Quantum electronics

5

Magnetic materials I

IFM PAN

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Magnetic materials I

- Diamagnetism
- Paramagnetism

Diamagnetism - susceptibility

All materials can be classified in terms of their magnetic behavior falling into one of several categories depending on their bulk magnetic susceptibility χ.

$$\chi=\frac{\vec{M}}{\vec{H}}$$

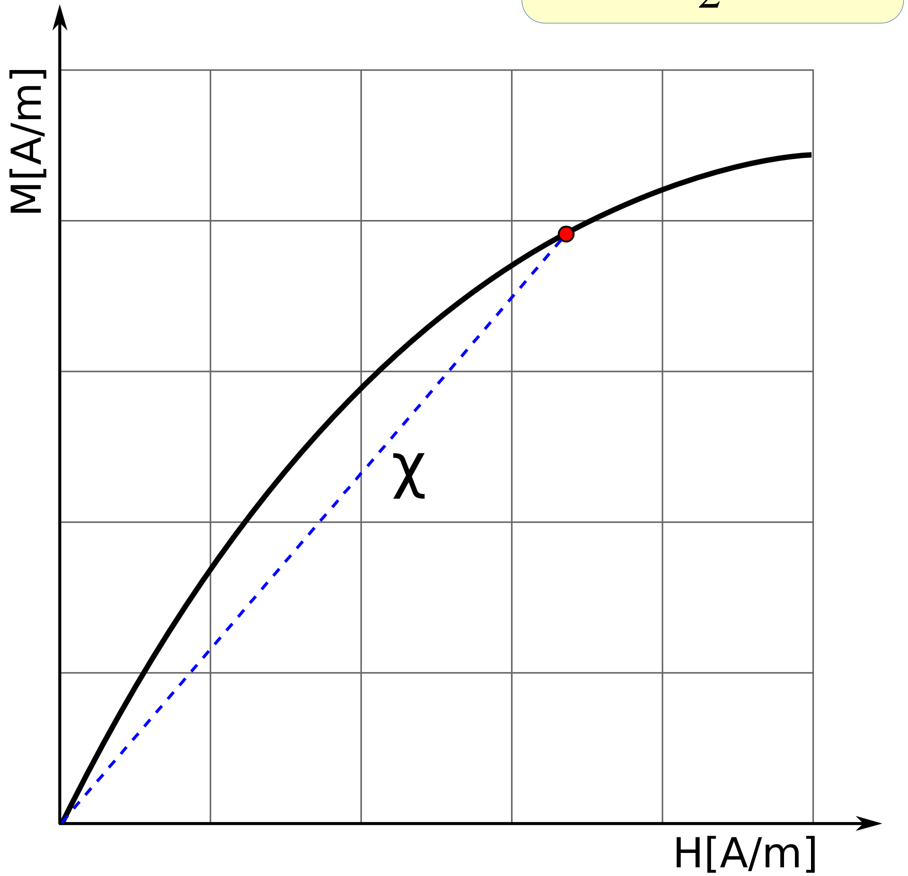
in general the susceptibility is a position dependent tensor

without spin

$$\vec{M}(\vec{r})=\frac{1}{2}\vec{r}\times\vec{J}(\vec{r})$$

In some materials the magnetization is not a linear function of field strength. In such cases the differential susceptibility is introduced:

$$\chi_d=\frac{d\vec{M}}{d\vec{H}}$$



We usually talk about isothermal susceptibility:

$$\chi_T=\left(\frac{\partial\vec{M}}{\partial\vec{H}}\right)_T$$

Theoreticians define magnetization as:

$$M=-\left(\frac{\partial\vec{F}}{\partial\vec{H}}\right)_T$$

$F=U-TS$ - Helmholtz free energy [4]

$$dU=T\,dS-p\,dV+\sum_{i=1}^{N}\mu_i\,dn_i$$

$$dF=T\,dS-p\,dV+\sum_{i=1}^{N}\mu_i\,dn_i-T\,dS-S\,dT=-S\,dT-p\,dV+\sum_{i=1}^{N}\mu_i\,dn_i$$

Diamagnetism - susceptibility

It is customary to define susceptibility in relation to volume, mass or mole:

$$\chi=\frac{\vec{M}}{\vec{H}}\quad[dimensionless],\qquad \chi_\rho=\frac{(\vec{M}/\rho)}{\vec{H}}\left[\frac{m^3}{kg}\right],\qquad \chi_{mol}=\frac{(\vec{M}/mol)}{\vec{H}}\left[\frac{m^3}{mol}\right]$$

$$1\,emu=1\times10^{-3}\,A\cdot m^2$$

The general classification of materials according to their magnetic properties

$\mu<1$	$\chi<0$	diamagnetic*
$\mu>1$	$\chi>0$	paramagnetic**
$\mu\gg1$	$\chi\gg1$	ferromagnetic***

$$\vec{B}=\mu\vec{H}=\mu_r\mu_0\vec{H}\qquad \vec{B}=\mu_o(\vec{H}+\vec{M})$$

$$\mu_r\mu_0\vec{H}=\mu_o(\vec{H}+\vec{M})\ \rightarrow\ \mu_r=1+\chi$$

*dia /daɪəmægˈnɛtɪk/ -Greek: “from, through, across” - repelled by magnets. We have from L2:

$$\vec{F}=\frac{1}{2\mu_0}\chi V\nabla(B^2)$$

the force is directed antiparallel to the gradient of ***B*²**
i.e. away from the magnetized bodies

- water is diamagnetic $\chi\approx-10^{-5}$ (see levitating frog - Ignoble)

** para- Greek: beside, near; for most materials $\chi\approx10^{-5}-10^{-3}$ [1].

***susceptibility ranges from several hundred for steels to 100,000 for soft magnetic materials (Permalloy)

In electronics only ferromagnetic materials are relevant (superconductors, with χ=-1 are used in some devices too)

Diamagnetism - susceptibility

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image source: С. В. Бонсовский, Магнетизм, Издательство ,,Наука", Москва 1971 [5]

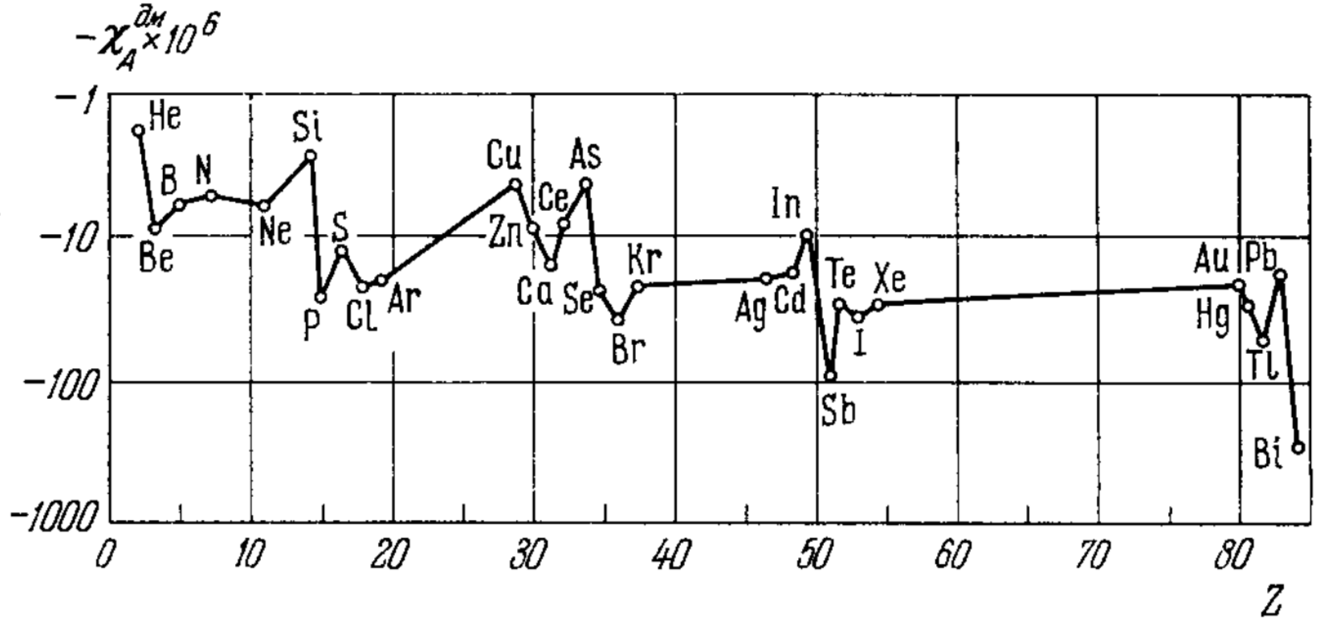

Рис. 7.3. Атомная диамагнитная восприимчивость элементов при комнатной температуре [данные взяты из книги Селвуда (1958)].

room temperature atomic magnetic susceptibility

Bohr–van Leeuwen Theorem

*At any finite temperature, and in all finite applied electric or magnetic fields, the net magnetization of a collection of **classical electrons** in thermal equilibrium vanishes identically*

or in other words

In classical mechanics, there can be no magnetization

or still in other words – see [1]

- Note that a single electron orbiting in magnetic field is a source of small magnetic moment with direction opposite to that of **B** [2] but this moment is independent of **B** [3]

“*The orbits of a cloud of electrons in space give no net current density in bulk, but build a surface current orthogonal to H. Only the outer electrons feed this diamagnetic field, but since their ratio to the total number vanishes for larger and larger clouds, in thermodynamic limit no magnetization per unit volume results. If the motion of several electrons is confined in a box, a current also develops along the boundary due to electrons that bounce on it. This current density is opposite and exactly cancels the surface current due to electrons that do not hit the walls. Thus paramagnetic and diamagnetic terms compensate and again, no magnetization survives (van Leeuwen’s theorem, 1921).*” [2]

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Bohr–van Leeuwen Theorem

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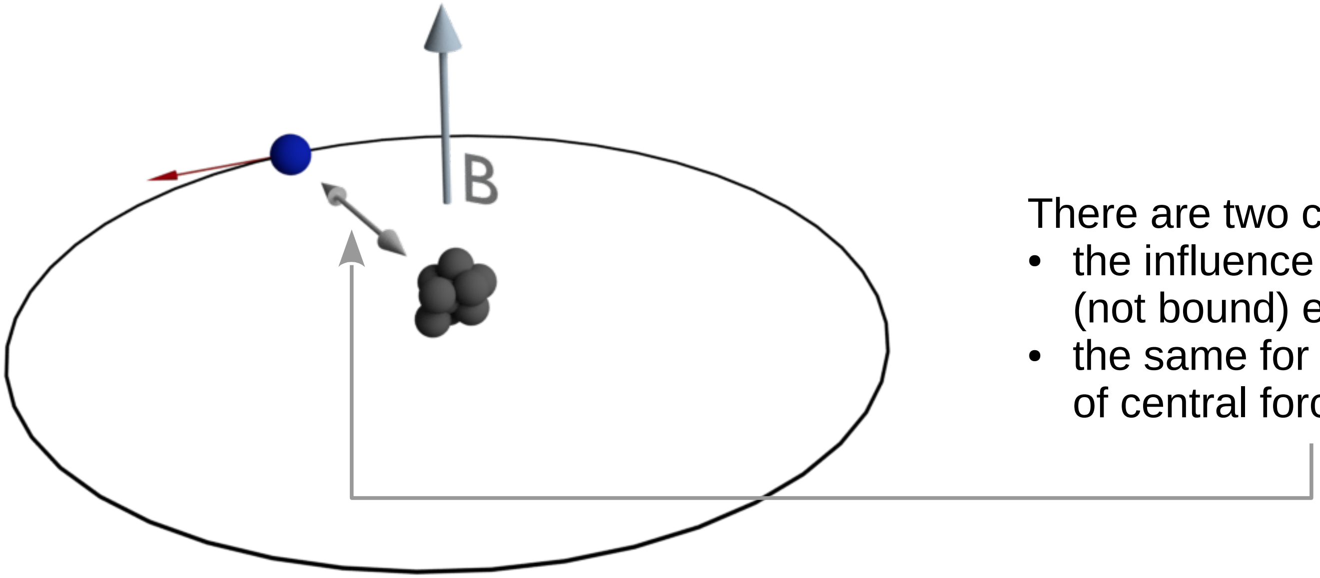
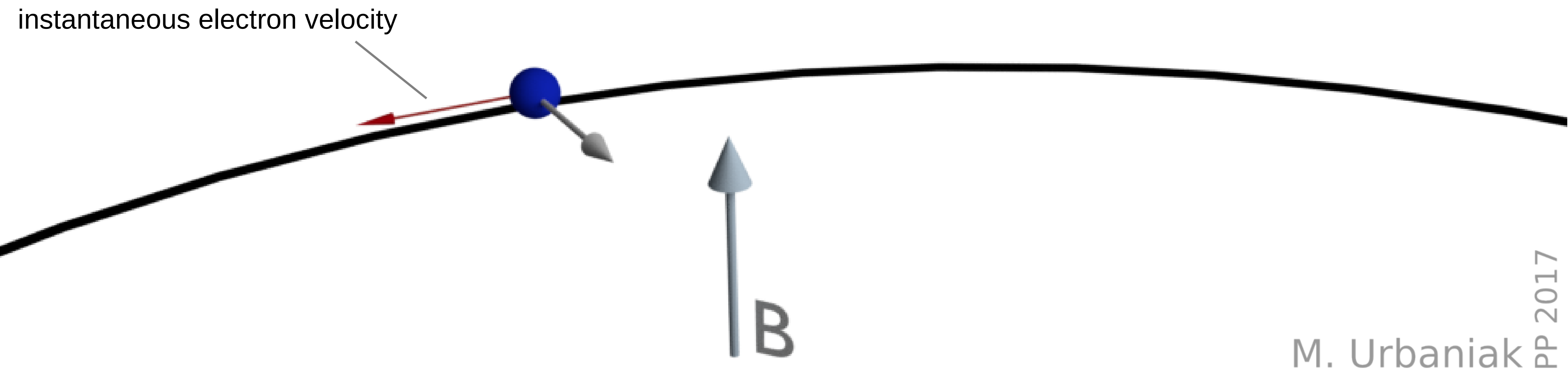
- For the electron orbiting in circle under the influence of **central force** adiabatic switching of the field (**slow increase of the field**, taking much longer than orbital period) does induce the additional moment that is opposite to the **B** direction [3]



There are two cases to consider:

- the influence of magnetic field on a free (not bound) electron
- the same for an electron under the action of central force from nucleus



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Faraday law gives emf induced in the "circular current loop"*

$$emf=-\pi r^2\frac{dB}{dt}$$

period of one tour

Magnetic moment of a loop is $\mu=I\,A,\quad \mathrm{I\ \text{-}\ loop\ current,\ A\ \text{-}\ loop\ area}\ ,\quad \mu=\pi r^2\ I=\pi r^2 q/\left(\frac{2\pi r}{v}\right)$

$$\mu=\frac{1}{2}r\,q\,v\quad \text{and angular momentum is}\quad J=m\,v\,r\rightarrow\mu=\frac{1}{2}(q/m)J$$

An induced emf force induces torque **τ** acting on the electron giving it an acceleration

$$\tau=\vec{r}\cdot\vec{F}=E_{cirle}\,q\,r=\frac{er^2}{2}\frac{dB}{dt}\qquad e\ \text{istead of}\ q\qquad\leftarrow\quad E_{cirle}=\frac{emf}{2\pi r}=-\frac{r}{2}\frac{dB}{dt}$$

and a torque is equal to time derivative of angular momentum l

$$\frac{dJ}{dt}=\frac{er^2}{2}\frac{dB}{dt}\quad\rightarrow\quad dJ=\frac{er^2}{2}dB$$

"This is the extra angular momentum from **the twist** given to the electrons as the field is turned on" - Feynman [4]

and the corresponding change of magnetic moment is (remember q=-e) is

$$d\mu=-\frac{e^2r^2}{4m}dB\quad\text{and because the field starts from zero}\quad\rightarrow\quad\boxed{\Delta\mu=-\frac{e^2r^2}{4m}B}$$

*please read the appropriate Feynman lecture – they are now free to read (www.feynmanlectures.caltech.edu/II_34.html)

Digression – time independent non-degenerate perturbation method

We have a system described by a Hamiltonian $H^{(0)}$ for which we know the solutions [6,7]

$$H^{(0)}\psi=E\psi \quad \rightarrow \quad E_1^{(0)},\ E_2^{(0)},\ E_3^{(0)},\ldots \qquad \psi_1^{(0)},\ \psi_2^{(0)},\ \psi_3^{(0)},\ldots$$

the eigenfunctions are orthonormal and a form complete set

The system is now perturbed so that the new Hamiltonian differs only slightly from $H^{(0)}$

$$\left(H^{(0)}+H^{(1)}\right)\psi=E\psi \quad \rightarrow \quad \left(H^{(0)}+\lambda\hat{V}\right)\psi=E\psi \tag{1}$$

We assume that the solutions of the perturbed equation can be expressed as a power series relative to λ

$$E_m=E_m^{(0)}+\lambda E_m^{(1)}+\lambda^2 E_m^{(2)}+\ldots$$

$$\psi_m=\psi_m^{(0)}+\lambda\psi_m^{(1)}+\lambda^2\psi_m^{(2)}+\ldots$$

Inserting the above solutions to (1) we get

$$\left(H^{(0)}+\lambda\hat{V}-E_m^{(0)}-\lambda E_m^{(1)}-\lambda^2E_m^{(2)}-\ldots\right)\left(\psi_m^{(0)}+\lambda\psi_m^{(1)}+\lambda^2\psi_m^{(2)}+\ldots\right)=0$$

Collecting terms according to the powers of λ we obtain [7]

$$\begin{aligned}
&\left(H^{(0)}-E_m^{(0)}\right)\psi_m^{(0)}=0 \longleftarrow \text{unperturbed equation}\\
&\left(H^{(0)}-E_m^{(0)}\right)\psi_m^{(1)}=\left(E_m^{(1)}-\hat{V}\right)\psi_m^{(0)} \longleftarrow \text{contains zeroth and first order terms}\\
&\left(H^{(0)}-E_m^{(0)}\right)\psi_m^{(2)}=\left(E_m^{(1)}-\hat{V}\right)\psi_m^{(1)}+E_m^{(2)}\psi_m^{(0)}
\end{aligned} \tag{2}$$

Digression – time independent non-degenerate perturbation method

We want to find the first order correction to the energy [7]
To that end we multiply (2) with $\psi_m^{(0)*}$ to get

$$\psi_m^{(0)*}(H^{(0)}-E_m^{(0)})\psi_m^{(1)}=\psi_m^{(0)*}(E_m^{(1)}-\hat{V})\psi_m^{(0)}$$

$$(H^{(0)}-E_m^{(0)})\psi_m^{(0)}=0$$

$$(H^{(0)}-E_m^{(0)})\psi_m^{(1)}=(E_m^{(1)}-\hat{V})\psi_m^{(0)} \qquad (2)$$

$$(H^{(0)}-E_m^{(0)})\psi_m^{(2)}=(E_m^{(1)}-\hat{V})\psi_m^{(1)}+E_m^{(2)}\psi_m^{(0)}$$

Integrating the above expression we have

$$\int\left(\psi_m^{(0)*}(H^{(0)}-E_m^{(0)})\psi_m^{(1)}\right)dV=\int\psi_m^{(0)*}E_m^{(1)}\psi_m^{(0)}dV-\int\psi_m^{(0)*}\hat{V}\psi_m^{(0)}dV$$

$$V_{lm}:=\int\psi_l^{(0)*}\hat{V}\psi_m^{(0)}dV$$

$$\int\left(\psi_m^{(0)*}(H^{(0)}-E_m^{(0)})\psi_m^{(1)}\right)dV=\int\psi_m^{(0)*}H^{(0)}\psi_m^{(1)}dV-\int\psi_m^{(0)*}E_m^{(0)}\psi_m^{(1)}dV=\int\psi_m^{(1)}(H^{(0)}\psi_m^{(0)})^*dV-\int\psi_m^{(0)*}E_m^{(0)}\psi_m^{(1)}dV=$$

$$\int\psi_m^{(1)}E_m^{(0)}\psi_m^{(0)*}dV-\int\psi_m^{(0)*}E_m^{(0)}\psi_m^{(1)}dV=0$$

becaues energy is a real number: $(E_m^{(0)})^*=E_m^{(0)}$

Hermitian operator is defined by the condition [8]

$$\int\psi_1^*\hat{x}\psi_2dV=\int\psi_2(\hat{x}\psi_1)^*dV$$

$$0=E_m^{(1)}-V_{mm}$$

and finally

$$\boxed{E_m^{(1)}=V_{mm}=\int\psi_m^{(0)*}\hat{V}\psi_m^{(0)}dV}$$

$$E_m=E_m^{(0)}+\lambda V_{mm} \qquad E_m=E_0+\langle 0\ \mathrm{m}|H^{(1)}|0\ \mathrm{m}\rangle$$

The correction to the eigenvalues in the first order approximation is the equal to the average energy of the perturbation in the unperturbed state

$\int\psi_m^{(0)*}E_m^{(1)}\psi_m^{(0)}dV=E_m^{(1)}\int\psi_m^{(0)*}\psi_m^{(0)}dV=E_m^{(1)}$, because eigenfunctions are normalized to 1 and $E_m^{(1)}$ is just a number

Digression – time independent non-degenerate perturbation method

To find eigenfunctions in the first order of perturbation we express them as the superpositions of the functions of the unperturbed Hamiltonian [7]

$$\psi_m^{(1)}=\sum_{l=1}\psi_l^{(0)}c_{lm}$$

and insert them to Eq. (2) to obtain

$$(H^{(0)}-E_m^{(0)})\sum_{l=1}\psi_l^{(0)}c_{lm}=(E_m^{(1)}-\hat{V})\psi_m^{(0)} \qquad (3)$$

$$(H^{(0)}-E_m^{(0)})\psi_m^{(1)}=(E_m^{(1)}-\hat{V})\psi_m^{(0)} \qquad (2)$$

To find coefficients c for k≠m we multiply (3) by $\psi_k^{(0)*}$ and integrate to get

$$\int\left[\psi_k^{(0)*}(H^{(0)}-E_m^{(0)})\sum_{l=1}\psi_l^{(0)}c_{lm}\right]dV=\int\psi_k^{(0)*}E_m^{(1)}\psi_m^{(0)}\,dV-\int\psi_k^{(0)*}\hat{V}\psi_m^{(0)}\,dV$$

$$V_{lm}:=\int\psi_l^{(0)*}\hat{V}\psi_m^{(0)}\,dV$$

$$H^{(0)}\sum_{l=1}\psi_l^{(0)}c_{lm}=\sum_{l=1}E_l^{(0)}\psi_l^{(0)}c_{lm}$$

orthogonality of $\psi_k^{(0)}$ and $\psi_m^{(0)}$ → =0

$$\mathrm{LHS}=\sum_{l=1}(E_l^{(0)}-E_m^{(0)})c_{lm}\int\psi_k^{(0)*}\psi_l^{(0)}\,dV=\sum_{l=1}(E_l^{(0)}-E_m^{(0)})c_{lm}\delta_{kl}=(E_k^{(0)}-E_m^{(0)})c_{km}$$

Kronecker delta:
$\delta_{ij}=0\ if\ i\neq j$

which gives $(E_k^{(0)}-E_m^{(0)})c_{km}=-V_{km}$

or

$$\boxed{c_{km}=\frac{V_{km}}{(E_m^{(0)}-E_k^{(0)})}\qquad \text{for } k\neq m}$$

Digression – time independent non-degenerate perturbation method

In order to obtain approximately normalized eigenfunction one assumes that $c_{mm}=0$ [7]. We have then

$$\psi_m^{(1)}=\sum_{l,l\neq m} c_{lm}\psi_l^{(0)}$$

$$c_{km}=\frac{V_{km}}{\left(E_m^{(0)}-E_k^{(0)}\right)} \quad \text{for } k\neq m$$

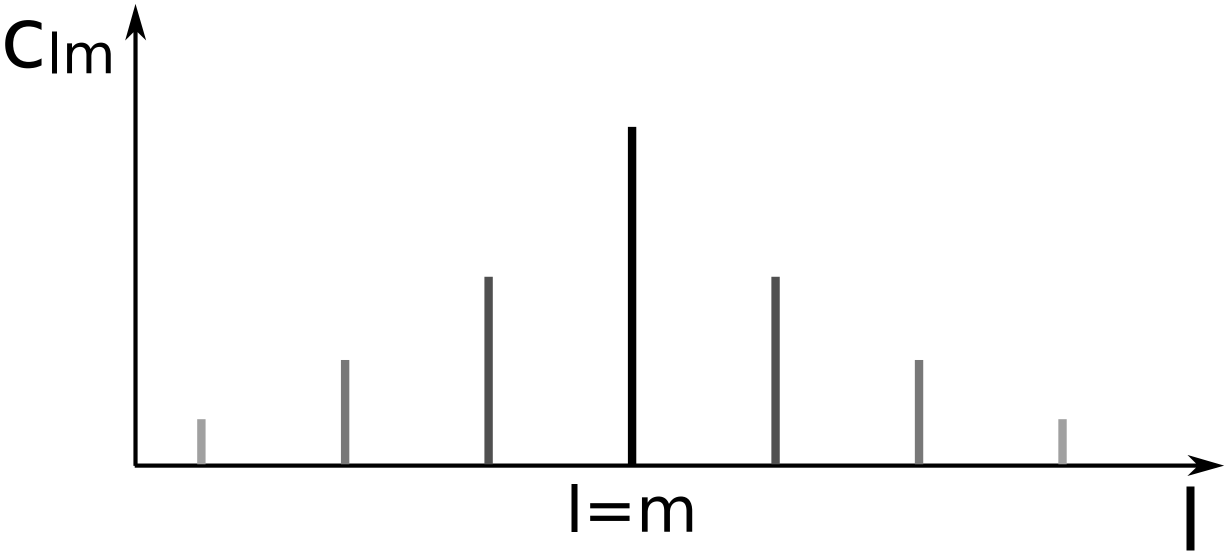
and finally, for the function in the first order of perturbation

$$\psi_m^{(0)}+\lambda\psi_m^{(1)}=\psi_m^{(0)}+\sum_{l,l\neq m}\frac{V_{lm}}{\left(E_m^{(0)}-E_l^{(0)}\right)}\psi_l^{(0)}$$

- note the the approximating series do not always converge [7] requiring more advanced methods
- for degenerate energy levels (eigenfunctions with the same energy) the above methods fails: some c coefficients go to infinity

$$E_m=E_m^{(0)}+\lambda E_m^{(1)}+\lambda^2 E_m^{(2)}+\ldots$$

$$\psi_m=\psi_m^{(0)}+\lambda\psi_m^{(1)}+\lambda^2\psi_m^{(2)}+\ldots$$



- perturbation mixes every unperturbed state with other states [9, Fig.11.1]
- the states in the vicinity (energy) are more strongly admixed than those farther away

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

Atom in magnetic field

Hamiltonian of an atom containing Z electrons reads [10]

$$H_0=\sum_{i=1}^{z}\left(\frac{p_i^2}{2m}+V_i\right),\qquad V_i\ \text{- potential energy}$$

The external magnetic field can be written using vector potential $\vec A(r)=\frac{1}{2}(\vec B\times\vec r)$

From previous lectures we have for the energy of an electron

$$H=\frac{1}{2}m(\vec p-e\vec A)^2+eV$$

$$\vec B=\nabla\times\vec A$$

$$\vec B\times\vec r=\hat x(-B_z y+B_y z)+\hat y(B_z x-B_x z)+\hat z(-B_y x+B_x y)$$

$$\nabla\times(\vec B\times\vec r)=2\vec B$$

Expanding the kinetic energy term we get

$$\frac{1}{2}m(\vec p-e\vec A)^2=\frac{p^2}{2m}-\frac{e}{m}\vec A\cdot\vec p+\frac{e^2}{2m}\vec A^2=\frac{p^2}{2m}-\frac{e}{2m}(\vec B\times\vec r)\cdot\vec p+\frac{e^2}{2m}\left(\frac{1}{2}(\vec B\times\vec r)\right)^2=$$

$$\frac{p^2}{2m}-\frac{e}{2m}\underbrace{(\vec r\times\vec p)}_{\text{orbital angular momentum }\hbar L}\cdot\vec B+\frac{e^2}{8m}(\vec B\times\vec r)^2$$

The complete Hamiltonian, including the spin of an electron, is then [10]

$$\boxed{H=\sum_{i=1}^{Z}\left(\frac{p_i^2}{2m}+V_i\right)\ +\ \underbrace{\mu_B(\vec L+g\vec S)\cdot\vec B}_{\text{paramagnetic term}}\ +\ \underbrace{\frac{e^2}{8m}\sum_{i=1}^{Z}(\vec B\times\vec r_i)^2}_{\text{diamagnetic term}}}$$

$$\mu_B=\frac{e\hbar}{2m}$$

$g\approx 2$ - g-factor of an electron

Atom in magnetic field - diamagnetism

To simplify the matters we assume that all electronic shells of the atom are filled so that orbital and spin momenta vanish [10] – the atom has no magnetic moment on its own

$$H=\sum_{i=1}^{Z}\left(\frac{p_i^2}{2m}+V_i\right) + \frac{e^2}{8m}\sum_{i=1}^{Z}(\vec{B}\times\vec{r}_i)^2 \quad \leftarrow \quad \vec{L}=0,\ \vec{S}=0$$

$$H=\sum_{i=1}^{Z}\left(\frac{p_i^2}{2m}+V_i\right) + \mu_B(\vec{L}+g\vec{S})\cdot\vec{B} + \frac{e^2}{8m}\sum_{i=1}^{Z}(\vec{B}\times\vec{r}_i)^2$$

We further assume the magnetic field is parallel to z-axis: **B**=(0,0,B)

$$\vec{B}\times\vec{r}_i=B(-\hat{x}\,y_i+\hat{y}\,x_i) \quad \rightarrow \quad (\vec{B}\times\vec{r}_i)^2=B^2(x_i^2+y_i^2)$$

Consequently (see previous slides on perturbation method) an energy shift due to the diamagnetic term is

$$\Delta E=B^2\frac{e^2}{8m}\sum_{i=1}^{Z}<0|\,x_i^2+y_i^2\,|0>$$

$|0>$ - ground state wave function

Perturbation correction

$$E_m^{(1)}=V_{mm}=\int\psi_m^{(0)*}\,\hat{V}\,\psi_m^{(0)}\,dV$$

For spherically symmetric electronic wave function we have

$$<x_i^2>=<y_i^2>=<z_i^2>=\frac{1}{3}<r_i^2> \quad \rightarrow \quad \Delta E=B^2\frac{e^2}{12m}\sum_{i=1}^{Z}<0|\,r_i^2\,|0>$$

and using a thermodynamic definition of magnetic moment we get (for T=0)

$$m=-\left(\frac{\partial\vec{F}}{\partial\vec{H}}\right)_T$$

$$F=U-TS$$

$$M=-\frac{N}{V}\left(\frac{\partial\vec{F}}{\partial\vec{H}}\right)_T=-B\,\frac{N}{V}\,\frac{e^2}{6m\mu_0^2}\sum_{i=1}^{Z}<0|\,r_i^2\,|0>$$

Number of atoms in a volume – to obtain magnetization

Atom in magnetic field - diamagnetism

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$$H=\sum_{i=1}^{Z}\left(\frac{p_i^2}{2m}+V_i\right) + \frac{e^2}{8m}\sum_{i=1}^{Z}(\vec{B}\times\vec{r}_i)^2 \leftarrow \vec{L}=0,\ \vec{S}=0 \quad H=\sum_{i=1}^{Z}\left(\frac{p_i^2}{2m}+V_i\right) + \mu_B(\vec{L}+g\vec{S})\cdot\vec{B} + \frac{e^2}{8m}\sum_{i=1}^{Z}(\vec{B}\times\vec{r}_i)^2$$

- the susceptibility is negative – diamagnetism
- the outermost shells contribute more to the the susceptibility due to $\chi\propto<r_i^2>$

$$M=-\frac{N}{V}\left(\frac{\partial\vec{F}}{\partial\vec{H}}\right)_T=-B\frac{N}{V}\frac{e^2}{6m\mu_0^2}\sum_{i=1}^{Z}<0|r_i^2|0>$$

$$\chi=-\frac{N}{V}\frac{e^2}{6m\mu_0^2}\sum_{i=1}^{Z}<0|r_i^2|0>$$

Pauli principle – fermions, bosons

In the system composed of indistinguishable particles the exchange of the particles does not change the wave function

$$H\psi(r_{1,}r_2)=E\psi(r_{1,}r_2) \qquad H\psi(r_{2,}r_1)=E\psi(r_{2,}r_1)$$

Since the observables do not change when particles are exchanged we must have*

$$<\psi(r_{1,}r_2)|\text{some operator}|\psi(r_{1,}r_2)>=a<\psi(r_{1,}r_2)|\text{some operator}|\psi(r_{1,}r_2)>$$

or

$$\psi(r_{1,}r_2)=a\psi(r_{1,}r_2)$$

But exchanging the particles twice brings us back to the initial state

$$\psi(r_{1,}r_2) \rightarrow a\psi(r_{1,}r_2) \rightarrow a^2\psi(r_{1,}r_2)$$

It follows **a=±1**

- **a=1** – symmetric wave functions – bosons
- **a=-1** – antisymmetric wave functions – fermions (electrons, protons, neutrons)

*argument, leading to identical conclusions, is different if energy levels are degenerate

Pauli principle – fermions, bosons

“*This brings up an interesting question: Why is it that particles with half-integral spin are Fermi particles whose amplitudes add with the minus sign, whereas particles with integral spin are Bose particles whose amplitudes add with the positive sign? We apologize for the fact that we cannot give you an elementary explanation. An explanation has been worked out by Pauli from complicated arguments of quantum field theory and relativity. He has shown that the two must necessarily go together, but we have not been able to find a way of reproducing his arguments on an elementary level. It appears to be one of the few places in physics where there is a rule which can be stated very simply, but for which no one has found a simple and easy explanation. The explanation is deep down in relativistic quantum mechanics. This probably means that we do not have a complete understanding of the fundamental principle involved.* ***For the moment, you will just have to take it as one of the rules of the world***.”

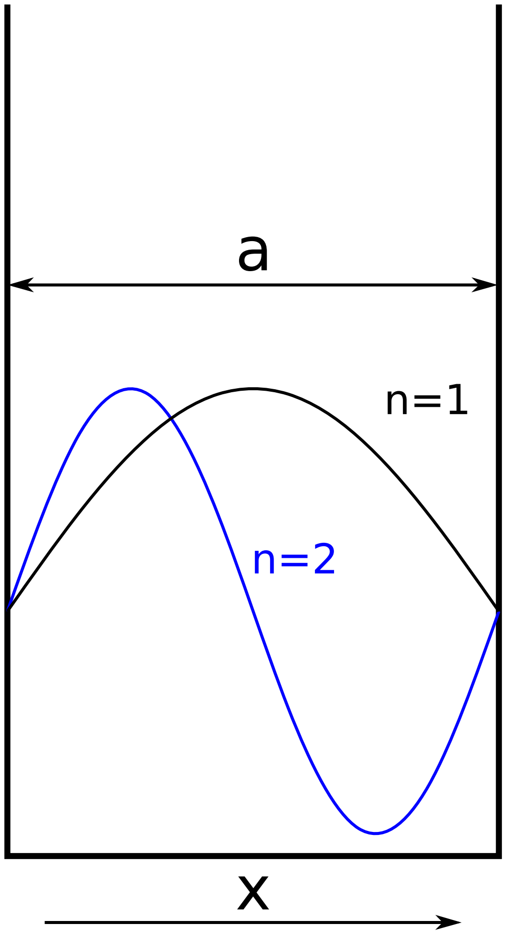
R. Feynman, *Feynman Lectures on Physics*, *Identical Particles*, III Ch.4, 1963

- **a=1** – symmetric wave functions – bosons
- **a=-1** – antisymmetric wave functions – fermions (electrons, protons, neutrons)

Fermions, bosons – an example; non-interacting particles

Assume that two identical particles are confined to a potential well of the **infinite** depth and width **a**. The normalized 1-D solutions to Schrödinger equation are of the form [9]:

$$\psi(x)=\sqrt{\frac{2}{a}}\sin\left(n\frac{\pi}{a}x\right), \qquad n=\pm1,\pm2,\ldots$$



Depending on whether the particles are distinguishable (classical case) or not and on whether they are bosons or fermions the wave function of two non-interacting particles can be written in one of three ways*:

- distinguishable particles

$$\psi(r_1,r_2)=\psi_{n1}(r_1)\,\psi_{n2}(r_2)$$

which means that particle no.1 is in state n1 at position r_1 and particle no.2 is in state n2 at position r_2

- bosons (symmetric wave function)

$$\psi(r_1,r_2)=\frac{1}{\sqrt{2}}\left[\psi_{n1}(r_1)\,\psi_{n2}(r_2)+\psi_{n1}(r_2)\,\psi_{n2}(r_1)\right]$$

- fermions (antisymmetric function)

$$\psi(r_1,r_2)=\frac{1}{\sqrt{2}}\left[\psi_{n1}(r_1)\,\psi_{n2}(r_2)-\psi_{n1}(r_2)\,\psi_{n2}(r_1)\right]$$

*see the video lectures 7.1-7.5 of Ron Reifenberger () [26]

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Depending on whether the particles are distinguishable (classical case) or not and on whether they are bosons or fermions the wave function of two non-interacting particles can be written in one of three ways*:

Both particles in the same quantum state [26]
probability density

- distinguishable particles

$$\psi(r_1,r_2)=\psi_{n1}(r_1)\psi_{n2}(r_2)$$

$$P(r_1,r_2)=\psi_n(r_1)\psi_n(r_2)\psi_n(r_1)^*\psi_n(r_2)^*$$

- bosons (symmetric wave function)

$$\psi(r_1,r_2)=\frac{1}{\sqrt{2}}\left[\psi_{n1}(r_1)\psi_{n2}(r_2)+\psi_{n1}(r_2)\psi_{n2}(r_1)\right]$$

$$P(r_1,r_2)=\left(\frac{1}{\sqrt{2}}\left[2\psi_n(r_1)\psi_n(r_2)\right]\right)\left(\frac{1}{\sqrt{2}}\left[2\psi_n(r_1)\psi_n(r_2)\right]\right)^*$$

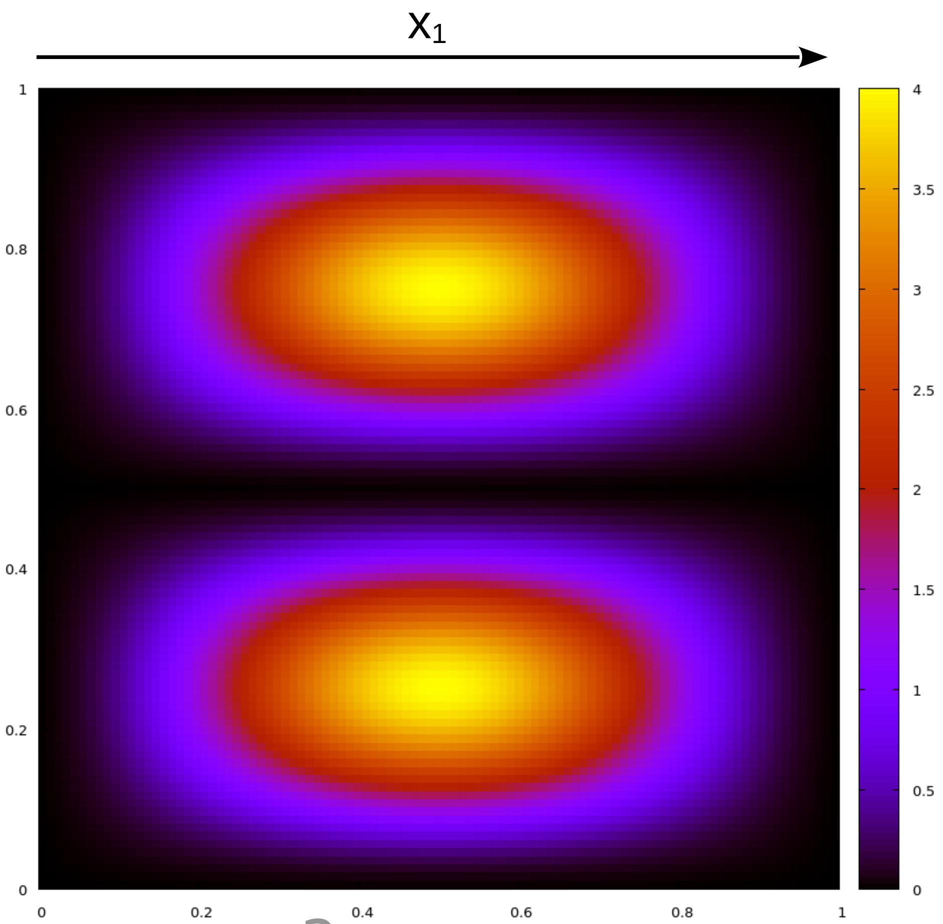
$$=2\psi_n(r_1)\psi_n(r_2)\psi_n(r_1)^*\psi_n(r_2)^*$$

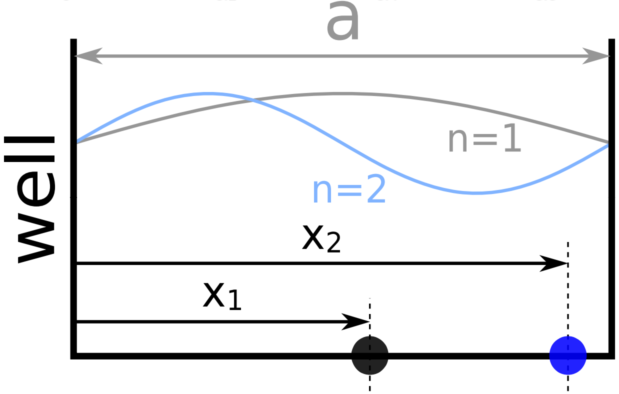
Bosons have enhanced probability of being in the same quantum state

Fermions, bosons – an example; non-interacting particles

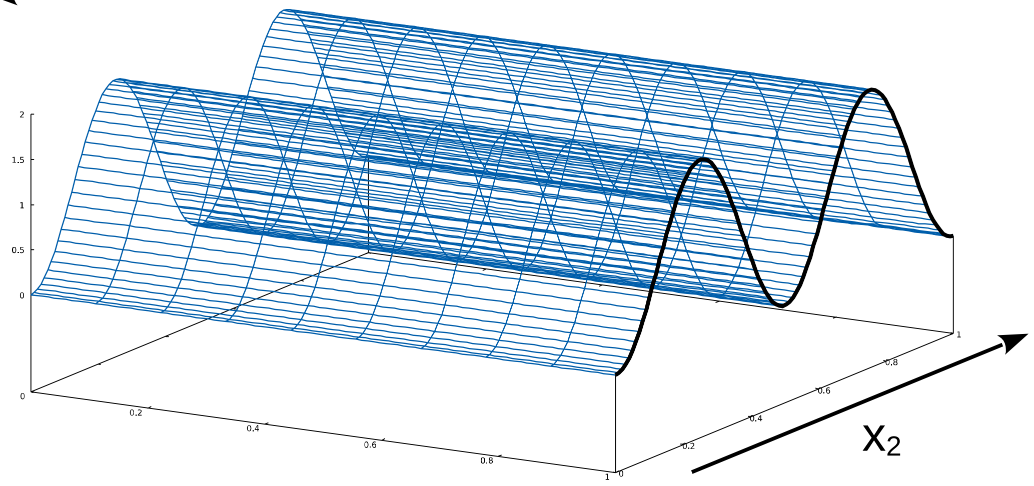
We consider first two levels in a well: one particle in state with n=1 and the other with n=2

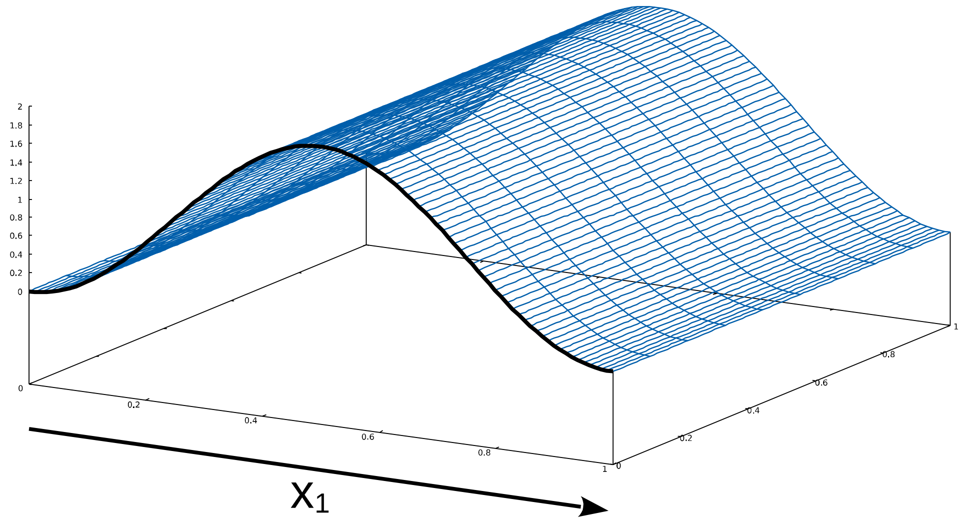
Distinguishable particles – classical description





$$P(x_1,x_2)=\left[\sqrt{\frac{2}{a}}\sin\left(1\,\frac{\pi}{a}\,x_1\right)\sqrt{\frac{2}{a}}\sin\left(2\,\frac{\pi}{a}\,x_2\right)\right]^2$$

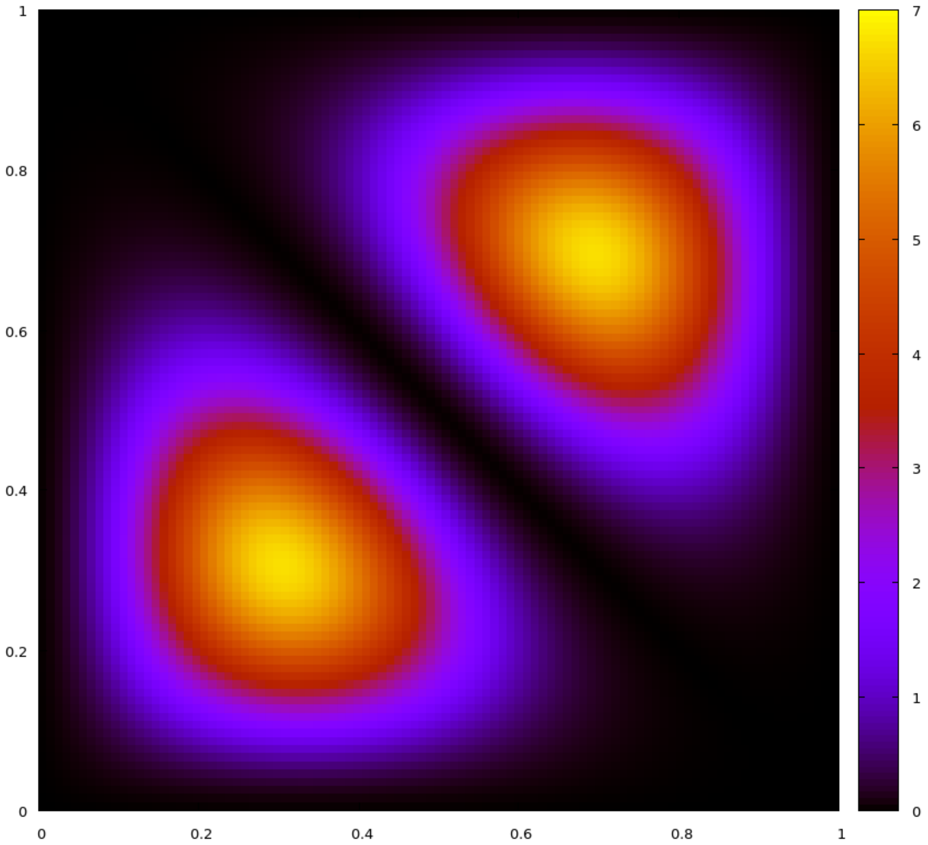




x_1 and x_2 denote the positions of particles along x-axis

Fermions, bosons – an example; non-interacting particles

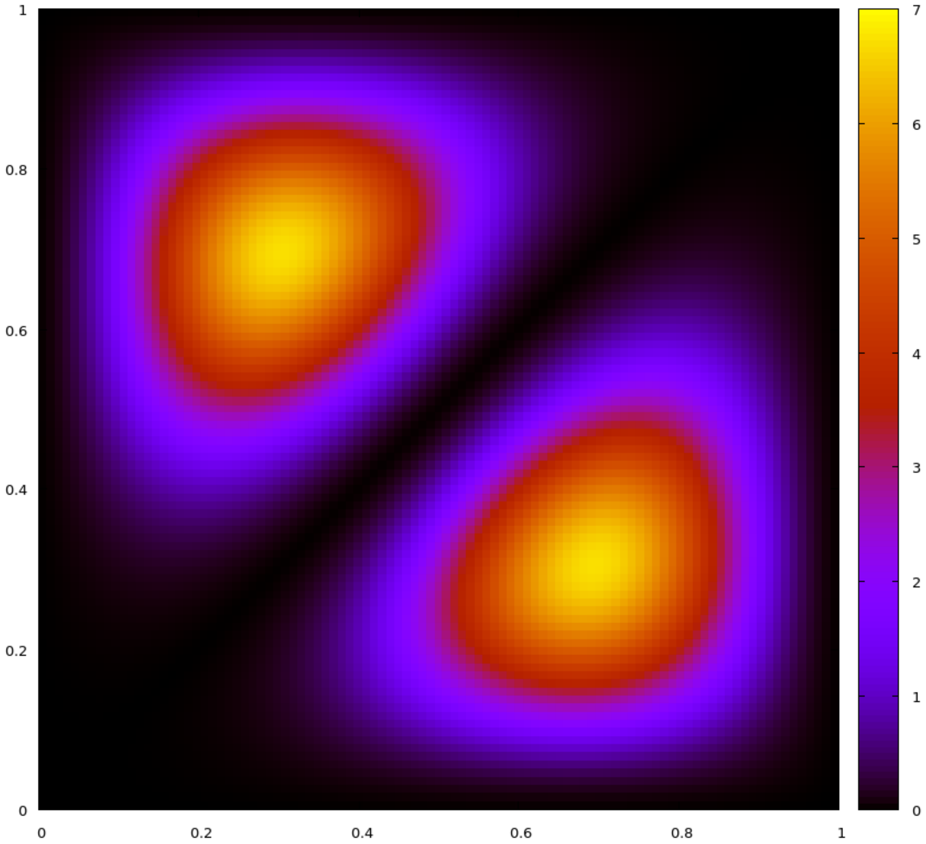
We consider first two levels in a well: one particle in state with n=1 and the other with n=2
Indistinguishable boson particles



$$P(x_1,x_2)=\left[\sqrt{\frac{2}{a}}\sin\left(1\,\frac{\pi}{a}\,x_1\right)\sqrt{\frac{2}{a}}\sin\left(2\,\frac{\pi}{a}\,x_2\right)\;+\;\sqrt{\frac{2}{a}}\sin\left(1\,\frac{\pi}{a}\,x_2\right)\sqrt{\frac{2}{a}}\sin\left(2\,\frac{\pi}{a}\,x_1\right)\right]^2$$

Fermions, bosons – an example; non-interacting particles

We consider first two levels in a well: one particle in state with n=1 and the other with n=2
Indistinguishable fermions



$$P(x_1,x_2)=\left[\sqrt{\frac{2}{a}}\sin\left(1\,\frac{\pi}{a}\,x_1\right)\sqrt{\frac{2}{a}}\sin\left(2\,\frac{\pi}{a}\,x_2\right)\quad-\quad\sqrt{\frac{2}{a}}\sin\left(1\,\frac{\pi}{a}\,x_2\right)\sqrt{\frac{2}{a}}\sin\left(2\,\frac{\pi}{a}\,x_1\right)\right]^2$$

Density of states

We define the density of states as a number of electron states per unit energy range [11]

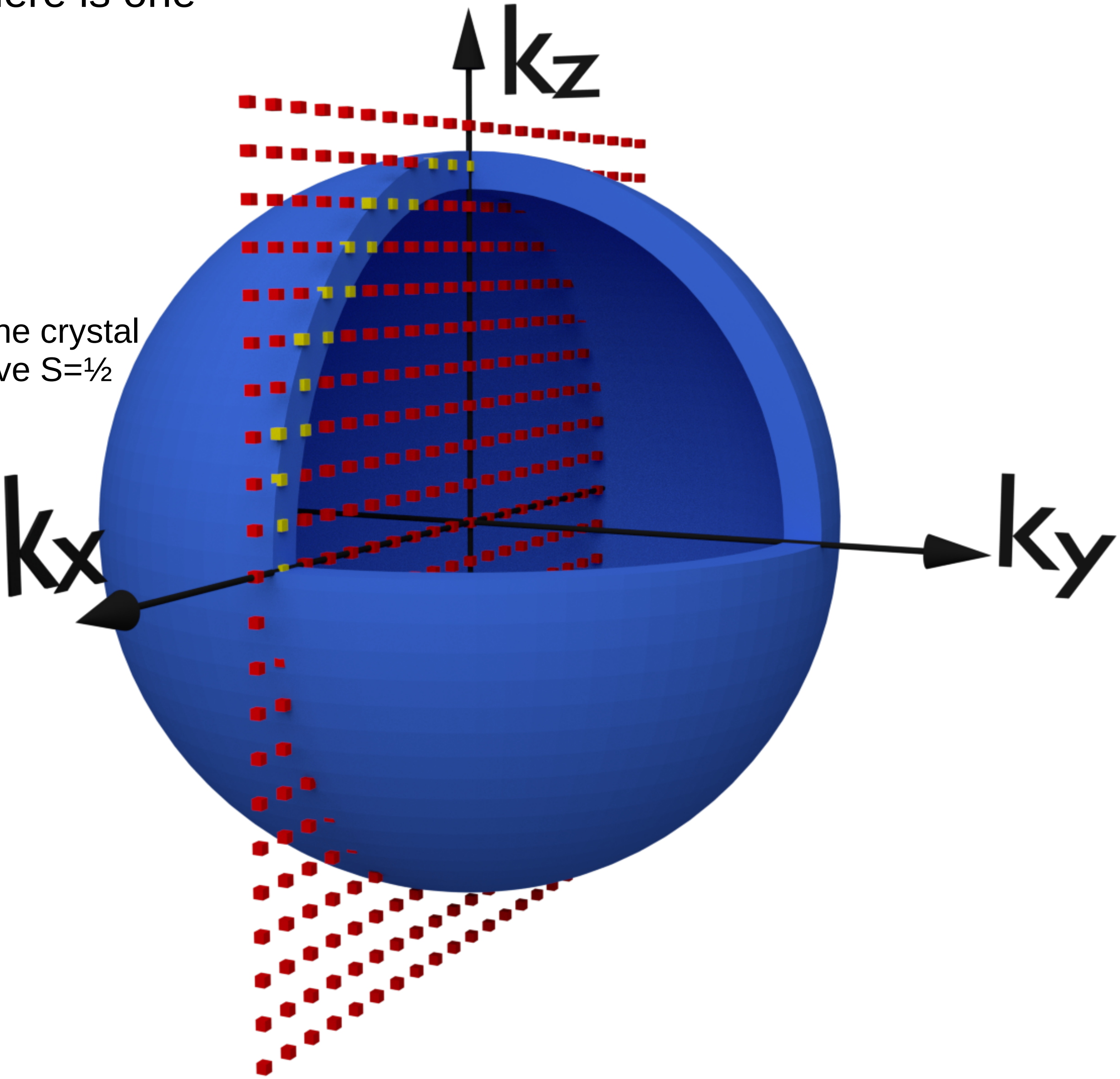
From previous lectures we know that there is one allowed wave vector (k_x,k_y,k_z) for

$$\left(\frac{2\pi}{L}\right)^3$$ volume of **k** space [12]

If we allow for the possible orientations of spin the density of states in k-space is [13]

$$d_{statee}=(2S+1)\left(\frac{L}{2\pi}\right)^3$$

L^3 is the volume of the crystal
For electrons we have S=½



- we assume that the space is isotropic
- and that the allowed **k** values are quasi continuous (macroscopic system [13]

The number of allowed states in the range 0 to k (see the sphere to the right) is given by

$$N=\frac{4}{3}\pi k^3\ d_{states}=\frac{4}{3}\pi k^3(2S+1)\left(\frac{L}{2\pi}\right)^3$$

volume of the k-sphere

Density of states

The number of states in the k to k+dk range is thus (surface of the sphere times its thickness,...)

$$dN=4\pi k^2\, d_{states}\, dk=(2S+1)\frac{L^3}{2\pi^2}k^2\, dk$$

$$d_{states}=(2S+1)\left(\frac{L}{2\pi}\right)^3$$

From the expression for the for the energy of free particles $\epsilon=\frac{p^2}{2m}=\frac{\hbar^2}{2m}k^2$ we get

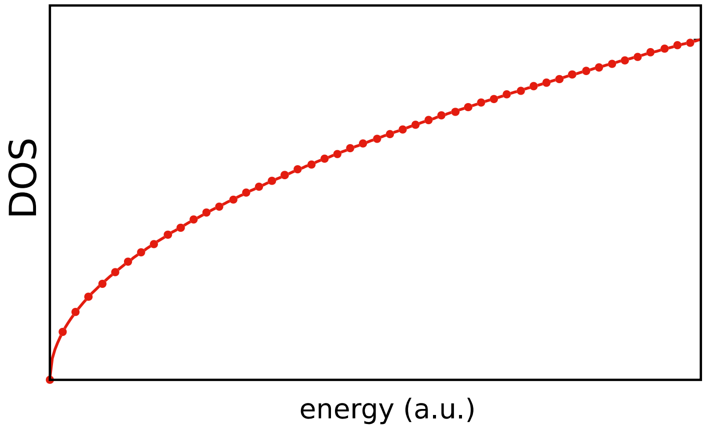
$$k=\sqrt{\frac{2m\epsilon}{\hbar^2}} \rightarrow dk=\frac{1}{2}\sqrt{\frac{2m}{\hbar^2}}\,\epsilon^{-1/2}\, d\epsilon$$

Combining last two expressions we obtain [13]

$$dN=(2S+1)\frac{L^3}{2\pi^2}k^2 \times \frac{1}{2}\sqrt{\frac{2m}{\hbar^2}}\,\epsilon^{-1/2}\, d\epsilon \rightarrow \rho(\epsilon)=\frac{dN}{d\epsilon}=(2S+1)\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{+1/2}$$

The density of states* in **three dimensional systems** is proportional to square of energy

$$\mathrm{DOS}(\epsilon) \propto \epsilon^{+1/2}$$



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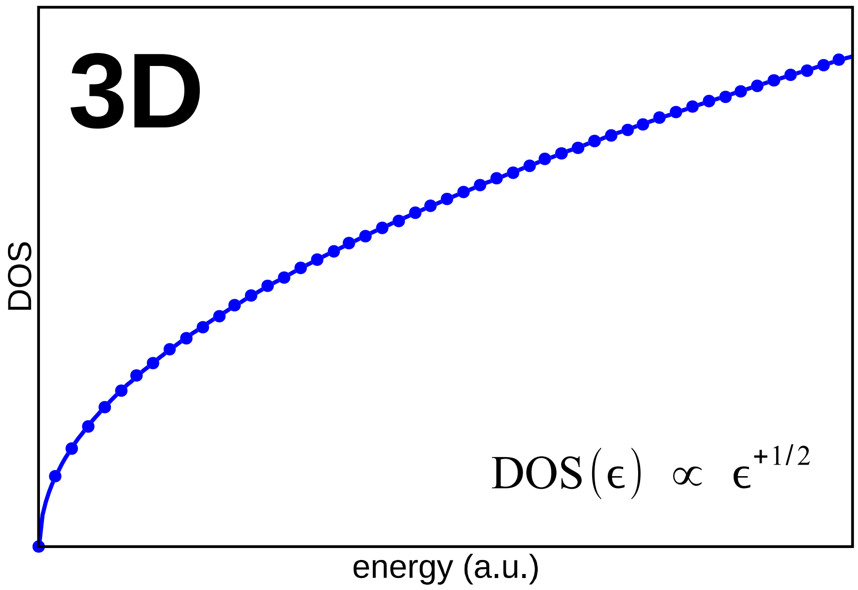
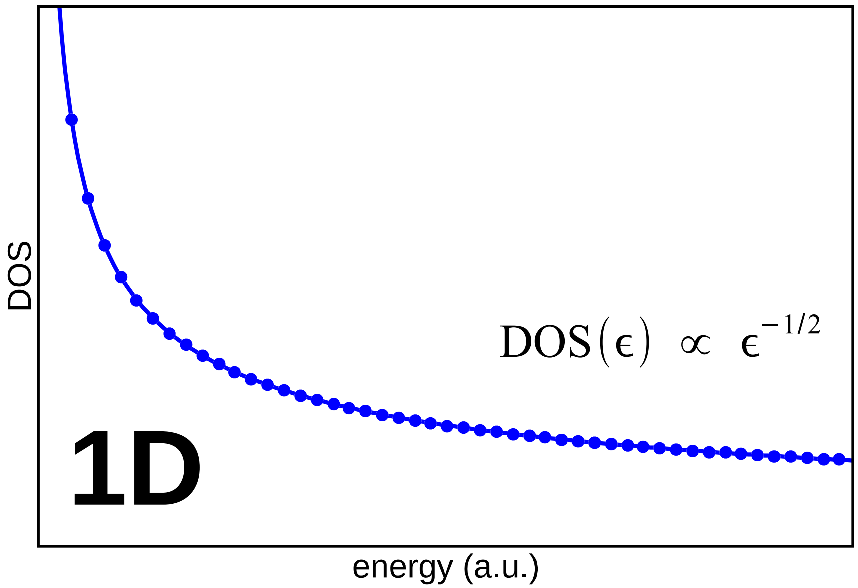
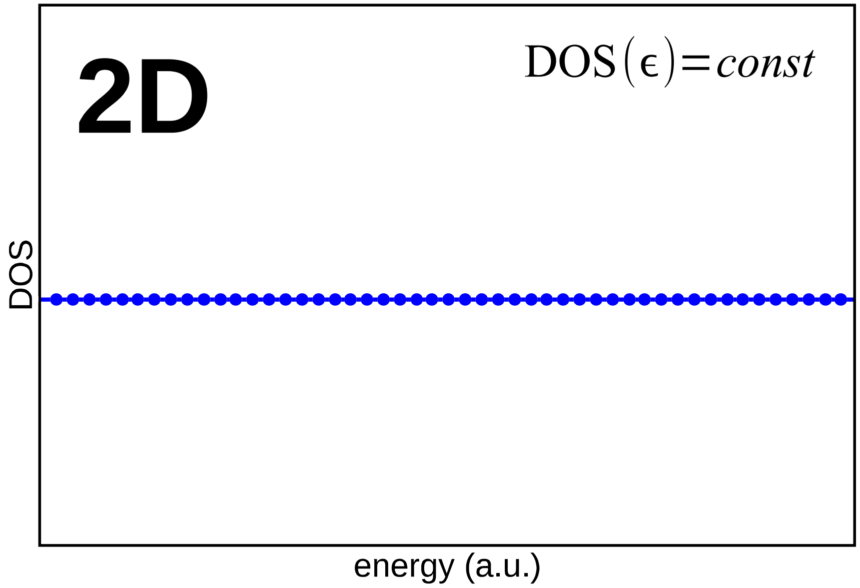
*often denoted as DOS

Density of states

The dependence of the DOS on energy depends on the dimensionality of the system [13]







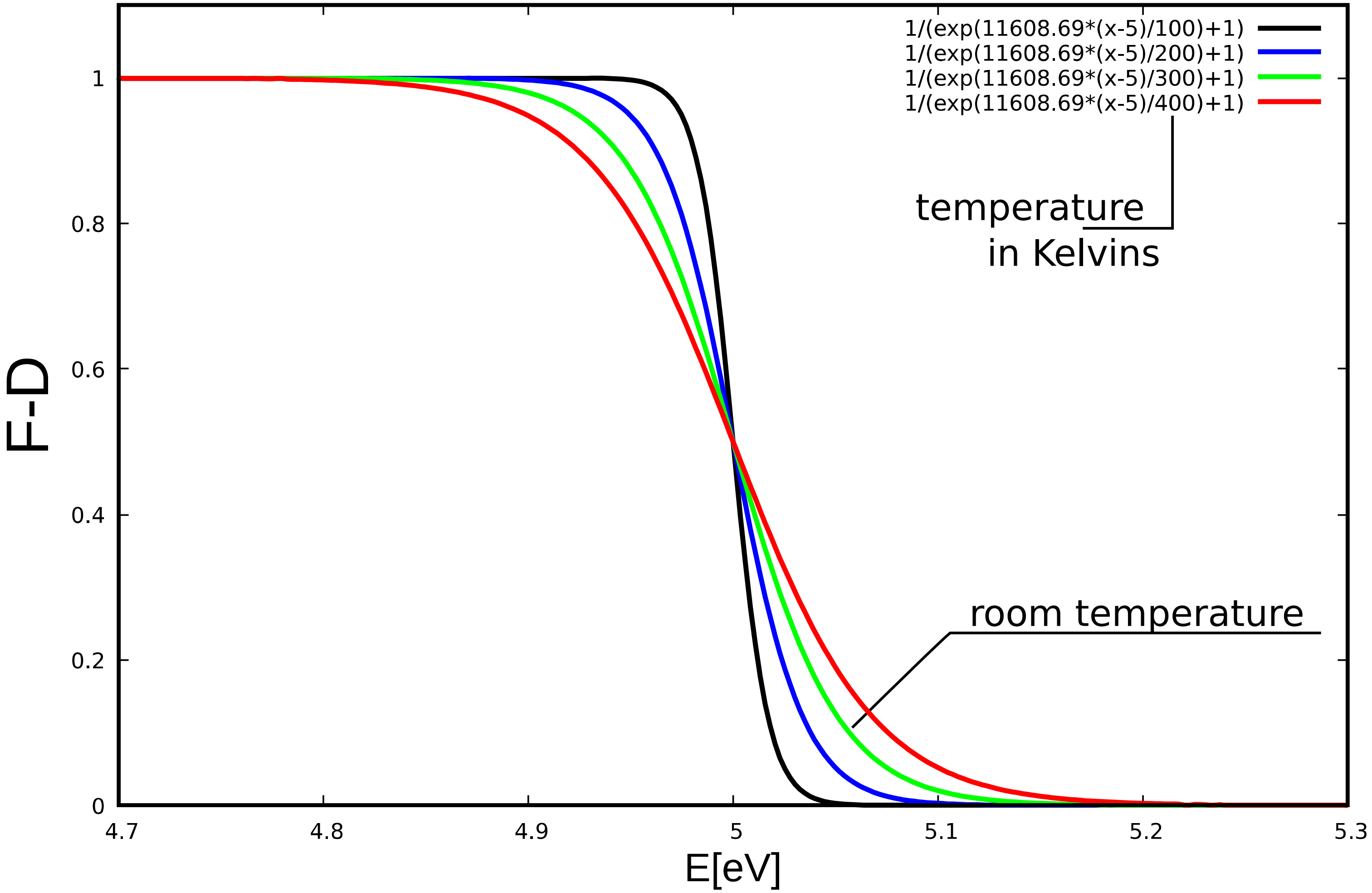
Fermi-Dirac distribution

The Fermi-Dirac distribution (*probability that a single state of a given energy is filled*) is given by the expression

$$F_{F-D}=\frac{1}{e^{(E-E_F)/k_b T}+1}$$

for T=0 this is Heaviside step function [13]

$$1\,eV/k_b \approx 11608.69$$



Gnuplot commands to get the graph (Version 5.0 patchlevel 4):

```
set samples 250;set xlabel "E[eV]" font "Arial,12";set ylabel "F-D"
font "Arial,18";set xrange [4.7:5.3];set yrange [0:1.1];plot 1/
(exp(11608.69*(x-5)/100)+1) with lines lw 3 lt rgb "black",1/
(exp(11608.69*(x-5)/200)+1) with lines lw 3 lt rgb "blue", 1/
(exp(11608.69*(x-5)/300)+1) with lines lw 3 lt rgb "green",1/
(exp(11608.69*(x-5)/400)+1) with lines lw 3 lt rgb "red"
```

- note that Fermi energy E_F for the graphs is 5 eV
- value of F-D function at E_F is 0.5 for any temperature

Fermi-Dirac distribution

The Fermi-Dirac distribution (*probability that a single state of a given energy is filled*) is given by the expression

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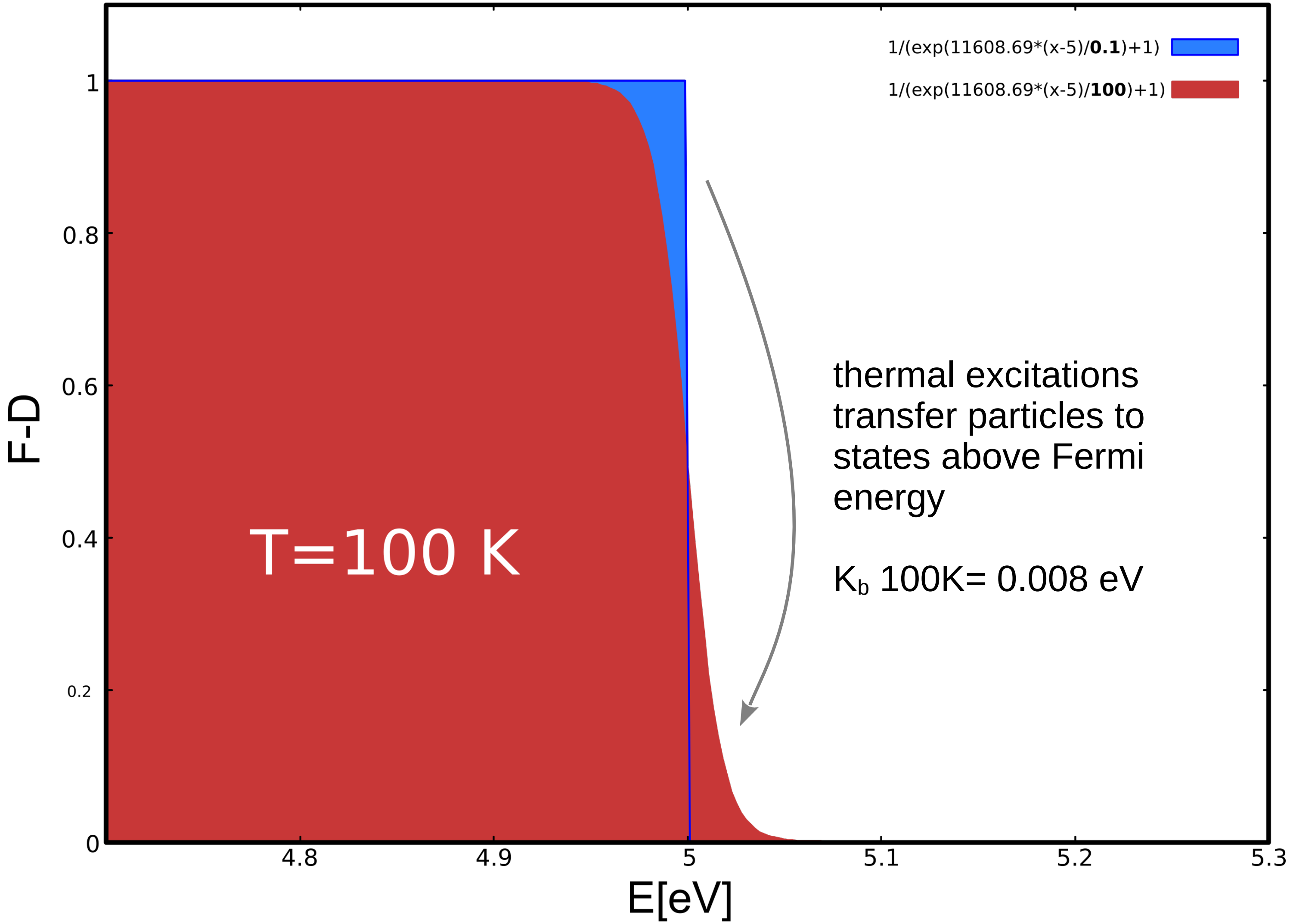


thermal excitations transfer particles to states above Fermi energy

K_b 100K= 0.008 eV

Fermi energy

Because of Pauli exclusion principle, at T=0K, the electrons fill the energy levels up to some maximum value which can be estimated from previously found expression for the number of allowed states for wave vectors less than k_F

$$N=\frac{4}{3}\pi k_F^3(2S+1)\left(\frac{L}{2\pi}\right)^3$$

For electrons (S=½) this transforms to

$N=\frac{V}{3\pi^2}k_F^3 \rightarrow k_F=\left(\frac{3\pi^2 N}{V}\right)^{1/3}$ and since $\epsilon=\frac{p^2}{2m}=\frac{\hbar^2}{2m}k^2$ we get [12]

$$\boxed{E_F=\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}}$$

$$v_F=\frac{\hbar k_F}{m}=\frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

Some Fermi vectors, energies and velocities (according to Kittel [12])

	E_F [eV*]	k_F [10^{10}m^{-1}]	v_F [10^6m/s]	N/V [10^{28} electrons/m^3]
Cu	7.0	1.35	1.56	8.5
Ag	5.5	1.19	1.38	5.8
Au	5.5	1.20	1.39	5.9

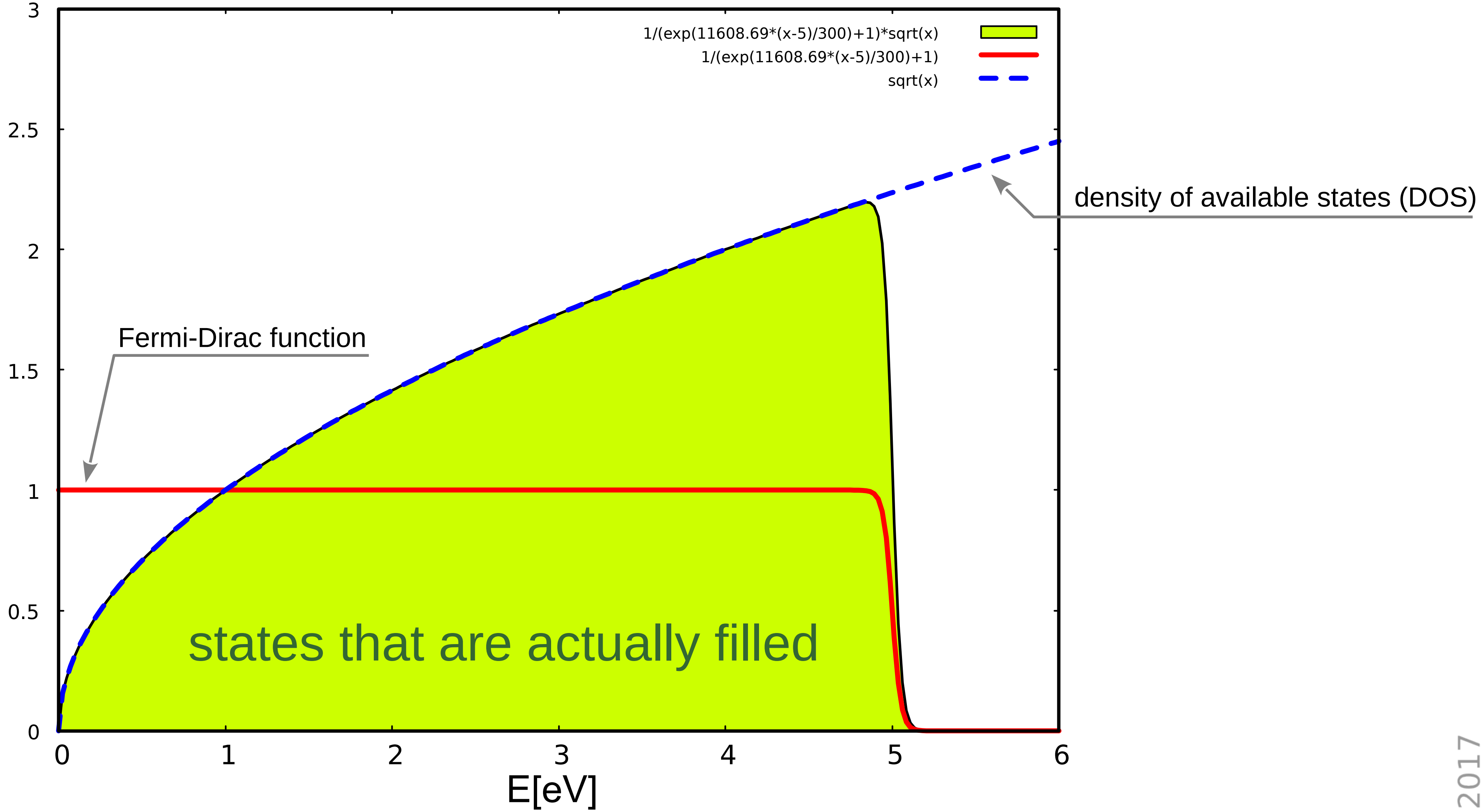
approx. 6 eV

approx. 0.5% velocity of light

F-D distribution - density of filled states

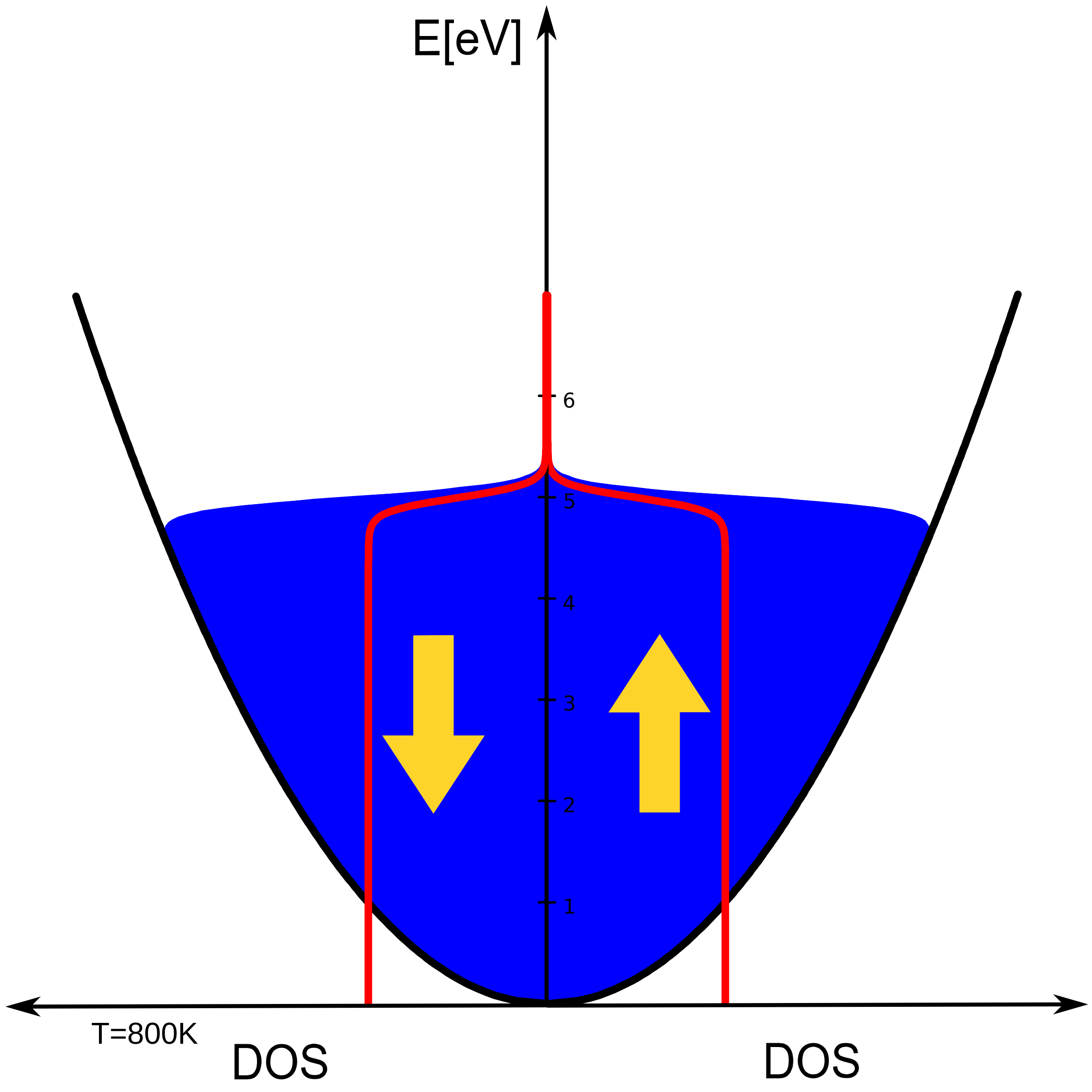
Number of particles/electrons with a given energy is a product of available states and the probability of finding a particle in a state characterized by a given energy [12]

$$N_{\text{filled states}} = F_{F-D}(\epsilon) * DOS(\epsilon)$$



F-D distribution - density of filled states

When dealing with magnetic properties of materials one often separates density of states with different spin orientation



Note the convention [13]:

- spin up (up spin) denotes the spins parallel to magnetic field
- spin down – antiparallel orientation

Note that depending on the convention for the sign of g-factor for an electron its magnetic moment can be parallel to the spin (g<0) or antiparallel [14]. Saying that spins align along the field direction is usually meant to mean the associated magnetic moments

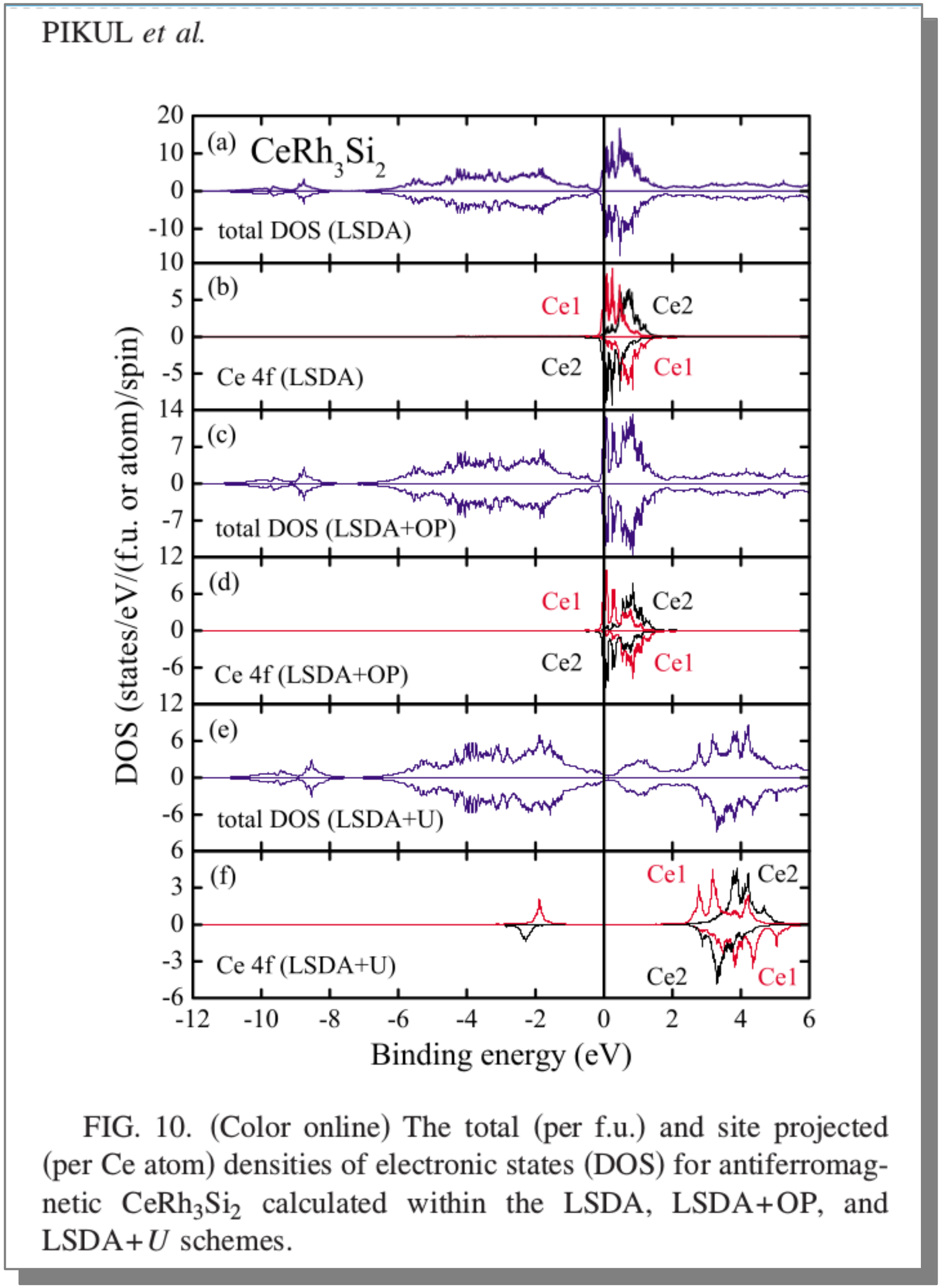
- NIST (USA) gives the g-factor as **-**2.002 319 304 361 82(52)*

$$\vec{\mu} = -g\,\mu_B\,\vec{S}$$

*http://physics.nist.gov/cgi-bin/cuu/Value?gem, retrieved 2017.01.17

F-D distribution - density of filled states

When dealing with magnetic properties of materials one often separates density of states with different spin orientation



PIKUL *et al.*

FIG. 10. (Color online) The total (per f.u.) and site projected (per Ce atom) densities of electronic states (DOS) for antiferromagnetic $CeRh_3Si_2$ calculated within the LSDA, LSDA+OP, and LSDA+U schemes.

Exemplary theoretical calculations of the DOS for **single-crystalline** $CeRh_3Si_2$

- note that density of states is determined for different non-equivalent positions of Ce atoms ("on cerium atoms forming two magnetic sublattices")

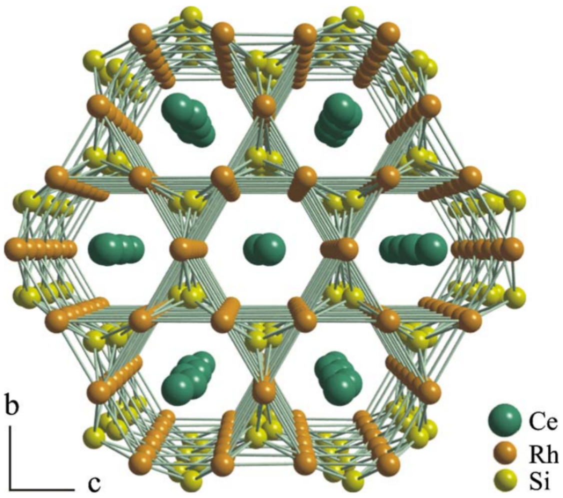
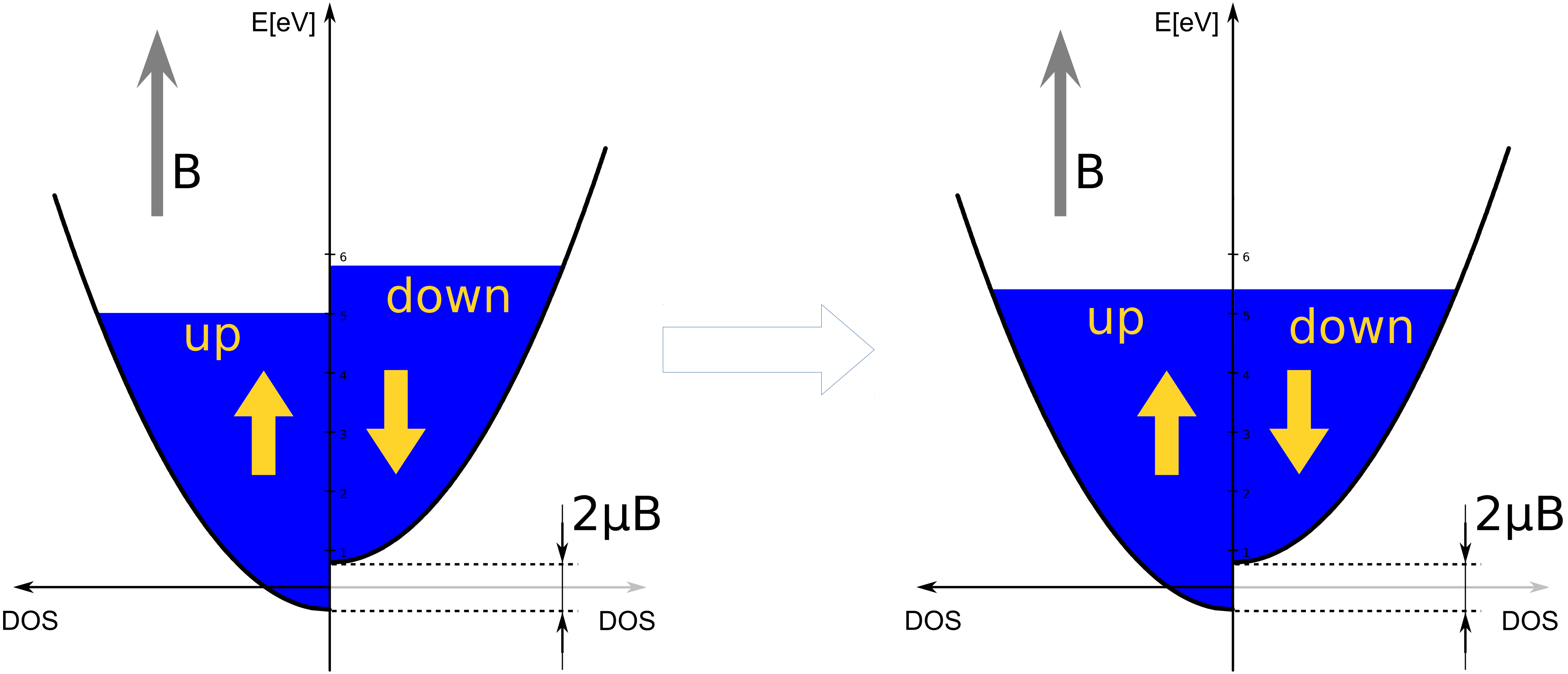


FIG. 1. (Color online) Crystal structure of $CeRh_3Si_2$.

images source: A. P. Pikul, D. Kaczorowski, Z. Gajek, J. Stępień-Damm, A. Ślebarski, M. Werwiński, A. Szajek, Phys.Rev B **81**, 174408 (2010)

Pauli susceptibility – magnetic susceptibility of itinerant electrons

- The susceptibility of the electron gas is largely overestimated if one assumes that spin of electrons are free to align with magnetic field [12]
- In metal most of the electrons, those lying far below Fermi level, can not change the orientation of their spins because the states with comparable energy (we assume that the magnetic field is weak*) are already filled



*meaning that it does not noticeably change the electronic structure of the material - bands

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- In metal most of the electrons, those lying far below Fermi level, can not change the orientation of their spins because the states with comparable energy (we assume that the magnetic field is weak*) are already filled

Concentration of electrons with magnetic moments “**parallel**” to the external magnetic field is given by [19]

$$N_{\mathrm{up}}=\frac{1}{2}\int_{-\mu B}^{E_F} F_{F-D}(\epsilon)*D(\epsilon+\mu B)\,d\epsilon$$

We expand the DOS: $D(\epsilon+\mu B)=D(\epsilon)+\mu B\frac{\partial}{\partial\epsilon}D(\epsilon)+\ldots$ and substitute

$$N_{\mathrm{up}}=\frac{1}{2}\int_{0}^{\infty} F_{F-D}(\epsilon)*D(\epsilon)\,d\epsilon+\frac{1}{2}\int_{-\mu B}^{0} F_{F-D}(\epsilon)*D(\epsilon)\,d\epsilon+\frac{\mu B}{2}\int_{-\mu B}^{\infty} F_{F-D}(\epsilon)*\frac{\partial}{\partial\epsilon}D(\epsilon)\,d\epsilon$$

integration by parts

integral divided into two integrals; the second one vanishes because D(E) is 0 for E<0

$$\frac{\partial}{\partial\epsilon}F_{F-D}(\epsilon)D(\epsilon)=F_{F-D}(\epsilon)\frac{\partial}{\partial\epsilon}D(\epsilon)+D(\epsilon)\frac{\partial}{\partial\epsilon}F_{F-D}(\epsilon)$$

$$\int_{-\mu B}^{\infty} F_{F-D}(\epsilon)*\frac{\partial}{\partial\epsilon}D(\epsilon)\,d\epsilon=F_{F-D}(\epsilon)D(\epsilon)\Big|_{-\mu B}^{\infty}-\int_{-\mu B}^{\infty} D(\epsilon)\frac{\partial}{\partial\epsilon}F_{F-D}(\epsilon)\,d\epsilon=$$

vanishes because D(E)=0 for E<0 (lower summation limit) and $F_{F\text{-}D}$ is zero at +∞

Dirac’ delta

$$\boxed{\frac{\partial}{\partial\epsilon}F_{F-D}(\epsilon)=-\delta(\epsilon-E_F)}$$

$$=D(E_F)$$

$$\boxed{N_{\mathrm{up}}=\frac{1}{2}n_0+\frac{\mu B}{2}D(E_F)}$$

n_0 – number of states up to Fermi energy in unperturbed system (B=0)

*meaning that it does not noticeably change the electronic structure of the material - bands

Pauli susceptibility – magnetic susceptibility of itinerant electrons

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Concentration of electrons with magnetic moments “**parallel**” to the external magnetic field is given by [12,19]

$$N_{\mathrm{up}}=\frac{1}{2}n_0+\frac{\mu B}{2}D(E_F)$$

Concentration of electrons with magnetic moments “**antiparallel**” to the external magnetic field is

$$N_{\mathrm{down}}=\frac{1}{2}n_0-\frac{\mu B}{2}D(E_F)$$

$$D(\epsilon)=\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{+1/2}$$

and the resultant magnetization is (μ - magnetic moment of a particle)

$$E_F=\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$M=\mu(N_{\mathrm{down}}-N_{\mathrm{down}})\approx\mu^2 D(E_F)B=\frac{3N\mu^2}{2E_F}\,B$$

$$\chi=\mu_0\frac{3N\mu^2}{2E_F}$$

$$D(E_F)=\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}\right)^{+1/2}=\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{\hbar^2}{2m}\right)^{1/2}\left(\frac{3\pi^2 N}{V}\right)^{1/3}=$$

$$\frac{V}{2\pi^2}\underbrace{\left(\frac{\hbar^2}{2m}\right)^{-1}\left(\frac{3\pi^2 N}{V}\right)^{-2/3}}_{1/E_F}\left(\frac{3\pi^2 N}{V}\right)^{+1}=\frac{3N}{2E_F}$$

$$\chi=\frac{\partial M}{\partial H}$$

*meaning that it does not noticeably change the electronic structure of the material - bands

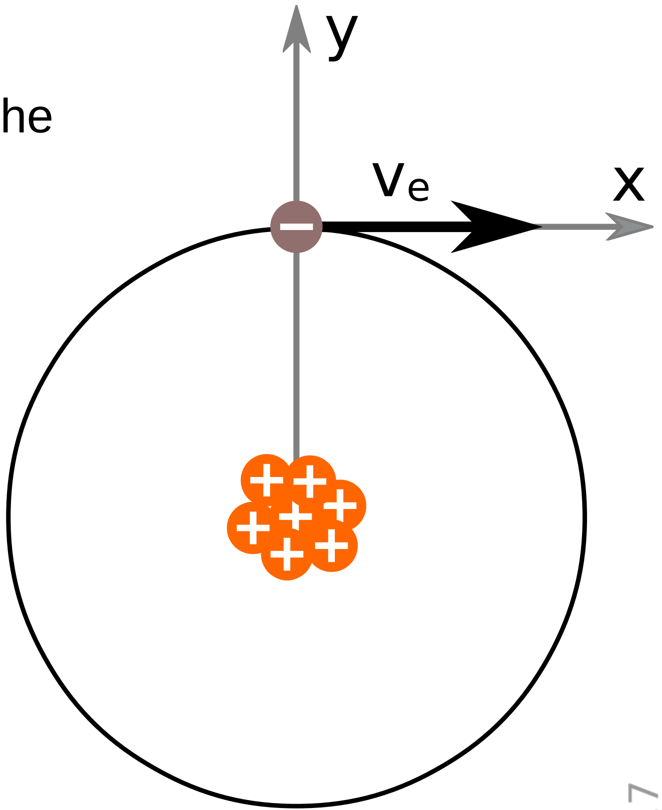
Spin-orbit interaction (coupling)

- The electron is orbiting the nucleus of the +Ze charge*
- Looking at the nucleus from electron we have the magnetic field due to the motion of the nucleus. The energy of electron in that field is

$$\vec{B}=-g\mu_B m_s B$$

Correspondingly every electronic state splits into two (with two orientations of the spin).
We assume that an electron is orbiting the nucleus in xy plane and that its instantaneous velocity is along x-direction.
The electric field of the nucleus at the place of an electron is along y-direction then

$$E_y=\frac{1}{4\pi\epsilon_0}\frac{Ze}{r^2}$$



From special relativity theory (A. Einstein) for the components of the magnetic field in the electron reference frame we have [16]

$$B_x^{\mathrm{el(ectron)}}=B_x=0$$

$$B_y^{\mathrm{el}}=\frac{1}{\sqrt{1-v^2/c^2}}\left(B_y+\frac{v_e}{c^2}E_z\right)=0 \qquad B_z^{\mathrm{el}}=\frac{1}{\sqrt{1-v^2/c^2}}\left(B_z-\frac{v_e}{c^2}E_y\right)\approx-\frac{v_e}{c^2}E_y$$

Electron feels then the magnetic field that is oriented along z-axis
Further, the field seen by the electron can be written as

$$B^{\mathrm{el}}=\frac{1}{c^2}(\vec{E}\times\vec{v})=\frac{1}{mc^2}(\vec{E}\times\vec{p}) \qquad \vec{p}=\frac{m_0\vec{v}}{\sqrt{1-v^2/c^2}}$$

---

*the derivation is taken from *Einführung in die Quantenmechanik* (Physik IV), ETH Zurich [16]

Spin-orbit interaction (coupling)

$$B^{el}=\frac{1}{c^2}(\vec{E}\times\vec{v})=\frac{1}{mc^2}(\vec{E}\times\vec{p})$$

Inserting the above calculated magnetic field into the expression for energy yields

$$\Delta E_{spin-orbit}=-g\mu_B m_s B=-g\mu_B m_s\frac{1}{mc^2}(\vec{E}\times\vec{p})=-g\mu_B m_s\frac{1}{mc^2}\left(\left[\frac{1}{4\pi\epsilon_0}\frac{Ze}{r^2}\right]\frac{\vec{r}}{r}\times\vec{p}\right)$$

this give the appropriate direction of electric field

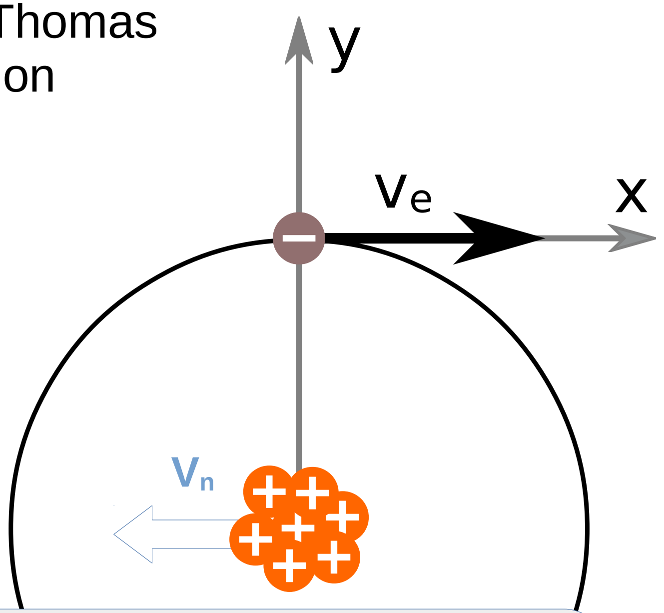
$$\Delta E_{spin-orbit}=-g\mu_B m_s\frac{1}{mc^2}\left(\left[\frac{1}{4\pi\epsilon_0}\frac{Ze}{r^3}\right]\vec{r}\times\vec{p}\right)=-g\mu_B m_s\frac{1}{mc^2}\left(\left[\frac{1}{4\pi\epsilon_0}\frac{Ze}{r^3}\right]\vec{L}\right)$$

angular momentum

More exact calculations require taking into account the so called Thomas precession* – this leads to factor ½ which leads to “final” expression

$$\boxed{\Delta E_{spin-orbit}=-\frac{g}{2}\mu_B\frac{1}{mc^2}\frac{1}{4\pi\epsilon_0}\frac{Ze}{r^3}\vec{L}}$$

- note that spin-orbit coupling is proportional to Z
- ...and to orbital moment of an electron



The direction of the magnetic field cal-calculated from **Biot-Savart law** for a moving charge is the same

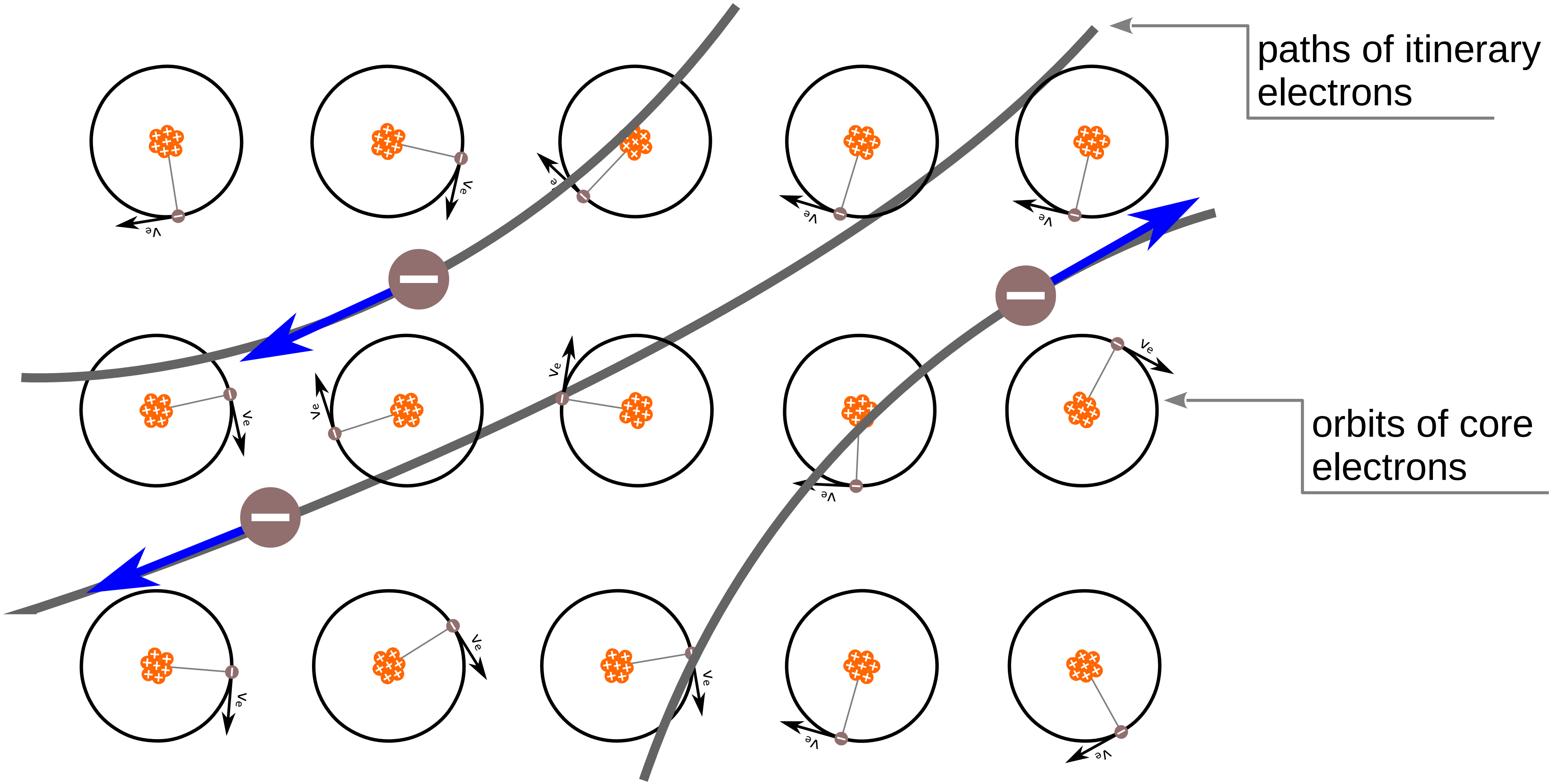
$$\vec{B}=\frac{\mu_0}{4\pi}\frac{q}{r^2}\vec{v}\times\vec{r}$$

---

*the derivation assumed that electron moves along straight line [16]

Spin-orbit interaction (coupling)

- **In a crystal** conducting electrons move in the average electric field of the atom cores and other electrons
- The core electrons that remain in the vicinity of the nucleus experience strong electric fields and, provided that the orbit is not centrosymmetric, they experience strong spin-orbit coupling (please see movies at https://staff.aist.go.jp/v.zayets/spin3_32_SpinOrbit.html)



paths of itinerary electrons

orbits of core electrons

Spin-orbit interaction (coupling)

- **In a crystal** conducting electrons move in the average electric field of the atom cores and other electrons
- The core electrons that remain in the vicinity of the nucleus experience strong electric fields and provided that the orbit is not centrosymmetric they experience strong spin-orbit coupling (please see movies at https://staff.aist.go.jp/v.zayets/spin3_32_SpinOrbit.html)
- The magnetic fields due the core electron movement can be huge [17]:

Linear velocity of an electron rotating around a nucleus is **$\sim 2.1*10^6$ m/s**
The electric field experienced by an electron in the vicinity of nucleus (calculated for 1s orbital of hydrogen atom) is roughly **$5*10^{11}$ V/m**
The effective magnetic field of the spin-orbit interaction is about **12 T**

For comparison we [17] estimate the effective field in devices in which we try to influence the behavior of itinerant electrons applying external electric fields
The maximal electron velocity (saturation velocity, maximal drift speed) **$\sim 1*10^7$ m/s**
The maximal available electric field (limited by breakdown voltage of the materials), for GaAs or Si it is roughly **$5*10^7$ V/m**
The effective magnetic field of the spin-orbit interaction is about 5**$*10^{-4}$ T** (about the strength of the earth magnetic field)

Spin-orbit interaction (coupling) – dependence on atomic number

The SO coupling depends indirectly on the charge of the nucleus (Z)
The dependence is different for different series

image source [19] PHYSICAL REVIEW B **90**, 165108 (2014)

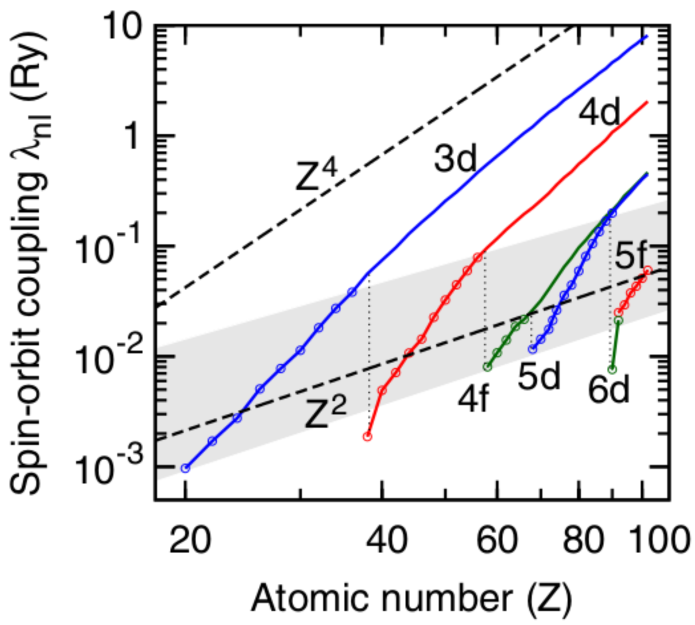


FIG. 1. (Color online) Dependence of the spin-orbit coupling strength λ_{nl} for atoms as a function of the atomic number Z. The calculated results of Herman and Skillman [24] using the Hartree-Fock method (colored lines) are compared to the hydrogenic Z^4 dependence, which is computed from Eq. (4) for the $3d$ series (upper dashed line). For the *outermost* electrons (indicated by the circles and the shaded area), which are the relevant electrons in the solid, the quantum numbers nl change with Z and the spin-orbit interaction increases much more slowly, following roughly the Landau-Lifshitz Z^2 scaling [lower dashed line, calculated from Eq. (5) with $A = 0.10$].

- The Z^4 dependence for SO in central field (near core electrons) comes from perturbative correction [18]:

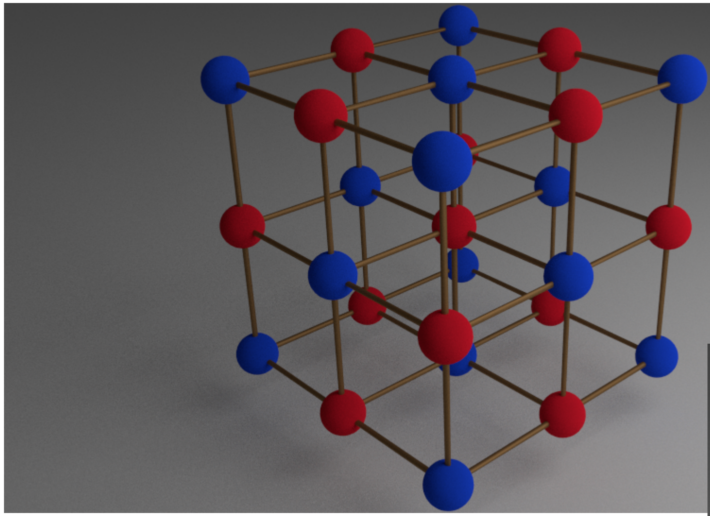
$$H_{SO}(r)=\frac{1}{2m^2c^2}\frac{\partial V(r)}{\partial r}\vec{L}\cdot\vec{S}$$

$$E_{nl}=E^0_{nl}+F(l,j)\;Z^4$$

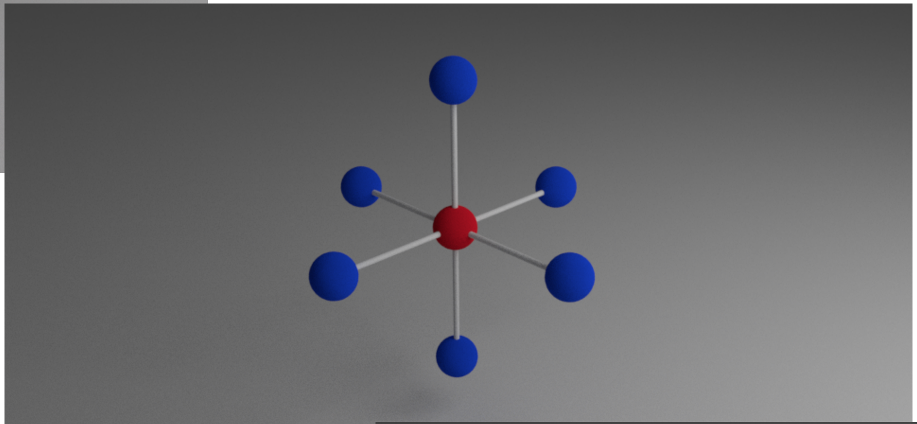
- The Z^2 dependence is more relevant for solids

Coordinational polyhedron

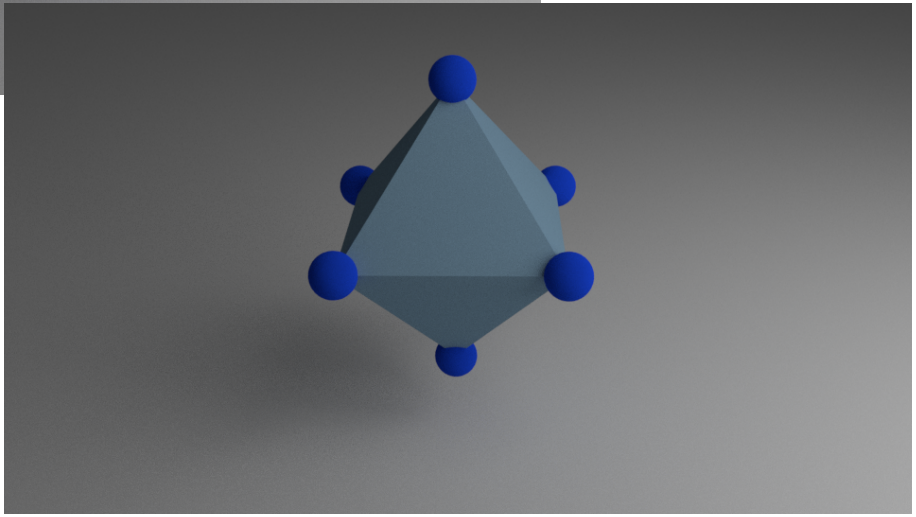
- The arrangement of nearest neighbors depends on the coordination number [21]



NaCl structure



six nearest
neighbors



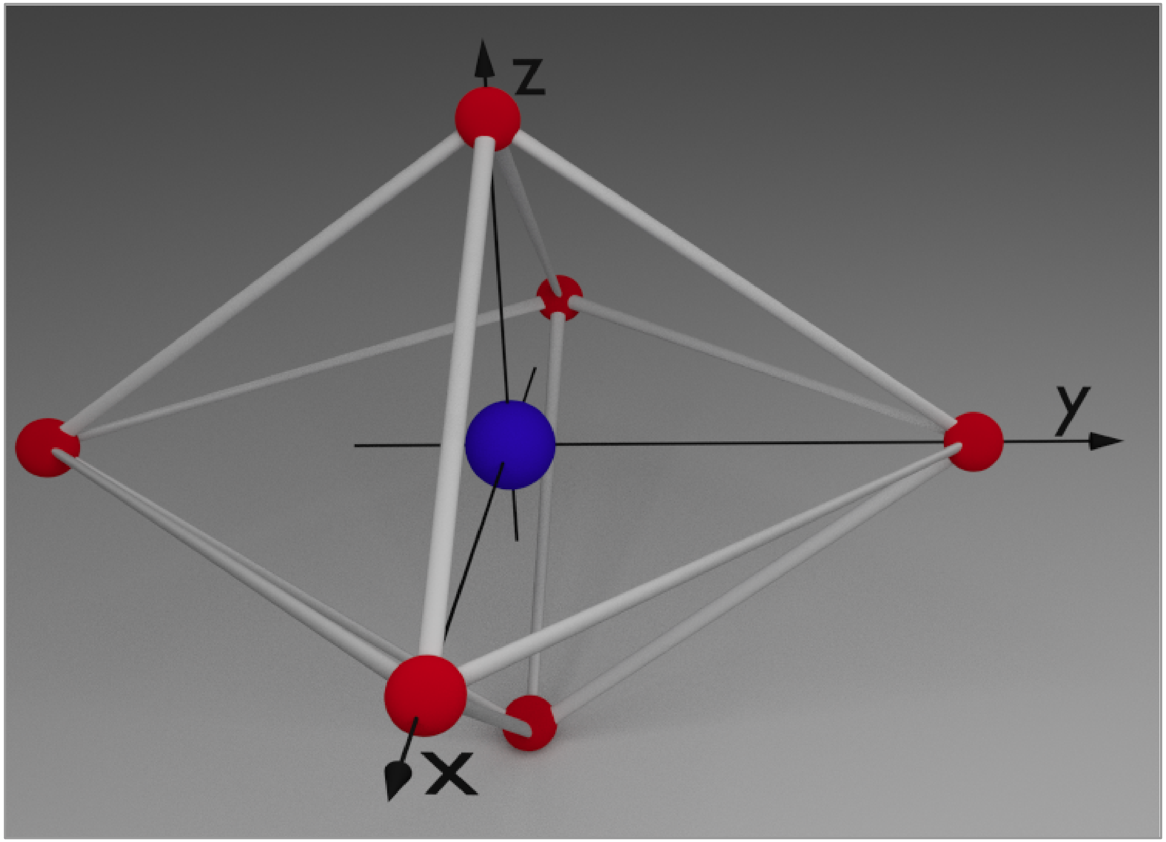
coordinational octahedron

Crystal field

- The basic assumption of crystal field theory (also called ligand field theory) is that the crystal is ionic
- The paramagnetic ion is surrounded by a set of point charges and the electric potential V produced by these ions is added to the Hamiltonian [19]

$$H=\sum_{i=1}^{n}\left[\frac{p_i^2}{2m}-\frac{Ze^2}{r_i}+e^2\sum_{j>i}\frac{1}{r_{ij}}\right]+\lambda\vec{L}\cdot\vec{S}+\sum_{i=1}^{n}eV_i$$

- The crystal field is calculated by summing the contributions of the nearest neighbors, next nearest neighbors etc. - it possesses thus the symmetry of the lattice
- This leads to lifting of some degeneracies of the electron levels



The central ion is surrounded by **nearest neighbors**

In this case six neighbors are arranged on the vertexes of octahedron

The neighbors produce some electric potential

Crystal field

- The basic assumption of crystal field theory (also called ligand field theory) is that the crystal is ionic
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$$H=\sum_{i=1}^{n}\left[\frac{p_i^2}{2m}-\frac{Ze^2}{r_i}+e^2\sum_{j>i}\frac{1}{r_{ij}}\right]+\lambda\vec{L}\cdot\vec{S}+\sum_{i=1}^{n}e\,V_i$$

source of **E**

- The crystal field is calculated by summing the contributions of the nearest neighbors, next nearest neighbors etc. - it possesses thus the symmetry of the lattice
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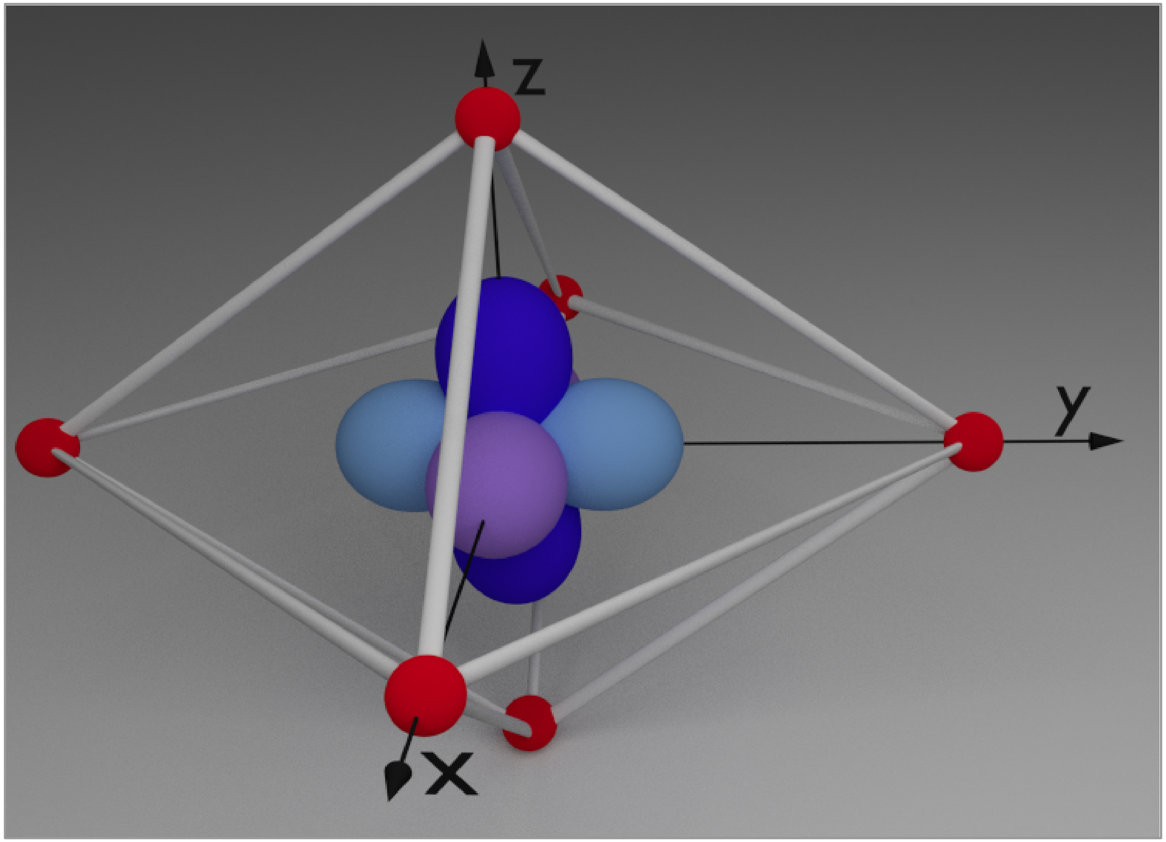
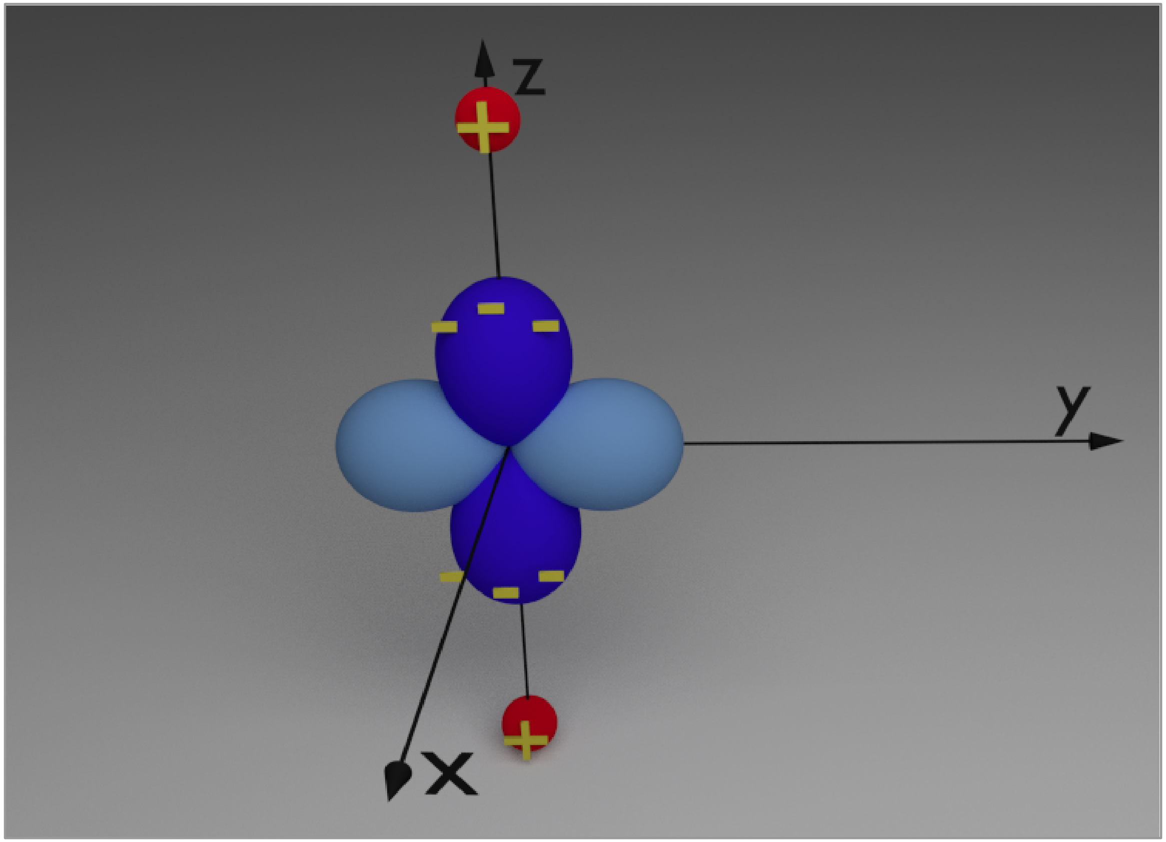


Various orbitals (p-orbitals in the image) can be oriented differently relative to the charges of neighboring ions

Consequently the electrostatic energies are different for p_x, p_y, and p_z orbitals

Crystal field

- The basic assumption of crystal field theory (also called ligand field theory) is that the crystal is ionic
- The paramagnetic ion is surrounded by a set of point charges and the electric potential V produced by these ions is added to the Hamiltonian [19]
- Assuming a simple model of point charges we see that purely electrostatic interactions cause the p_z orbital to have lower energy (than the p_y orbital) – the potential energy of *electron cloud* is lowered as electron is closer to positive ions (see Jahn-Teller effect at https://chem.libretexts.org...Jahn-Teller_Distortions)
- Similar situation exists for other orbitals: five **d orbitals**, depending on the symmetry of the surrounding , can split into 4-levels (https://en.wikipedia.org/wiki/Crystal_field_theory)



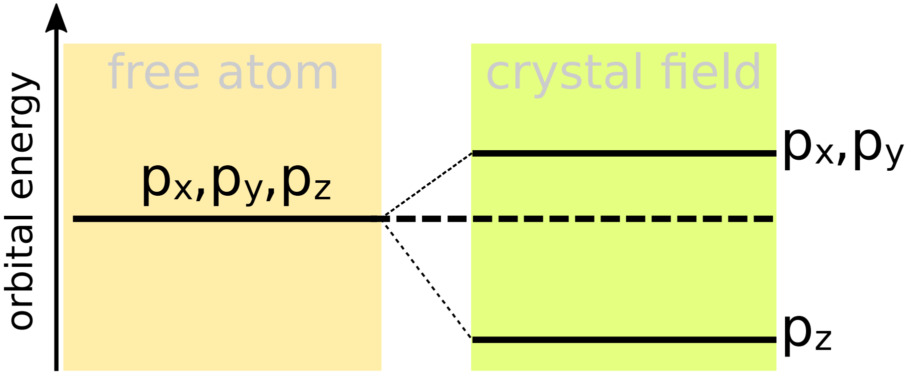


image based of Fig. 3.7 from [19]

Degeneracy in crystal field

- Wigner theorem [5,p.134]: *if eigenfunction φ of operator H corresponds to eigenvalue E and H is invariant under a symmetry operation T then the function Tφ will be the eigenfunction of H corresponding to the same eigenvalue E*

The set of functions transforms under the action of operation T into new set of functions [5]

$$(\phi_1,\phi_2,\ldots,\phi_f)=(\psi_1,\psi_2,\ldots,\psi_f)\begin{pmatrix} T_{11} & T_{12} & \ldots & T_{1f} \\ T_{21} & T_{22} & \ldots & T_{2f} \\ \ldots & \ldots & \ldots & \ldots \\ T_{f1} & T_{f2} & \ldots & T_{ff} \end{pmatrix}$$

Group [20]:
- the product of any two elements in the group must be an element of the group (square of each of them too)
- one element of he group must commute with all others and leave them unchanged (identity element)
- the associative law of multiplication holds: A(BC)=(AB)C
- every element must have a reciprocal within the group

If the set of transformation forms a group the set of functions $(\psi_1,\psi_2,\ldots,\psi_f)$ is its base

In general the matrices representing transformations can be transformed int a new set of matrices

$$T^{(k)} \rightarrow Q^{-1}\,T^{(k)}\,Q,$$

k numbers members of the group (e.g. rotation, reflection etc.)

$$\begin{pmatrix} T_{11} & T_{12} & T_{13} & T_{14} & T_{15} & T_{16} & T_{17} \\ T_{21} & T_{22} & T_{23} & T_{24} & T_{25} & T_{26} & T_{27} \\ T_{31} & T_{32} & T_{33} & T_{34} & T_{35} & T_{36} & T_{37} \\ T_{41} & T_{42} & T_{43} & T_{44} & T_{45} & T_{46} & T_{47} \\ T_{51} & T_{52} & T_{53} & T_{54} & T_{55} & T_{56} & T_{57} \\ T_{61} & T_{62} & T_{63} & T_{64} & T_{65} & T_{66} & T_{67} \\ T_{71} & T_{72} & T_{73} & T_{74} & T_{75} & T_{76} & T_{77} \end{pmatrix} \Longrightarrow \begin{pmatrix} T_{11} & T_{12} & 0 & 0 & 0 & 0 & 0 \\ T_{21} & T_{22} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & T_{33} & T_{34} & 0 & 0 & 0 \\ 0 & 0 & T_{43} & T_{44} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & T_{55} & T_{56} & T_{57} \\ 0 & 0 & 0 & 0 & T_{65} & T_{66} & T_{67} \\ 0 & 0 & 0 & 0 & T_{75} & T_{76} & T_{77} \end{pmatrix}$$

if all matrices of the group can be transformed into similar blocked out matrices by the same Q matrix then

the group representation is **reducible** [20]

Degeneracy in crystal field

Using the block matrix we get (by standard matrix multiplication of vector by matrix)

$$(\psi_1,\psi_2,\dots,\psi_7)\begin{pmatrix} T_{11} & T_{12} & 0 & 0 & 0 & 0 & 0 \\ T_{21} & T_{22} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & T_{33} & T_{34} & 0 & 0 & 0 \\ 0 & 0 & T_{43} & T_{44} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & T_{55} & T_{56} & T_{57} \\ 0 & 0 & 0 & 0 & T_{65} & T_{66} & T_{67} \\ 0 & 0 & 0 & 0 & T_{75} & T_{76} & T_{77} \end{pmatrix} = \begin{matrix}(\psi_1 T_{11}+\psi_2 T_{21},\ \psi_1 T_{12}+\psi_2 T_{22}, \\ \psi_3 T_{33}+\psi_4 T_{43},\ \psi_3 T_{34}+\psi_4 T_{44}, \\ \psi_5 T_{55}+\psi_6 T_{65}+\psi_7 T_{75}, \\ \psi_5 T_{56}+\psi_6 T_{66}+\psi_7 T_{76}, \\ \psi_5 T_{57}+\psi_6 T_{67}+\psi_7 T_{77})\end{matrix}$$

row vector
(i.e. not a matrix)

… and for each of the blocks we have something like that

$$(\psi_5,\psi_6,\psi_7)\begin{pmatrix} T_{55} & T_{56} & T_{57} \\ T_{65} & T_{66} & T_{67} \\ T_{75} & T_{76} & T_{77} \end{pmatrix} = (\psi_5 T_{55}+\psi_6 T_{65}+\psi_7 T_{75},\ \psi_5 T_{56}+\psi_6 T_{66}+\psi_7 T_{76},\ \psi_5 T_{57}+\psi_6 T_{67}+\psi_7 T_{77})$$

Which means that functions ψ_5, ψ_6 ,ψ_7 will be transformed only between themselves (they won't get contribution from function ψ_1 for example) [5]

Degeneracy in crystal field

Atom in the crystal field of a cubic symmetry (a tetrahedron group) – we take the hydrogen orbitals in real form (combination of complex orbitals) [5]:

$R_0, R_1, R_2^{(1)}, R_2^{(2)}$ depend only on the module of $\vec{r}$

$\psi_s = R_0$ s orbitals

$\psi_{1p} = R_1 x \quad \psi_{2p} = R_1 y \quad \psi_{3p} = R_1 z$ p orbitals

$\psi_{1d} = R_2^{(1)} xy \quad \psi_{2d} = R_2^{(1)} yz \quad \psi_{3d} = R_2^{(1)} zx \quad \psi_{4d} = R_2^{(2)}(x^2 - y^2) \quad \psi_{5d} = R_2^{(2)}(2z^2 - x^2 - y^2)$ d orbitals

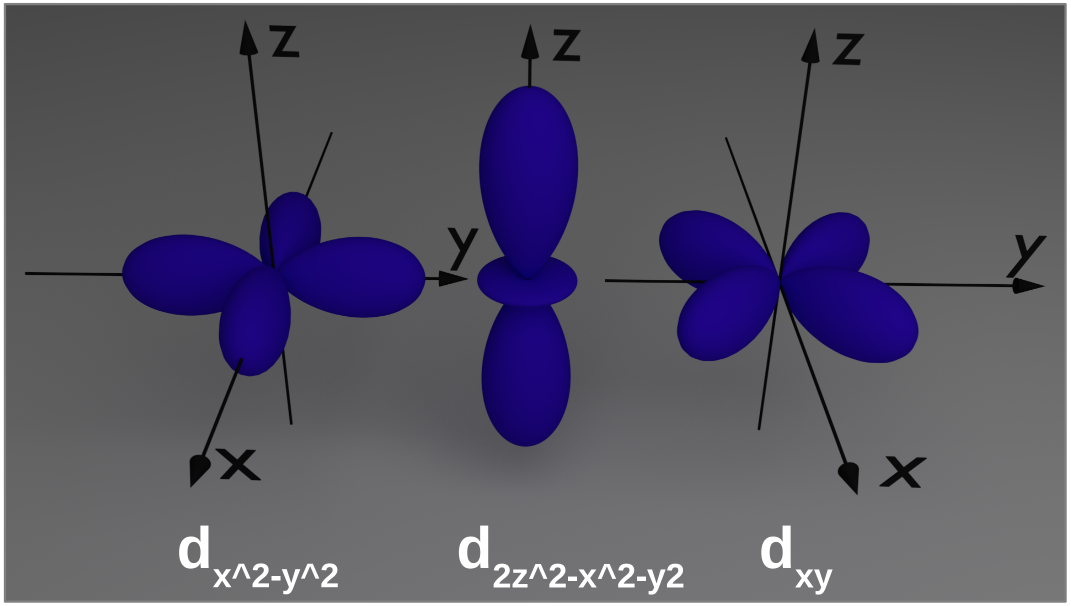
The operation of the rotation by (120Deg) around the diagonal of the cube

$$T(2\pi/3,(111)) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

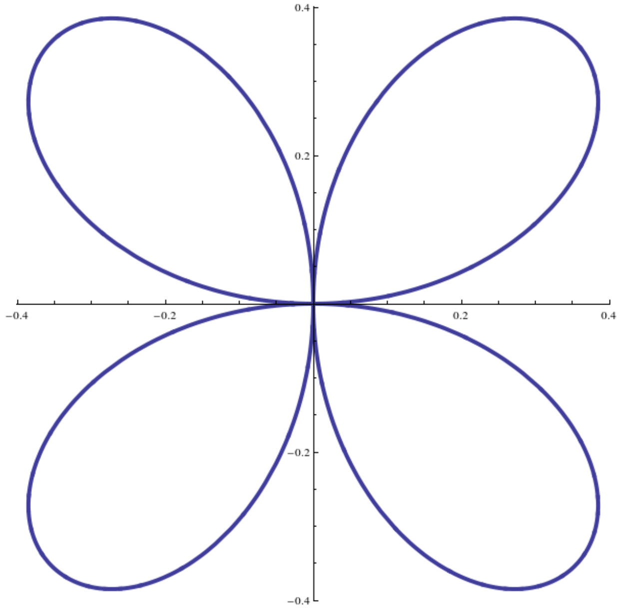
$x = r \sin\theta \cos\phi$
$y = r \sin\theta \sin\phi$
$z = r \cos\theta$

$d_{xz} \propto \sin(\theta)\cos(\theta)\cos(\phi) =$
$\sin(\theta)\cos(\phi)\ \cos(\theta) = (x/r)\ (z/r) = \text{const}\ xz$

Cyclically exchanges the axes of the cube: x→z→y
It follows, using Wigner theorem, that all p-orbitals belong to the same eigenvalue of energy.



Polar plot of a function xy



Degeneracy in crystal field

Analogous arguments lead to the conclusion that the fivefold degeneracy of d-level of free ion is split into two levels [5]:

$\psi_{1d}=R_2^{(1)}xy \qquad \psi_{2d}=R_2^{(1)}yz \qquad \psi_{3d}=R_2^{(1)}zx$

$\psi_{4d}=R_2^{(2)}(x^2-y^2) \qquad \psi_{5d}=R_2^{(2)}2z^2-x^2-y^2$

d orbitals

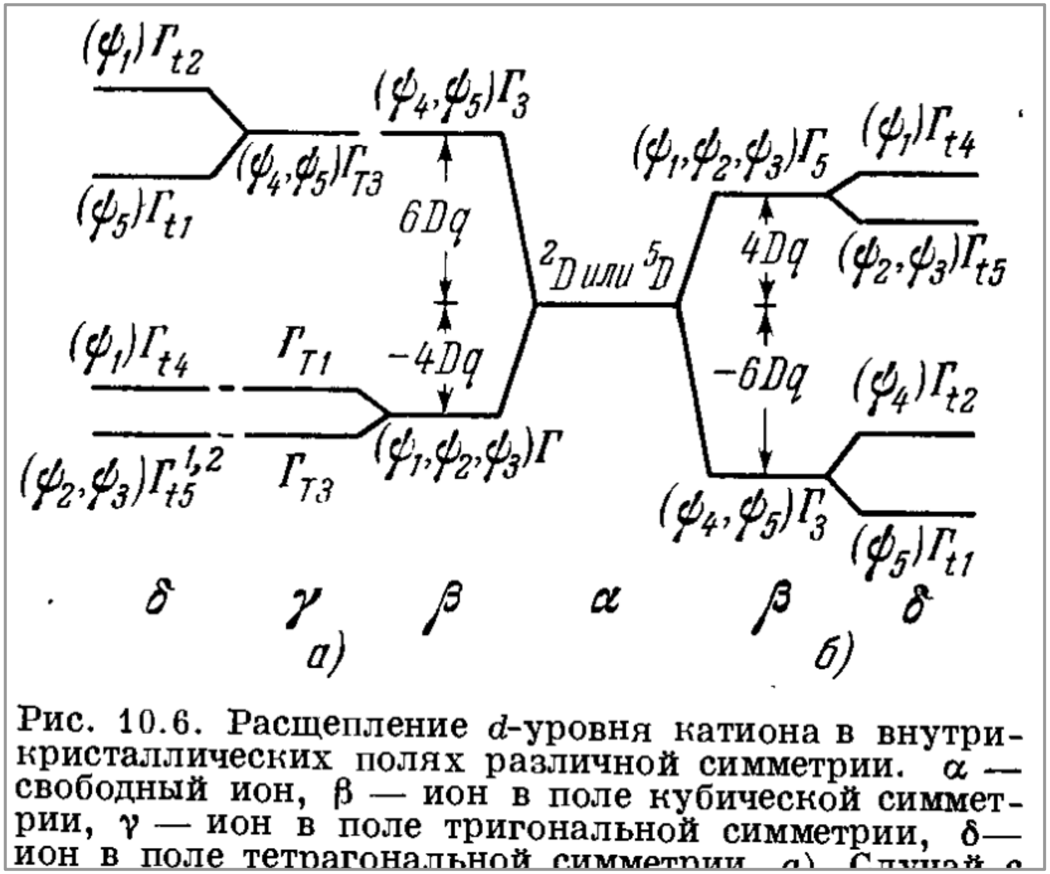


Рис. 10.6. Расщепление *d*-уровня катиона в внутрикристаллических полях различной симметрии. α — свободный ион, β — ион в поле кубической симметрии, γ — ион в поле тригональной симметрии, δ— ион в поле тетрагональной симметрии. а) Случай с

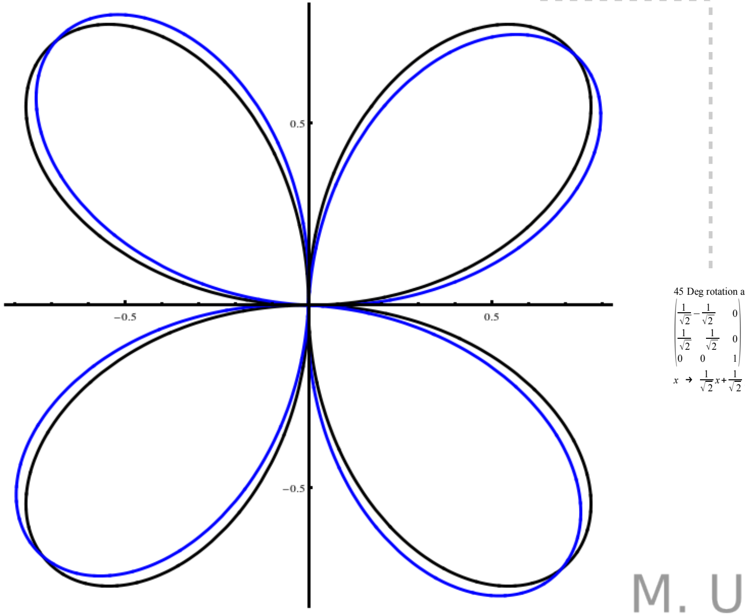
image source С. В. Бонсовский, Магнетизм, Издательство ,,Наука", Москва 1971 [5]

Note that although the function x^2-y^2 can be transformed into xy with the rotation by 45 Deg such a rotation is not present in the octahedron group

Stark splitting of d-energy levels depends on the symmetry of the crystal field
β - cubic symmetry
γ – trigonal (rhombohedral*) symmetry
δ – tetragonal symmetry – stretching of a cube

a – 6 nearest neighbors
б – 4, 8 or 12 nearest neighbors

Polar plot of a functions xy and x^2-y^2 (the second function is rotated by π/2 – 0.05)



45 Deg rotation around z axis :

$$\begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$x \rightarrow \frac{1}{\sqrt{2}}x+\frac{1}{\sqrt{2}}y \qquad y \rightarrow -\frac{1}{\sqrt{2}}x+\frac{1}{\sqrt{2}}y$newlign¿ $x^2-y^2 \rightarrow 2xy$

Quenching of orbital moments

- Experiments show that in many important cases (for ions of transition metals, like copper or iron) magnetic properties of ions placed in crystal structure are predominantly determined by their spins.
- In solid Fe, Co, Ni the orbital moment is only about 5% of the spin moment [22] as a result of the interaction of 3d electrons with the crystal field
- Other effects, like spin-orbit or Coulomb interactions, can lead to partial restoring of the orbital moments [22]

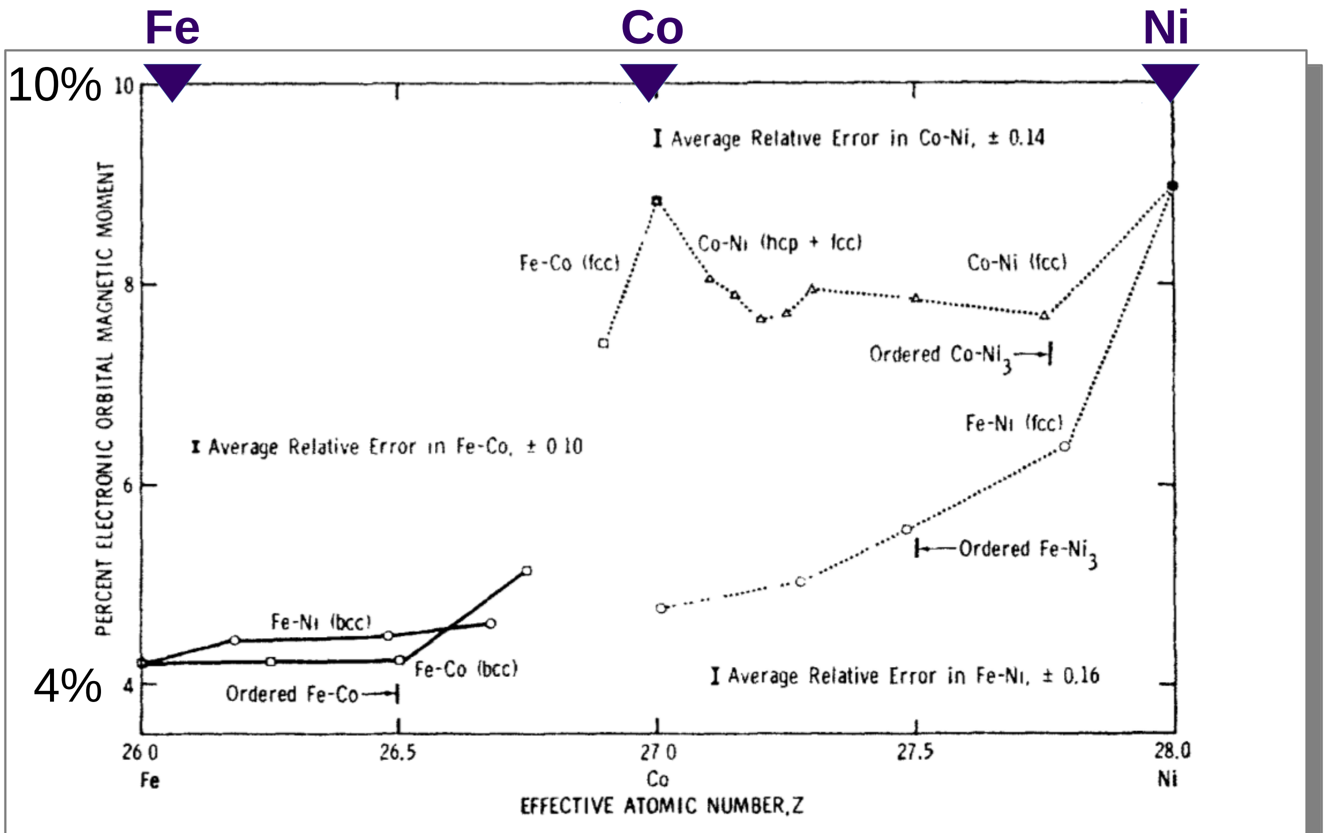


FIG. 1. Percent orbital magnetization $(M_0/M_t \times 10^2)$, as a function of the effective atomic number. Note: $[(M_s/M_t)\times 10^2 = (1-M_0/M_t)\times 10^2]$.

values determined from magnetomechanical ratio - g factor

image source: A. Reck, D. L. Fry, Phys. Rev. **184**, 492 (1969)

Quenching of orbital moments

The degree of moment quenching depends on the size of the “solid” - in clusters containing less than few hundred atoms the magnetic moment per atom may be much higher than in the bulk

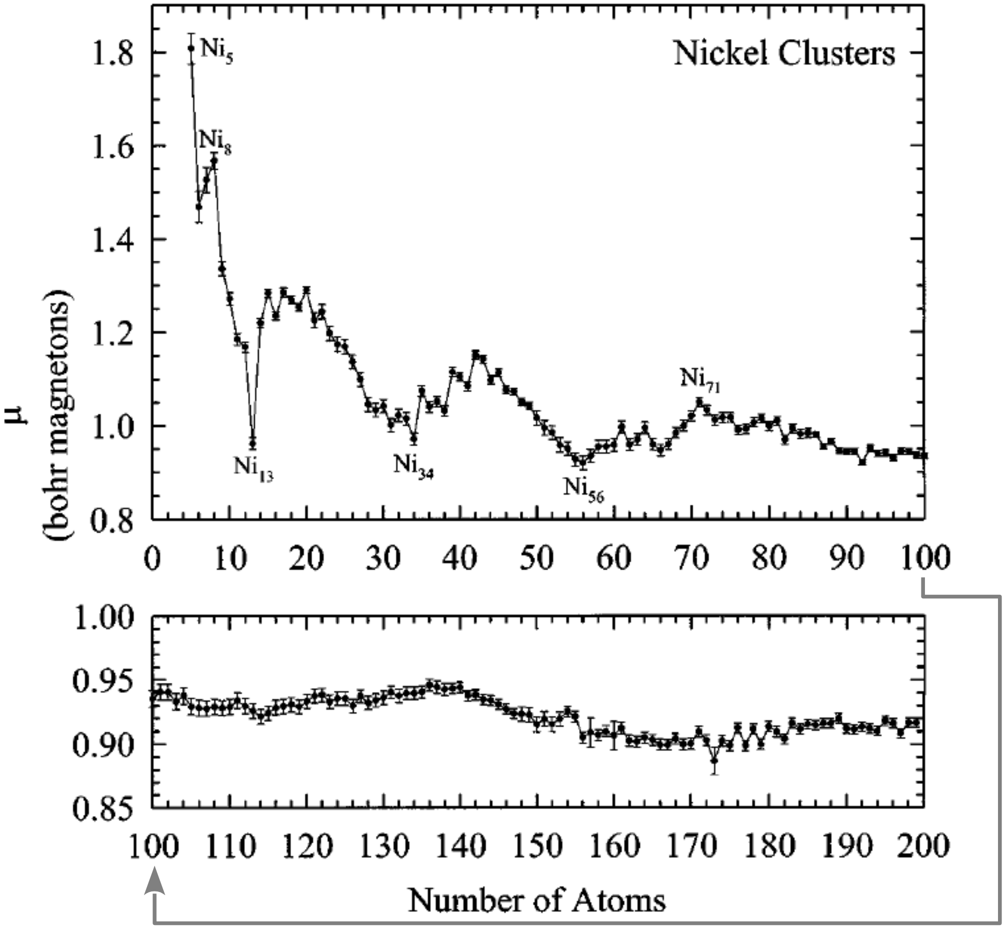


FIG. 1. Nickel cluster magnetic moment per atom (μ) as a function of cluster size, at temperatures between 73 and 198 K. The error bars reflect statistical uncertainty (1 s.d.). The systematic uncertainty in these measurements is $\pm 0.05\mu_B$.

- 0.61μ_B/atom - bulk value of magnetic moment of Ni
- observations support theoretical predictions of enhanced magnetization in systems with decreased coordination between atoms, increased symmetry, and reduced dimensionality
- the similar behavior is observed in clusters of Co, Fe and Rhodium

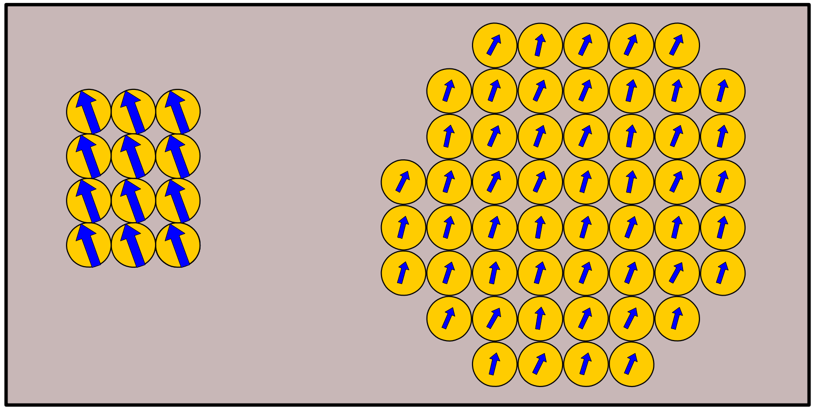


image source: S. E. Apsel, J. W. Emmert, J. Deng, and L. A. Bloomfield, Phys. Rev. Lett. **76**, 1441 (1996)

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