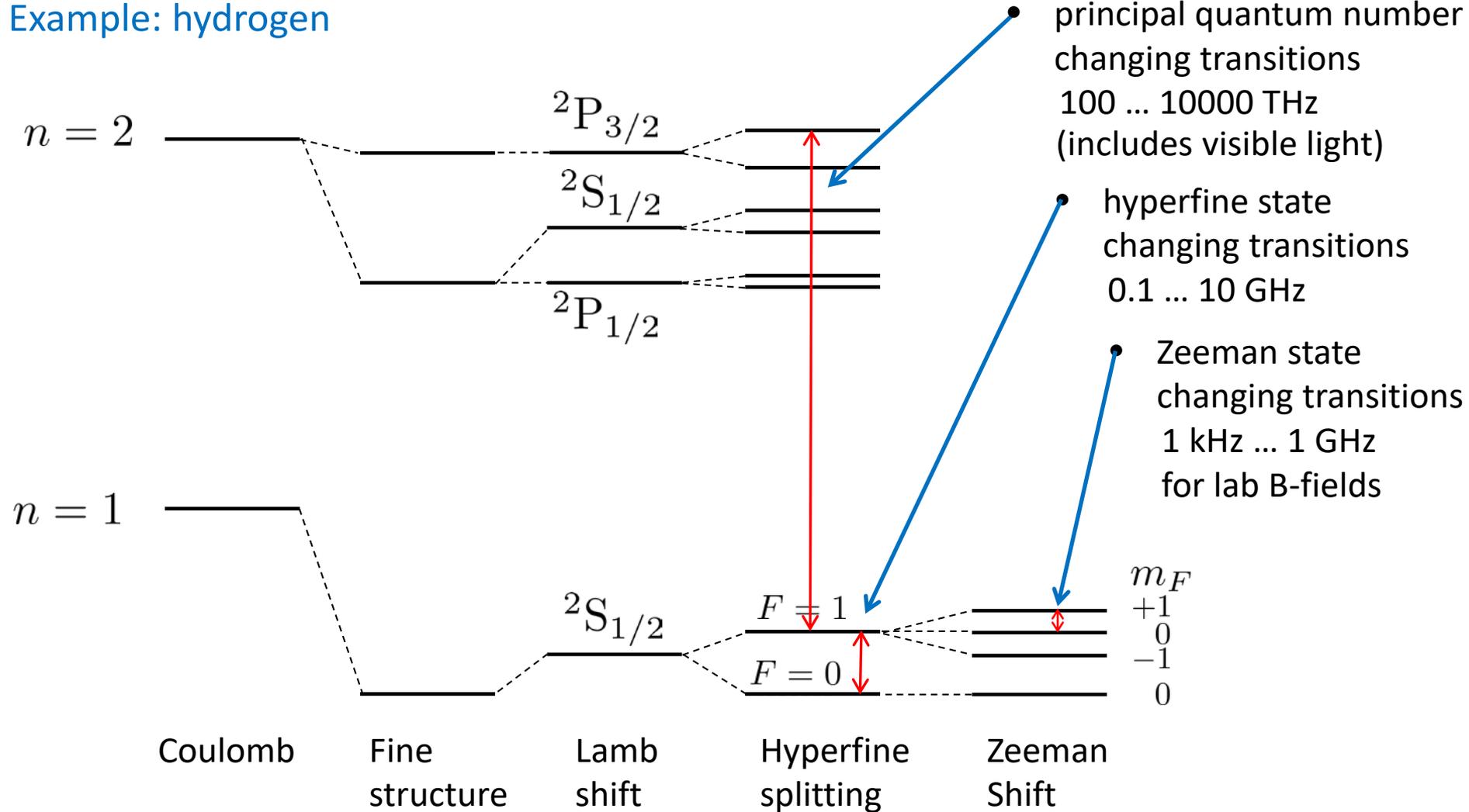
Reminder



Atomic transitions

Electromagnetic radiation can drive different types of transitions in atoms:

Example: hydrogen



In the following: principal quantum number changing transitions

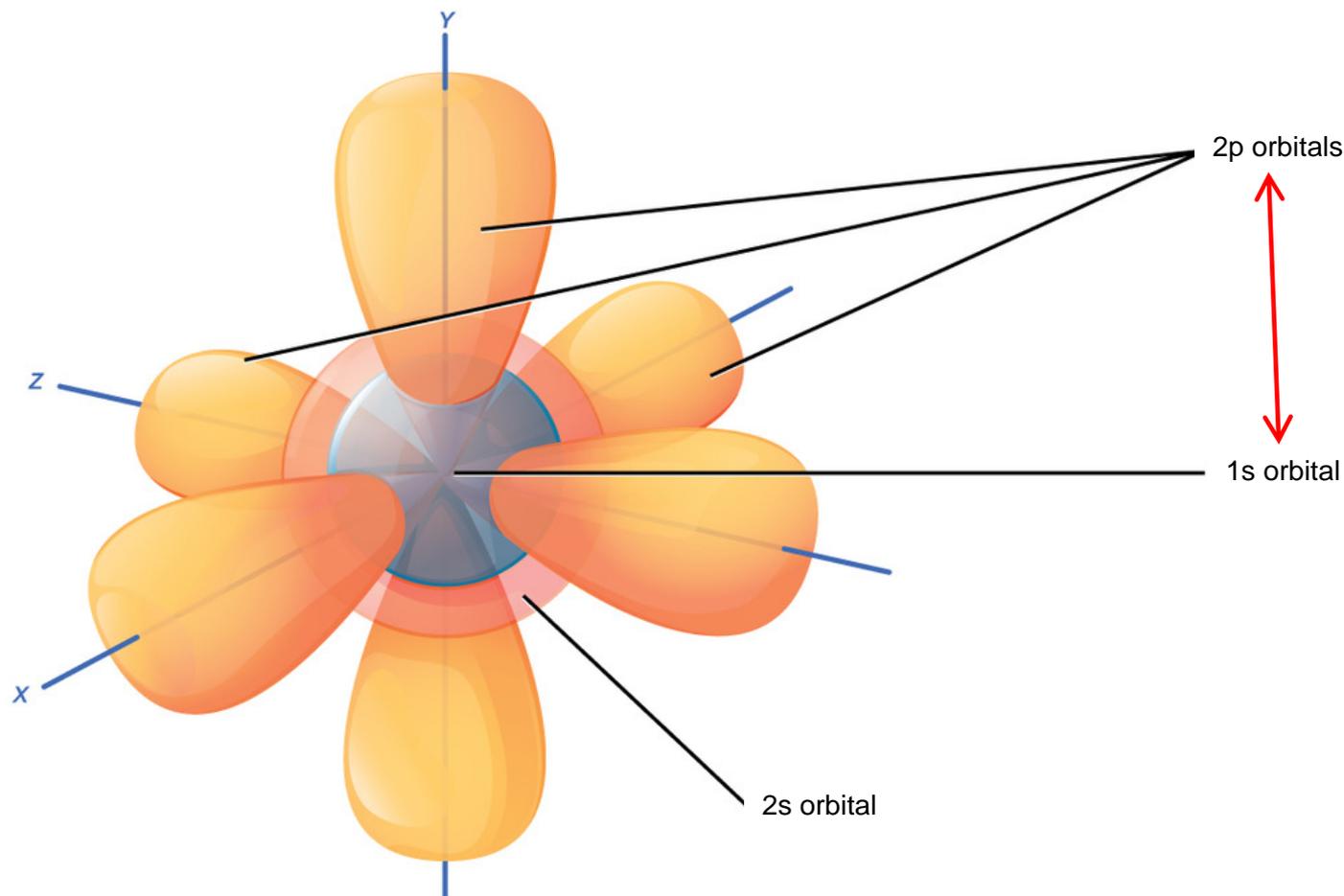
Principal quantum number changing transition

(Valence) electron has to change it's 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

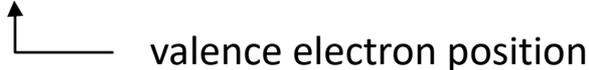
E-field of monochromatic, linearly polarized plane wave:

$$\vec{E}_L(\vec{r}, t) = \vec{E}_0 \cos(\vec{k} \cdot \vec{r} - \omega_L t + \varphi_l)$$

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

Energy $E = -e \vec{r}_e \cdot \vec{E}_L(\vec{r}_e, t)$
 valence electron position

Simplifications:

- wavelength of light much larger than size of atom
 (blue: 400 nm, red: 700 nm ; Bohr radius: 0.05 nm)

→ E-field homogeneous accross atom $\vec{E}_L(\vec{r}, t) \sim \vec{E}_L(\vec{r}_n, t)$
 nucleus position

- chose z-axis parallel to E-field polarization
- atom position fixed in space during transition → no Doppler effect
- light phase φ_L chosen such that $\vec{k} \cdot \vec{r}_n + \varphi_l = 0$

Energy $E = -eE_0 \cos(\omega_L t) z_e \equiv H'$

thorough derivation:
 Sakurai 5.7, Cohen-Tannoudji A_{XIII},...

Hamiltonian of valence e^- and E-field

Bonus material

$$\hat{H}(\vec{r}, t) = \frac{1}{2m_e} \left[\hat{\vec{p}} + e\vec{A}(\vec{r}, t) \right]^2 - e\Phi(\vec{r}, t) + V(r) - \frac{e}{m_e} \hat{S} \cdot \vec{B}(\vec{r}, t)$$

\vec{A} vector potential

$$\vec{E} = -\vec{\nabla}\Phi - \frac{\partial\vec{A}}{\partial t}$$

Φ scalar potential

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

V Coulomb potential of nucleus and inner electrons on valence electron

$-e$ electron charge

m_e electron mass

\hat{S} electron spin operator

Dipole approximation

Bonus material

$$\hat{H}(\vec{r}, t) = \frac{1}{2m_e} \left[\hat{\vec{p}} + e\vec{A}(\vec{r}, t) \right]^2 - e\Phi(\vec{r}, t) + V(r) - \frac{e}{m_e} \hat{\vec{S}} \cdot \vec{B}(\vec{r}, t)$$

Calculation steps and approximations

- Find gauge of EM field that simplifies Hamiltonian.
- Show that terms $\propto A^2$ can be neglected.
- Show that interaction between electron magnetic moment and B field can be neglected.
- Note that spatial extent 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

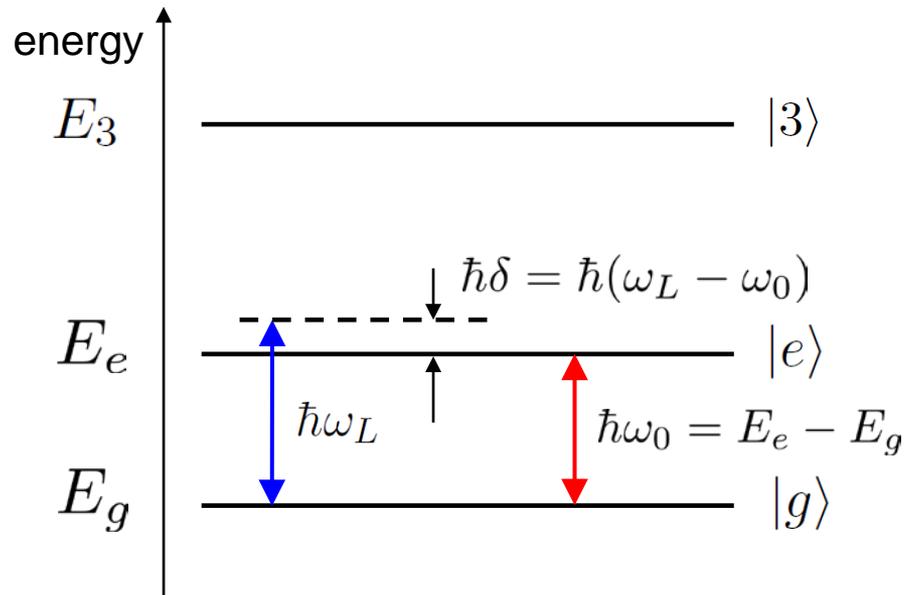
$$\hat{H} = \hat{H}_{\text{at}} + \hat{H}_{\text{int}}$$

$$\hat{H}_{\text{at}} = \frac{\hat{\vec{p}}^2}{2m} + V(r)$$

$$\hat{H}_{\text{int}} = -e\vec{E}(\vec{r} = \vec{0}, t) \cdot \hat{\vec{r}} = -eE_0 \cos(\omega_L t + \varphi_L) \hat{x}$$

Two-level approximation

Atoms have many internal states.



We assume that atom initially in state $|g\rangle$ or $|e\rangle$.

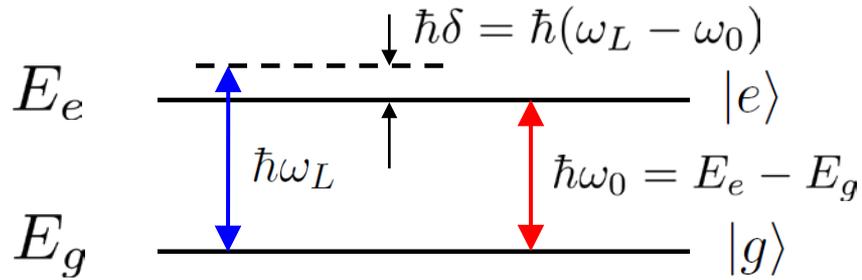
We want to describe transitions between states by light with frequency $\omega_L \sim \omega_0$.

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:



$$H = H^0 + H'(t)$$

$$\begin{array}{c} \uparrow \\ H'(t) = -eE_0 \cos(\omega_L t) z_e \end{array}$$

$$H^0 |i\rangle = E_i |i\rangle \quad ; \quad \langle i|j\rangle = \delta_{ij} \quad ; \quad i, j \in \{g, e\}$$

Compare to calculation „Sinusoidal perturbation“

Sinusoidal perturbation

Reminder

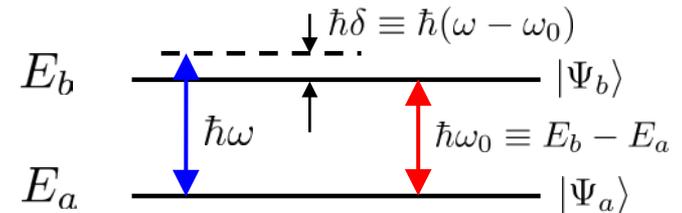
$$H = H^0 + H'(t)$$

static $\underbrace{\quad}$ $\underbrace{\quad}$ **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: $H'_{ij}(t) \equiv V_{ij} \cos(\omega t)$

$$c_a(t) \cong 1$$

$$c_b(t) \cong -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t') e^{i\omega_0 t'} dt' = -\frac{iV_{ba}}{2\hbar} \int_0^t \left[e^{i(\omega_0 + \omega)t'} + e^{i(\omega_0 - \omega)t'} \right] dt'$$

$$= -\frac{V_{ba}}{2\hbar} \left[\frac{e^{i(\omega_0 + \omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0 - \omega)t} - 1}{\omega_0 - \omega} \right]$$

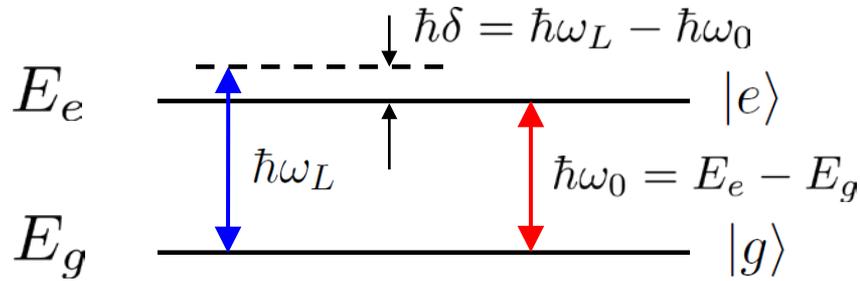
Simplifying assumption: $\omega_0 + \omega \gg |\omega_0 - \omega| = |\delta|$, i.e. detuning small compared to transition frequency

$$c_b(t) \cong -\frac{V_{ba}}{2\hbar} \frac{e^{i(\omega_0 - \omega)t/2}}{\omega_0 - \omega} \left[e^{i(\omega_0 - \omega)t/2} - e^{-i(\omega_0 - \omega)t/2} \right]$$

$$= -i \frac{V_{ba}}{\hbar} \frac{\sin[(\omega_0 - \omega)t/2]}{\omega_0 - \omega} e^{i(\omega_0 - \omega)t/2}$$

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“

$$\longrightarrow V_{ab} = -\wp E_0 \quad \text{with „transition dipole moment“} \quad \wp \equiv e \langle e|z_e|g\rangle$$

Perturbation theory transition probability (valid if $P \ll 1$)

$$\text{Atom starts in } |g\rangle. \text{ Probability of transition to } |e\rangle: P_{g \rightarrow e}(t) \cong \left(\frac{|\wp| E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2}$$

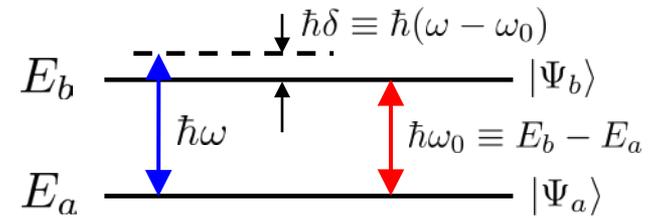
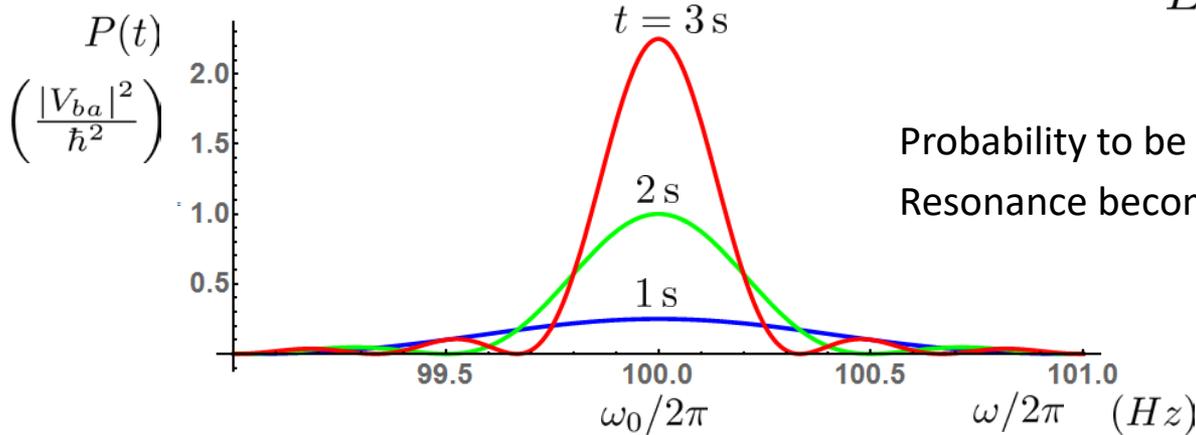
Transition probability

Reminder

$$P_{a \rightarrow b}(t) = |c_b(t)|^2 \cong \frac{|V_{ba}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}$$

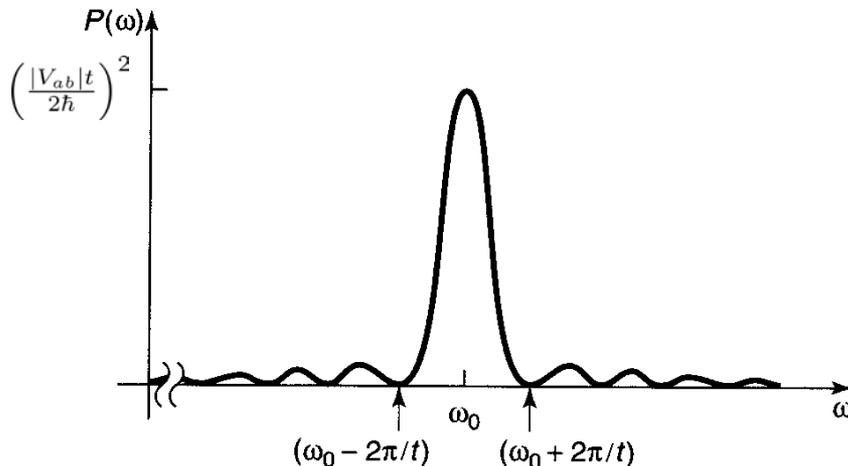
$$\frac{|V_{ba}|^2}{\hbar^2} \ll 1 \text{ for perturbation theory to be valid}$$

Spectrum:

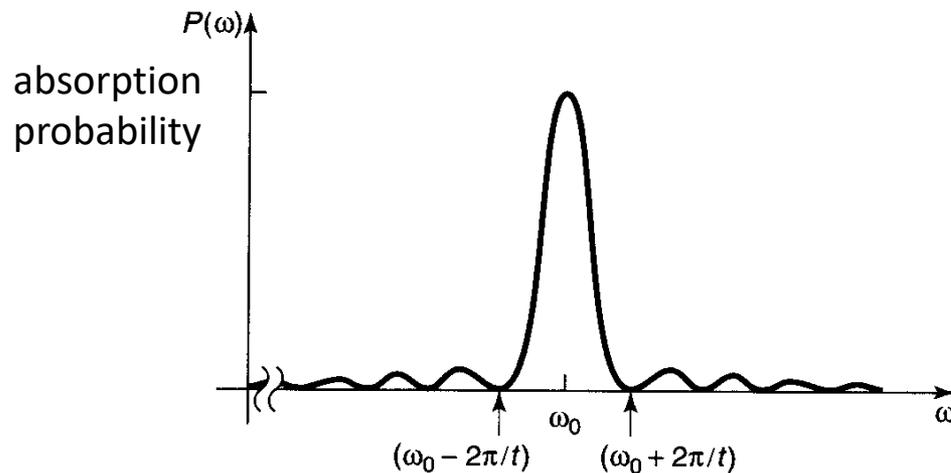
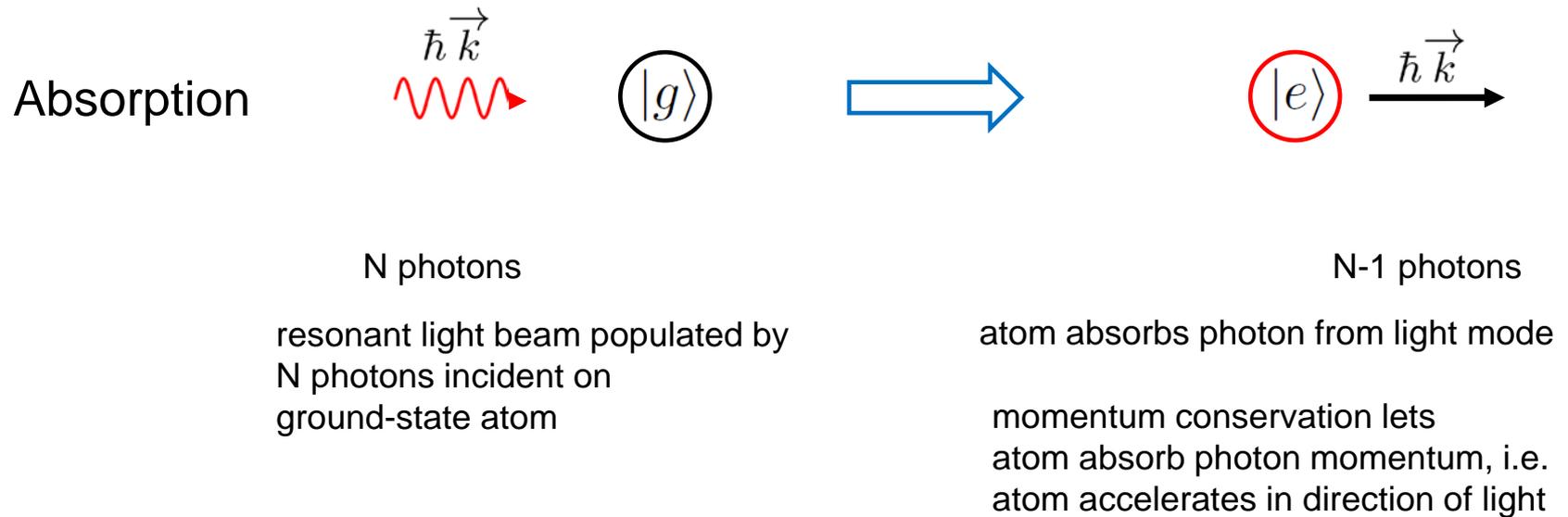


Probability to be in $|\Psi_b\rangle$ higher if detuning δ small.
Resonance becomes narrower and higher over time.

Rescaling collapses resonances for all times on one graph:

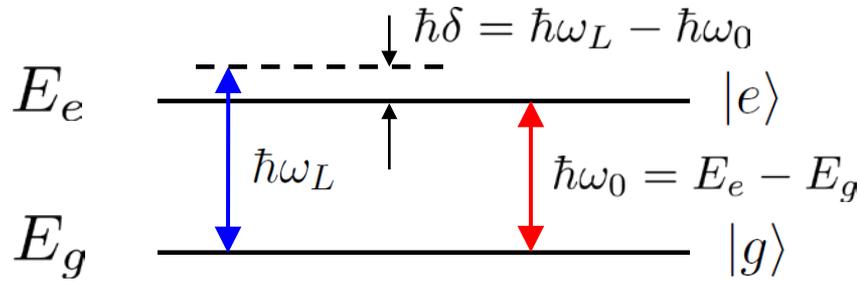


Basic atom-light interaction processes



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“

$$\longrightarrow V_{ab} = -\wp E_0 \quad \text{with „transition dipole moment“} \quad \wp \equiv e \langle e|z_e|g\rangle$$

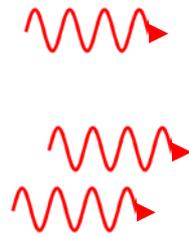
Perturbation theory transition probability (valid if $P \ll 1$)

$$\text{Atom starts in } |g\rangle. \text{ Probability of transition to } |e\rangle: P_{g \rightarrow e}(t) \cong \left(\frac{|\wp| E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2}$$

$$\text{Atom starts in } |e\rangle. \text{ Probability of transition to } |g\rangle: P_{e \rightarrow g}(t) \cong \left(\frac{|\wp| E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2}$$

Stimulated emission

Stimulated emission



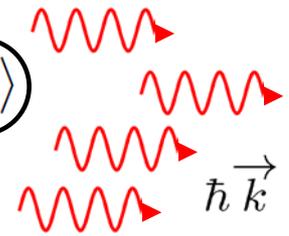
N photons

$|e\rangle$



$-\hbar \vec{k}$

$|g\rangle$

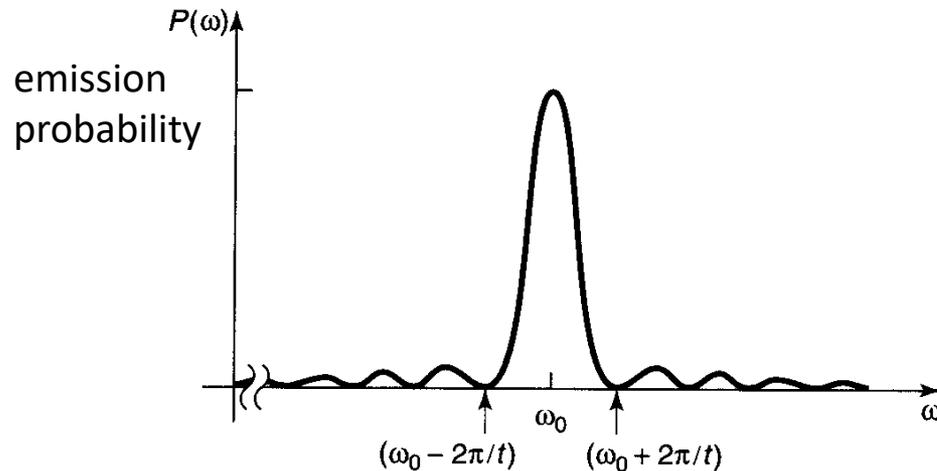


N+1 photons

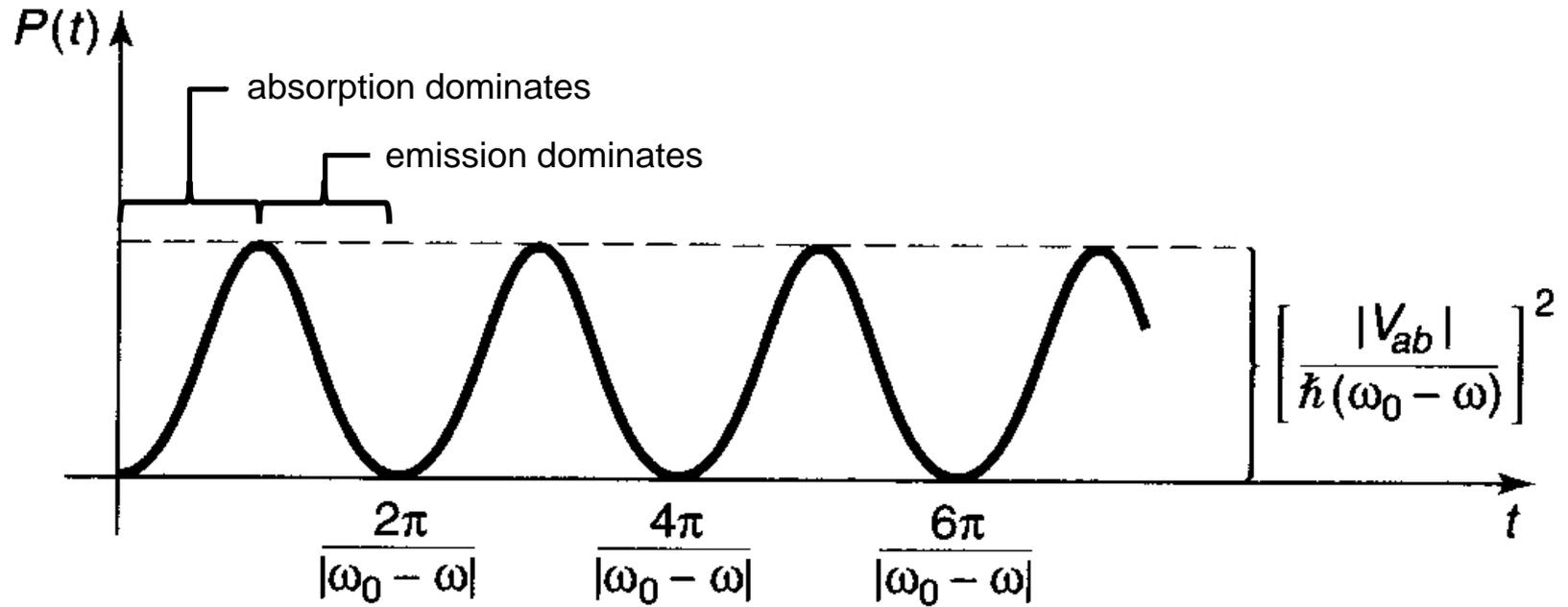
resonant light beam populated by N photons incident on excited-state atom

atom emits photon into light mode

momentum conservation lets atom recoil in direction opposite to photon momentum, i.e. opposite to light direction



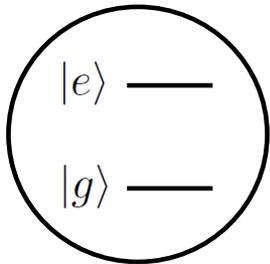
Rabi oscillations



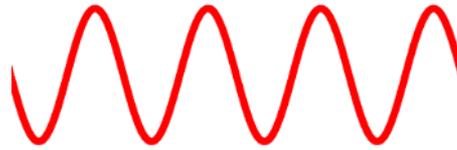
Meet the players

Reminder

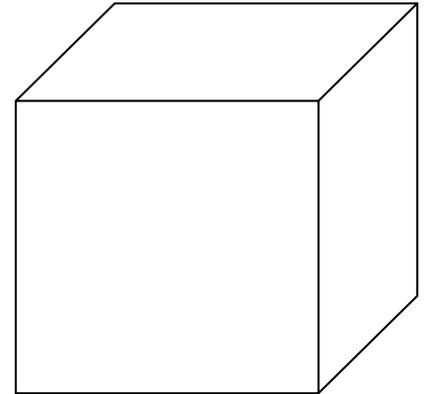
Atom



Laser beam

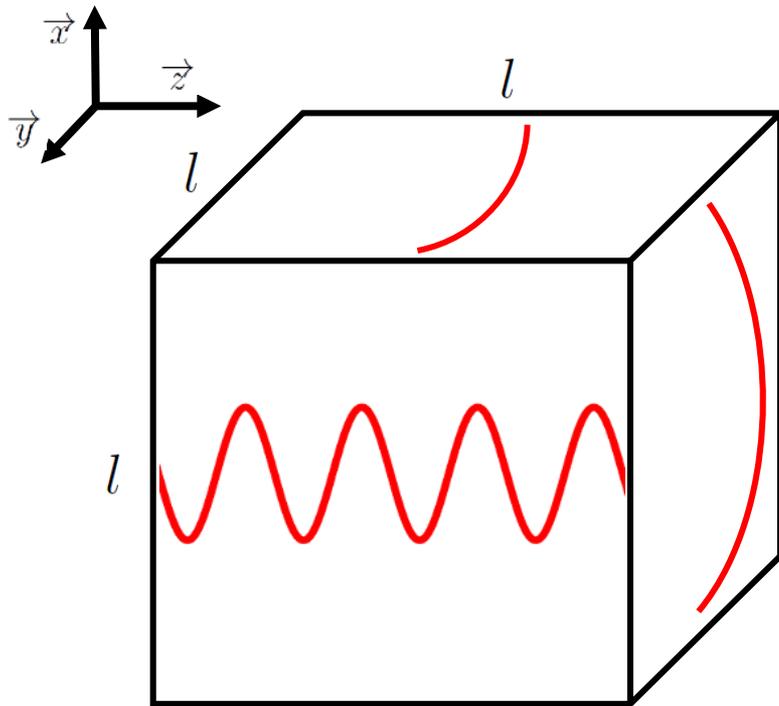


EM field modes



The 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

$$\vec{E} = \vec{E}_0 \sin\left(\frac{n_x \pi x}{l}\right) \sin\left(\frac{n_y \pi y}{l}\right) \sin\left(\frac{n_z \pi z}{l}\right) \sin(\omega t)$$

Example shown:

red lines symbolize sine term along respective direction
 $n_x = n_y = 1$ and $n_z = 8$

Two polarizations $\vec{E}_{1,2}$:
e.g. linear with $\vec{E}_{1,2} \perp \vec{k}$ and $\vec{E}_1 \perp \vec{E}_2$

Each mode can be populated with $n = 0 \dots \infty$ photons.

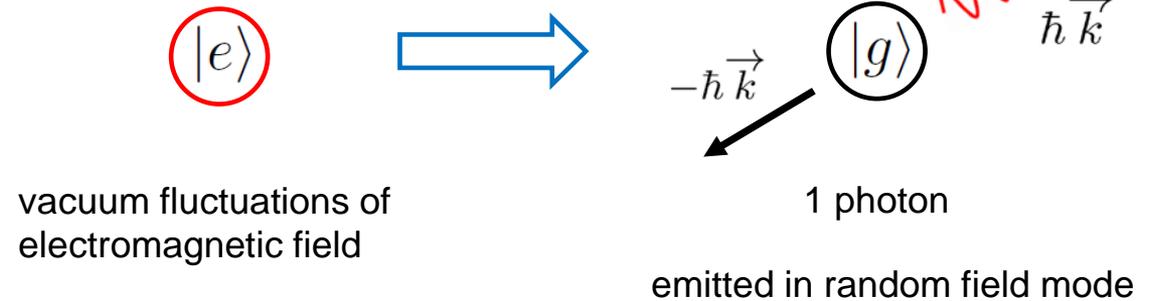
The energy of each mode is $E = \left(\frac{1}{2} + n\right) \hbar \omega$ (just like harmonic oscillator)

↑ quantum fluctuations of vacuum

The electromagnetic vacuum $|0\rangle$ consists of these modes in their groundstate, $n = 0$ for every mode.

Spontaneous emission

Spontaneous emission



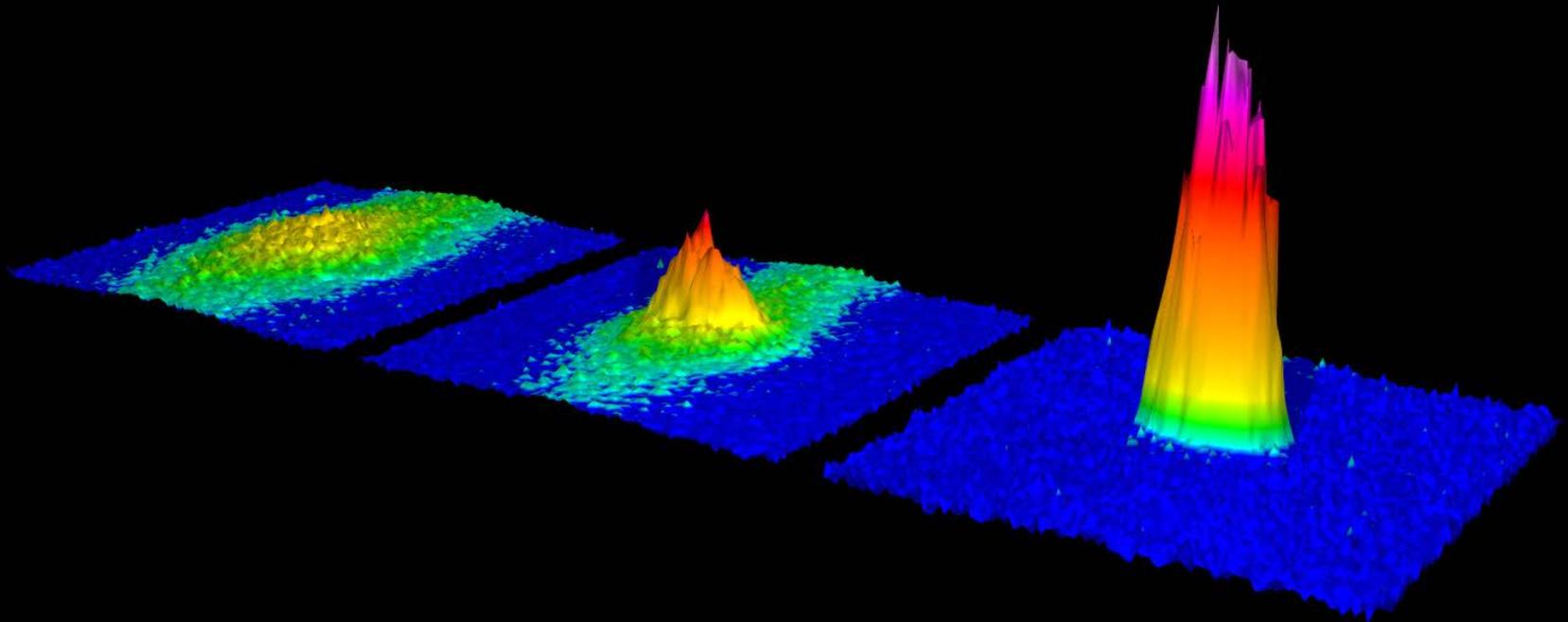
Spontaneous emission is stimulated emission driven by vacuum fluctuations of EM field modes.

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

Griffiths 3rd 5.1, 5.2

Crystalline solids

5.3.2

Time-independent perturbation theory

7.1, 7.2

Structure of hydrogen

7.3 – 7.5

Variational principle

8.1 – 8.3

today → Time-dependent perturbation theory, atom-light interaction 11.1 – 11.4

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.

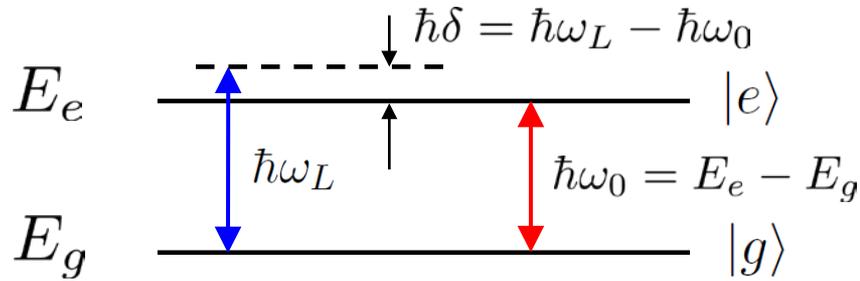
Plan of this section

- 1) Introduction Griffiths 3rd 11.0
- 2) Two-level system with time-dependent H 11.1
 - time-dependent perturbation theory
 - sinusoidal perturbation
- 3) Emission and absorption of radiation 11.2 - 3
 - - 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

Reminder

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“

$$\longrightarrow V_{ab} = -\wp E_0 \quad \text{with „transition dipole moment“} \quad \wp \equiv e \langle e|z_e|g\rangle$$

Perturbation theory transition probability (valid if $P \ll 1$)

$$\text{Atom starts in } |g\rangle. \text{ Probability of transition to } |e\rangle: P_{g \rightarrow e}(t) \cong \left(\frac{|\wp| E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2}$$

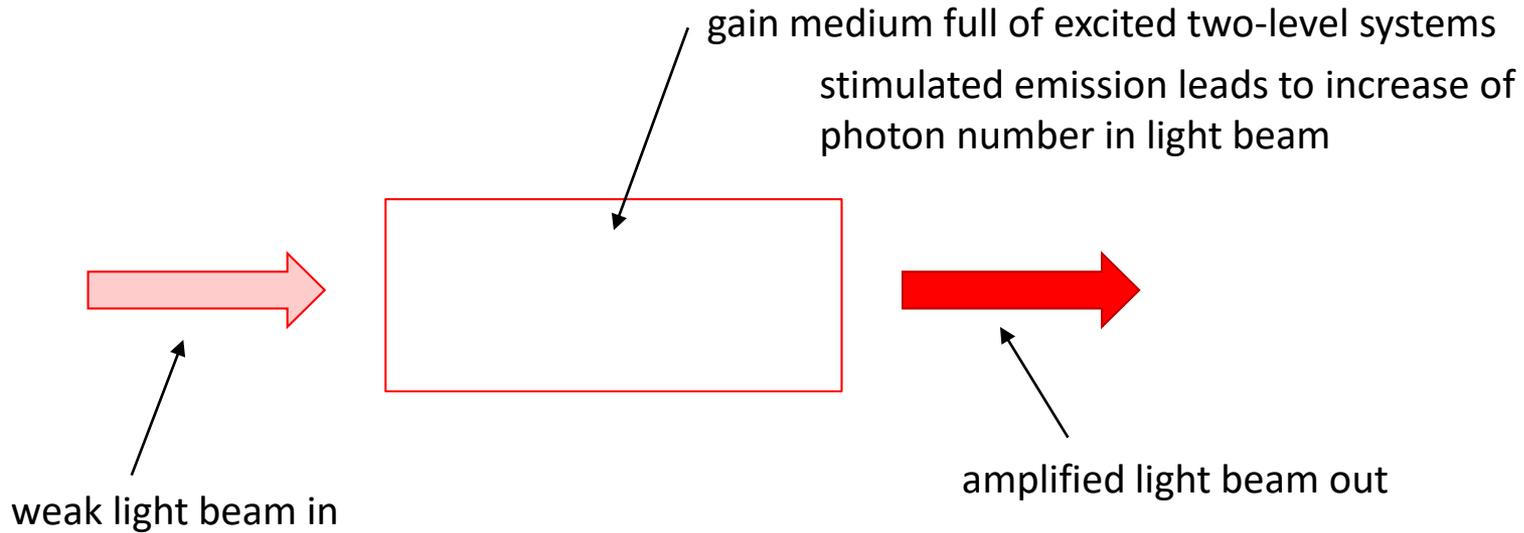
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Basic atom-light interaction processes



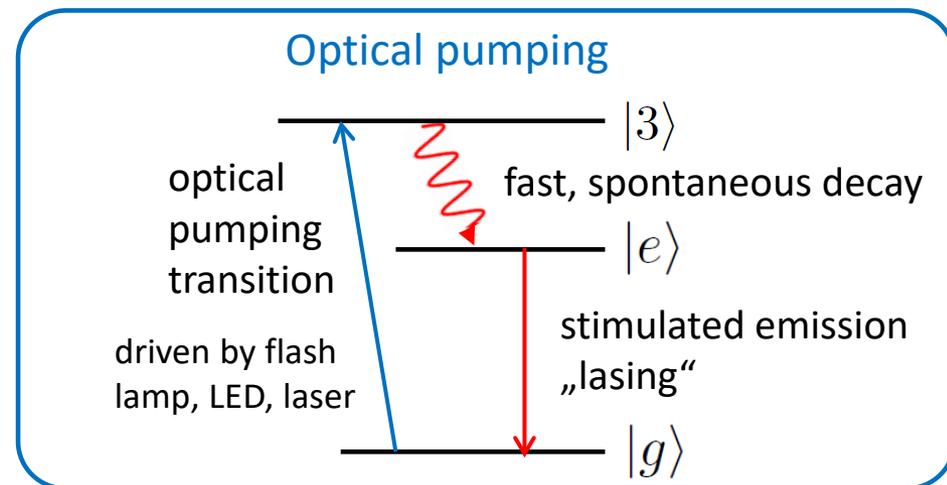
Laser amplifier

LASER: Light Amplification by Stimulated Emission of Radiation



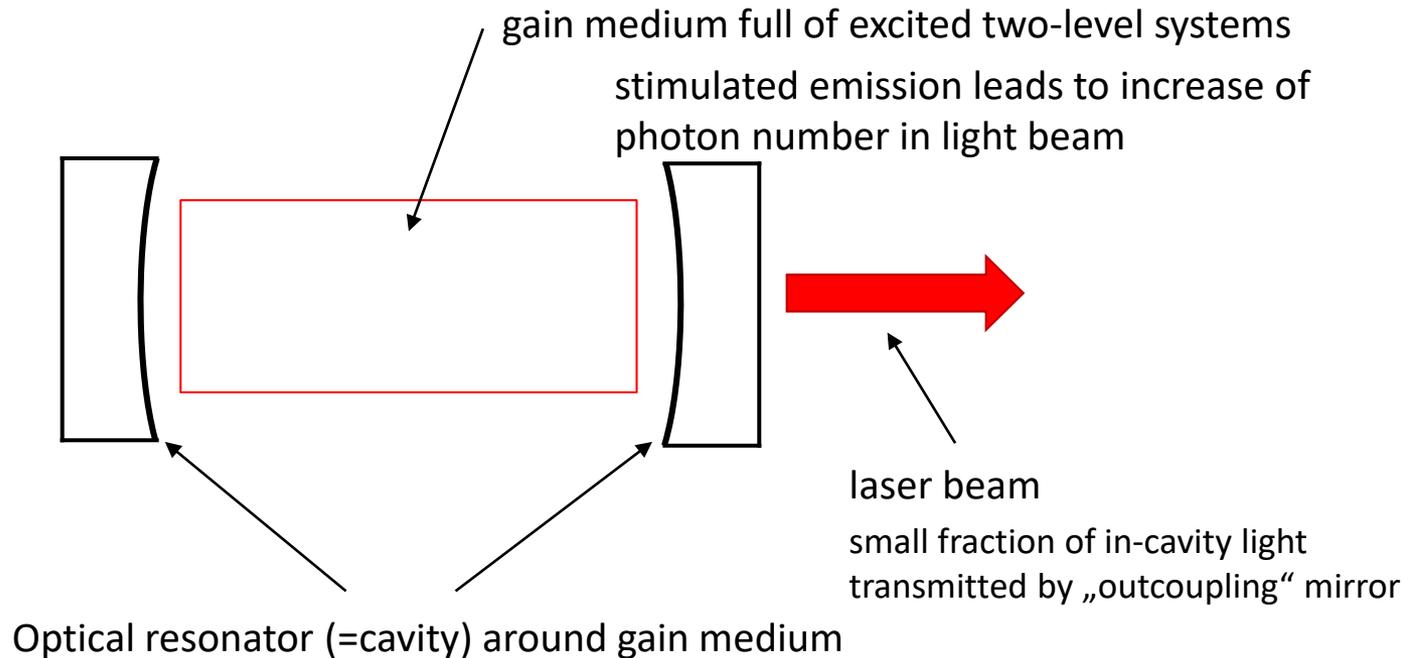
Excited two-level systems are created

- optically („optical pumping“)
- electronically (laser diode)
- chemically (excimer laser)



Laser

LASER: Light Amplification by Stimulated Emission of Radiation



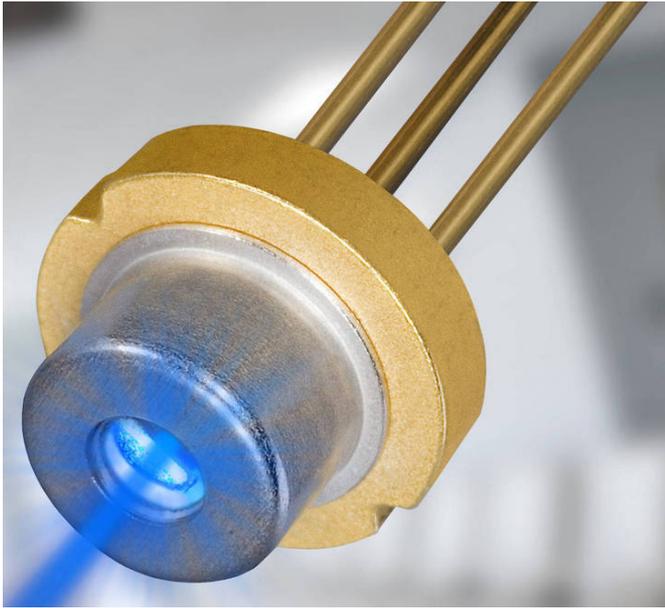
Photons travel many times forwards and backwards, each time leading to amplification by spontaneous emission

Lasing process starts by spontaneous emission

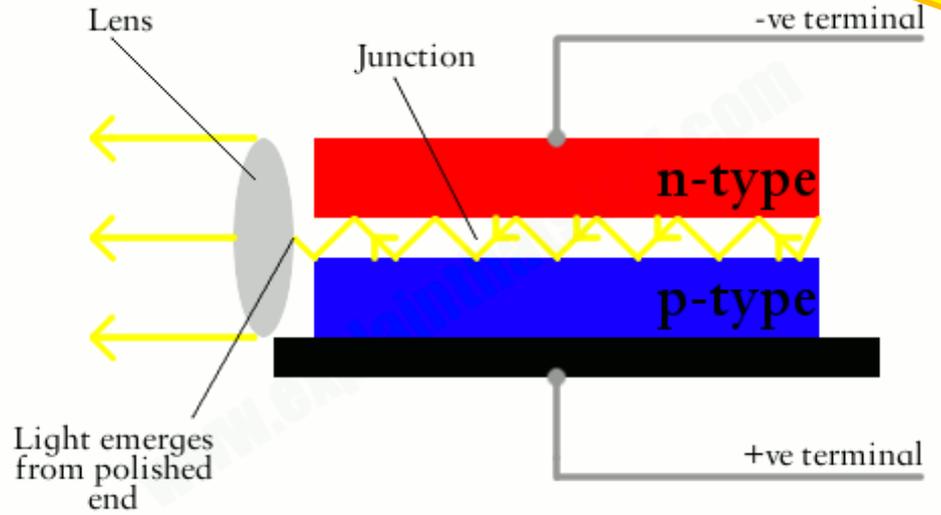
Lasing only possible on modes of the electromagnetic field that are resonant with cavity

Laser diode

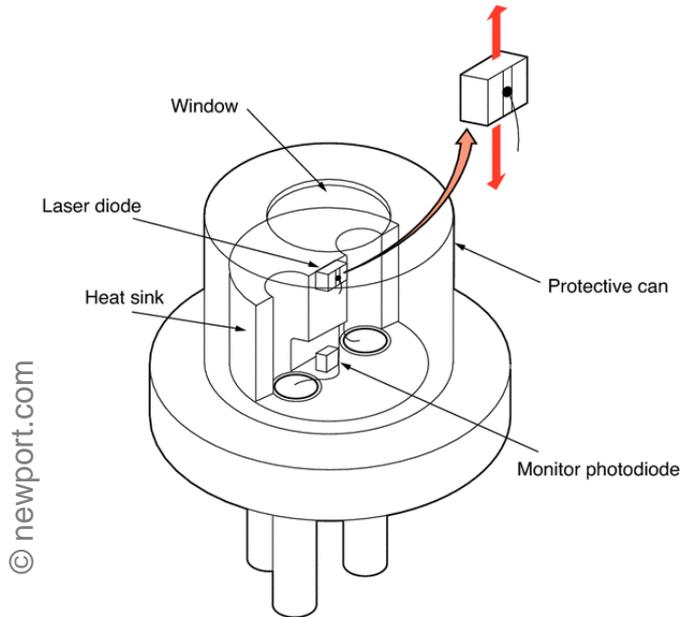
Bonus material



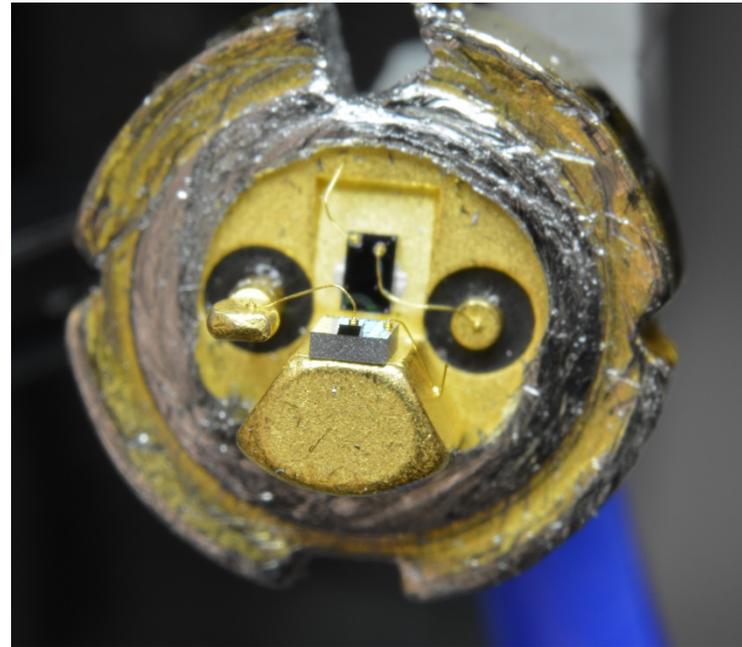
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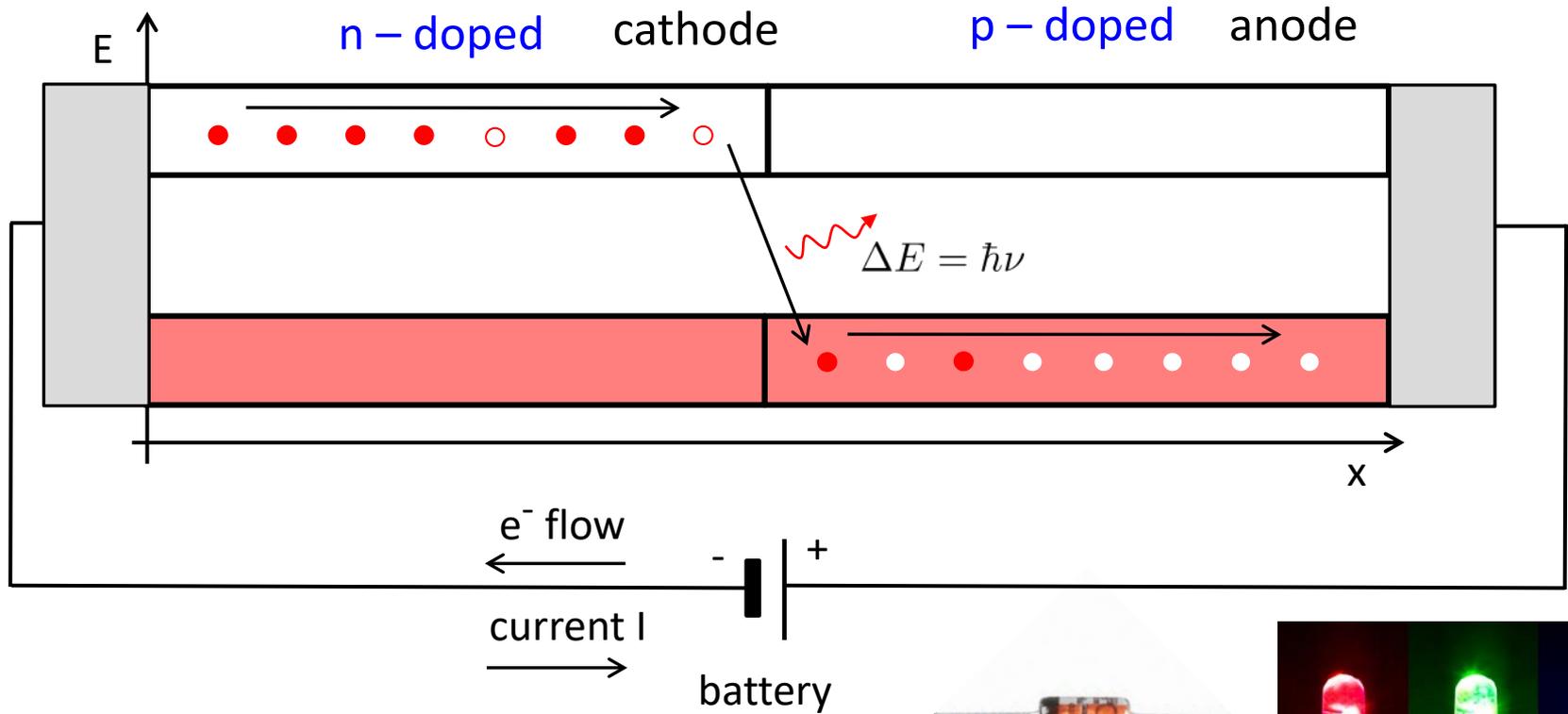


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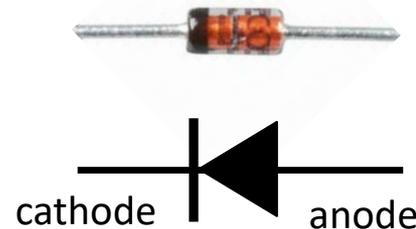
Light-emitting Diode (LED)

Reminder

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.

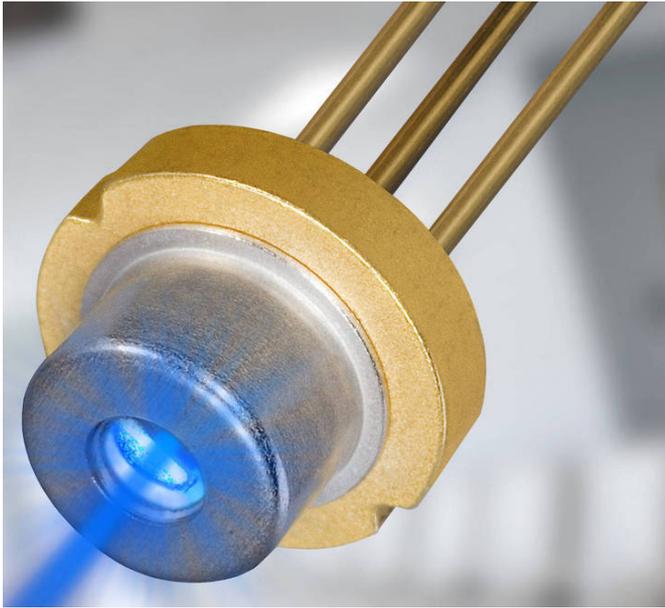


In LEDs energy of electron combining with hole liberated as photon.

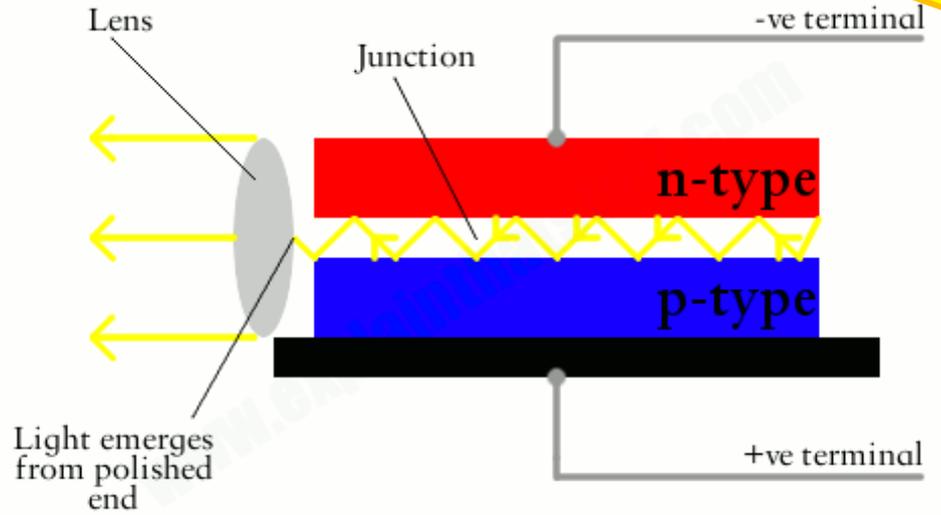


Laser diode

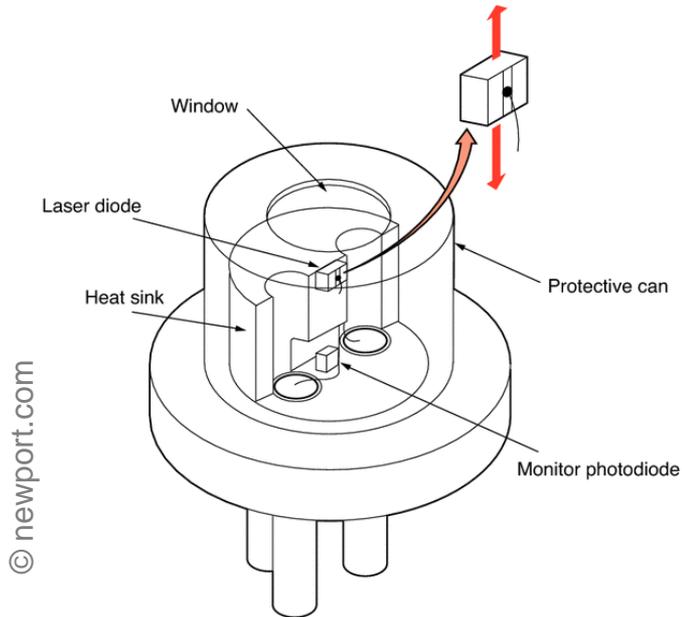
Bonus material



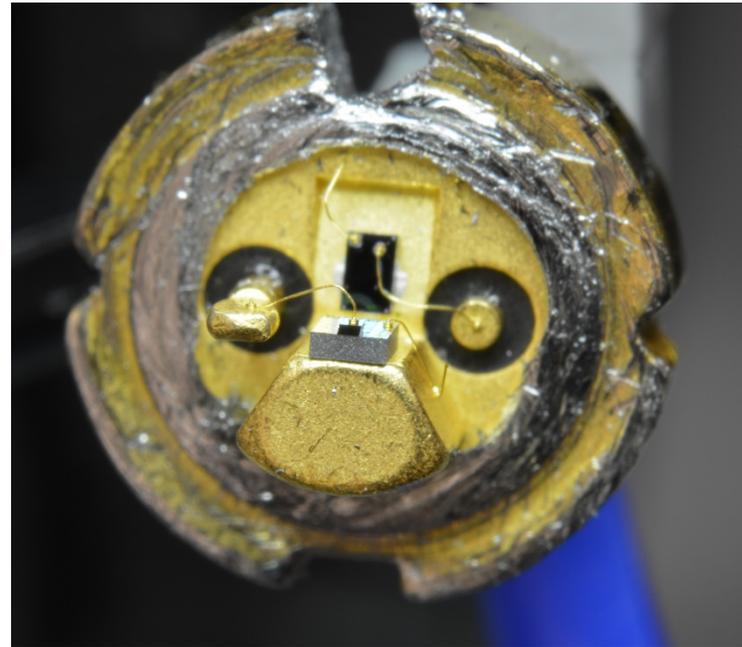
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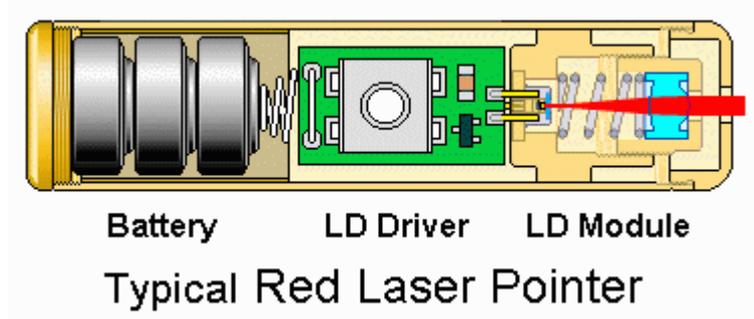
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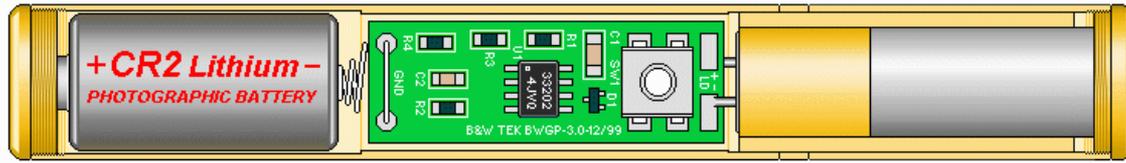
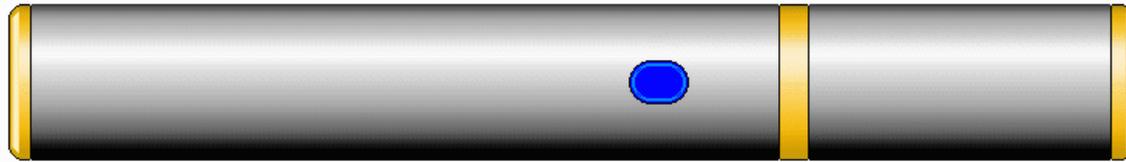
Red laser pointer

Bonus material



Green laser pointer

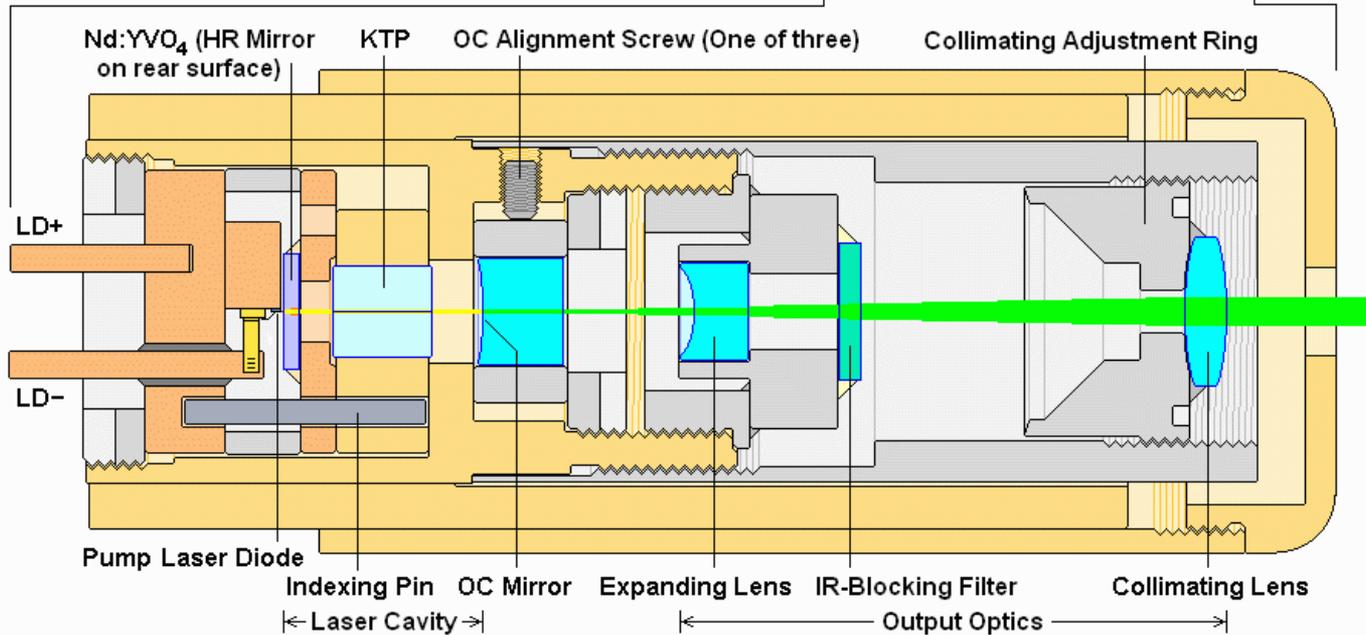
Bonus material



Battery

Pump LD Driver

DPSS Laser Module

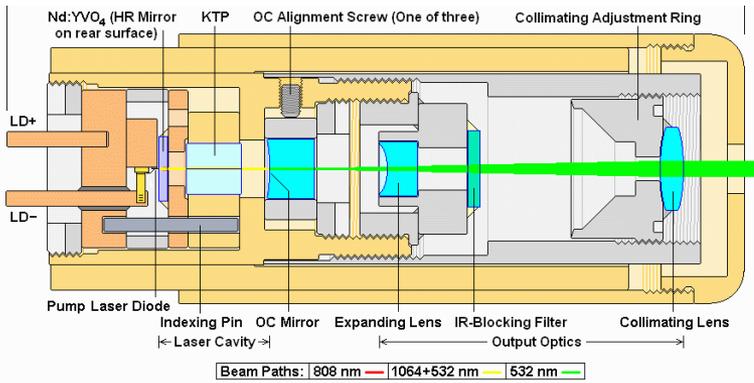


Beam Paths: 808 nm — 1064+532 nm — 532 nm —

Edmund Scientific L54-101 Green DPSS Laser Pointer

Components of green laser pointer

Bonus material



Pump Diode Driver Board



Collimating Lens



Pump Diode on Block on Copper Disk



Indexing Pin



OC Mirror



Vanadate on Copper Disk



KTP on Brass Disk



IR Filter, Expanding Lens below

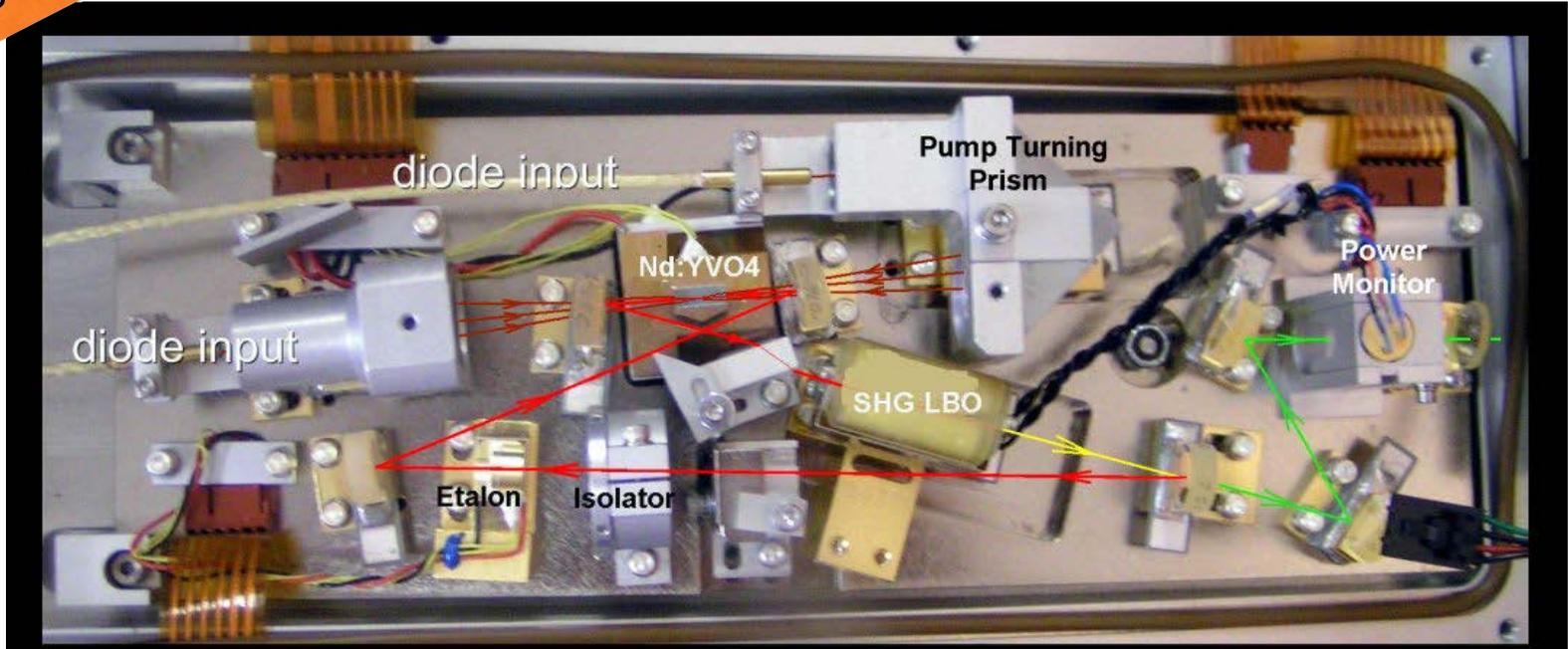
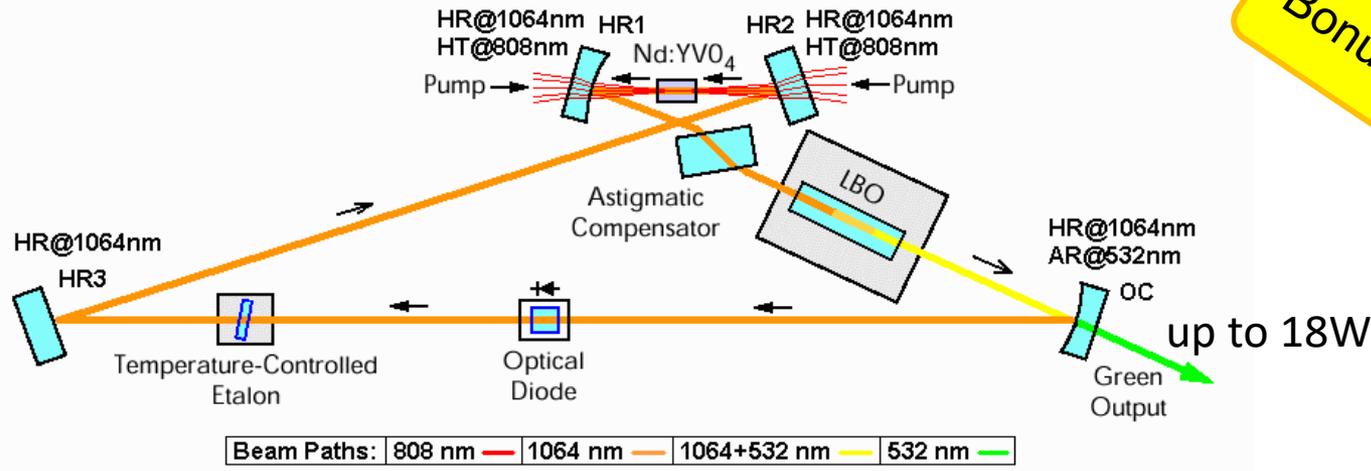


OC Adjusting Set Screws

20W frequency doubled Nd:YAG laser

Bonus material

100k€



Coherent Verdi DPSS Laser Cavity with Components Labeled

© <http://greyghost.mo00.com>

<http://donkclipstein.com>

Overview of „*Time-dependent perturbation theory*“

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Spontaneous emission limits lifetime of $|e\rangle$

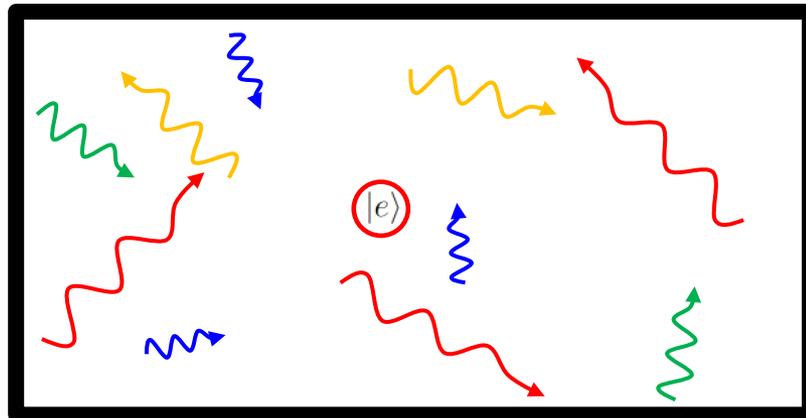
Goals:

- 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.

$|e\rangle$

In reality atom decays by spontaneous emission driven by vacuum fluctuations.



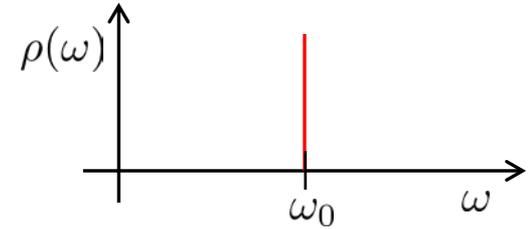
Vacuum fluctuations happen in each electromagnetic field mode, not just one.

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: $u = \frac{\epsilon_0}{2} E_0^2$

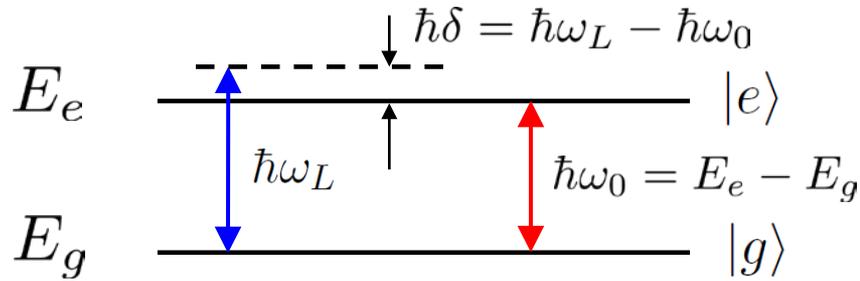


energy density in range $d\omega$ is $\rho(\omega)d\omega$

Atom-light interaction

Reminder

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“

$$\longrightarrow V_{ab} = -\wp E_0 \quad \text{with „transition dipole moment“} \quad \wp \equiv e \langle e|z_e|g\rangle$$

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$$\text{Atom starts in } |g\rangle. \text{ Probability of transition to } |e\rangle: P_{g \rightarrow e}(t) \cong \left(\frac{|\wp| E_0}{\hbar} \right)^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2}$$

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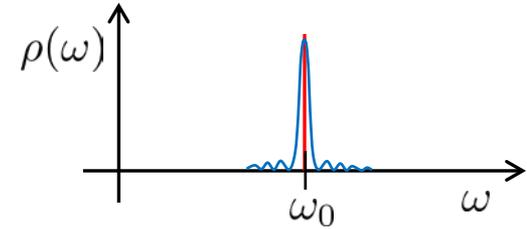
Incoherent perturbation

So far: coherent, monochromatic, electromagnetic plane wave

Energy density: $u = \frac{\epsilon_0}{2} E_0^2$

Transition probability, expressed using energy density:

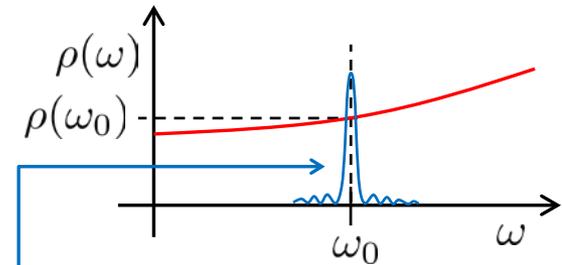
$$P_{e \rightarrow g}(t) = \frac{2u}{\epsilon_0 \hbar^2} |\mathcal{D}|^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2}$$



energy density in range $d\omega$ is $\rho(\omega)d\omega$

Incoherent electromagnetic wave:

$$P_{e \rightarrow g}(t) = \frac{2}{\epsilon_0 \hbar^2} |\mathcal{D}|^2 \int_0^\infty \rho(\omega) \left\{ \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2} \right\}$$



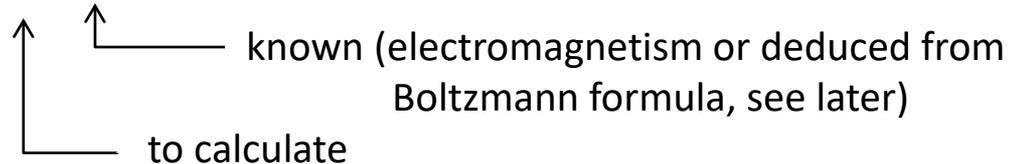
atom absorbs resonantly around ω_0

$$\cong \frac{2}{\epsilon_0 \hbar^2} |\mathcal{D}|^2 \rho(\omega_0) \int_0^\infty \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2}$$

$$\cong \frac{\pi |\mathcal{D}|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) t$$

Transition rate:

$$R_{e \rightarrow g}(t) \equiv \frac{dP_{e \rightarrow g}(t)}{dt} = \frac{\pi}{\epsilon_0 \hbar^2} |\mathcal{D}|^2 \rho(\omega_0)$$



Radiation from all directions, with all polarizations

Transition rate:

$$R_{e \rightarrow g}(t) \equiv \frac{dP_{e \rightarrow g}(t)}{dt} = \frac{\pi}{\epsilon_0 \hbar^2} |\mathcal{D}|^2 \rho(\omega_0)$$

So far: single plane wave, polarized along z direction

$$|\mathcal{D}|^2 \text{ calculated with } \mathcal{D} = e \langle e | z_e | g \rangle ; V_{ge} = -\mathcal{D} E_0 ; H'_{eg}(t) = V_{eg} \cos(\omega t)$$

Now: radiation from all directions, all polarization directions per mode

Todo: Average over $|\mathcal{D}|^2$ calculated for all directions and polarizations

First: Generalize $|\mathcal{D}|^2$ to one wave with wavevector \vec{k} and polarization direction \hat{n} .

i.e. repeat calculation „sinusoidal perturbation“, but keep polarization general.

$$\text{Perturbation } H'(t) = -e \vec{r}_e \cdot \vec{E}_L(\vec{r}_e, t)$$

Electric dipole transitions

Reminder

E-field of light acting on charge of electron

E-field of monochromatic, linearly polarized plane wave:

$$\vec{E}_L(\vec{r}, t) = \vec{E}_0 \cos(\vec{k} \cdot \vec{r} - \omega_L t + \varphi_l)$$

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

Energy $E = -e \vec{r}_e \cdot \vec{E}_L(\vec{r}_e, t)$

↑
valence electron position

Simplifications:

- wavelength of light much larger than size of atom
(blue: 400 nm, red: 700 nm ; Bohr radius: 0.05 nm)

→ E-field homogeneous accross atom $\vec{E}_L(\vec{r}, t) \sim \vec{E}_L(\vec{r}_n, t)$

↑
nucleus position

- chose z-axis parallel to E-field polarization
- atom position fixed in space during transition → no Doppler effect
- light phase φ_L chosen such that $\vec{k} \cdot \vec{r}_n + \varphi_l = 0$

Energy $E = -e E_0 \cos(\omega_L t) z_e \equiv H'$

thorough derivation:
Sakurai 5.7, Cohen-Tannoudji A_{XIII},...

Radiation from all directions, with all polarizations

Transition rate:

$$R_{e \rightarrow g}(t) \equiv \frac{dP_{e \rightarrow g}(t)}{dt} = \frac{\pi}{\epsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0)$$

So far: single plane wave, polarized along z direction

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Now: radiation from all directions, all polarization directions per mode

Todo: Average over $|\wp|^2$ calculated for all directions and polarizations

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i.e. repeat calculation „sinusoidal perturbation“, but keep polarization general.

$$\text{Perturbation } H'(t) = -e \vec{r}_e \cdot \vec{E}_L(\vec{r}_e, t) = -e \vec{r}_e \cdot \vec{n} E_0 \cos(\omega_L t)$$

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 $H'_{eg}(t) = V_{eg} \cos(\omega t)$:

$$V_{ge} = -\vec{\wp} \cdot \hat{n} E_0 \text{ with } \vec{\wp} \equiv e \langle e | \vec{r}_e | g \rangle$$

Sinusoidal perturbation

Reminder

$$H = H^0 + H'(t)$$

static $\left\{ \begin{array}{l} \text{small time-dependent perturbation } H'(t) = V \cos(\omega t) \end{array} \right.$

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:

$$H'_{ij}(t) \equiv V_{ij} \cos(\omega t)$$

$$c_a(t) \cong 1$$

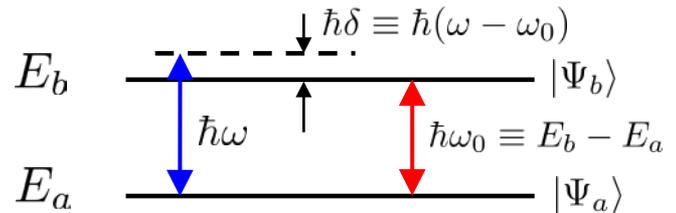
$$c_b(t) \cong -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t') e^{i\omega_0 t'} dt' = -\frac{iV_{ba}}{2\hbar} \int_0^t \left[e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'} \right] dt'$$

$$= -\frac{V_{ba}}{2\hbar} \left[\frac{e^{i(\omega_0+\omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega} \right]$$

Simplifying assumption: $\omega_0 + \omega \gg |\omega_0 - \omega| = |\delta|$, i.e. detuning small compared to transition frequency

$$c_b(t) \cong -\frac{V_{ba}}{2\hbar} \frac{e^{i(\omega_0-\omega)t/2}}{\omega_0-\omega} \left[e^{i(\omega_0-\omega)t/2} - e^{-i(\omega_0-\omega)t/2} \right]$$

$$= -i \frac{V_{ba}}{\hbar} \frac{\sin[(\omega_0-\omega)t/2]}{\omega_0-\omega} e^{i(\omega_0-\omega)t/2}$$



Radiation from all directions, with all polarizations

Transition rate:

$$R_{e \rightarrow g}(t) \equiv \frac{dP_{e \rightarrow g}(t)}{dt} = \frac{\pi}{\epsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0)$$

So far: single plane wave, polarized along z direction

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Note: direction of light \vec{k} doesn't influence atom-light interaction, only polarization \hat{n} does.

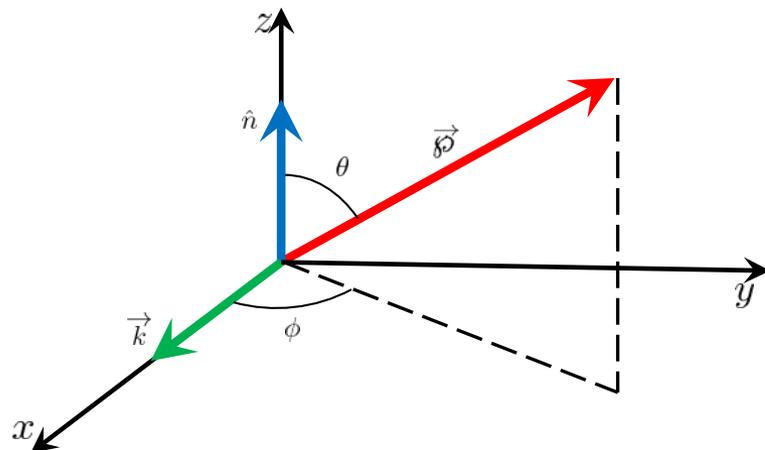
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$$V_{ge} = -\vec{\wp} \cdot \hat{n} E_0 \text{ with } \vec{\wp} \equiv e \langle e | \vec{r}_e | g \rangle$$

Next: Average over $|\vec{\wp} \cdot \hat{n}|^2$ calculated for all directions and all polarizations

Radiation from all directions, with all polarizations

Next: Average over $|\vec{\mathcal{P}} \cdot \vec{n}|^2$ calculated for all directions and all polarizations



$$\vec{\mathcal{P}} \cdot \vec{n} = \mathcal{P} \cos \theta$$

Hold $\vec{\mathcal{P}}$ 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 $\vec{\mathcal{P}}$.

$$\begin{aligned} |\vec{\mathcal{P}} \cdot \vec{n}|^2_{\text{average}} &= \frac{1}{4\pi} \int |\mathcal{P}|^2 \cos^2 \theta \sin \theta d\theta d\phi \\ &= \frac{|\mathcal{P}|^2}{4\pi} \left(-\frac{\cos^3 \theta}{3} \right) \Big|_0^\pi (2\pi) = \frac{1}{3} |\mathcal{P}|^2 \end{aligned}$$

↑ factor 1/3 different from before.

Final result: transition rate

$$R_{e \rightarrow g}(t) = \frac{\pi}{3\epsilon_0 \hbar^2} |\mathcal{P}|^2 \rho(\omega_0)$$

Incoherent perturbation

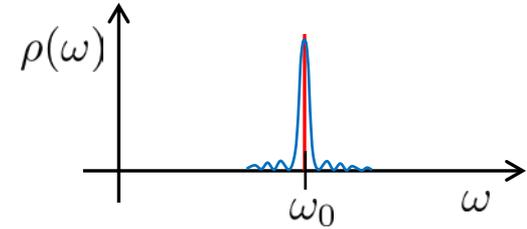
Reminder

Energy density of monochromatic, electromagnetic plane wave:

$$u = \frac{\epsilon_0}{2} E_0^2$$

Transition probability:

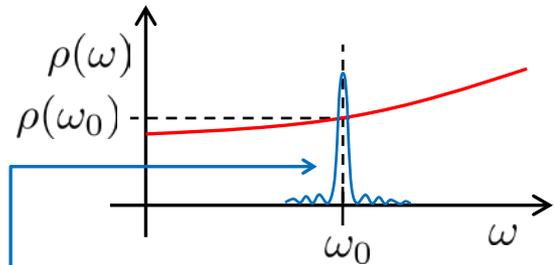
$$P_{e \rightarrow g}(t) = \frac{2u}{\epsilon_0 \hbar^2} |\mathcal{D}|^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2}$$



energy density in range $d\omega$ is $\rho(\omega)d\omega$

Incoherent electromagnetic wave:

$$P_{e \rightarrow g}(t) = \frac{2}{\epsilon_0 \hbar^2} |\mathcal{D}|^2 \int_0^\infty \rho(\omega) \left\{ \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2} \right\} d\omega$$



atom absorbs resonantly around ω_0

$$\approx \frac{2}{\epsilon_0 \hbar^2} |\mathcal{D}|^2 \rho(\omega_0) \int_0^\infty \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2}$$

$$\approx \frac{\pi |\mathcal{D}|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) t$$

Transition rate:

$$R_{e \rightarrow g}(t) \equiv \frac{dP_{e \rightarrow g}(t)}{dt} = \frac{\pi}{\epsilon_0 \hbar^2} |\mathcal{D}|^2 \rho(\omega_0)$$

known (electromagnetism or deduced from Boltzmann formula, now)

done

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

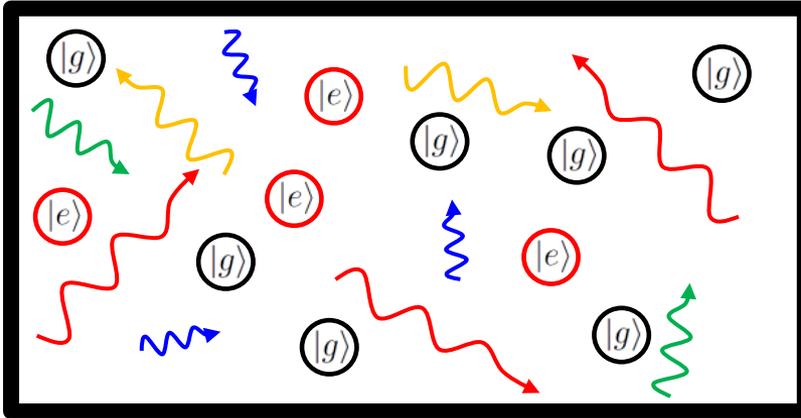
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Spontaneous emission rate after Einstein

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.



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:

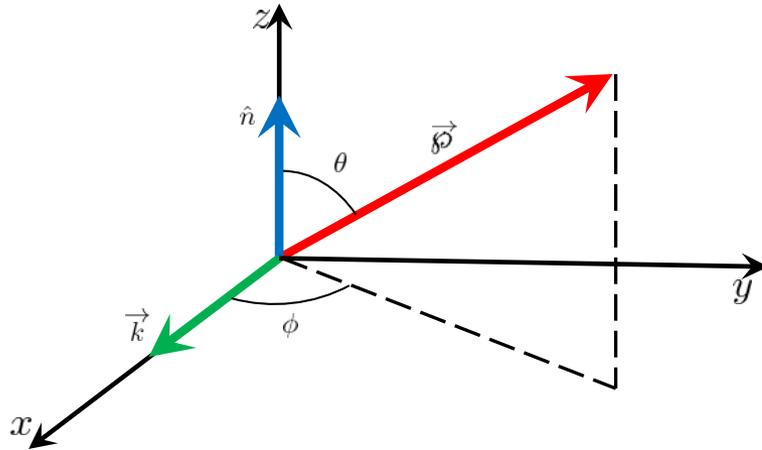
$$\frac{dN_b}{dt} = \underbrace{-N_b A}_{\text{spontaneous emission}} \quad \underbrace{-N_b B_{ba} \rho(\omega_0)}_{\text{stimulated emission}}$$

$$B_{ba} = \frac{\pi |\mathcal{D}|^2}{3\epsilon_0 \hbar^2}$$

Radiation from all directions, with all polarizations

Reminder

Next: Average over $|\vec{\mathcal{P}} \cdot \vec{n}|^2$ calculated for all directions and all polarizations



$$\vec{\mathcal{P}} \cdot \vec{n} = \mathcal{P} \cos \theta$$

Hold $\vec{\mathcal{P}}$ 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 $\vec{\mathcal{P}}$.

$$\begin{aligned} |\vec{\mathcal{P}} \cdot \vec{n}|^2_{\text{average}} &= \frac{1}{4\pi} \int |\mathcal{P}|^2 \cos^2 \theta \sin \theta d\theta d\phi \\ &= \frac{|\mathcal{P}|^2}{4\pi} \left(-\frac{\cos^3 \theta}{3} \right) \Big|_0^\pi (2\pi) = \frac{1}{3} |\mathcal{P}|^2 \end{aligned}$$

↑ factor 1/3 different from before.

Final result: transition rate

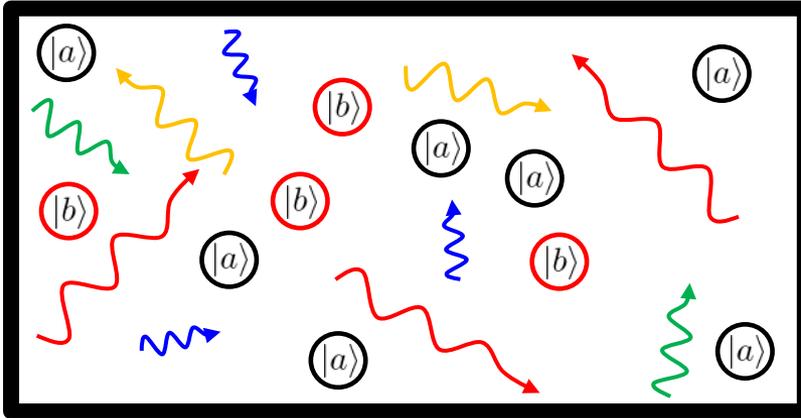
$$R_{e \rightarrow g}(t) = \frac{\pi}{3\epsilon_0 \hbar^2} |\mathcal{P}|^2 \rho(\omega_0)$$

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:

A, B_{ba}, B_{ab} : „Einstein's A and B coefficients“

$$\frac{dN_b}{dt} = \underbrace{-N_b A}_{\text{spontaneous emission}} \quad \underbrace{-N_b B_{ba} \rho(\omega_0)}_{\text{stimulated emission}} \quad \underbrace{+N_a B_{ab} \rho(\omega_0)}_{\text{stimulated absorption}}$$

$$B_{ba} = \frac{\pi |\mathcal{D}|^2}{3\epsilon_0 \hbar^2}$$

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.

$$\longrightarrow \rho(\omega_0) = \frac{A}{(N_a/N_b)B_{ab} - B_{ba}}$$

From statistical mechanics we know that occupation proportional to Boltzmann factor $e^{-E/k_B T}$:

$$\frac{N_a}{N_b} = \frac{e^{-E_a/k_B T}}{e^{-E_b/k_B T}} = e^{\hbar\omega_0/k_B T}$$

$$\longrightarrow \rho(\omega_0) = \frac{A}{e^{\hbar\omega_0/k_B T} B_{ab} - B_{ba}}$$

Compare to Planck's blackbody formula, which also gives energy density of thermal radiation $\rho(\omega)$:

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1}$$

$$\longrightarrow B_{ba} = B_{ab} \quad , \quad A = \frac{\omega_0^3 \hbar}{\pi^2 c^3} B_{ba} \quad , \quad \text{where we know } B_{ba} = \frac{\pi |\mathcal{D}|^2}{3\epsilon_0 \hbar^2}$$

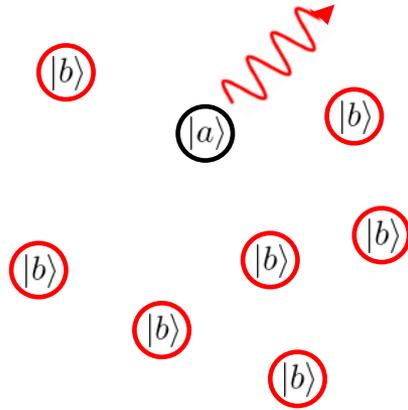
Spontaneous emission

$$\frac{dN_b}{dt} = -AN_b \quad \text{with spontaneous emission rate } A = \frac{\omega_0^3 |\mathcal{D}|^2}{3\pi\epsilon_0 \hbar c^3}$$

Note: modern symbol Γ
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)

$$\frac{dN_b}{dt} = -AN_b$$

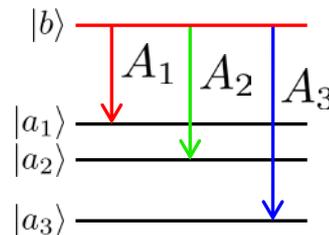
Number of excited emitters over time:

$$N_b(t) = N_b(0)e^{-t/\tau} \quad \text{with } \tau = 1/A$$

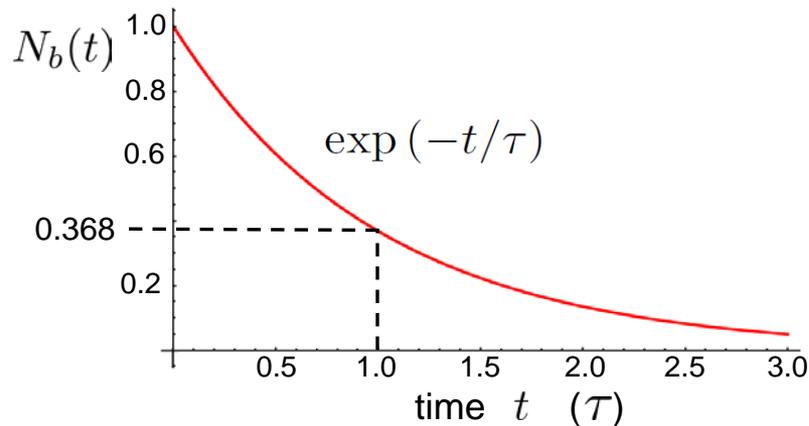
Rate of photon emission:

$$N_\Gamma(t) = AN_b(t)$$

In case there are several lower states:

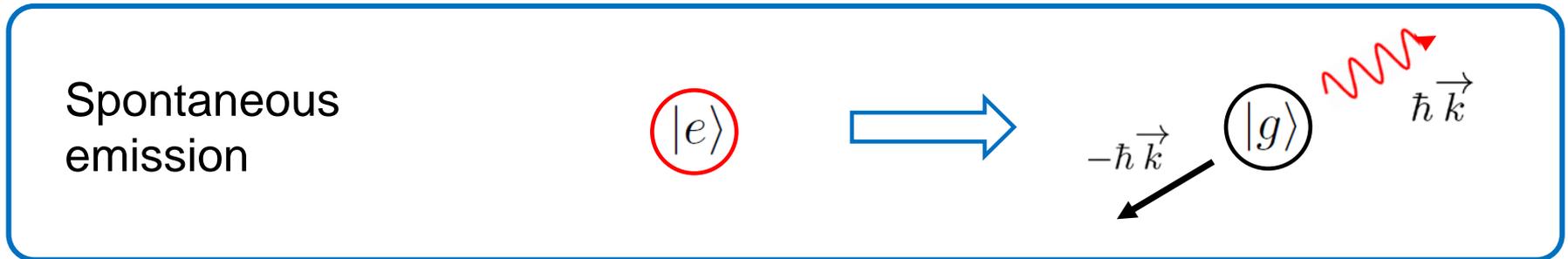
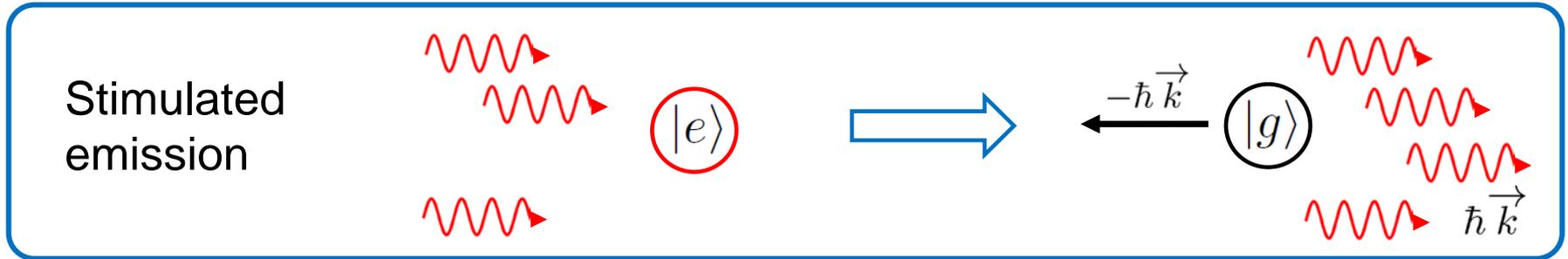
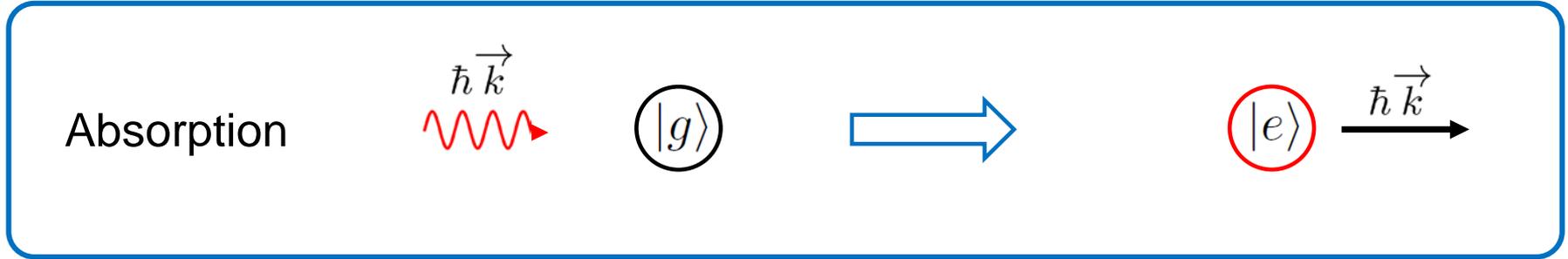


$$\tau = \frac{1}{A_1 + A_2 + A_3 + \dots}$$



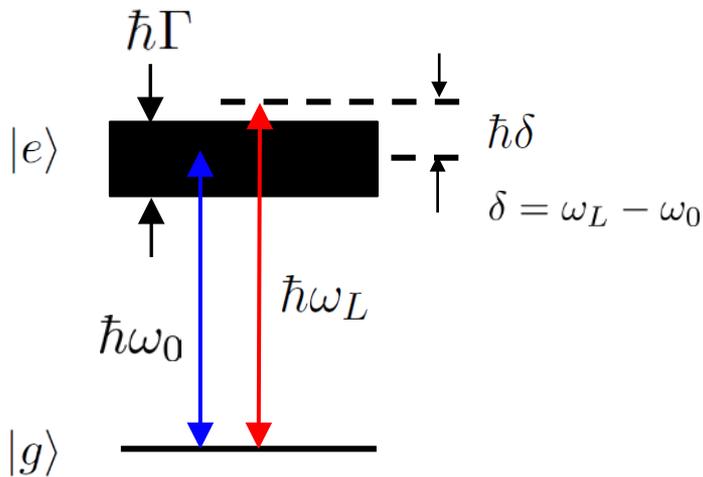
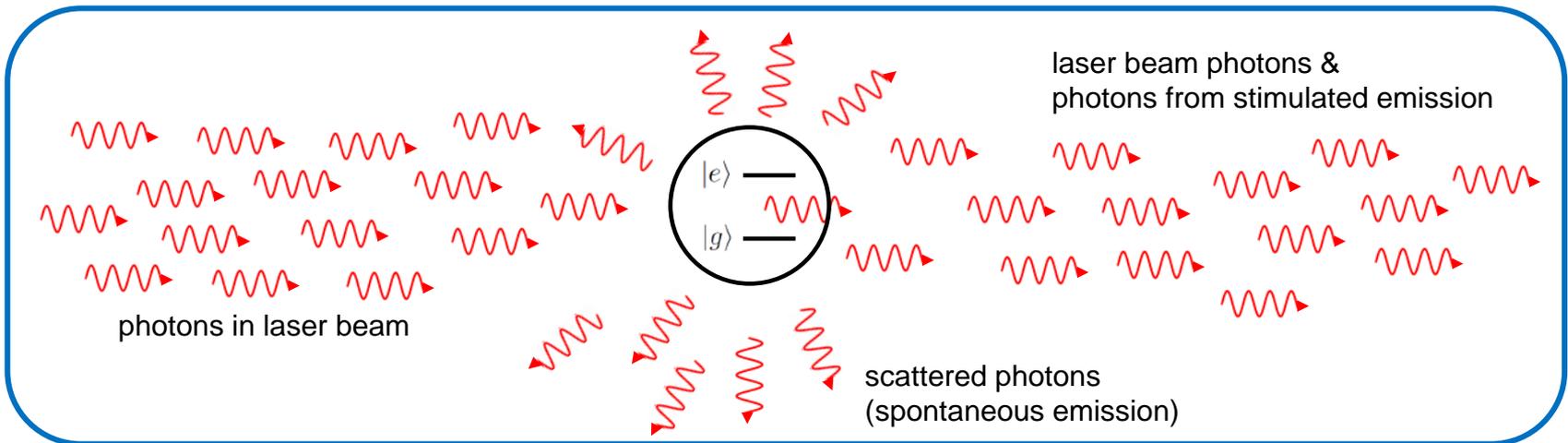
Basic atom-light interaction processes

Reminder



All together now: fluorescence

Bonus material

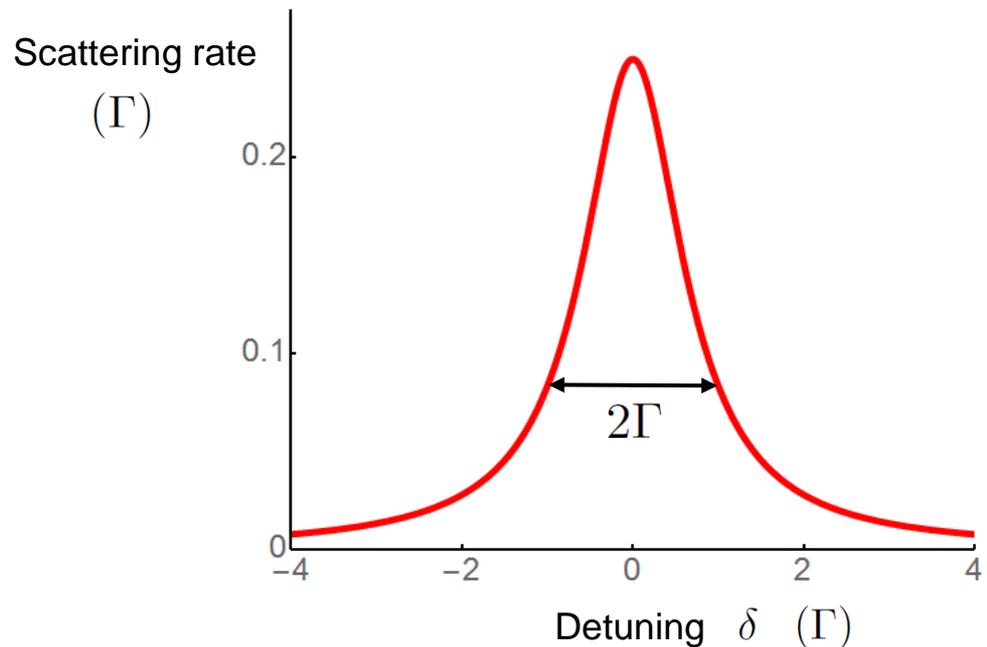


Minimum linewidth $\Gamma = 1/\tau$

Linewidth often broadened by

- Doppler effect
- collisions
- saturation of resonance

Typical resonance in scattering rate



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 Griffiths 3rd 11.0
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 - 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:

$$\vec{\rho} = e \langle a | \vec{r}_e | b \rangle$$

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: $|nlm\rangle$

$$\langle a | \vec{r}_e | b \rangle = \langle n'l'm' | \vec{r}_e | nlm \rangle$$

Selection rules involving m and m'

Commutators between angular momentum and position:

$$[L_z, x] = i\hbar y \quad , \quad [L_z, y] = -i\hbar x \quad , \quad [L_z, z] = 0$$

$$[L_z, z] = 0:$$

$$0 = \langle n'l'm' | [L_z, z] | nlm \rangle = \langle n'l'm' | L_z z - z L_z | nlm \rangle = (m' - m)\hbar \langle n'l'm' | z | nlm \rangle$$

→ either $m' = m$ or $\langle n'l'm' | z | nlm \rangle = 0$

$$[L_z, x] = i\hbar y:$$

$$\langle n'l'm' | [L_z, x] | nlm \rangle = \underbrace{(m' - m)\hbar \langle n'l'm' | x | nlm \rangle = i\hbar \langle n'l'm' | y | nlm \rangle}_{(*)}$$

Note:
(*) can calculate $\langle n'l'm' | x | nlm \rangle$ from $\langle n'l'm' | y | nlm \rangle$

$$[L_z, y] = -i\hbar x:$$

$$\langle n'l'm' | [L_z, y] | nlm \rangle = \underbrace{(m' - m)\hbar \langle n'l'm' | y | nlm \rangle = -i\hbar \langle n'l'm' | x | nlm \rangle}_{(**)}$$

$$(m' - m)^2 \langle n'l'm' | x | nlm \rangle \stackrel{(*)}{=} i(m' - m) \langle n'l'm' | y | nlm \rangle \stackrel{(**)}{=} \langle n'l'm' | x | nlm \rangle$$

→ either $(m' - m) = 1$ 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:

$$[L^2, [L^2, \vec{r}]] = 2\hbar^2(\vec{r}L^2 + L^2\vec{r}) \quad (\text{no proof here})$$

$$\begin{aligned} \langle n'l'm' | [L^2, [L^2, \vec{r}]] | nlm \rangle &= 2\hbar^2 \langle n'l'm' | (\vec{r}L^2 + L^2\vec{r}) | nlm \rangle \\ \parallel & \\ \dots & \qquad \qquad \qquad \parallel \\ & \qquad \qquad \qquad 2\hbar^4[l(l+1) + l'(l'+1)] \langle n'l'm' | \vec{r} | nlm \rangle \\ \parallel & \\ & \hbar^4[l'(l'+1) - l(l+1)]^2 \langle n'l'm' | \vec{r} | nlm \rangle \end{aligned}$$

→ either $2[l(l+1) + l'(l'+1)] = [l'(l'+1) - l(l+1)]^2$ or $\langle n'l'm' | \vec{r} | nlm \rangle = 0$

↕ 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 $\Delta l = \pm 1$.

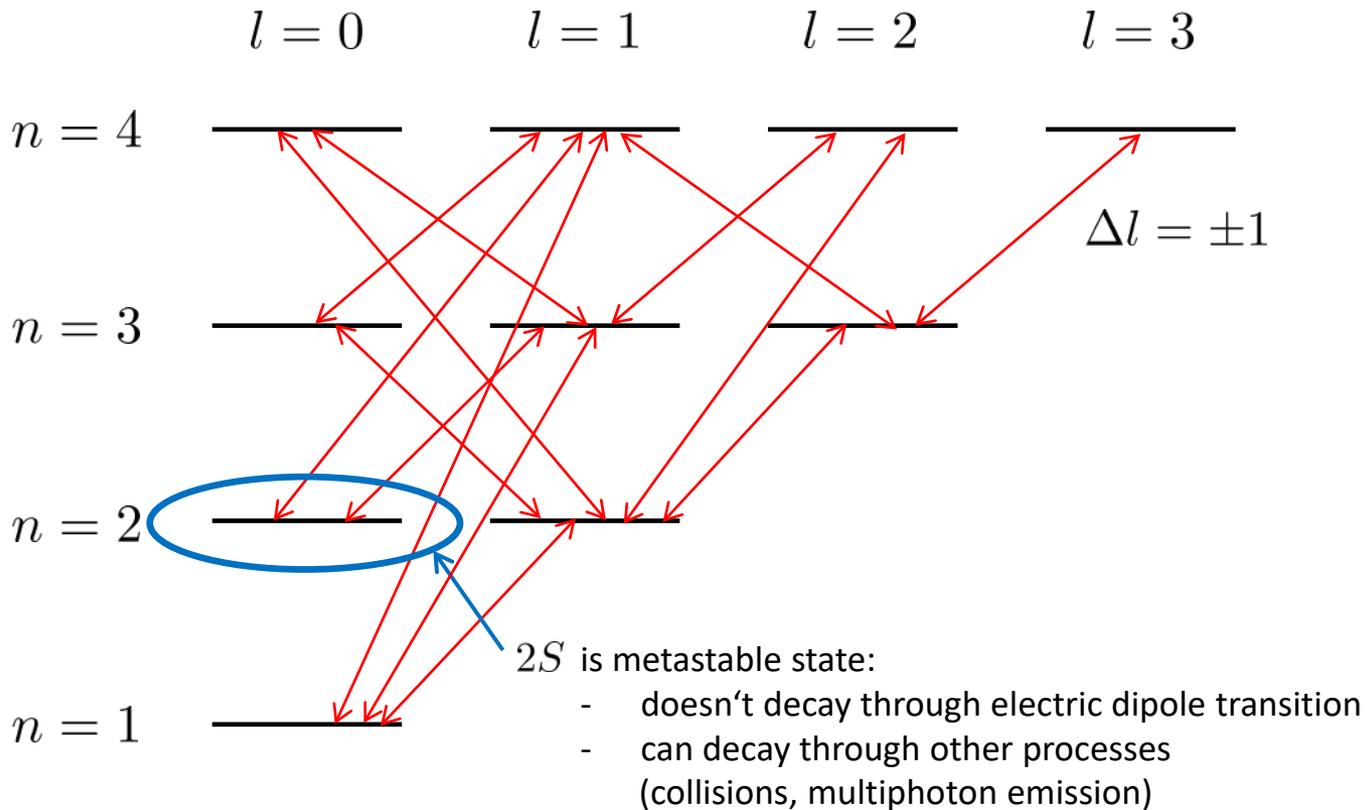
Interpretation:

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.

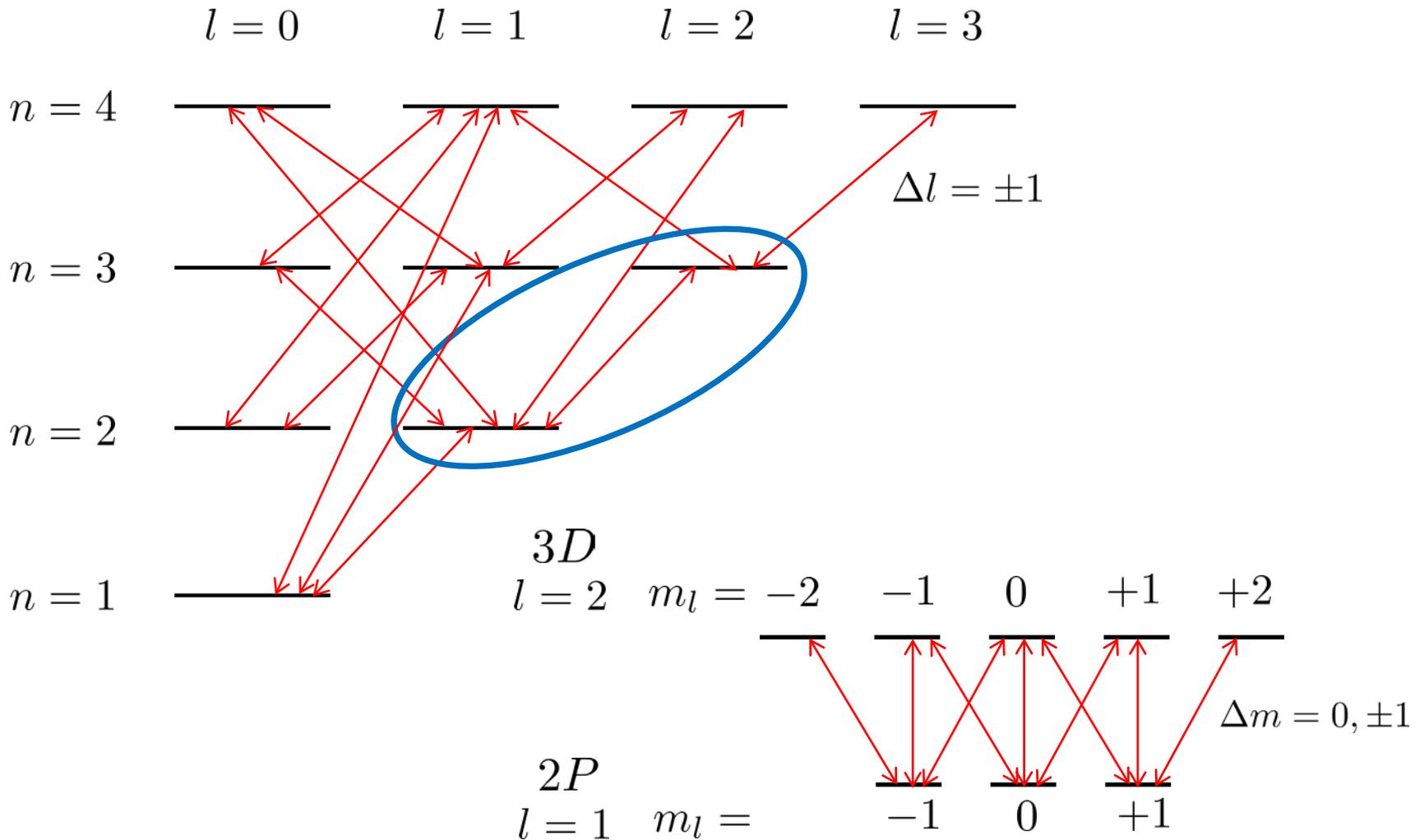
l selection rules in hydrogen

Neglecting electron and nuclear spin



m_l selection rules in hydrogen

Neglecting electron and nuclear spin



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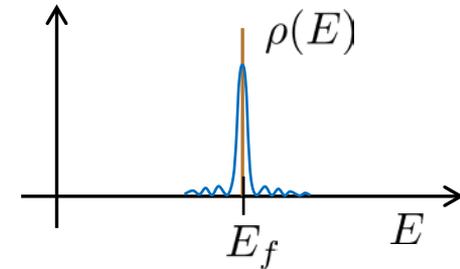
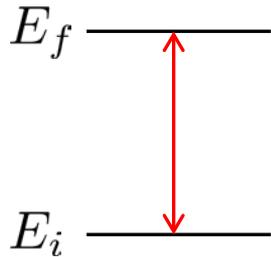
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Fermi's golden rule

Bonus material
Griffiths 3rd edition

So far: transitions between **two discrete states**

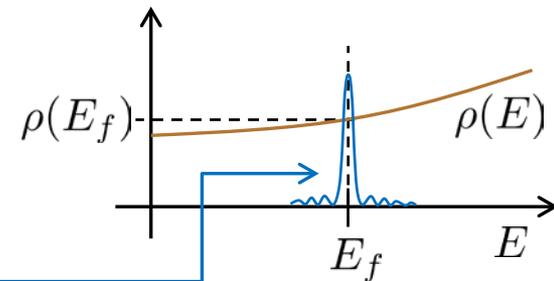
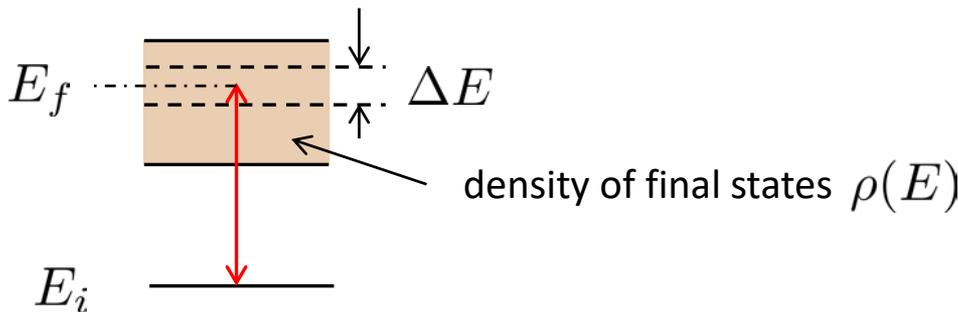
Example: transition of e^- from H ground state to higher orbital



Transition probability:
$$P = \frac{|V_{ba}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}$$

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:
$$P = \int_{E_f - \Delta E/2}^{E_f + \Delta E/2} \frac{|V_{in}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \rho(E_n) dE_n$$

Incoherent perturbation

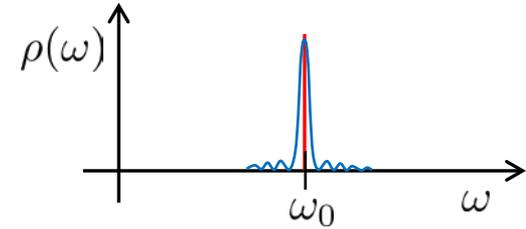
Reminder

Energy density of monochromatic, electromagnetic plane wave:

$$u = \frac{\epsilon_0}{2} E_0^2$$

Transition probability:

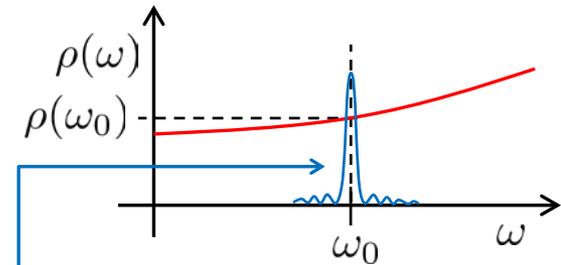
$$P_{e \rightarrow g}(t) = \frac{2u}{\epsilon_0 \hbar^2} |\wp|^2 \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2}$$



energy density in range $d\omega$ is $\rho(\omega)d\omega$

Incoherent electromagnetic wave:

$$P_{e \rightarrow g}(t) = \frac{2}{\epsilon_0 \hbar^2} |\wp|^2 \int_0^\infty \rho(\omega) \left\{ \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2} \right\}$$



atom absorbs resonantly around ω_0

$$\approx \frac{2}{\epsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0) \int_0^\infty \frac{\sin^2[(\omega_0 - \omega_L)t/2]}{(\omega_0 - \omega_L)^2}$$

$$\approx \frac{\pi |\wp|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) t$$

Transition rate:

$$R_{e \rightarrow g}(t) \equiv \frac{dP_{e \rightarrow g}(t)}{dt} = \frac{\pi}{\epsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0)$$

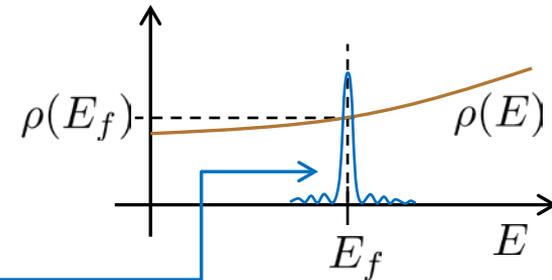
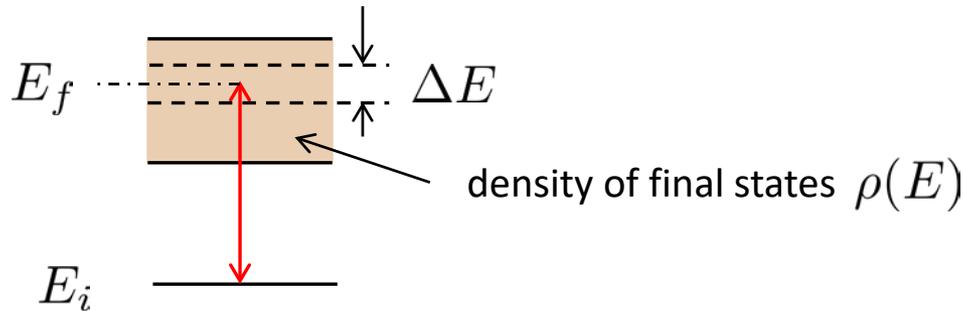
Attention
don't confuse with
incoherent perturbation

Fermi's golden rule

Bonus material
Griffiths 3rd edition

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 ():

$$\begin{aligned} &\cong \frac{|V_{if}|^2}{\hbar^2} \rho(E_f) \int_{-\infty}^{\infty} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} dE_n \\ &= \frac{2\pi}{\hbar} \left| \frac{V_{if}}{2} \right|^2 \rho(E_f) t \end{aligned}$$

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*“

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Describe the reaction of a system to a time-dependent perturbation, especially absorption and emission of photons by atoms.

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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	Griffiths 3 rd 5.1, 5.2
Crystalline solids	5.3.2
Time-independent perturbation theory	7.1, 7.2
Structure of hydrogen	7.3 – 7.5
Variational principle	8.1 – 8.3
Time-dependent perturbation theory, atom-light interaction	11.1 – 11.4

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*“

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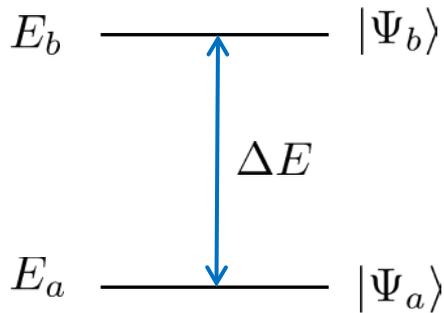
- 1) Introduction Griffiths 9.0
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Rotating wave approximation

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

Two level system



$$H\Psi_i = E_i\Psi_i \quad ; \quad \langle\Psi_i|\Psi_j\rangle = \delta_{ij} \quad ; \quad i, j \in \{a, b\}$$

Initial state: $\Psi(t = 0) = c_a(0)\Psi_a + c_b(0)\Psi_b$ $|c_a(0)|^2 + |c_b(0)|^2 = 1$

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

Reminder

$$H = H^0 + H'(t)$$

$\left\{ \begin{array}{l} \text{time-dependent perturbation (not necessarily small)} \\ \text{static} \end{array} \right.$

Solve $H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$ with ansatz $\Psi(t) = c_a(t)e^{-iE_a t/\hbar}\Psi_a + c_b(t)e^{-iE_b t/\hbar}\Psi_b$

$$\begin{aligned}
 & \cancel{c_a[H^0\Psi_a]e^{-iE_a t/\hbar} + c_b[H^0\Psi_b]e^{-iE_b t/\hbar}} + c_a[H'\Psi_a]e^{-iE_a t/\hbar} + c_b[H'\Psi_b]e^{-iE_b t/\hbar} \\
 & = i\hbar \left[\dot{c}_a\Psi_a e^{-iE_a t/\hbar} + \dot{c}_b\Psi_b e^{-iE_b t/\hbar} + \cancel{c_a\Psi_a \left(\frac{-iE_a t}{\hbar}\right) e^{-iE_a t/\hbar}} + \cancel{c_b\Psi_b \left(\frac{-iE_b t}{\hbar}\right) e^{-iE_b t/\hbar}} \right]
 \end{aligned}$$

$$c_a[H'\Psi_a]e^{-iE_a t/\hbar} + c_b[H'\Psi_b]e^{-iE_b t/\hbar} = i\hbar \left[\dot{c}_a\Psi_a e^{-iE_a t/\hbar} + \dot{c}_b\Psi_b e^{-iE_b t/\hbar} \right]$$

$\langle \Psi_a | \cdot :$

$$c_a \langle \Psi_a | H' | \Psi_a \rangle e^{-iE_a t/\hbar} + c_b \langle \Psi_b | H' | \Psi_b \rangle e^{-iE_b t/\hbar} = i\hbar \dot{c}_a e^{-iE_a t/\hbar}$$

$$H'_{ij} \equiv \langle \Psi_i | H' | \Psi_j \rangle : \quad \dot{c}_a = -\frac{i}{\hbar} \left[c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar} \right]$$

$$\langle \Psi_b | \cdot : \quad \dot{c}_b = -\frac{i}{\hbar} \left[c_a H'_{ba} e^{i(E_b - E_a)t/\hbar} + c_b H'_{bb} \right]$$

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

Reminder

$$H = H^0 + H'(t)$$

└── static
└── time-dependent perturbation (not necessarily small)

Solve $H\Psi = i\hbar \frac{\partial\Psi}{\partial t}$ with ansatz $\Psi(t) = c_a(t)e^{-iE_a t/\hbar}\Psi_a + c_b(t)e^{-iE_b t/\hbar}\Psi_b$

$$\dot{c}_a = -\frac{i}{\hbar} [c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar}]$$

$$\dot{c}_b = -\frac{i}{\hbar} [c_a H'_{ba} e^{i(E_b - E_a)t/\hbar} + c_b H'_{bb}]$$

Often $H'_{aa} = H'_{bb} = 0$:

$$\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b$$

$$\dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a$$

with $\omega_0 \equiv \frac{E_b - E_a}{\hbar}$

Time-dependent perturbation theory

Reminder

$$H = H^0 + H'(t)$$

static \perp \perp small time-dependent perturbation

Initial condition: system in ground state $c_a(0) = 1$, $c_b(0) = 0$

Iteratively solve $\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b$; $\omega_0 \equiv \frac{E_b - E_a}{\hbar}$

$$\dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a$$

Zeroth Order: $(H' = 0)$

$$c_a^{(0)}(t) = 1 , \quad c_b^{(0)}(t) = 0$$

First Order:

Note: $|c_a^{(1)}(t)|^2 + |c_b^{(1)}(t)|^2 = 1 + \mathcal{O}(H'_{ab}{}^2) \neq 1$

$$\dot{c}_a^{(1)} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b^{(0)} = 0 \quad \Rightarrow \quad c_a^{(1)}(t) = 1$$

$$\dot{c}_b^{(1)} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a^{(0)} \quad \Rightarrow \quad c_b^{(1)}(t) = -\frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt'$$

Second Order:

$$\dot{c}_a^{(2)} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} \left(-\frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt' \right)$$

$$\Rightarrow c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2} \int_0^t H'_{ab}(t') e^{-i\omega_0 t'} \left[\int_0^{t'} H'_{ba}(t'') e^{i\omega_0 t''} dt'' \right] dt'$$

$$\dot{c}_b^{(2)} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a^{(1)} \Rightarrow c_b^{(2)}(t) = c_b^{(1)}(t)$$

etc.

Sinusoidal perturbation

Reminder

$$H = H^0 + H'(t)$$

static $\underbrace{\quad}$ $\underbrace{\quad}$ 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 $\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b$; $\omega_0 \equiv \frac{E_b - E_a}{\hbar}$

$$\dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a$$

First Order: $H'_{ij}(t) \equiv V_{ij} \cos(\omega t)$

$$c_a(t) \cong 1$$

$$\begin{aligned} c_b(t) &\cong -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t') e^{i\omega_0 t'} dt' = -\frac{iV_{ba}}{2\hbar} \int_0^t \left[e^{i(\omega_0 + \omega)t'} + e^{i(\omega_0 - \omega)t'} \right] \\ &= -\frac{V_{ba}}{2\hbar} \left[\frac{e^{i(\omega_0 + \omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0 - \omega)t} - 1}{\omega_0 - \omega} \right] \end{aligned}$$

Simplifying assumption: $\omega_0 + \omega \gg |\omega_0 - \omega|$

$$\begin{aligned} c_b(t) &\cong -\frac{V_{ba}}{2\hbar} \frac{e^{i(\omega_0 - \omega)t/2}}{\omega_0 - \omega} \left[e^{i(\omega_0 - \omega)t/2} - e^{i(\omega_0 + \omega)t/2} \right] \\ &= -\frac{V_{ba}}{\hbar} \frac{\sin[(\omega_0 - \omega)t/2]}{\omega_0 - \omega} e^{i(\omega_0 - \omega)t/2} \end{aligned}$$

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

Reminder

$$H = H^0 + H'(t)$$

└── static
└── time-dependent perturbation (not necessarily small)

Solve $H\Psi = i\hbar \frac{\partial\Psi}{\partial t}$ with ansatz $\Psi(t) = c_a(t)e^{-iE_a t/\hbar}\Psi_a + c_b(t)e^{-iE_b t/\hbar}\Psi_b$

$$\dot{c}_a = -\frac{i}{\hbar} [c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar}]$$

$$\dot{c}_b = -\frac{i}{\hbar} [c_a H'_{ba} e^{i(E_b - E_a)t/\hbar} + c_b H'_{bb}]$$

Often $H'_{aa} = H'_{bb} = 0$:

$$\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b$$

$$\dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a$$

with $\omega_0 \equiv \frac{E_b - E_a}{\hbar}$

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 $\varphi = 0$

$$c_e(t) = -i \frac{\Omega}{\Omega'} \sin \frac{\Omega' t}{2} e^{-i\delta t/2}$$

$$c_g(t) = \left(\cos \frac{\Omega' t}{2} - i \frac{\delta}{\Omega'} \sin \frac{\Omega' t}{2} \right) e^{i\delta t/2}$$

$$\text{with } \Omega' \equiv \sqrt{\Omega^2 + \delta^2}$$

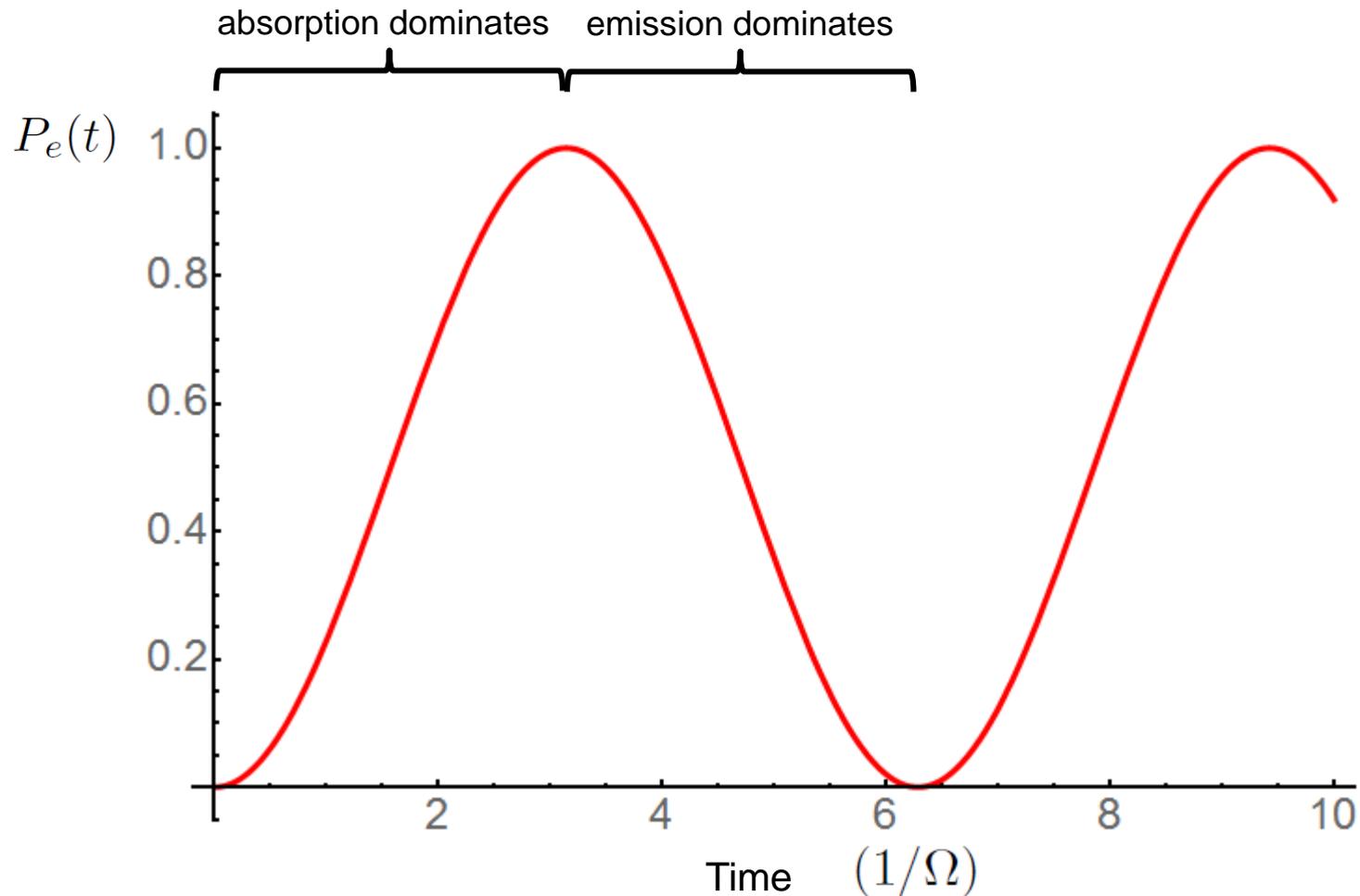
Probability of finding atom in $|e\rangle$:

$$P_e(t) = |c_e(t)|^2 = \left(\frac{\Omega}{\Omega'} \sin \frac{\Omega' t}{2} \right)^2$$

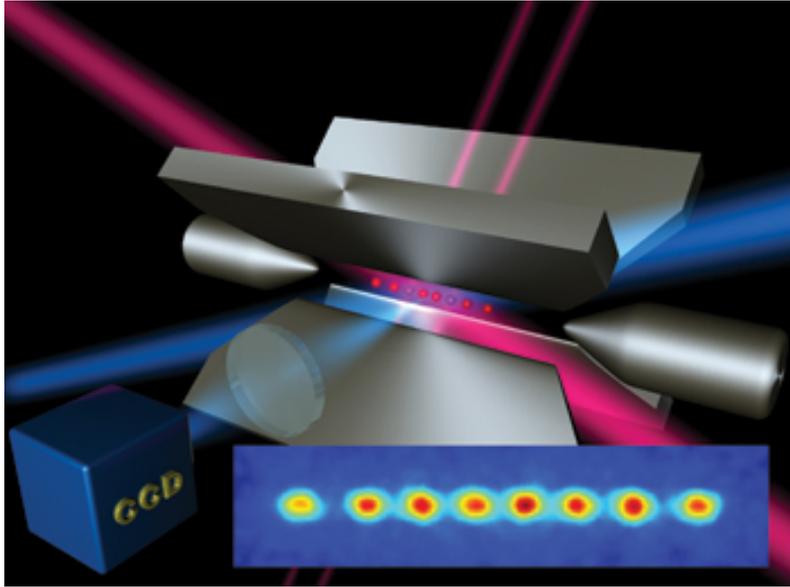
Resonant behavior

$$P_e(t) = |c_e(t)| = \left(\frac{\Omega}{\Omega'} \sin \frac{\Omega t}{2} \right)^2 \quad \text{with} \quad \Omega' \equiv \sqrt{\Omega^2 + \delta^2}$$

On resonance: $P_e(t) = \sin^2 \frac{\Omega t}{2}$ Sine oscillations with period $2\pi/\Omega$.



Experiment: ion qubit

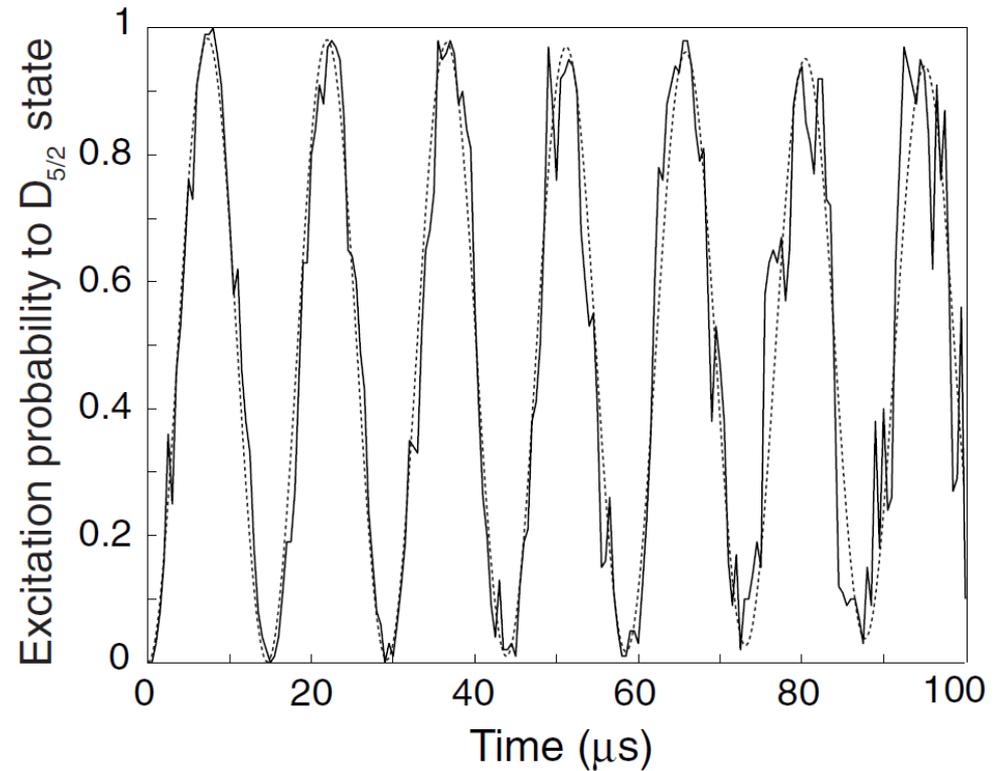


J. Phys. B: At. Mol. Opt. Phys. **36** (2003) 623–636

The coherence of qubits based on single Ca^+ ions

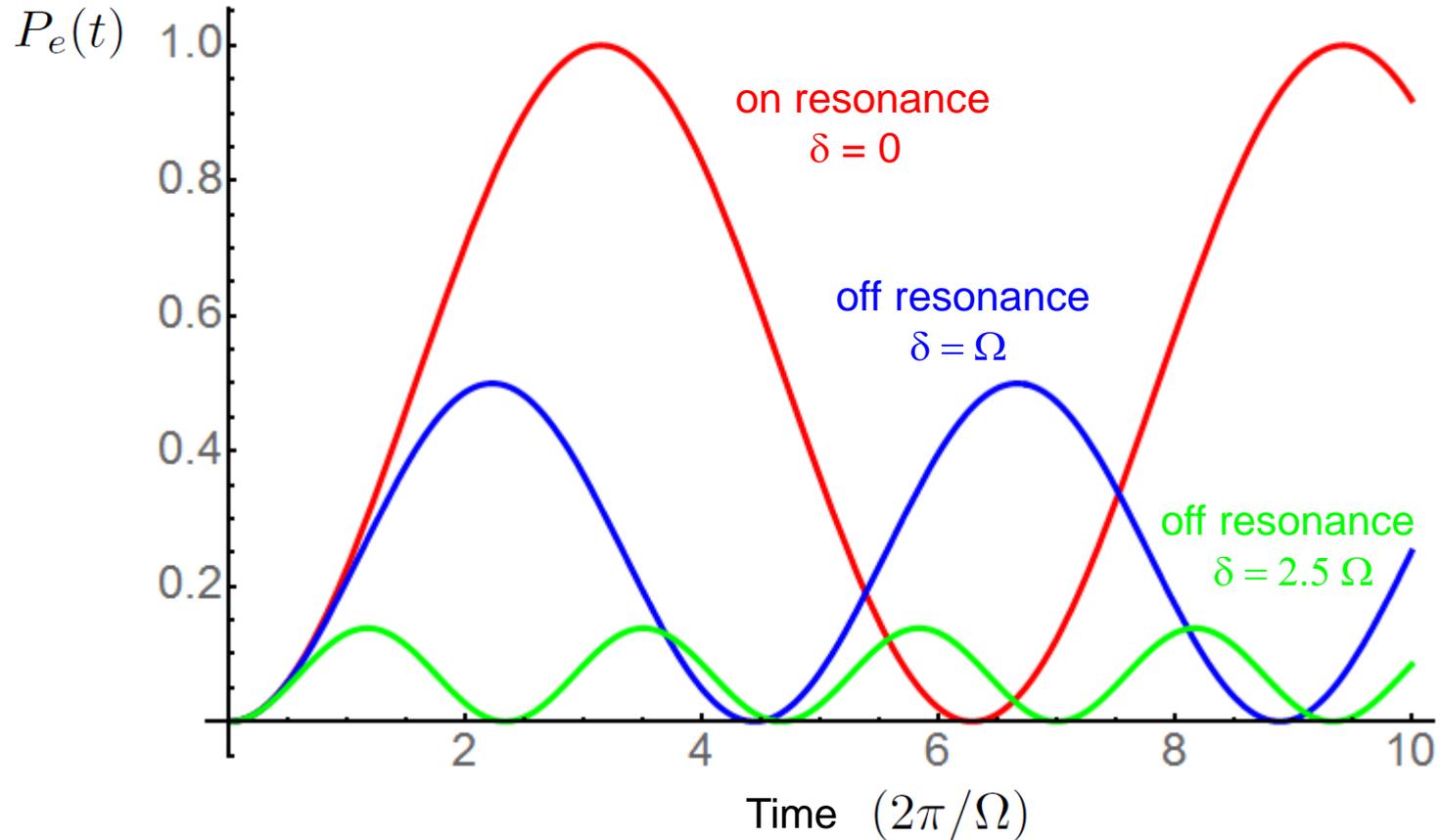
F Schmidt-Kaler¹, S Gulde, M Riebe, T Deuschle, A Kreuter,
G Lancaster, C Becher, J Eschner, H Häffner and R Blatt

Institut für Experimentalphysik, 6020 Innsbruck, Austria



Off resonant behavior

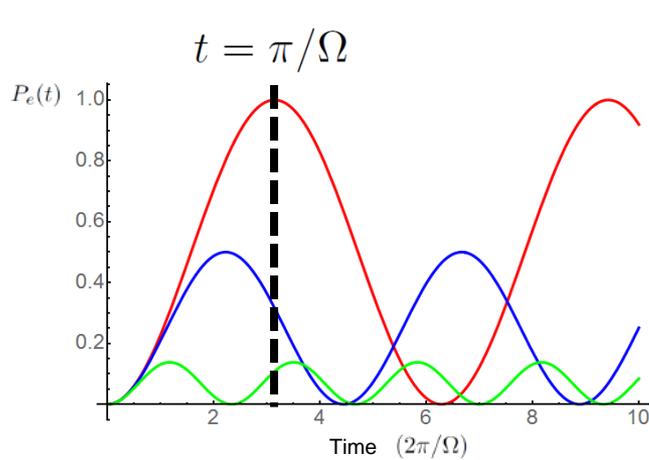
$$P_e(t) = |c_e(t)| = \left(\frac{\Omega}{\Omega'} \sin \frac{\Omega' t}{2} \right)^2 \quad \text{with} \quad \Omega' \equiv \sqrt{\Omega^2 + \delta^2}$$



- Oscillations faster.
- Atom never fully in excited state.

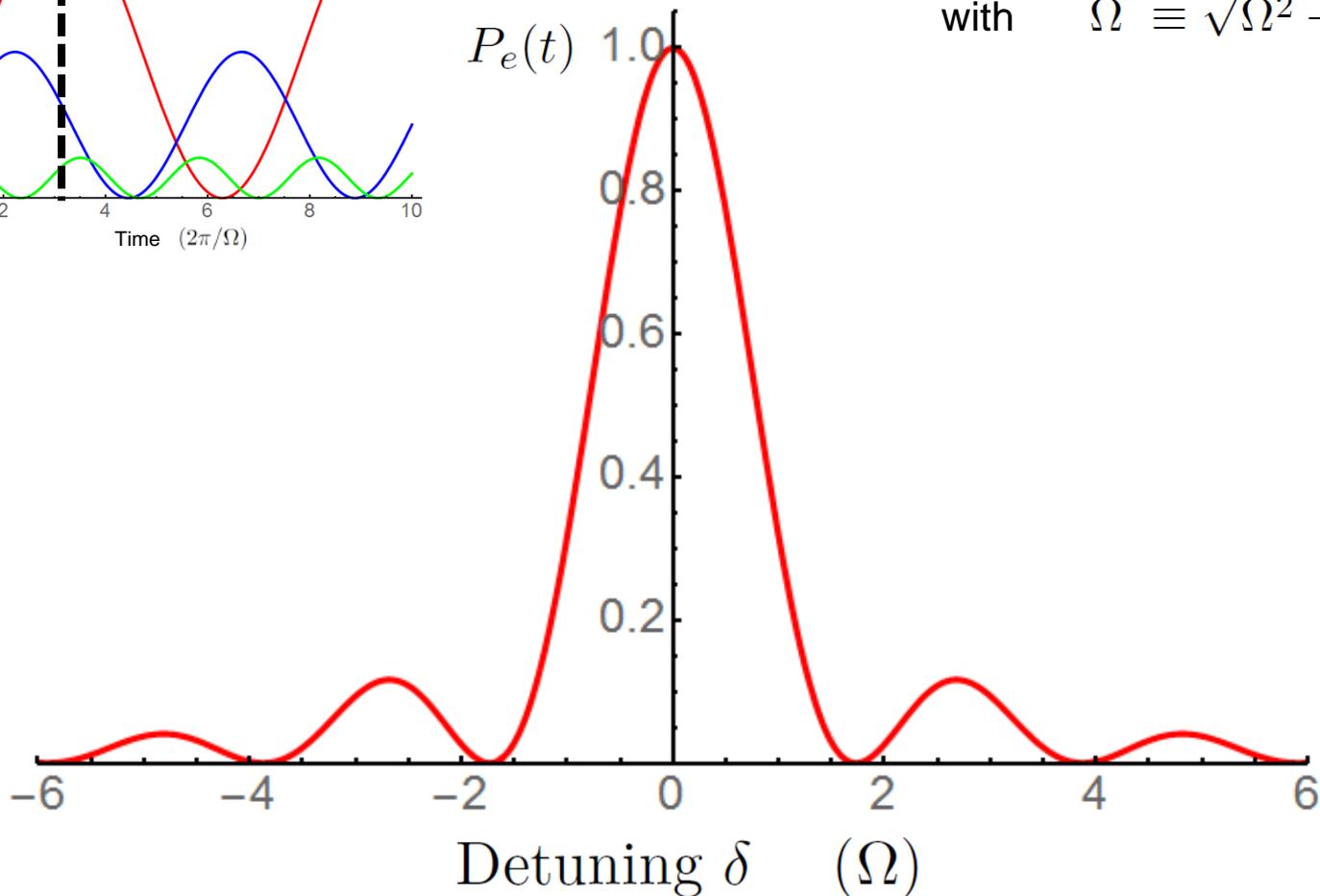
Resonance

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

→ four real parameters.

Normalization $|c_e|^2 + |c_g|^2 = 1$ removes one parameter.

Overall phase is unimportant.

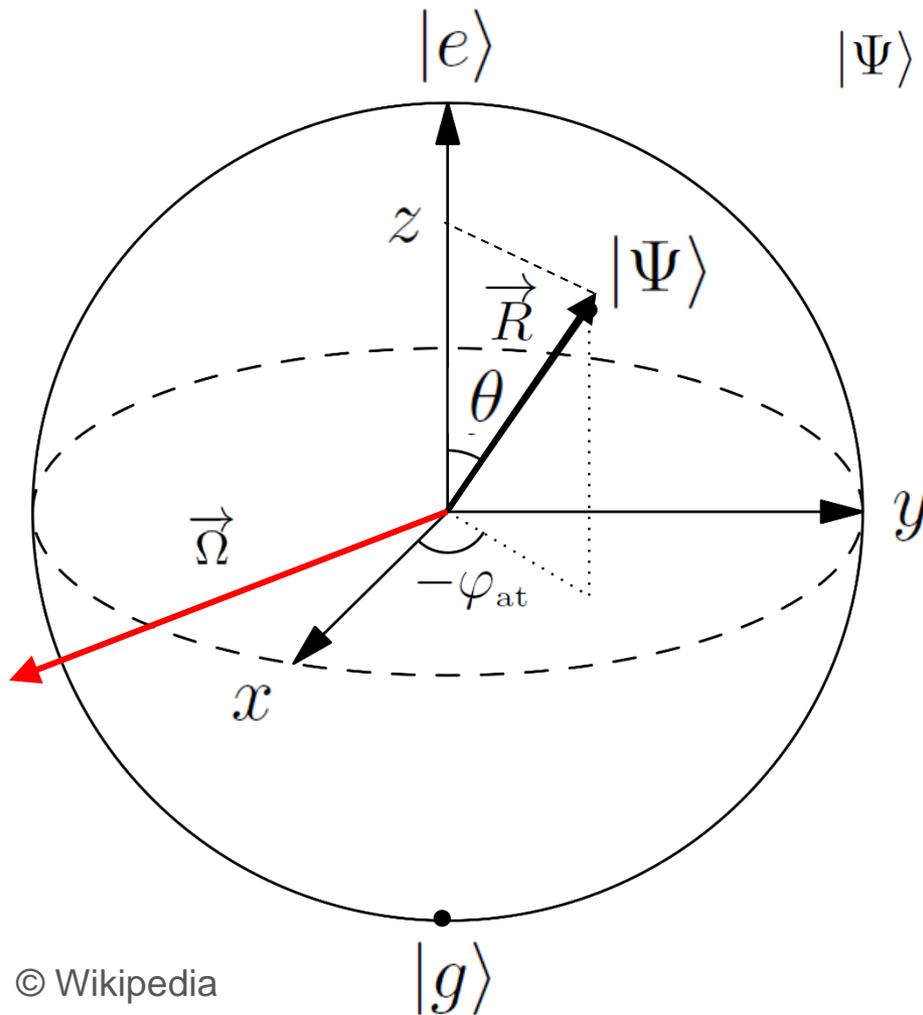
→ only two relevant real parameters.

Express $|\Psi\rangle$ with two real parameters, φ_{at} and z :

$$|\Psi\rangle = \underbrace{\sqrt{\frac{1+z}{2}} e^{i\varphi_{\text{at}}/2}}_{c_e} |e\rangle + \underbrace{\sqrt{\frac{1-z}{2}} e^{-i\varphi_{\text{at}}/2}}_{c_g} |g\rangle \quad \text{with} \quad z \equiv |c_e|^2 - |c_g|^2$$

Can be represented as a point on a unit sphere!

The Bloch sphere



$$|\Psi\rangle = \sqrt{\frac{1+z}{2}} e^{i\varphi_{\text{at}}/2} |e\rangle + \sqrt{\frac{1-z}{2}} e^{-i\varphi_{\text{at}}/2} |g\rangle$$

Represent $|\Psi\rangle$ by Bloch vector

$$\vec{R} = \begin{pmatrix} \sqrt{1-z^2} \cos(-\varphi_{\text{at}}) \\ \sqrt{1-z^2} \sin(-\varphi_{\text{at}}) \\ z \end{pmatrix}$$

We will show that equation of motion is

$$\frac{\partial \vec{R}}{\partial t} = \vec{\Omega} \times \vec{R}$$

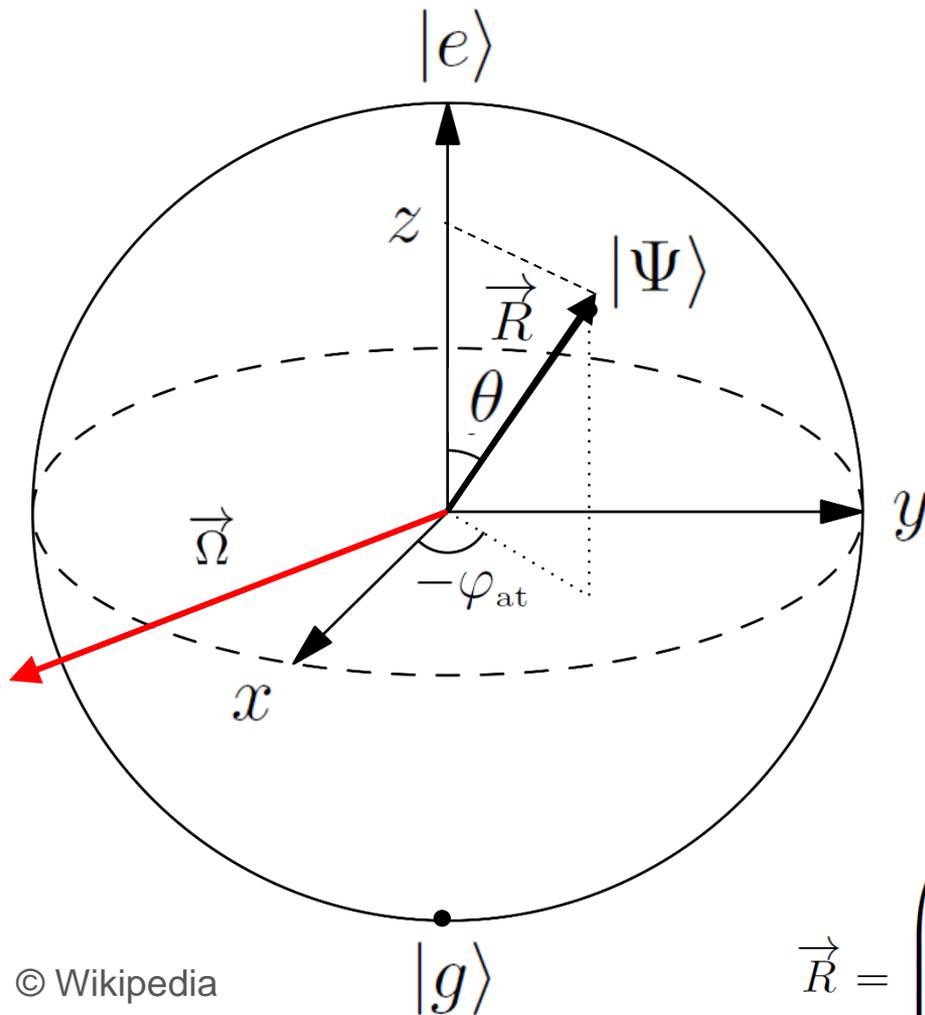
with field vector

$$\vec{\Omega} = \begin{pmatrix} |\Omega| \cos \varphi_{\text{L}} \\ |\Omega| \sin \varphi_{\text{L}} \\ -\delta \end{pmatrix}$$

© Wikipedia

Surface of Bloch sphere represents the Hilbert space of the two-level system.

The Bloch sphere



Equation of motion of Bloch vector:

$$\frac{\partial \vec{R}}{\partial t} = \vec{\Omega} \times \vec{R}$$

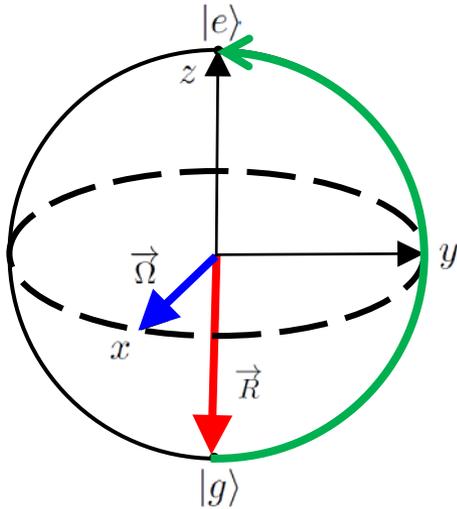
The Bloch vector moves under the influence of a driving field in the direction orthogonal to the field vector and the Bloch vector itself.

This is analogous to the evolution of an angular momentum under the influence of a torque.

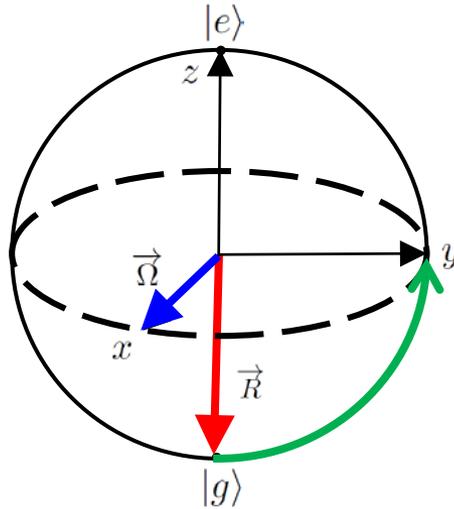
$$\vec{R} = \begin{pmatrix} \sqrt{1-z^2} \cos(-\varphi_{at}) \\ \sqrt{1-z^2} \sin(-\varphi_{at}) \\ z \end{pmatrix} \quad \vec{\Omega} = \begin{pmatrix} |\Omega| \cos \varphi_L \\ |\Omega| \sin \varphi_L \\ -\delta \end{pmatrix}$$

Examples

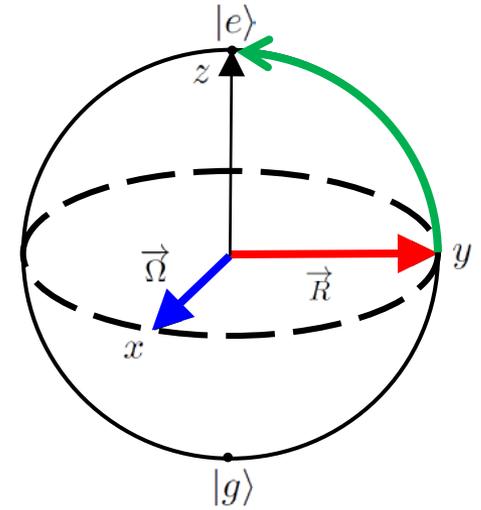
π -pulse



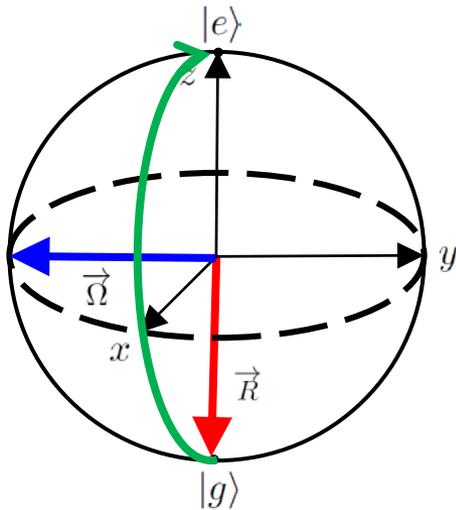
$\pi/2$ -pulse



$\pi/2$ -pulse
(different starting condition)



π -pulse with π phase



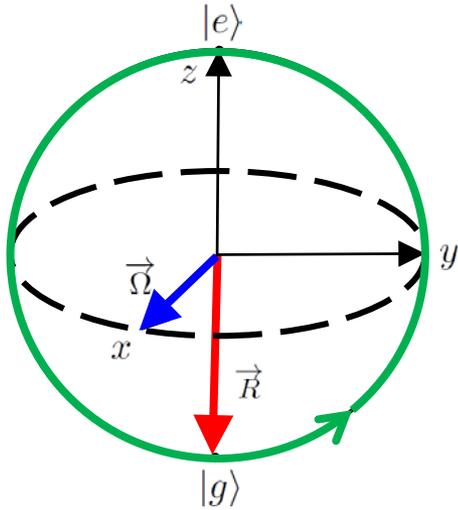
π -pulse:

Switch laser on for as long as necessary to bring atom to excited state.

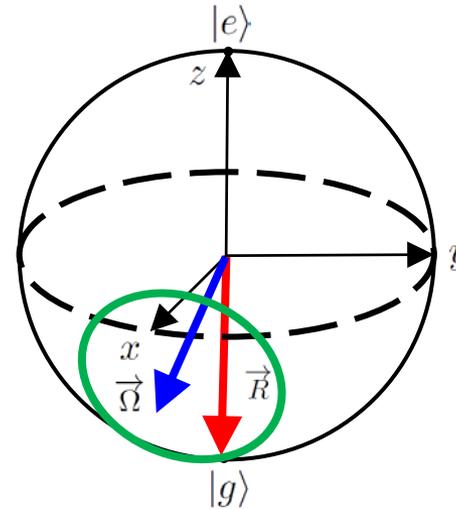
For weaker laser, longer time needed.

Rabi oscillations

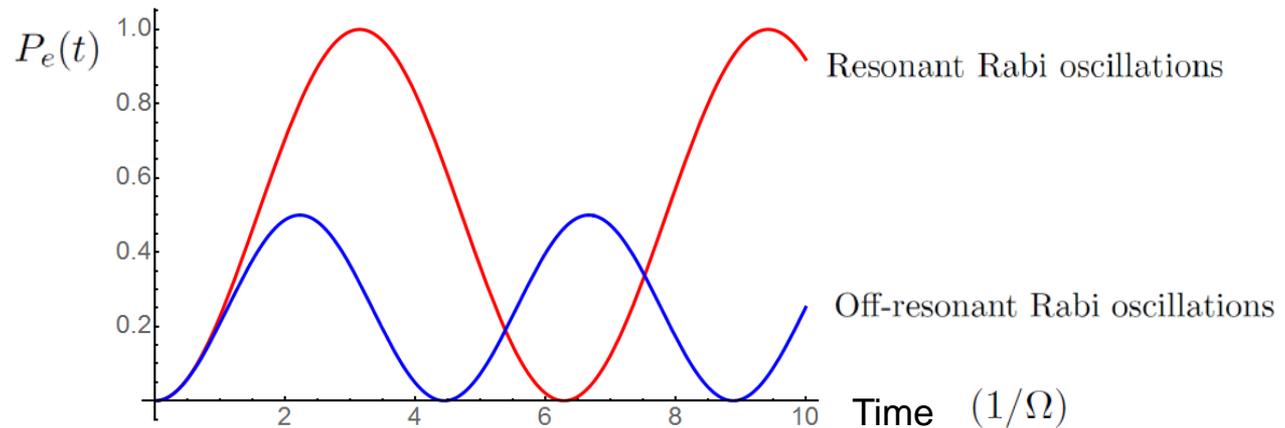
Resonant Rabi oscillations



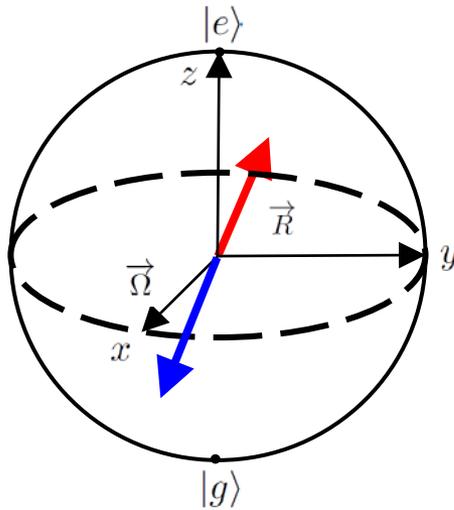
Off-resonant Rabi oscillations



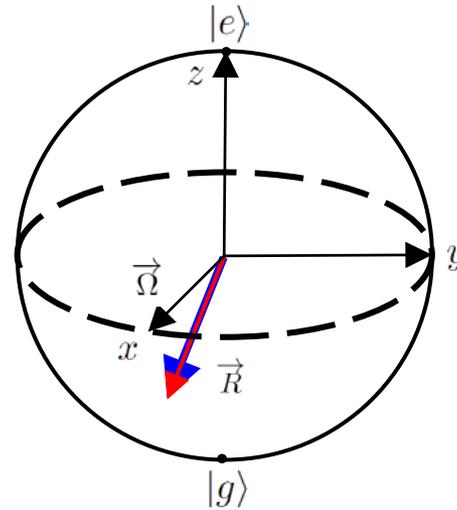
Compare to our calculation from before:



Stationary states



$$\vec{R} = -\vec{\Omega}/|\Omega|$$

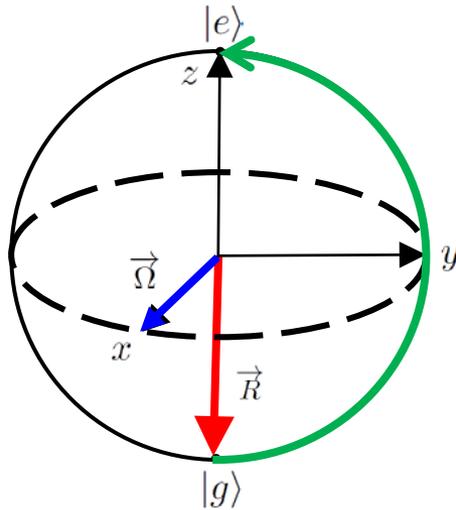


$$\vec{R} = \vec{\Omega}/|\Omega|$$

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

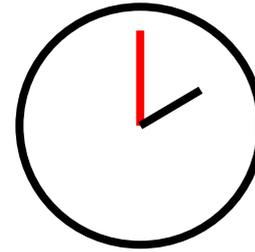
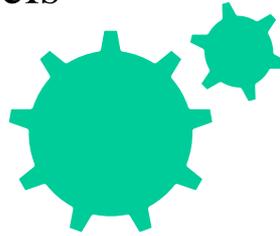




Basic structure of any clock



**clockwork
gearwheels**



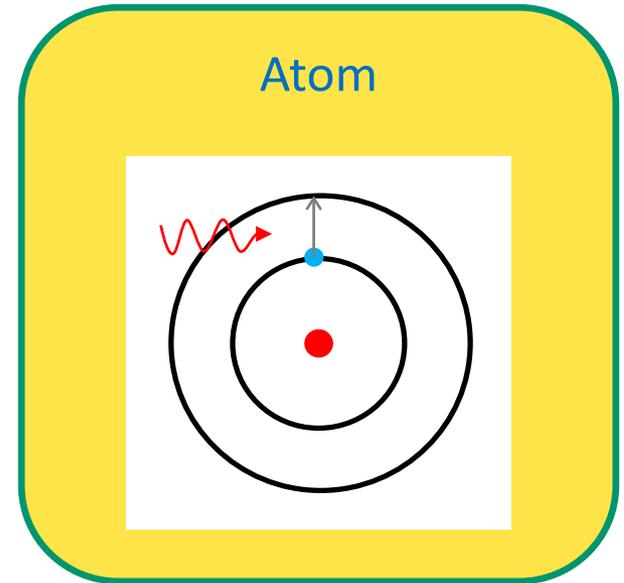
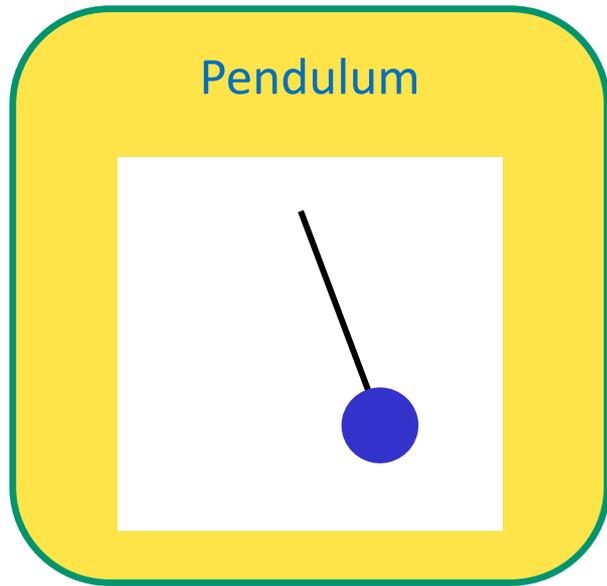
**do something useful
display elapsed time on dial**

**frequency reference
pendulum**





Atomic clock



Highest accuracy

- | | | |
|----------------------------|---|--------------------------|
| High transition frequency | → | optical transitions |
| Narrow transition | → | mHz linewidth |
| Large signal | → | use many atoms |
| Undisturbed by other atoms | → | use gas of atoms |
| Observe for long time | → | cool atoms to standstill |

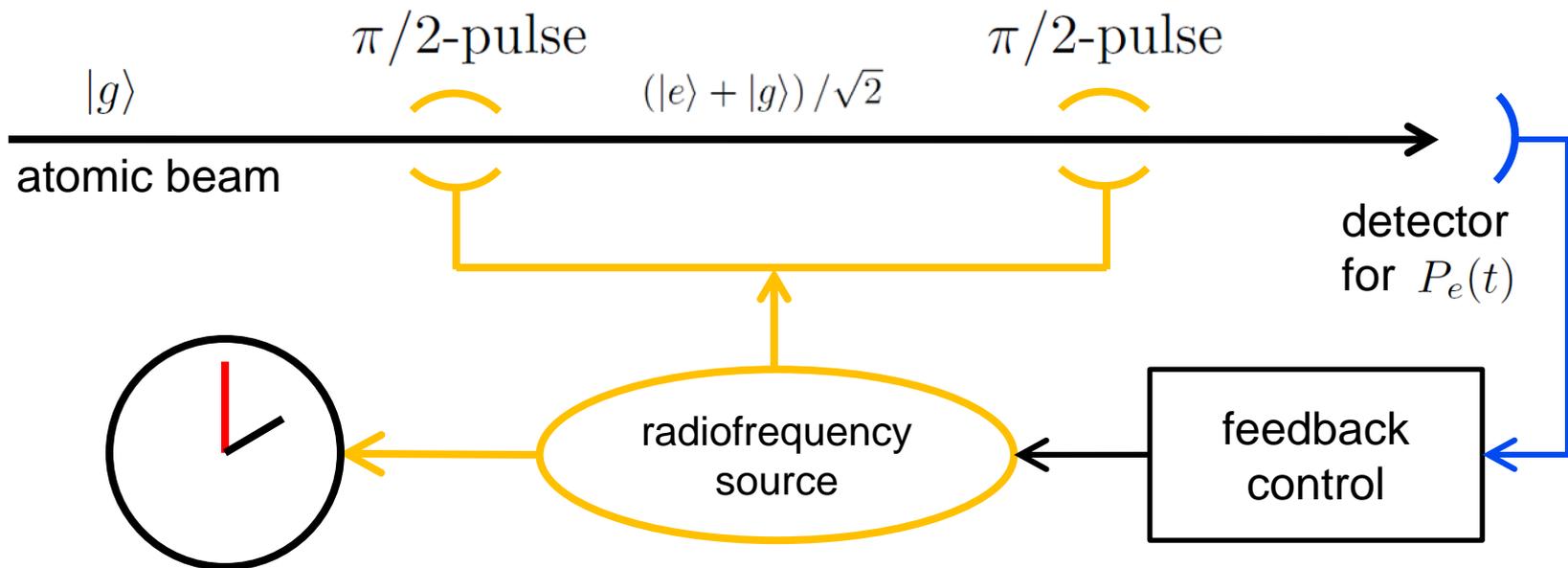
Atomic clock

Definition of second:

9 192 631 770 periods of the radiation corresponding to the transition between the cesium hyperfine levels

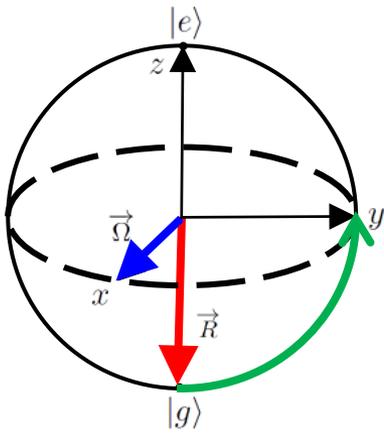
Challenge: measure this transition precisely

Use Ramsey spectroscopy:

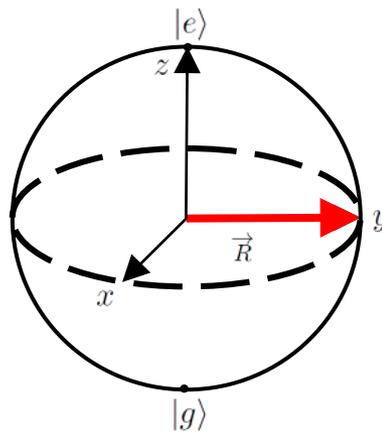


Ramsey spectroscopy on resonance

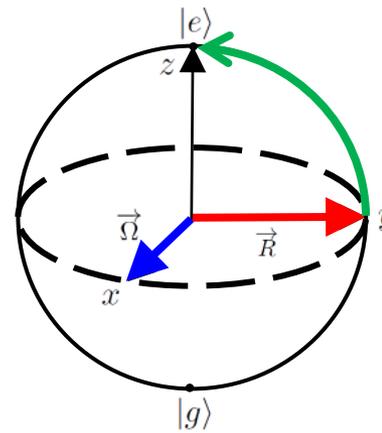
$\pi/2$ -pulse



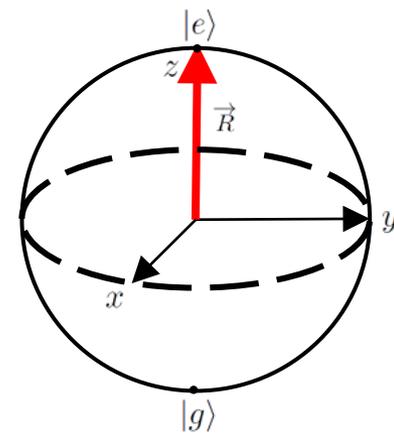
wait time



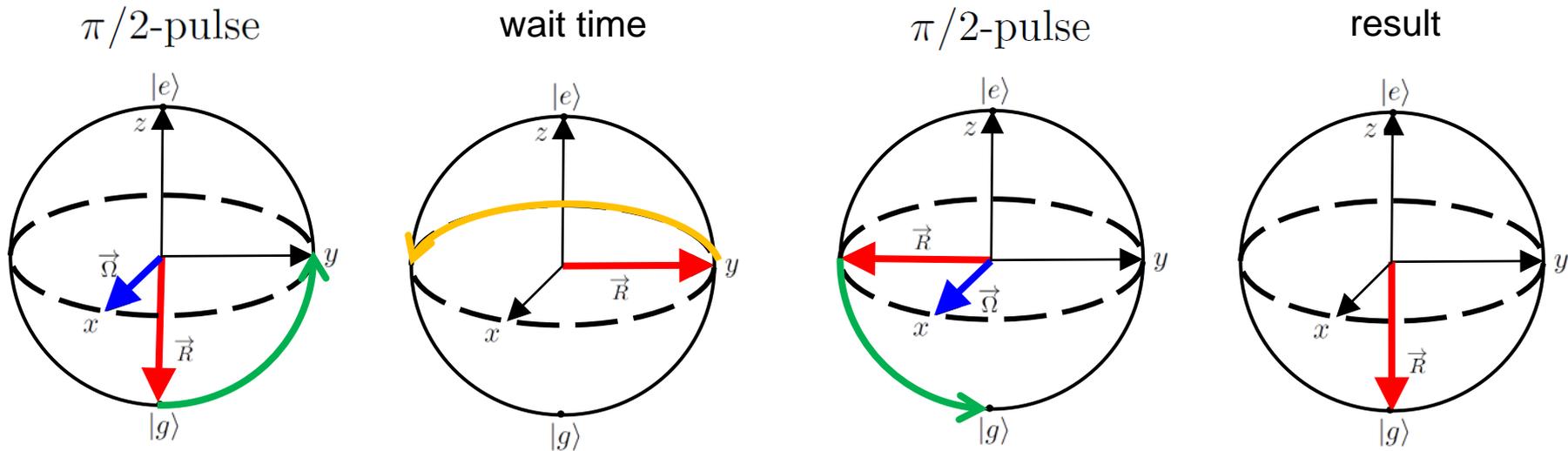
$\pi/2$ -pulse



result

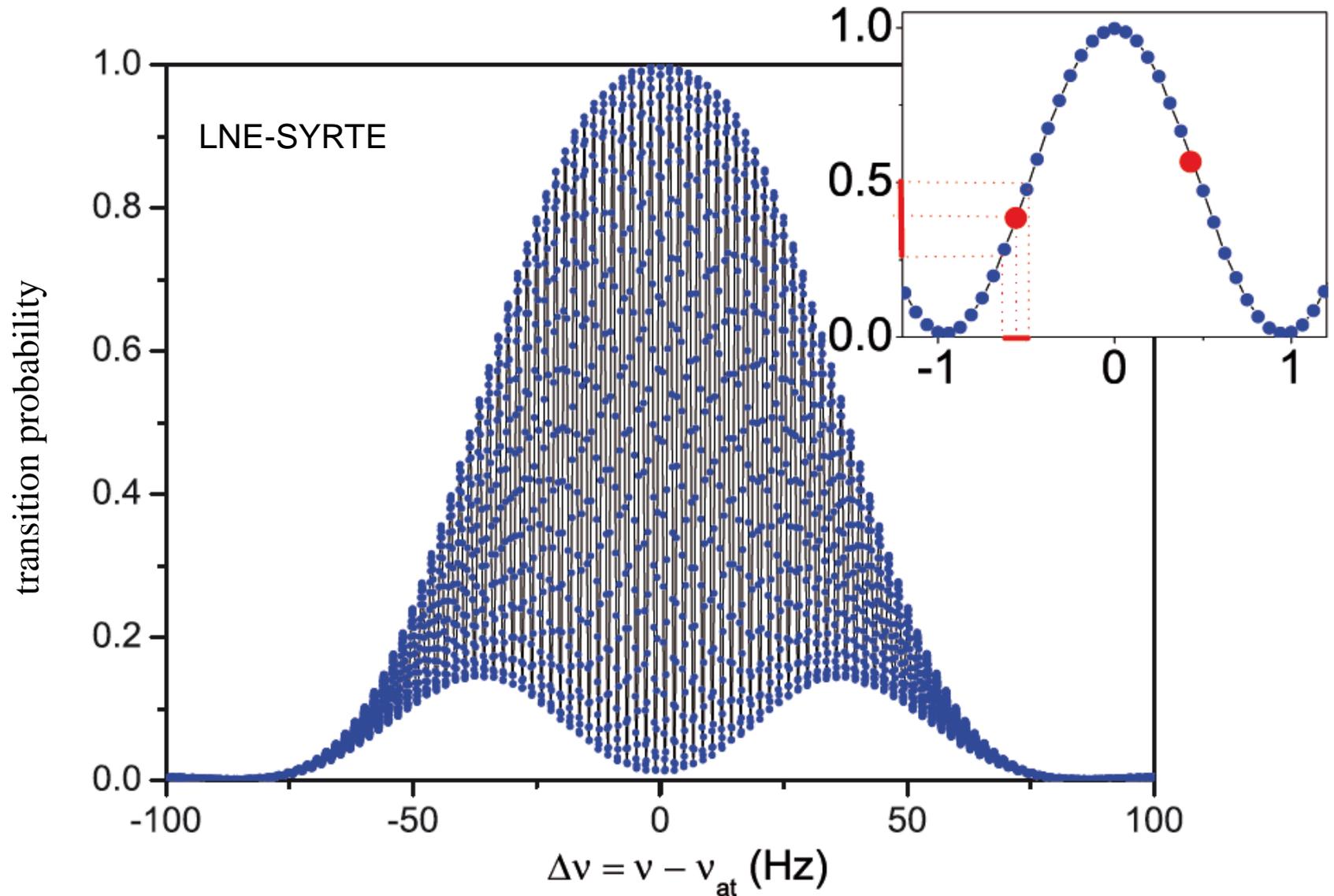


Ramsey spectroscopy off resonance



Frequency difference between
rf source and atomic transition leads
to phase shift between $\vec{\Omega}$ and \vec{R} ,
in this example by π .

Ramsey spectroscopy signal



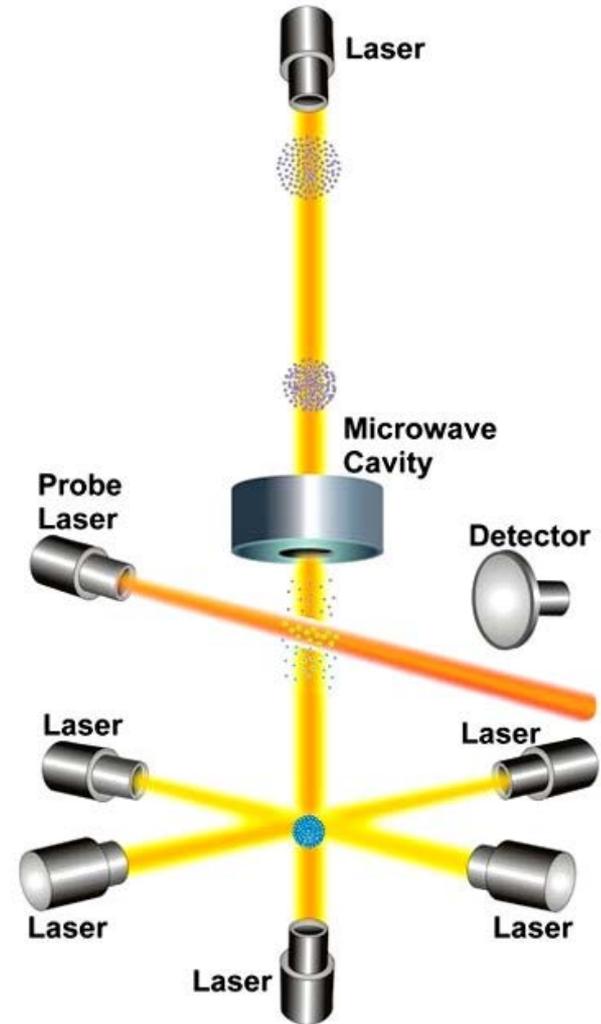
To determine if rf source is too low or too high in frequency, execute two measurements, with frequencies slightly above and below the rf source frequency.

Fountain clock

Long interrogation time (~ 1 s) through slow (few cm/s), ultracold (few μK) atoms.



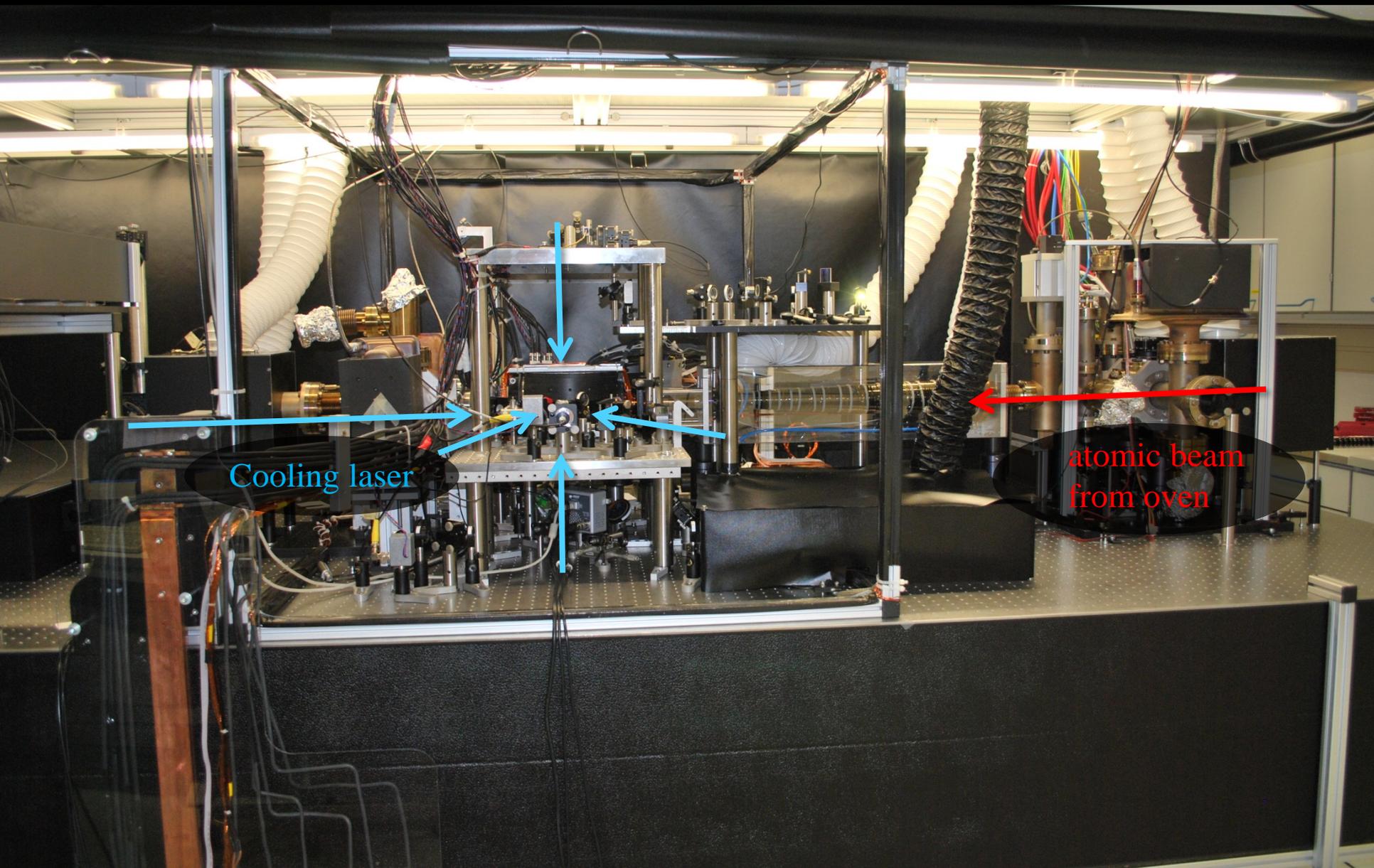
Atomic fountain clock,
BNM-SYRTE, Paris



NIST



Ultracold fridge

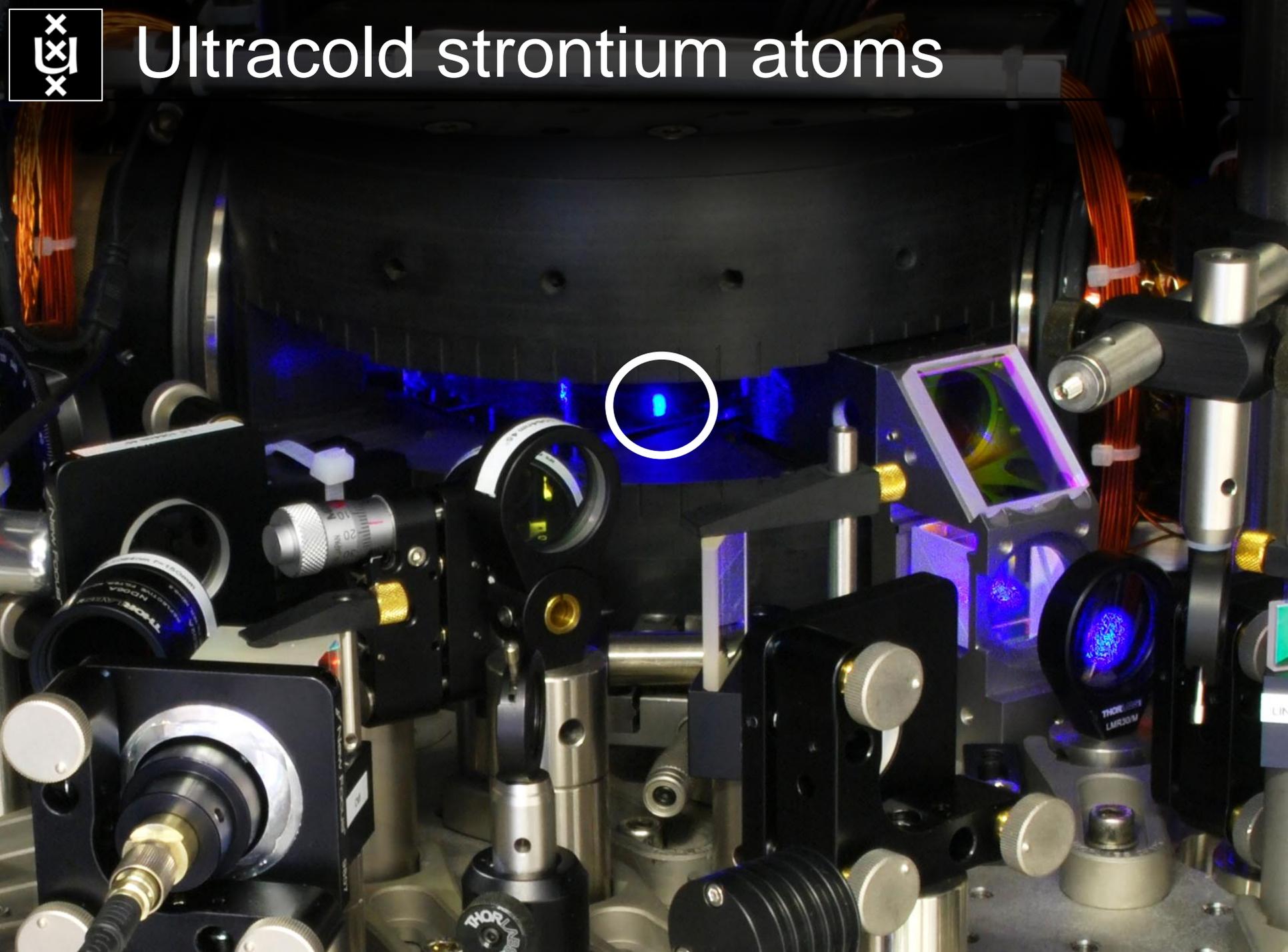


Cooling laser

atomic beam
from oven



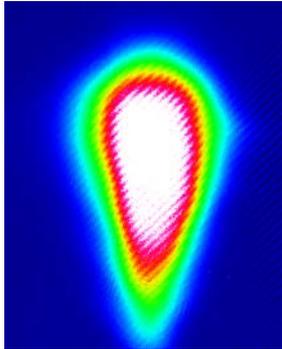
Ultracold strontium atoms



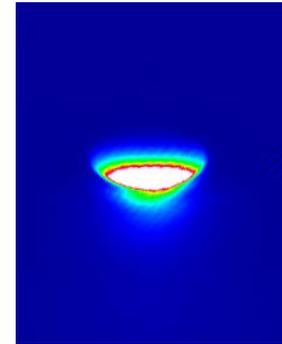
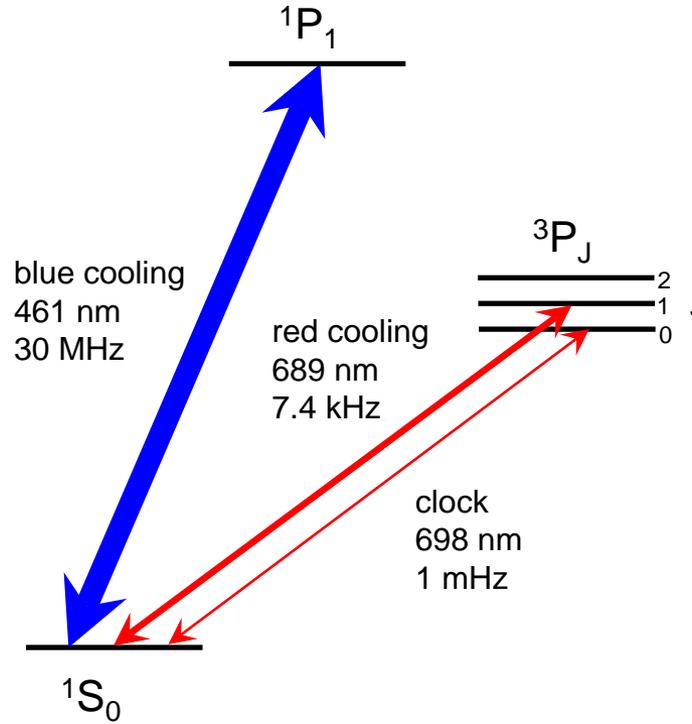


Sr transitions

← 2 mm →



blue laser cooling
hot gas $T \sim 1$ mK



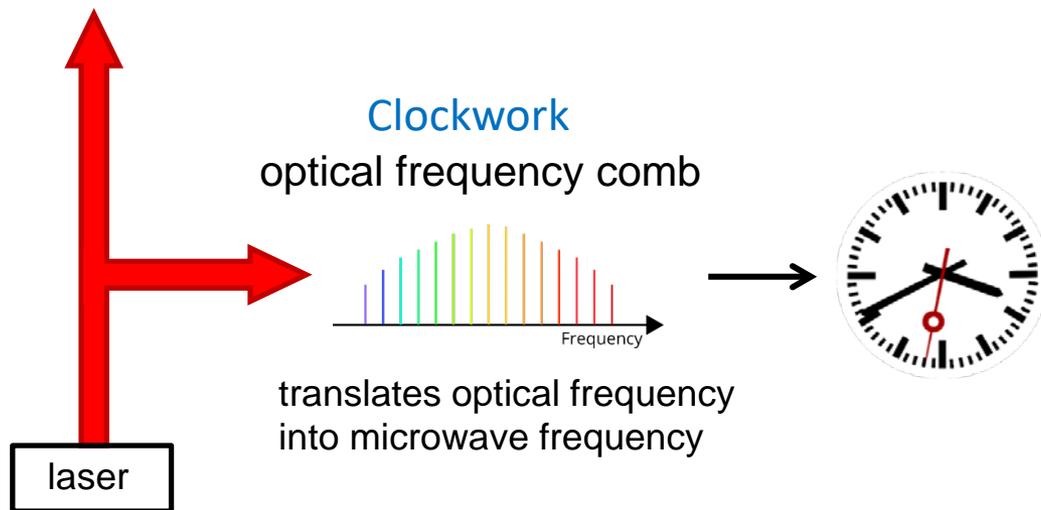
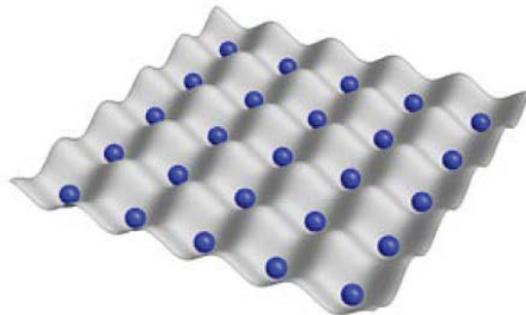
red laser cooling
cold gas $T \sim 1$ μ K



Optical clock scheme

Frequency reference

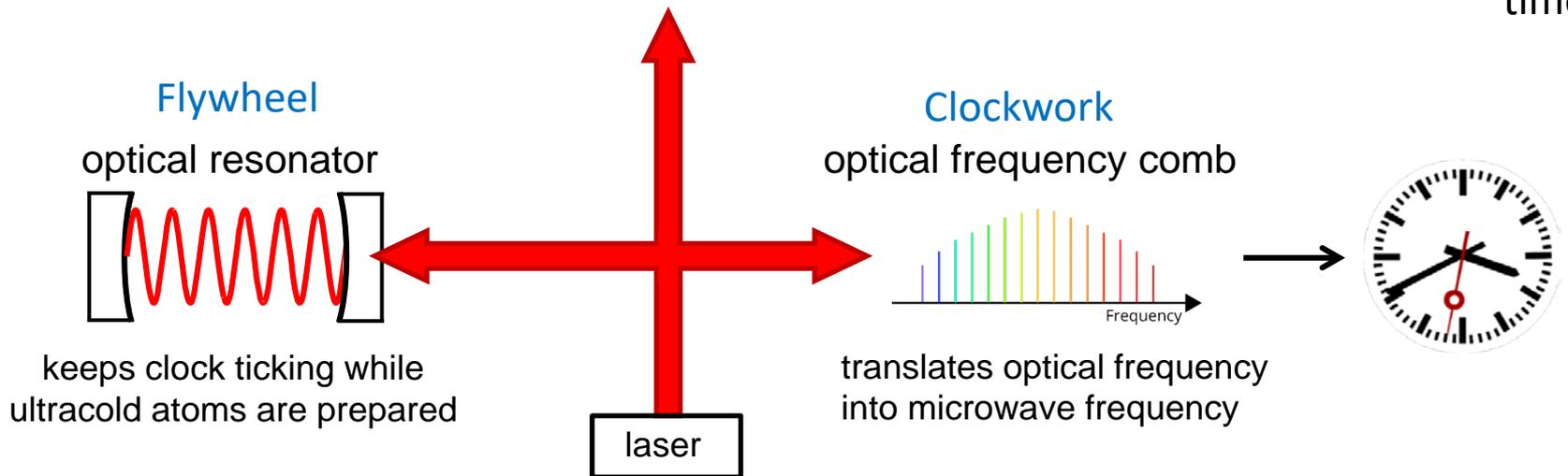
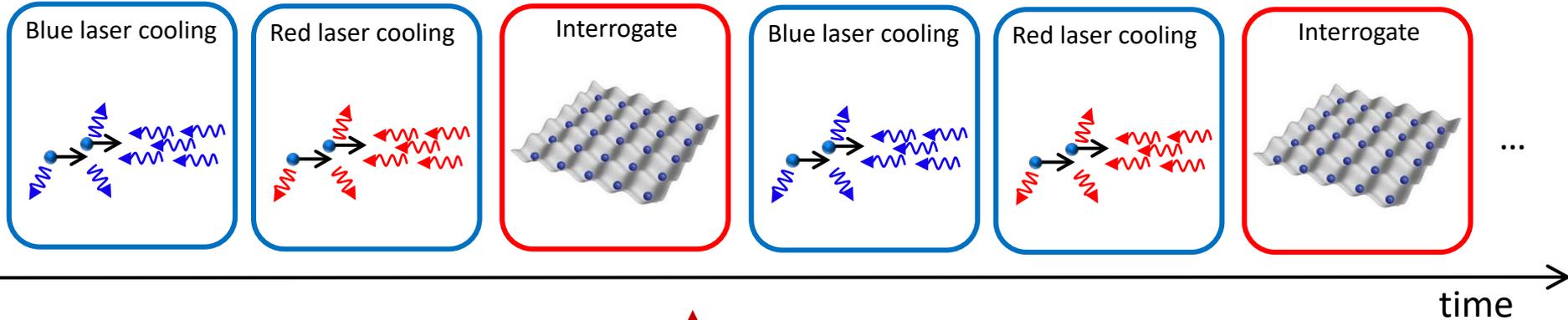
ultracold Sr atoms in lattice





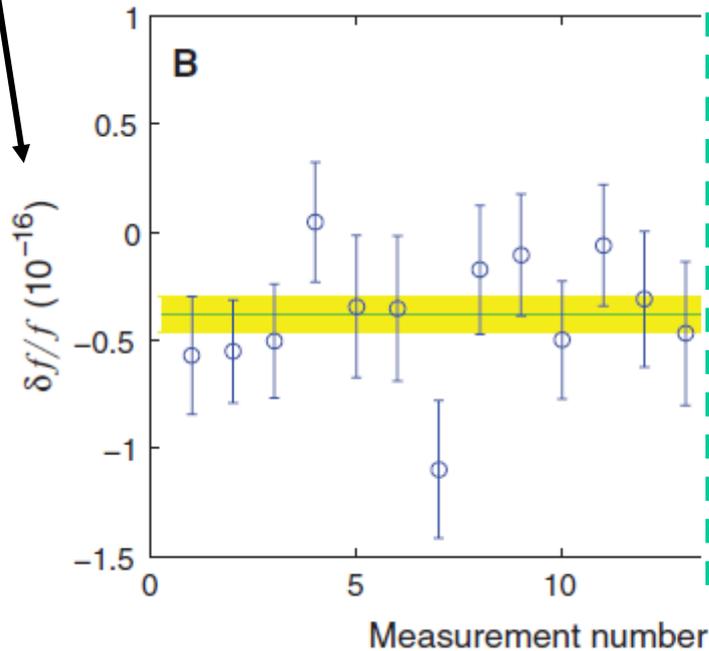
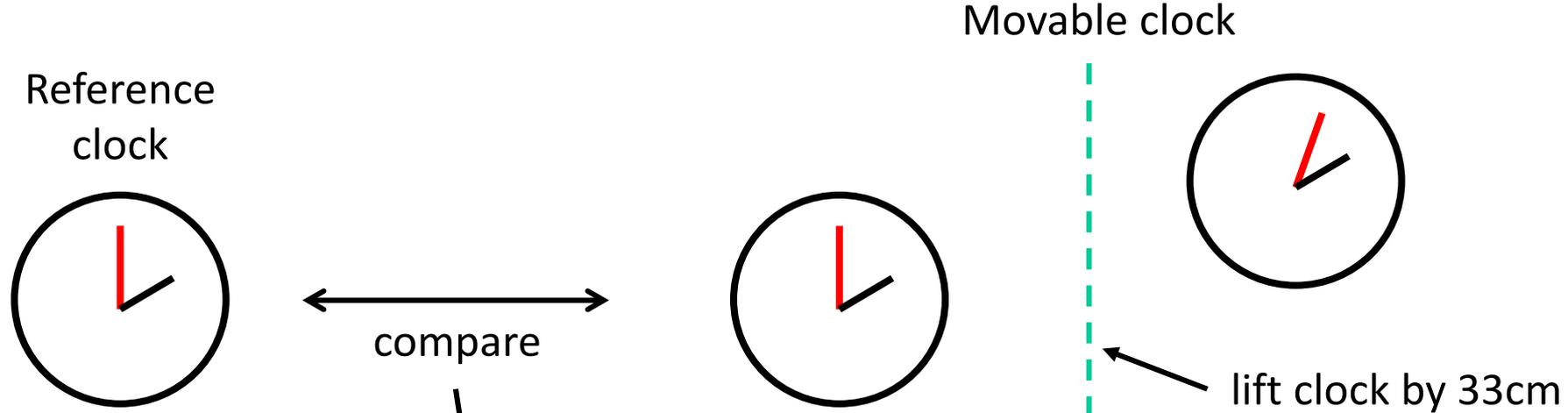
Optical clock scheme

Frequency reference
ultracold Sr atoms in lattice





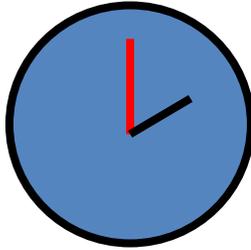
Time and gravity





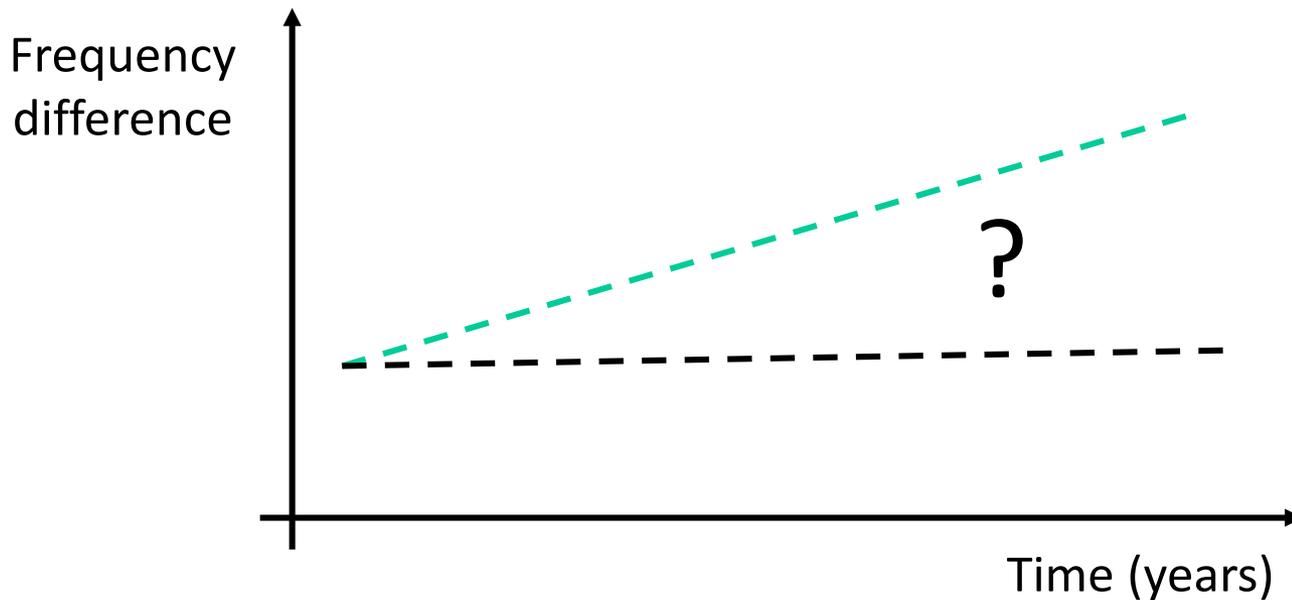
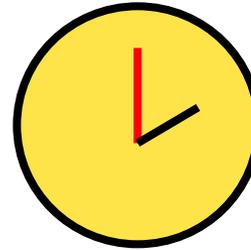
Are the „constants of nature“ constant?

Clock
using Sr



← →
compare

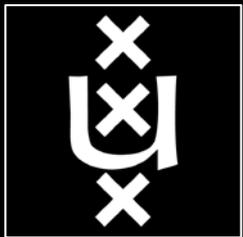
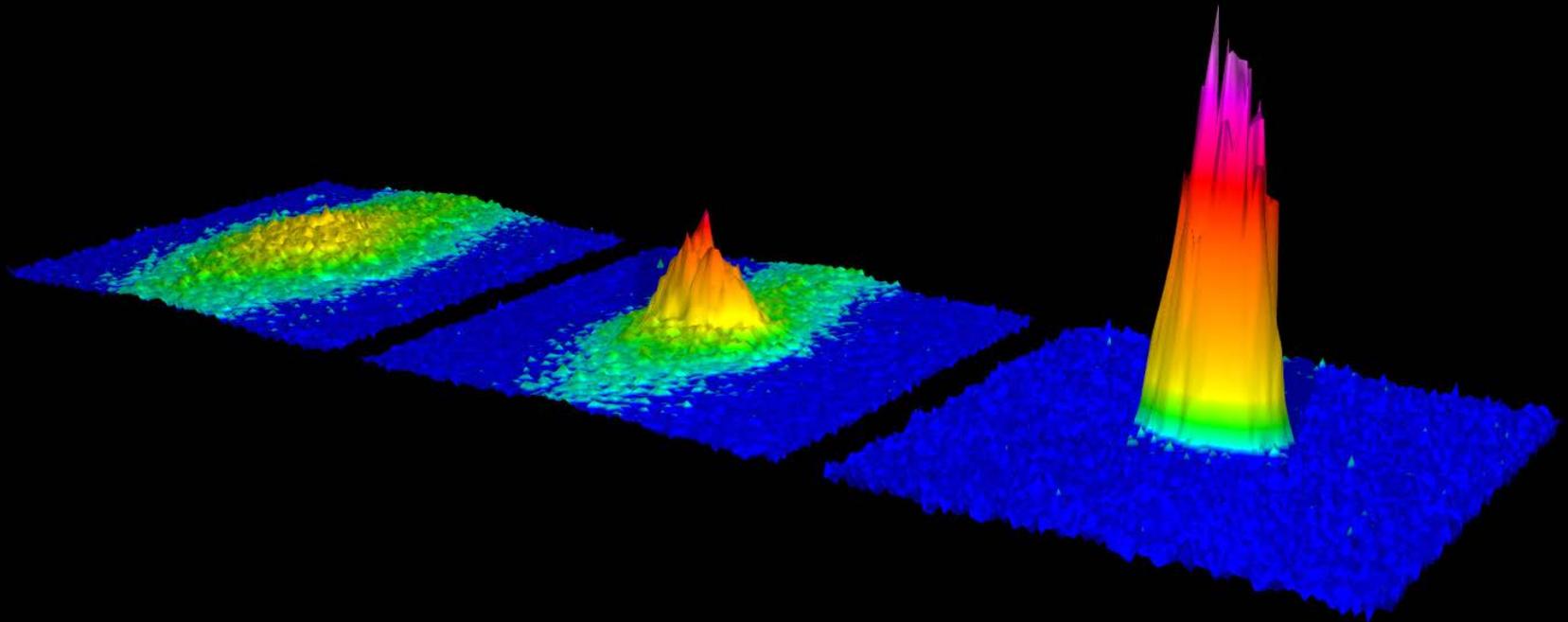
Clock
using Yb



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	Griffiths 5.1, 5.2
Solids	5.3
Time-independent perturbation theory	6.1, 6.2
Structure of hydrogen	6.3 – 6.5
Variational principle	7.1 – 7.3
today → Time-dependent perturbation theory, atom-light interaction	9

Lecture notes, problem sets and link to video recordings of C0.05 lectures
available on Canvas

Questions: schreck@StrontiumBEC.com