# 2. Quantum physics

## 2.1. Quantum behaviour

Consequences of the above chapter:

    i)    Microsystems behave as waves and as particles as well –

**wave-particle dualism**

    ii)    States of microsystems may be expressed as linear combinations

of other states – combination or **superposition principle**

    iii)    Energies, angular momenta and perhaps other physical quantities

may be quantized – **quantification**

    iv)    Measurements modify the state of a system in a non-controlled

manner; conjugated quantities can not be defined with arbitrary

precision – **uncertainty principle.** These conjugated quantities

are e.g. *the coordinate and the associated linear momentum.*

## 2.2. Quantum postulates

*Remark: the following postulates do not form a complete family of logically consistent propositions from which all the theory could be deduced. They are rather a way to construct quantum world and are based on experiments as well as on inferences tested a posteriori.*

**1. S**tates of a system are elements of a linear space called the state space. They are symbolized: by Greek letters $\varphi,\ \psi,\ \Psi,\ \Phi$; by Greek letters with variable specifications, $\Psi(x, y, z, t)$; by symbols in brackets, $\langle\Phi(x,\ y,\ z)|,\ |\psi(\vec{r}, t)\rangle,\ |3, 2, 0\rangle$. In the last forms they are known as *bras* and *kets*.

The interpretation of the wave function: its modulus squared gives the probability density for the system to be in a certain region, or to have a certain momentum:

$$\left|\psi(\vec{r})\right|^2 = \left\langle\psi^*\middle|\psi\right\rangle = \text{density of probability to have the system around the position vector}$$

$\vec{r}$, i.e. between $x$ and $x+\mathrm{d}x$, $y$ and $y+\mathrm{d}y$, $z$ and $z+\mathrm{d}z$.     (QM2.1)

The state functions are usually normalized:

$$\int\left|\psi(\vec{r})\right|^2 \mathrm{d}x\mathrm{d}y\mathrm{d}z = 1 \qquad\qquad \text{(QM2.2)}$$

State functions must be *finite, continuous, with continuous derivatives* (with one exception, points in which the potential has infinite discontinuities).

**2.** To each physical quantity $\mathcal{A}$ is associated a certain Hermitian operator $\hat{A}$. The measurement of the physical quantity $\mathcal{A}$ in the state $\psi$ is represented by the action of the operator $\hat{A}$ on this state. Such operators have real eigenvalues and their eigenvectors form a base of the space. They are called *observables*.

As the result of the measurement the state of the system changes in a chaotic way. A new measurement completed immediately after the first leaves the state unchanged. The results of the measurements are the eigenvalues of the observables.

**3**. The limit of quantum relations should be the classical results (*correspondence principle*)

**4.** *Fundamental commutators*:

$$[\hat{x},\,\hat{p}_x] = i\hbar,\; [\hat{y},\,\hat{p}_y] = i\hbar,\; [\hat{z},\,\hat{p}_z] = i\hbar \qquad \text{(QM2.3)}$$

All the other are zero.

### 2.3. The Schrödinger equation

If the system evolves freely, without any perturbation – such as measurements – the state at a later moment $t + \mathrm{d}t$ is perfectly defined by the state at a previous moment $t$. We get the state at the moment $t + \mathrm{d}t$ using an *evolution operator* $\hat{T}(\Delta t)$ which must keep the same norm and the superposition relations:

$$\left|\Psi(t + dt)\right\rangle = \hat{T}(\Delta t)\left|\Psi(t)\right\rangle \qquad \text{(QM2.4)}$$

To simplify notations we have not indicate the spatial dependence of the function, which should be written in full-form $\left|\Psi(\vec{r},t)\right\rangle$.

As $\left\langle \Psi^*(t + dt) \middle| \Psi(t + dt) \right\rangle = \left\langle \Psi^*(t) \middle| \hat{T}^+(\Delta t)\hat{T}(\Delta t) \middle| \Psi(t) \right\rangle = \left\langle \Psi^*(t) \middle| \Psi(t) \right\rangle$,

$$\hat{T}^+(\Delta t)\hat{T}(\Delta t) = \hat{I}, \text{ and } \hat{T}(\Delta t) \text{ is unitary.}$$

Assuming $\Delta t$ small, we develop

$$\hat{T}(\Delta t) = \hat{I} - i\hat{\omega}\Delta t \qquad \text{and} \qquad \hat{T}^+(\Delta t) = \hat{I} + i\hat{\omega}^+\Delta t$$

The above condition shows that $\hat{\omega}$ is hermitian. Denote $\hat{H} = \hbar\hat{\omega}$. (QM2.4) gives:

$$\left|\Psi(t + dt)\right\rangle = \left(\hat{I} - \frac{i}{\hbar}\hat{H}\Delta t\right)\left|\Psi(t)\right\rangle = \left|\Psi(t)\right\rangle - \frac{i}{\hbar}\Delta t\hat{H}\left|\Psi(t)\right\rangle$$

Eventually we get the Schrödinger equation:

$$i\hbar\frac{\mathrm{d}\left|\Psi(t)\right\rangle}{\mathrm{d}t} = \hat{H}\left|\Psi(t)\right\rangle \qquad \text{(QM2.5)}$$

One may show that $\hat{H} = \hat{E}_k + \hat{U}$ is the *Hamiltonian* of the system. Assume $|\psi_n(\vec{r},t)\rangle$ is an eigenfunction of $\hat{H}$, belonging to the eigenvalue $E_n$: $\hat{H}|\psi_n(\vec{r},t)\rangle = E_n|\psi_n(\vec{r},t)\rangle$. For such a state Eq. (QM2.54) gives:

$$i\hbar\frac{d|\psi_n(\vec{r},t)\rangle}{dt} = \hat{H}|\psi_n(\vec{r},t)\rangle = E_n|\psi_n(\vec{r},t)\rangle$$

with a simple solution

$$|\psi_n(\vec{r},t)\rangle = \exp\left[-\frac{i}{\hbar}E_n t\right]|\psi_n(\vec{r})\rangle \tag{QM2.6}$$

The temporal dependence factorizes out. Such states are known as *stationary states,* because their modulus squared is constant. They are the eigenfunctions of the equation with eigenvalues for the Hamilton operator. The *time-independent* Schrödinger equation $\hat{H}\psi = E\psi$ is written as: $\left(\frac{\hat{p}^2}{2m} + \hat{U}\right)\psi = E\psi$, or, for potential energy depending only on coordinates:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\psi = E\psi \tag{QM2.7}$$

## 2.4. One-dimensional examples
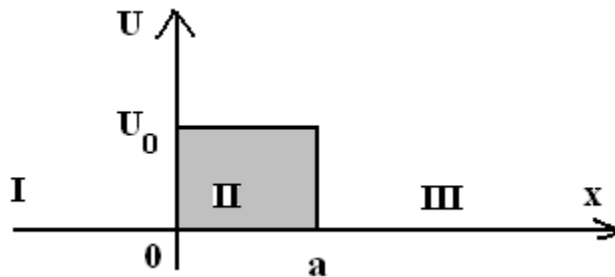
### 2.4.1. *The rectangular potential barrier*



Fig. 1. 1D square potential barrier

The Schrödinger equation (QM2.7) writes

$$\psi'' + \frac{2m}{\hbar^2}(E - U(x))\psi = 0$$

In the three regions we write:

$$\psi_I'' + \frac{2m}{\hbar^2} E \psi_I = 0 \qquad \text{with solution} \quad \psi_I(x) = A_1 e^{ikx} + B_1 e^{-ikx} \quad \text{(QM2.8')}$$

$$\psi_{II}'' + \frac{2m}{\hbar^2}(E - U_0)\psi_{II} = 0 \quad \text{with solution} \quad \psi_{II}(x) = A_2 e^{k_2 x} + B_2 e^{-k_2 x}$$

$$\text{(QM2.8'')} \quad \psi_{III}'' + \frac{2m}{\hbar^2} E \psi_{III} = 0 \qquad \text{with solution} \quad \psi_{III}(x) = A_3 e^{ikx}$$

(QM2.8''')

(see lectures for details). Here

$$k_1^2 = \frac{2mE}{\hbar^2} \qquad\qquad k_2^2 = \frac{2m}{\hbar^2}(U_0 - E) \qquad \text{(QM2.9)}$$

Continuity conditions:

$$\psi_I(0) = \psi_{II}(0), \qquad \psi_{II}(a) = \psi_{III}(a), \qquad \psi_I'(0) = \psi_{II}'(0), \qquad \psi_{II}'(a) = \psi_{III}'(a)$$

The interesting quantity is the *transparency*

$$D = \frac{A_3^* A_3}{A_1^* A_1}$$

which measures the probability to find the particle on the right if initially it moves towards the barrier from $x = -\infty$. If we could neglect the term proportional to $e^{-k_2 a}$ with regard to the term proportional to $e^{k_2 a}$ the final result is:
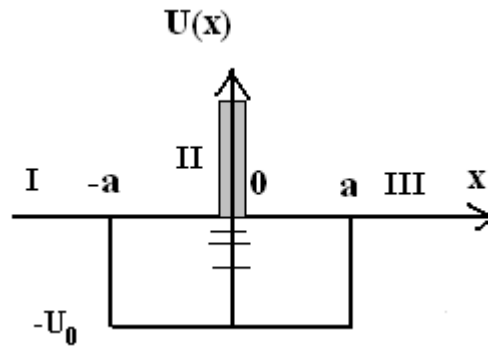
$$D = 16 \frac{E(U_0 - E)}{U_0^2} \exp\left[ -\frac{2}{\hbar}\sqrt{2m(U_0 - E)}\, a \right] \qquad \text{(QM2.10)}$$

For the general barrier described by a function $U(x)$, the result is (see lectures):

$$D \approx 16 \frac{E(U_0 - E)}{U_0^2} \exp\left[ -\frac{2}{\hbar}\int_{x_1}^{x_2} \sqrt{2m(U_0 - E)}\, dx \right] \qquad \text{(QM2.10')}$$

The factor $D_0 = 16 \frac{E(U_0 - E)}{U_0^2}$ is close to the unity.

*Potential well*



For $E > 0$ the energetic spectrum is continuous. We are interested in the situation $E < 0$. Inside the well $-a < x < a$ the Schrödinger equation is identical with that in (QM2.8'), outside it is the same as that from (QM2.8''). As the potential is symmetric, solutions may be symmetric (even) or anti-symmetric (odd).

Even solutions:                     Odd solutions

$$\psi_1^{(+)} = Ce^{+k_1 x} \qquad\qquad \psi_1^{(-)} = Ce^{+k_1 x}$$

$$\psi_2^{(+)} = A\cos k_2 x \qquad\qquad \psi_2^{(-)} = B\sin k_2 x$$

$$\psi_3^{(+)} = Ce^{-k_1 x} \qquad\qquad \psi_3^{(-)} = -Ce^{-k_1 x}$$

with notations from (QM2.9): $k_1^2 = \dfrac{2m|E|}{\hbar^2}$, $k_2^2 = \dfrac{2m}{\hbar^2}(U_0 - |E|)$. Continuity conditions in $-a/2$ and $a/2$ give eventually:

for even solutions –     $\tan k_2 a = \dfrac{k_1}{k_2}$

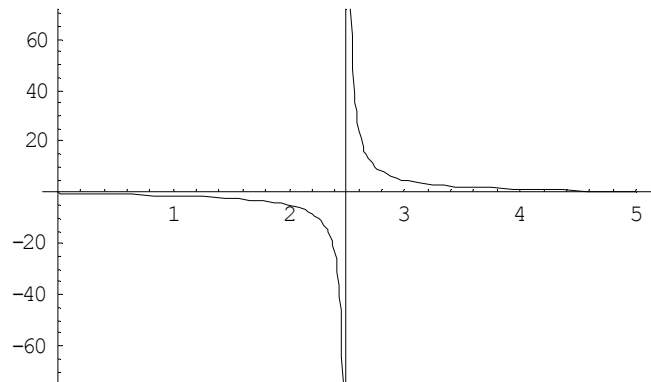for odd solutions –     $\cot k_2 a = -\dfrac{k_1}{k_2}$

Both relations may be written in the form $\tan k_2 a = \dfrac{2k_1 k_2}{k_1^2 - k_2^2}$. But $k_1$ and $k_2$ are both functions of the energy $E$. The last equation gives the possible values for this energy, which is *quantified*. The program below shows the graphs:
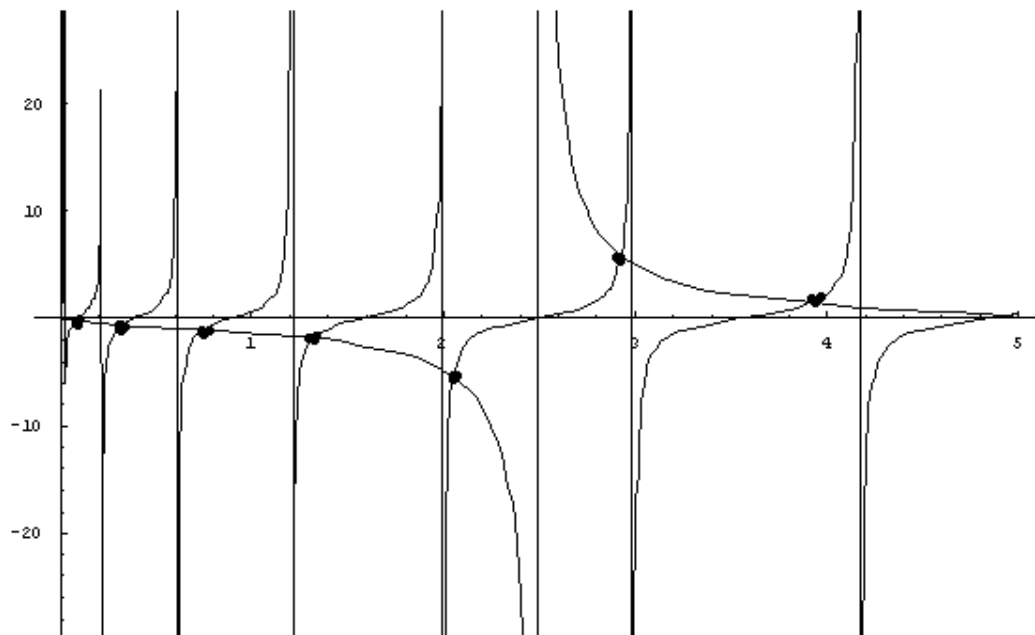
```
ClearAll[x,k1,k2,e,u0]
a=10;u0=5;
k1[e_]=Sqrt[e]
k2[e_]=Sqrt[u0-e]
f[e_]=Tan[k1[e]*a]
g[e_]=2*k1[e]*k2[e]/((k1[e])^2-(k2[e])^2)
 Plot[f[e],{e,0,u0}]
```
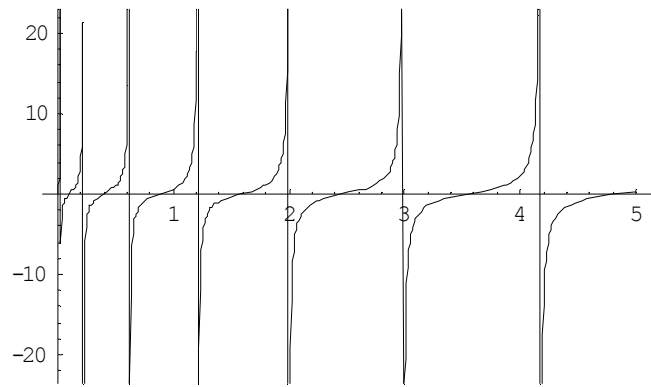
**`Plot[g[e],{e,0,u0}]`**



**`Show[%,%%]`**



Points give the allowed energies. In the example there are only 7 discrete energy levels in the well. They are called *bound states*.

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### 2.4.2. Quantum harmonic oscillator

$$\hat{H}\psi(x) = -\frac{\hbar^2}{2m}\psi''(x) + \frac{m\omega^2 x^2}{2}\psi(x) = E\psi(x)$$

With notations $\varepsilon = \dfrac{\hbar\omega}{2}$ and $x = \sqrt{\dfrac{\hbar}{m\omega}}\,\xi = \dfrac{\xi}{x_0}$ :

$$\frac{d^2\psi}{dx^2} + (\varepsilon - \xi^2)\psi = 0$$

Finite solutions depend on a quantum number $n = 0, 1, 2, 3, \ :$

$$\psi_n(\xi) = C_n H_n(\xi)e^{-\xi^2/2} \qquad\qquad \text{(QM2.11)}$$

with

$$H_n(\xi) = (2\xi)^n - \frac{n(n-1)}{1!}(2\xi)^{n-2} + \frac{n(n-1)(n-2)(n-3)}{2!}(2\xi)^{n-4} - \ldots \text{(QM2.12)}$$

the Hermite polynomials.

Energies are quantified as

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \qquad\qquad \text{(QM2.13)}$$

To compute the normalization constants, use the *normalization condition*:

$$\int_{-\infty}^{\infty}\left|\psi(\xi)\right|^2 d\xi = 1 \qquad\qquad \text{(QM2.14)}$$

One finds $C_n = \left[2^n n!\sqrt{\pi}\right]^{-1/2}$, so the first three normalized eigenfunctions are:

$$\psi_0(x) \equiv |0\rangle = \frac{1}{\left(\sqrt{\pi}x_0\right)^{1/2}}\exp\left[-\frac{1}{2}\left(\frac{x}{x_0}\right)^2\right]$$

$$\psi_1(x) \equiv |1\rangle = \frac{1}{\left(2\sqrt{\pi}x_0\right)^{1/2}}\frac{2x}{x_0}\exp\left[-\frac{1}{2}\left(\frac{x}{x_0}\right)^2\right]$$

$$\psi_2(x) \equiv |2\rangle = \frac{1}{\left(8\sqrt{\pi}x_0\right)^{1/2}}\left[4\left(\frac{x}{x_0}\right)^2 - 2\right]\exp\left[-\frac{1}{2}\left(\frac{x}{x_0}\right)^2\right]$$

### 2.5. Electron in a central field

#### 2.5.1. *The Scrödinger equation in spherical coordinates*

$$-\frac{\hbar^2}{2m_0}\Delta\psi(\vec{r})+U(r)\psi(\vec{r})=E\psi(\vec{r}) \qquad \text{(QM2.15)}$$

Go to spherical variables and get for the Laplace operator:

$$\Delta=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]=$$
$$=\Delta_r+\frac{1}{r^2}\Delta_{\theta,\varphi} \qquad \text{(QM2.16)}$$

(15) becomes: $\left(\Delta_r+\dfrac{1}{r^2}\Delta_{\theta,\varphi}\right)\psi(r,\theta,\varphi)+k^2(r)\psi(r,\theta,\varphi)=0$ (QM2.15')

with

$$k^2(r)=\frac{2m_0}{\hbar^2}\left[E-U(r)\right]$$

Separation of variables: $\psi(r,\theta,\varphi)=R(r)Y(\theta,\varphi)=R(r)\Theta(\theta)\Phi(\varphi)$.

The simplest equation is the one for $\Phi(\varphi)$:

$$\frac{d^2\Phi}{d^2\varphi}+m_l^2\Phi=0$$

with solutions $\Phi(\varphi)=Ce^{im\varphi}$. The periodicity condition $\Phi(\varphi+2\pi)=\Phi(\varphi)$ gives

$$m_l=0,\pm1,\pm2,\pm3... \qquad \text{(QM2.17)}$$

The number $m_l$ is called *the magnetic quantum number*.

The equation in $\Theta(\theta)$ is difficult:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left(\lambda-\frac{m^2}{\sin^2\theta}\right)\Theta=0, \qquad \text{(QM2.18)}$$

with *m* the *magnetic quantum number* and $\lambda$ another quantum number, coming from equation:

$$\Delta_{\theta,\varphi}Y(\theta,\varphi)+\lambda Y(\theta,\varphi)=0 \qquad \text{(QM2.19)}$$

Conditions for continuous, single-valued and finite solutions imply

$$\lambda=l(l+1), \qquad l=0,1,2,\dots \qquad \text{(QM2.20)}$$

Another condition is $\qquad\qquad |m_l|\leq l$ (QM2.21)

Solutions of Eq. (QM2.19) with the above limitations are known as *spherical harmonics*. Some expressions of the spherical functions are:

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta \qquad\qquad Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\varphi}$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right) \qquad Y_{2\pm1} = \sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta e^{\pm i\varphi} \qquad Y_{2\pm2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{\pm 2i\varphi}$$

It turns out that spherical functions $Y_{lm}$ are eigenfunctions of the operator square of the angular momentum $\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$. The exact eigenvalue equation is:

$$\hat{l}^2 Y_{lm}(\theta, \varphi) = l(l+1)\hbar^2 Y_{lm_l}(\theta, \varphi), \qquad\qquad \text{(QM2.22)}$$

$$\text{with} \quad l=0, 1, 2, \ldots \quad\text{and}\quad m_l = 0, \pm1, \pm2, \ldots, \pm l \qquad \text{(QM2.23)}$$

*The magnitude of the angular momentum takes only quantized values equal to*

$$\sqrt{l(l+1)}\hbar \qquad\qquad l=0, 1, 2, \ldots \qquad\qquad \text{(QM2.24)}$$

For the operator $\hat{l}_z$ one finds the eigenvalue equation

$$\hat{l}_z\psi = l_z\psi$$

with eigenvalues $\qquad\qquad l_z = m_l\hbar, \qquad m_l = 0, \pm1, \pm2, \ldots, \pm l \qquad \text{(QM2.25)}$

### 2.5.2. *The Hydrogen atom (and hydrogen-like atoms)*

*For more graphs see e.g.* [http://undergrad-ed.chemistry.ohio-state.edu/H-AOs/](http://undergrad-ed.chemistry.ohio-state.edu/H-AOs/)

The potential energy is $U(r) = \dfrac{Ze^2}{4\pi\varepsilon_0 r}$. The radial equation could be solved analytically and the finite, continuous solutions are the Laguerre polynomials. They depend on a single *principal quantum number $n$=1, 2, 3, ….* If we put together all the preceding results, we see that the eigenfunctions $\psi_{nlm_l}(r, \theta, \varphi) \equiv |n, l, m_l\rangle$ depend on three different quantum numbers:

The principal q.n. $\qquad n=1, 2, 3, \ldots.$

The azimuthal q.n. $\qquad l=0, 1, 2, \ldots, n\text{-}1$

The magnetic q.n. $\qquad m_l = 0, \pm1, \pm2, \ldots, \pm l$

See attached files H eigenfunc 1 & 2.

### 2.5.3. *Characterization of stationary states of H atoms.*

Each state of a *H* atom is described by three quantum numbers, *n*, *l*, and $m_l$. Therefore the notation $\psi_{nlm}(r, \theta, \varphi) \equiv |n, l, m\rangle$. These q.n. fix the quantified values of the energy (see below), the magnitude of the angular momentum and of its projection on the *Oz* axis, Eqs. (24, 25). Energy is given by the expression from Bohr's theory:

$$E_n = -\frac{1}{n^2}\frac{m_0 e_0^4}{2\hbar^2} = -\frac{1}{n^2}\frac{m_0 e^4}{2\hbar^2(4\pi\varepsilon_0)^2} = -\frac{13.6}{n^2}\text{ eV} = -\frac{Ry}{n^2} \qquad \text{(QM2.26)}$$

Here
$$Ry = \frac{m_0 e^4}{2\hbar^2(4\pi\varepsilon_0)^2} = \frac{1}{2}m_0 c^2\left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)^2 = \alpha^2\frac{1}{2}m_0 c^2 \qquad \text{(QM2.26')}$$

is the *rydberg*. The factor in the bracket is a dimensionless quantity called the *fine structure constant*:

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137} \qquad \text{(QM2.27)}$$

Because the energy does not depend on *l* and $m_l$ each level is degenerated and to each value of the principal q.n. *n* correspond $n^2$ different states with *l*=0, 1, 2, …, *n*-1 and $m_l = 0, \pm 1, \pm 2, ..., \pm l$.

*Spectral notation*:     *l*=0     *s*-states

                       *l*=1     *p*-states

                       *l*=2     *d*-states

                       *l*=3     *f*-states

Possible states:   1*s*;   2*s*, 2*p*;   3*s*, 3*p*, 3*d*;   4*s*, 4*p*, 4*d*, 4*f*;

The three observables $\hat{H}$, $\hat{l}^2$ and $\hat{l}_z$ form a complete set of commutative operators and their eigenvalues give the maximum information we could have on the state.

See the applet http://www.falstad.com/qmatom/  for atomic orbitals and 1-D periodic potentials.

### 2.6. Emission and absorption of radiation

2.6.1 *Quantum transitions.* Eigenstates of the Hamiltonian described above are *stationary*, i.e. a system being in such a state will remain there. But quantum systems experience transitions from one stationary state to another and doing so they emit or absorb energy, usually under the form of photons. That means the microsystem has

not the simple Hamiltonian we used before; it is *perturbed* by some extra terms describing the interaction with other systems. As a result transitions occur. Let's study a system which at $t=0$ is in a stationary state $\left|\psi_n^0\right\rangle$ of a Hamiltonian $\hat{H}_0$: $\hat{H}_0\left|\psi_n^0\right\rangle = E_n^0\left|\psi_n^0\right\rangle$. During a finite time $t$ the system is acted upon by a perturbation described by the operator for the interaction energy $\hat{W}$. The system evolves following the Schrödinger equation: $i\hbar\dfrac{d\left|\psi\right\rangle}{dt} = \left(\hat{H}_0 + \hat{W}\right)\left|\psi\right\rangle$. $\left|\psi\right\rangle$ is no more an eigenstate of $\hat{H}_0$. But because $\hat{H}_0$ is an observable, one can develop any state function $\left|\psi\right\rangle = \sum c_k\left|\psi_k^0\right\rangle$. Assume we measure the state of the system at the moment $t$. What is the *transition probability* $P_{mn}$ to find the system in the state $\left|\psi_m^0\right\rangle$ if it was initially in the state $\left|\psi_n^0\right\rangle$? The result is given by *the Fermi golden rule*:

$$P_{mn} = \frac{1}{\hbar^2}\left|\left\langle\psi_m^0\left|\hat{W}\right|\psi_n^0\right\rangle\right|^2 \qquad \text{(QM2.28)}$$

There is a supplementary condition: the perturbation must contain a frequency given by Bohr's condition:

$$\omega_{mn} = \frac{E_m^0 - E_n^0}{\hbar} \qquad \text{(QM2.28')}$$

For each perturbation we have to compute the square of the matrix element $W_{mn}^0 = \left\langle\psi_m^0\left|\hat{W}\right|\psi_n^0\right\rangle = \int \psi_m^{0^*}\hat{W}\psi_n^0\,dxdydz$. If this element is zero, the transition is *forbidden*. If it is non-zero, the transition is *allowed*. These computations lead to *selection rules* controlling the variations of the quantum numbers.

2.6.2. *Selection rules*. The most encountered perturbations are given by electric or magnetic interactions. They could be classified following the type of field: dipole, quadrupole,... The most intense elmgn transitions in atoms and molecules are the *dipolar-electric transitions*. The selection rules for such transitions are:

$$\Delta l = \pm 1 \qquad\qquad \Delta m_l = 0,\ \pm 1 \qquad\qquad \text{(QM2.29)}$$

There are no selection rules for the principal q.n. Selection rules explain thoroughly atomic and molecular spectra, as well as nuclear gamma spectra.

2.6.3. *Einstein's theory of emission and absorption*. Assume identical atoms in an external elmgn field. To make simple, atoms have but two energy levels with energies $E_m$ and $E_n$. Levels have degeneracy $g_m$ and $g_n$. The number of atoms are $N_m$ and $N_n$ The field may have many frequencies but we suppose that the Bohr frequency of the transition (QM2.28') is present. The spectral density of energy of the elmgn field is $u_\omega(T) \equiv u(\omega_{mn})$
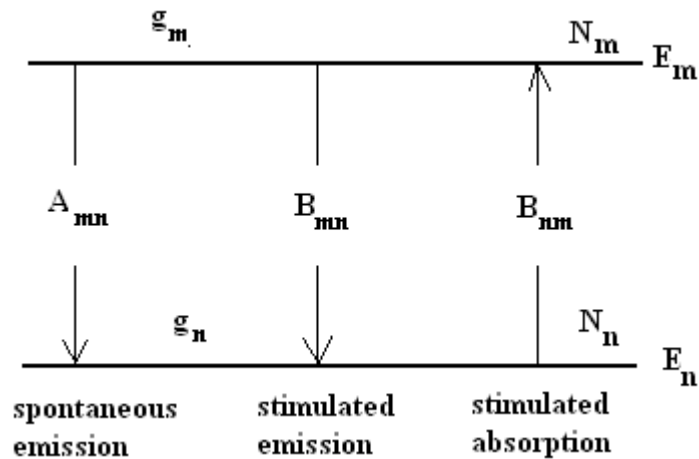


Three processes: *spontaneous* and *stimulated emission* and *stimulated absorption*. Denote by $A_{mn}$ the probability for an atom to suffer a spontaneous emission in a time $\Delta t$. For stimulated processes such a probability should be proportional to $u(\omega_{mn})$ and also to the corresponding *Einstein coefficient* $B_{mn}$ or $B_{nm}$. Assume for ease that $g_m = g_n$ The *detailed balance* equation is:

$$\left[A_{mn} + B_{mn}u(\omega_{mn})\right]N_m \Delta t = B_{nm}u(\omega_{mn})N_n \Delta t \qquad (*)$$

Hence

$$\frac{N_n}{N_m} = \exp\left[\frac{\hbar\omega_{mn}}{k_B T}\right] = \frac{A_{mn}}{B_{mn}u(\omega_{mn})} + \frac{B_{mn}}{B_{nm}}$$

This relation holds even for $T \to \infty$, hence $B_{mn} = B_{nm}$.

At equilibrium use the Boltzmann distribution:

$$\frac{N_m}{N_n} = \frac{g_m}{g_n}\exp\left[-\frac{E_m - E_n}{k_B T}\right] = \frac{g_m}{g_n}\exp\left[-\frac{\omega_{mn}}{k_B T}\right] = \exp\left[-\frac{\omega_{mn}}{k_B T}\right]$$

The final result is the Planck relation:

$$u(\omega_{mn}) = \frac{A_{mn}}{B_{mn}} \frac{1}{\exp\left[\dfrac{\hbar\omega_{mn}}{k_B T}\right] - 1}$$

It follows also that
$$\frac{A_{mn}}{B_{mn}} = \frac{\omega_{mn}^3}{\pi^2 c^3} \qquad\qquad \text{(QM2.30)}$$

The spontaneous coefficient $A$ has s$^{-1}$ as MU. If during $dt$ a number $dN_m$ atoms suffer transitions from the state $m$ to the state $n$, one can write: $-dN_m = A_{mn} N_m dt$, hence

$$N_m(t) = N_m(0)e^{-t/\tau} \qquad\qquad \text{(QM2.31)}$$

The duration $\tau$ is the average time the atom stays in the excited state, *the lifetime* of the state.

### 2.7. Magnetic interaction. Electronic spin

2.7.1. *The orbital magnetic moment of the electron.* If an atom is put in en external magnetic field its spectrum becomes more complex. Many spectral lines split into several closed components with different polarizations. This effect was discovered by Zeeman in 1897. Soma lines split in just three components; this is the *normal effect* and is explained classically. Indeed in classical electromagnetism each magnetic moment interacts with a magnetic field through an energy term

$$E_{mgn} = -\vec{\mu} \cdot \vec{B} \qquad\qquad \text{(QM2.32)}$$

Here $\vec{\mu}$ is the magnetic moment defined in analogy with the same quantity for a small loop as $\vec{\mu} = i\vec{A}$ (see figure below)
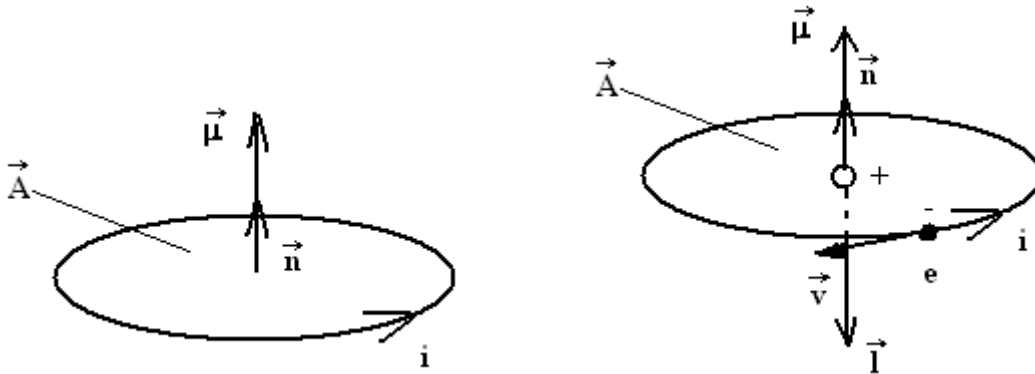
The vector $\vec{A} = A\vec{n}$ is associated with the sense of the current $i$ by the usual rule. If the current is given by an electron revolving around the nucleus at a distance $r$ with speed $v$, its magnetic moment would be: $\mu = -\dfrac{e}{2\pi r/v}\pi r^2 = -\dfrac{evr}{2} = -\dfrac{em_0 vr}{2m_0} = -\dfrac{el}{2m_0}$, with $l$ the angular momentum. One may write also:

$$\vec{\mu} = -\frac{e}{2m_0}\vec{l} = -\gamma_{orb}\vec{l} \qquad (QM2.33)$$

The quantity $\gamma_{orb}$ is the *orbital gyromagnetic factor*. The magnetic energy is

$$E_{mgn} = -\vec{\mu}\cdot\vec{B} = \frac{e}{2m_0}\vec{l}\cdot\vec{B} = \gamma_{orb}\vec{l}\cdot\vec{B} \qquad (QM2.34)$$

In quantum mechanics:

$$\hat{H}_{mgn} = -\hat{\vec{\mu}}\cdot\vec{B} = \frac{e}{2m_0}\hat{\vec{l}}\cdot\vec{B} = \gamma_{orb}\hat{\vec{l}}\cdot\vec{B} \qquad (QM2.34')$$

Assume the magnetic field along $Oz$ and use results from 2.5 to find:

$$\hat{H}_{mgn} = \gamma_{orb}\hat{l}_z\cdot B = m\frac{e\hbar}{2m_0}B = \{0,\ \pm 1,\ \pm 2,..\}\frac{e\hbar}{2m_0}B \qquad (QM2.35)$$
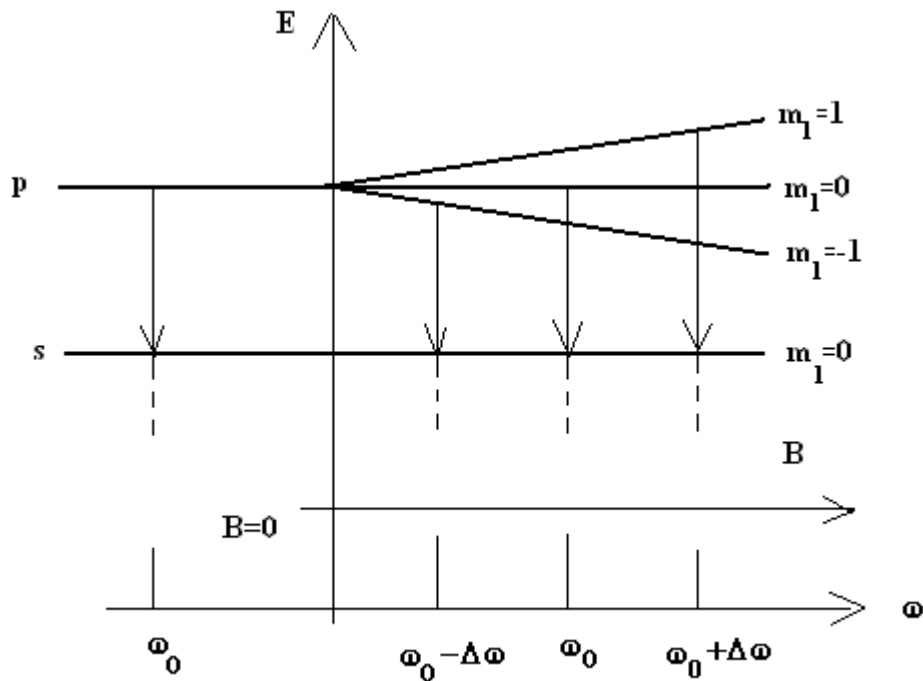
The quantity (*taken from CODATA*, a site giving last values for physical constants)

$$\mu_B = \frac{e\hbar}{2m_0} \cong 9.27400915(23)\times 10^{-24}\ \ J\cdot T^{-1} \qquad (QM2.36)$$

is the *Bohr magneton*. For a *H atom* the quantified energy of a level becomes

$$E_n \rightarrow E_n + E_{mgn} = -\frac{Ry}{n^2} + m_l\mu_B B \qquad (QM2.37)$$

The splitting of atomic levels and of spectral lines is shown below for a $p \rightarrow s$ transition.

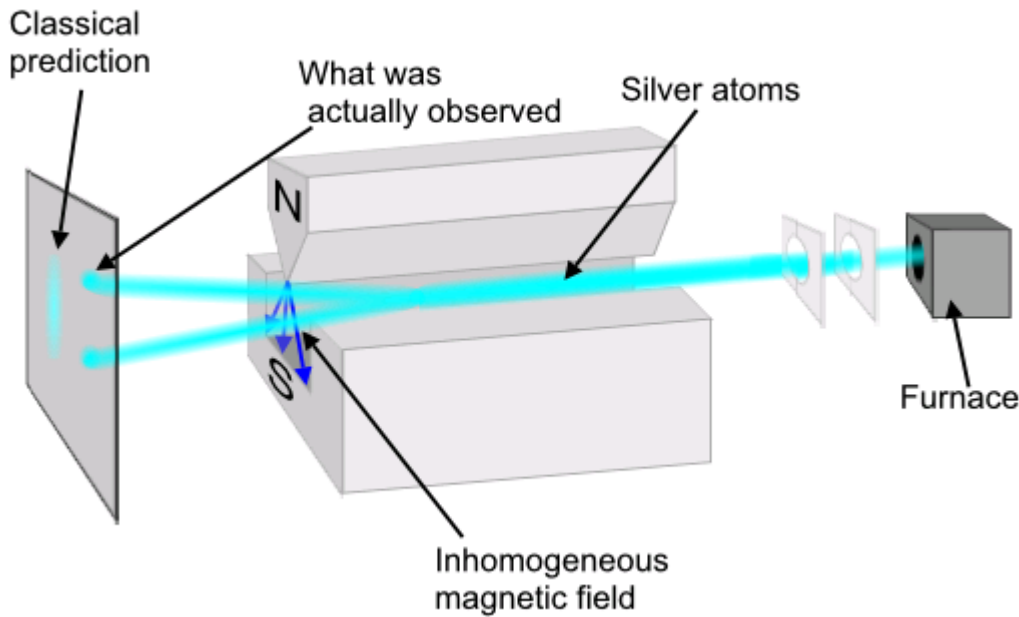The deviation $\boxed{\Delta\omega = \mu_B B = \dfrac{e\hbar}{2m_0}B}$ is the value found experimentally.

*Exercise:* show that even for more complex spectra (e.g. for a $d \to p$ transition) one get a three-fold splitting of spectral lines.

2.7.2. *Electronic spin.* So in magnetic field each spectral line should split in three components. But this is not true: one finds doublets, quartets … This is the *anomalous Zeeman effect.* The explanation is given by the existence of *electronic spin*. This hypothesis set forth by Uhlenbeck and Goudsmit in 1925 is based on spectroscopy and on the experiment of Stern and Gerlach made in 1922. The sketch of the experiment is shown below (from Wikipedia).

*Exercise*: **read and learn** the explanation in
http://www.upscale.utoronto.ca/GeneralInterest/Harrison/SternGerlach/SternGerlach.html, or http://hyperphysics.phy-astr.gsu.edu/hbase/spin.html#c2

Classical prediction · What was actually observed · Silver atoms · N · S · Furnace · Inhomogeneous magnetic field

The inhomogeneous magnetic field exercise upon a beam of atoms a vertical force along the $z$ direction given by $F = \vec{\mu}_{atom} \cdot \dfrac{\partial \vec{B}}{\partial z} = \mu_{atom} \dfrac{\partial B}{\partial z} \cos(\vec{\mu}_{atom}, \vec{B})$. Atoms (Ag) were chosen to have no magnetic moment, so the force ought to be zero. However deviations were observed. Assumptions were made to take into account some nonzero orbital magnetic moment. Classical theory allows any angle between the relevant vectors hence the classical prediction in the drawing. An orbital magnetic moment should conduct to an *odd* number of lines. What was actually observed was just a pair of spots as if the magnetic moment may have just two orientations, up and down. The corresponding value for the intrinsic – or spin – quantum number have to be $s = \dfrac{1}{2}$, so as to get $2s + 1 = 2$ possible orientation. The values oh the corresponding magnetic moment are $\pm \mu_B$. The *spin hypothesis* says:

a)  The electron has an intrinsic angular momentum, called *spin*, described by operators $\hat{s}^2$, $\hat{s}_x$, $\hat{s}_y$, $\hat{s}_z$. They fulfill the usual commutation relations of angular moments and commute with all coordinate and momentum operators.

b)  The operator $\hat{s}^2$ has but one eigenvalue

$$s = \frac{1}{2} : \hat{s}^2 \psi = s(s+1)\hbar^2 \psi = \frac{3}{4}\hbar^2 \psi \qquad \text{(QM2.38')}$$

Its projection along $Oz$ axis has two eigenvalues:

$$\hat{s}_z \psi = m_s \hbar \psi \qquad \text{with} \qquad m_s = \pm\frac{1}{2} \qquad \text{(QM2.38'')}$$

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c) To this spin angular momentum is associated a magnetic moment with quantified projections $\mu_{sz} = \pm\mu_B$.

The gyromagnetic ratio for the spin is twice as big as for the orbital case (gyromagnetic spin anomaly):
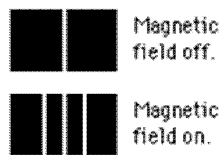
$$\gamma_{orb} = \frac{e}{2m_0} \qquad\qquad \gamma_s = \frac{\left(\dfrac{e\hbar}{2m_0}\right)}{\hbar/2} = \frac{e}{m_0} = g_s\frac{e}{2m_0} = g_s\gamma_{orb} \qquad (QM.2.39)$$

*Consequences*: doublets, quadruplets … are allowed and explained; complex spectra are explained; the periodic table is explained.

Examples of Zeeman splitting (from http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/zeeman.html )

"Normal" Zeeman effect

This type of splitting is observed with hydrogen and the zinc singlet.



This type of splitting is observed for spin 0 states since the spin does not contribute to the angular momentum.

"Anomalous" Zeeman effect

When electron spin is included, there is a greater variety of splitting patterns.
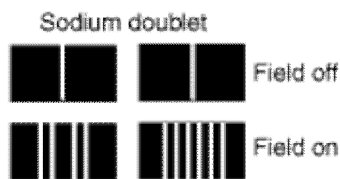
## 3. Quantum statistics

### 3.1. Types of quantum statistics

It turns out that every microscopic particle (elementary particles, atoms, molecules) has spin. For a complex particle the spin builds up from the individual spins of the components. Pauli shown that there are two very different families of particles:

-   Particles with integer spins, $s=0, 1, 2, 3, \ldots$ They are called *bosons* and obey the Bose-Einstein statistics: at equilibrium the average number of particles with energy $\varepsilon_i$ is given by:

$$\boxed{\langle n_i \rangle_{B-E} = \frac{g_i}{\exp\left[\dfrac{\varepsilon_i - \mu_{B-E}}{k_B T}\right] - 1}} \qquad \text{(QM2.40)}$$

Here $g_i$ is the degeneracy and $\mu_{B-E}$ the chemical potential. Examples: photons, an even number of electrons or of protons. Bosons may occupy in any number a given state. Their functions of state are symmetric to the particle permutations:

$$\psi(1, 2, \ldots j, \ldots k, \;) = +\psi(1, 2, \ldots k, \ldots j, \;)$$

-   Particles with half-integer spins, $s=1/2, 3/2, 5/2, \ldots$ They are called *fermions* and obey the Fermi-Dirac statistics: at equilibrium the average number of particles with energy $\varepsilon_i$ is given by:

$$\boxed{\langle n_i \rangle_{F-D} = \frac{g_i}{\exp\left[\dfrac{\varepsilon_i - \mu_F}{k_B T}\right] + 1}} \qquad \text{(QM2.41)}$$

Here $g_i$ is the degeneracy and $\mu_F$ the chemical potential or the *Fermi level*. Examples: electrons, protons, neutrons, an odd number of fermions. Fermions could be at most one in a state (the *Pauli exclusion principle*). Their functions of state are anti-symmetric to the particle permutations:

$$\psi(1, 2, \ldots j, \ldots k, \;) = -\psi(1, 2, \ldots k, \ldots j, \;)$$

A comparison between classical (Boltzmann) and quantum statistics is given in the following figure. At large values of the quantity at the exponent $\dfrac{\varepsilon_i - \mu_F}{k_B T} \gg 1$ both quantum statistics have the same classical limit.
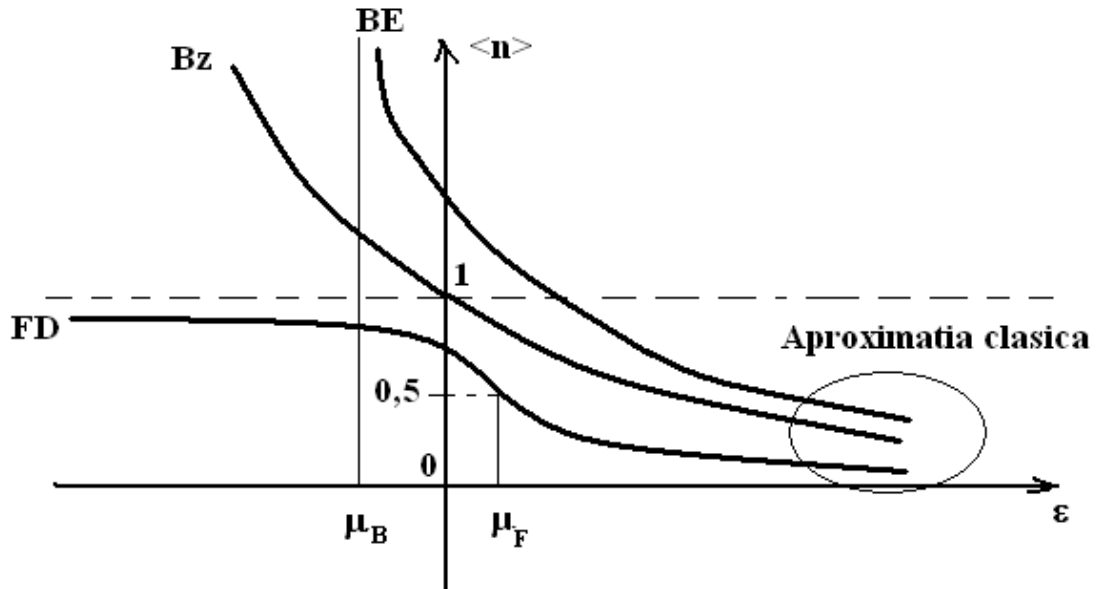
### 3.3. Electrons in solids. Semiconductors.

3.3.1. *Band structure of solids*

From Wikipedia:

"The electrons of a single isolated atom occupy atomic orbitals, which form a discrete set of energy levels. If several atoms are brought together into a molecule, their atomic orbitals split, as in a coupled oscillation. This produces a number of molecular orbitals proportional to the number of atoms. When a large number of atoms (of order $\times\ 10^{20}$ or more) are brought together to form a solid, the number of orbitals becomes exceedingly large, and the difference in energy between them becomes very small, so the levels may be considered to form continuous *bands* of energy rather than the discrete energy levels of the atoms in isolation. However, some intervals of energy contain no orbitals, no matter how many atoms are aggregated, forming *band gaps*.

Within an energy band, energy levels are so numerous as to be a near continuum. First, the separation between energy levels in a solid is comparable with the energy that electrons constantly exchange with phonons (atomic vibrations). Second, it is comparable with the energy uncertainty due to the Heisenberg uncertainty principle, for reasonably long intervals of time. As a result, the separation between energy levels is of no consequence."

Any solid has a large number of bands. In theory, it can be said to have infinitely many bands (just as an atom has infinitely many energy levels). However, all but a few lie at energies so high that any electron that reaches those energies escapes from the solid. These bands are usually disregarded.

Bands have different widths, based upon the properties of the atomic orbitals from which they arise. Also, allowed bands may overlap, producing (for practical purposes) a single large band.

Figure 1 shows a simplified picture of the bands in a solid that allows the three major types of materials to be identified: metals, semiconductors and insulators.

*Metals* contain a band that is partly empty and partly filled regardless of temperature. Therefore they have very high conductivity.

The lowermost, almost fully occupied band in an *insulator* or *semiconductor*, is called the *valence band* by analogy with the valence electrons of individual atoms. The uppermost, almost unoccupied band is called the *conduction band* because only when electrons are excited to the conduction band can current flow in these materials. The difference between insulators and semiconductors is only that the forbidden band gap between the valence band and conduction band is larger in an insulator, so that fewer electrons are found there and the electrical conductivity is lower. Because one of the main mechanisms for electrons to be excited to the conduction band is due to thermal energy, the conductivity of semiconductors is strongly dependent on the temperature of the material.
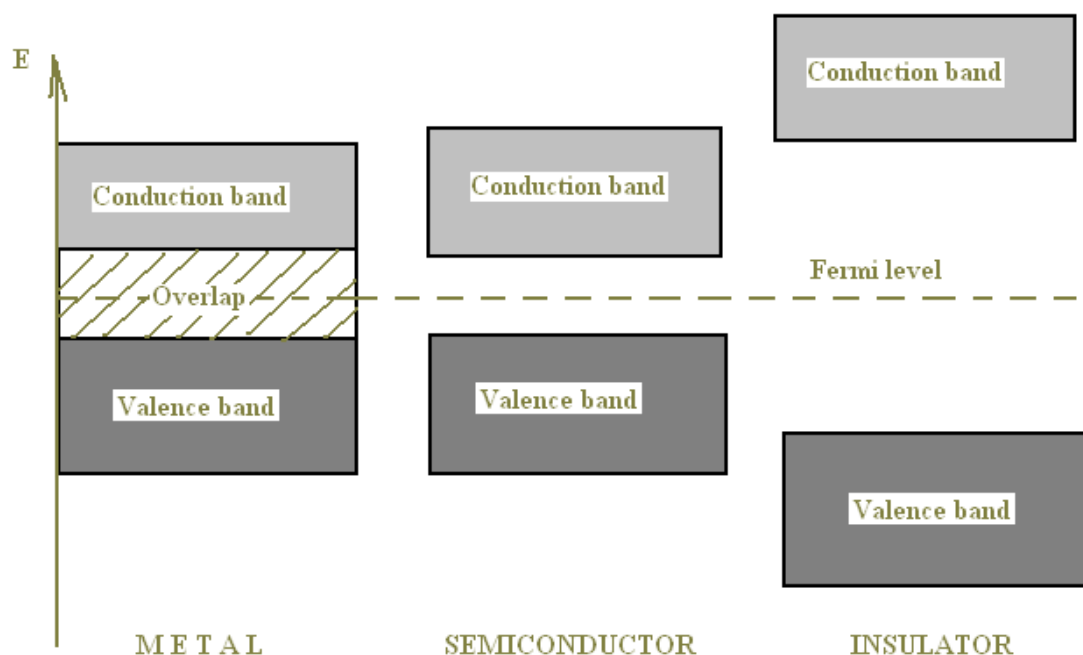


This band gap is one of the most useful aspects of the band structure, as it strongly influences the electrical and optical properties of the material. Electrons can transfer from one band to the other by means of carrier generation and recombination processes. The band gap and defect states created in the band gap by doping can be used to create semiconductor devices such as solar cells, diodes, transistors, laser diodes, and others." (End of Wikipedia)

*General statement: states above the Fermi level are mostly empty; states below are typically filled with electrons.* (see lectures)
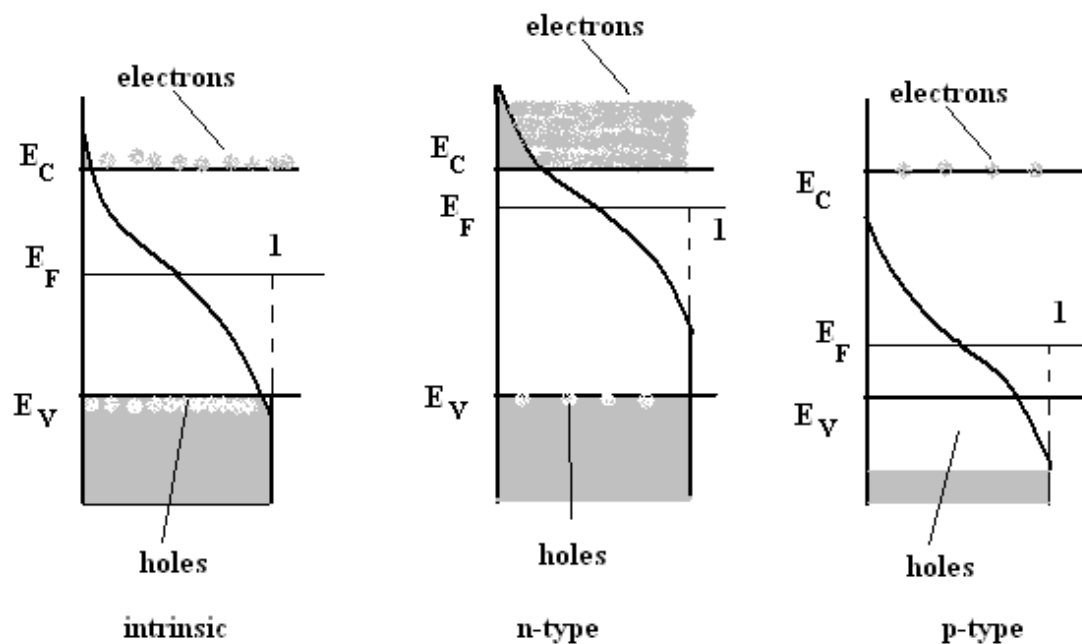
*Metals*: The Fermi level is in the middle of allowed bands. Electrons easily acquire energy from an external electric field and may participate to the conduction. The density of carriers is $10^{22} - 10^{23}$ cm$^{-3}$. It does not vary much with *T*.

*Semiconductors*. The Fermi level is in the middle of the forbidden gap, whose energy is $E_g \approx 1$ eV. Carriers are electrons in the conduction band (CB) and holes in the valence band (VB). To participate to conduction an *e-* must "jump" from VB to CB and for this it needs energy, e.g. thermal energy. At room temperature $k_B T = \dfrac{1}{40}$ eV. The carrier density varies mainly exponentially with temperature, between $10^{12}$ and $10^{20}$ cm$^{-3}$.

*Insulators*. The Fermi level is in the middle of the forbidden gap, whose energy is $E_g \approx 5$ eV. At usual *T* an insulator does not conduct electrical currents.

*3.3.2. Carrier statistics in semiconductors*



intrinsic          n-type          p-type

For intrinsic scond the Fermi level is roughly in the middle of the gap. For doped scond the Fermi level moves towards the CB (n-type) or VB (p-type) as in Fig. above. In this figure we see that the concentrations of carriers in both bands depend very much on the position of the Fermi level:

- they are equal in the intrinsic case

- the $e^-$ concentration in CB is much bigger that holes concentration in the VB for $n$-type semiconductors
- the concentration pf holes in the VB is much bigger that $e^-$ concentration in the CB for $p$-type semiconductors

Electrons in CB are "quasi-particles" which may be different from free electrons. In particular their mass depends to a great extent on the particular structure of the CB. We may find (sometimes even in the same material) light electrons, with *effective mass $m^*$* smaller than the mass of free electrons $m_0$ and heavy electrons, with $m^* > m_0$. The same is true for the holes in the VB.

In *nondegenerate semiconductors*: the Fermi level is well into the forbidden band and the Fermi distribution is approximated with the Boltzmann's:

$$E_C - E_F > 5k_BT, \qquad\qquad E_F - E_V > 5k_BT \qquad\qquad (QM2.49)$$

It can be shown that in this case the densities of electrons in the CB and holes in the VB are given by:

$$n = 2\left(\frac{2\pi m_n^* k_B T}{h^2}\right)^{3/2} \exp\left[\frac{E_F - E_C}{k_B T}\right] = N_C(T)\exp\left[\frac{E_F - E_C}{k_B T}\right] \qquad (QM2.50')$$
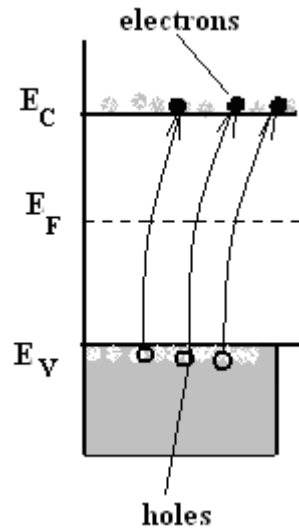
$$p = 2\left(\frac{2\pi m_p^* k_B T}{h^2}\right)^{3/2} \exp\left[\frac{E_V - E_F}{k_B T}\right] = N_V(T)\exp\left[\frac{E_V - E_F}{k_B T}\right] \qquad (QM2.50'')$$

In such nondegenerate semiconductors the product $np$ is constant:

$$np = N_C N_V \exp\left[-\frac{E_C - E_V}{k_B T}\right] = N_C N_V \exp\left[-\frac{E_g}{k_B T}\right] = n_i^2 \qquad (QM2.51)$$

where $E_g$ is the energy gap. Quantities $N_C$ and $N_V$ are the *effective concentrations* of $e^-$ in the CB and of holes in the VB. In Si at 300 K they are of the order of $10^{19}$ cm$^{-3}$.
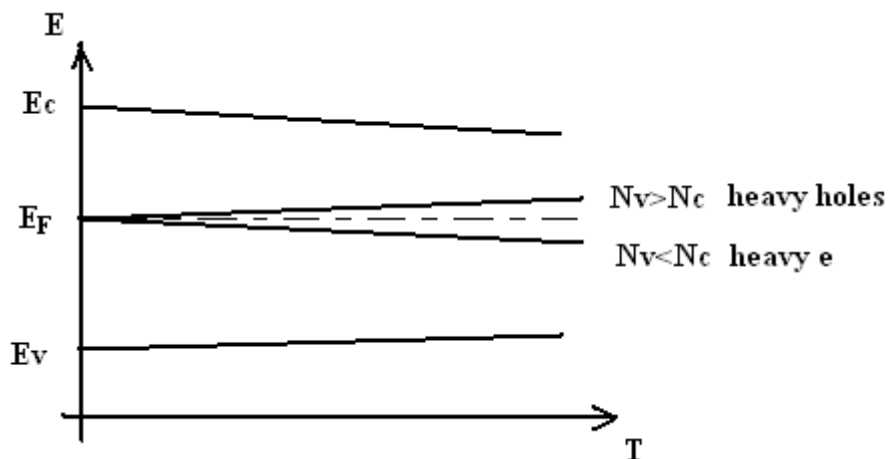
a) *Intrinsic semiconductors.*

The *neutrality condition*: $\boxed{n = p}$ writes with (QM2.50):

$N_C \exp\left[\dfrac{E_F - E_C}{k_B T}\right] = N_V \exp\left[\dfrac{E_V - E_F}{k_B T}\right]$. The position of the Fermi level is:

$$E_F = \frac{E_V + E_C}{k_B T} + \frac{k_B T}{2} \ln \frac{N_V}{N_C} = \frac{E_V + E_C}{k_B T} + \frac{3 k_B T}{4} \ln \frac{m_p^*}{m_n^*} \qquad \text{(QM2.52)}$$
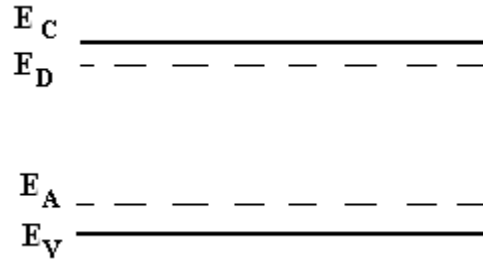
The position of $E_F$ when $T$ varies is shown below:



The intrinsic concentration is

$$\boxed{n_i = \sqrt{N_C N_V} \, \exp\left[-\frac{E_g}{2kT}\right]} \qquad \text{(QM2.53)}$$

*Exercise:* Draw the graph of $\ln(n_i) = f(1/T)$. What quantity could be computed from the slope of this graph ?

*b) Impurified semiconductors*

The most general case: donors and acceptors *compensated semiconductor*.



Taking into account spin degeneration of *e* on the impurities levels and the fact that a ionized donor level means the absence of an *e* the *neutrality condition* is roughly:
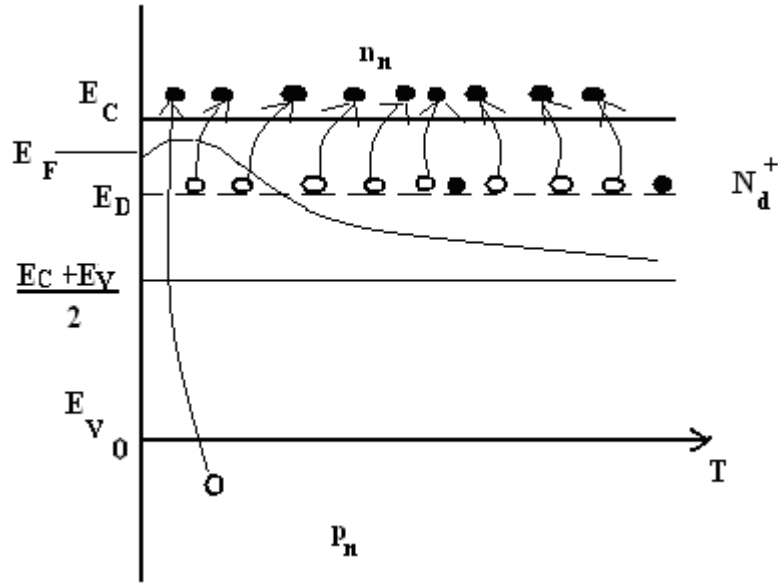
No. of *e* in CB + No. ionized acceptors = No. of holes in VB + No. ionized donors

$$n + N_A^- = p + N_D^+ \qquad\qquad \text{(QM2.54)}$$

(The numbers are actually concentrations)

*b1) Type-n semiconductors.*

Impurities from the V$^{th}$ group e.g. *P, As.* have extra levels in the gap close to $E_C$ as in the drawing below:

The *neutrality condition*: $\boxed{n_n = N_d^+ + p_n}$. $N_d^+$ is the concentration of ionized donors. These ionized donors have lost their electrons, so their concentration is (up to a degeneration factor 2 in the denominator)

$$N_d^+ = \frac{N_d}{2\exp\left[\dfrac{E_F - E_d}{k_B T}\right] + 1}$$

Neglecting the minority concentration $p_n$ one finds:

$$N_C \exp\left[\frac{E_F - E_C}{kT}\right] = \frac{N_D}{\exp\left[\dfrac{E_F - E_D}{kT}\right] + 1}.$$

Denoting $x = \exp\left[\dfrac{E_F}{kT}\right]$

$$2N_C \exp\left[-\frac{E_D + E_C}{kT}\right] x^2 + N_C \exp\left[-\frac{E_C}{kT}\right] x - N_D = 0 \text{, or}$$

$$x^2 + \frac{\exp\left[\dfrac{E_D}{kT}\right]}{2} x - \frac{N_D}{2N_C}\exp\left[\frac{E_C + E_D}{kT}\right] = 0$$

Keeping only the positive root:

$$x = \frac{\exp\left[\dfrac{E_D}{kT}\right]}{4}\left(-1 + \sqrt{1 + \frac{8N_D}{N_C}\exp\left[\frac{E_C - E_D}{kT}\right]}\right) \quad \text{or}$$

$$E_F = E_D + kT\ln\left\{\frac{1}{4}\left(-1 + \sqrt{1 + \frac{8N_D}{N_C}\exp\left[\frac{E_C - E_D}{kT}\right]}\right)\right\} \qquad \text{(QM2.55)}$$

*Limit Cases.*

A) *Very low T* (a few K). Condition: $\dfrac{8N_D}{N_C}\exp\left[\dfrac{E_C - E_D}{kT}\right] \gg 1$. We neglect the

unity in (QM2.55) and find

$$E_F = \frac{E_C + E_D}{2} + \frac{kT}{2}\ln\left[\frac{N_D}{2N_C}\right] \qquad \text{(QM2.55')}$$

At $T{=}0$ K the Fermi level is at half the distance between $E_C$ and $E_D$. When $T$ grows $E_F$ approaches the conduction band and later drops as in the figure above.

The $e^-$ concentration is

$$n_n(\text{very low } T) \approx \sqrt{\frac{N_C N_D}{2}}\exp\left[-\frac{E_C - E_D}{2kT}\right] \qquad \text{(QM2.56')}$$

The graph $\ln n = f\left(\dfrac{1}{T}\right)$ is virtually a straight line with the slope $-\dfrac{E_C - E_D}{2kT}$.

This is a method to find the position of the donor level below $E_C$.

*Question*: what is the situation in an intrinsic semiconductor?

B) *Low temperatures* (from several tens of K to room temperatures). Condition:

$\dfrac{8N_D}{N_C}\exp\left[\dfrac{E_C - E_D}{kT}\right] \ll 1$, hence $N_C \gg 8N_D$. We develop the square root

and eventually find

$$E_F = E_C + kT\ln\left[\frac{N_D}{N_C}\right] \qquad \text{(QM2.55'')}$$

The argument of ln is negative, so the Fermi level comes close to the middle of the gap. The $e^-$ concentration is

$$n_n(\text{low } T) \approx N_C\exp\left[\ln\left(\frac{N_D}{N_C}\right)\right] = N_D \qquad \text{(QM2.56'')}$$

This is the *depletion region* when all the donors are ionized and the intrinsic generation is low. The majority carriers have an almost constant concentration; the concentration of the minority carriers grows rapidly with $T$:

$$p_n = \frac{n_i^2}{n_n} = \frac{n_i^2}{N_D} = N_C N_V \exp\left[-\frac{E_g}{2kT}\right]$$

*C) High temperatures.* We go back to the neutrality condition and assume all the donors are ionized $n_n = N_D + p_n = N_D + \frac{n_i^2}{n_n}$. The positive solution is:

$$n_n = \frac{N_D}{2}\left(1 + \sqrt{1 + \frac{4n_i^2}{N_D^2}}\right), \text{ and hence } p_n = \frac{2n_i^2}{N_D\left(1 + \sqrt{1 + \frac{4n_i^2}{N_D^2}}\right)}$$
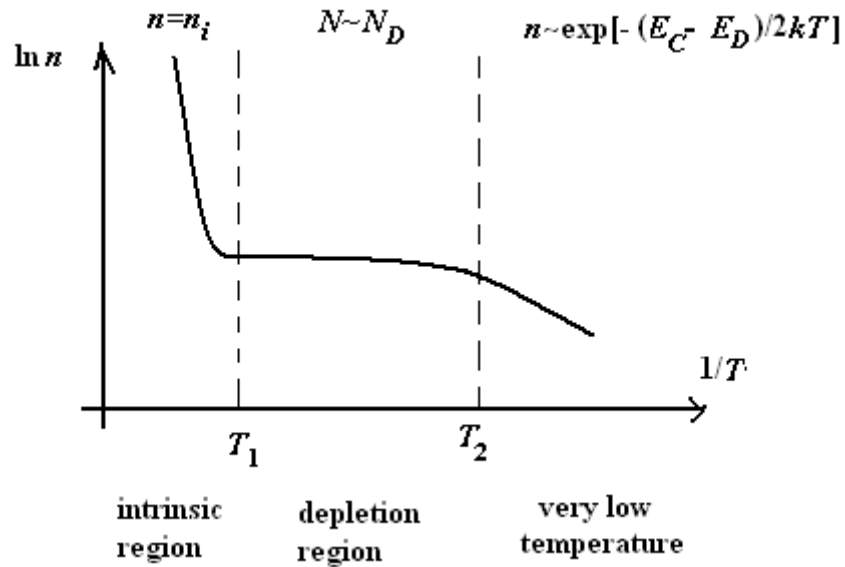
The Fermi level is given by:

$$E_F = E_C + kT \ln\left\{\left[\frac{N_D}{2N_C}\right]\left(1 + \sqrt{1 + \frac{4N_C N_V}{N_D^2}\exp\left[-\frac{E_g}{kT}\right]}\right)\right\}$$

For high $T$ but with $\frac{4n_i^2}{N_D^2} \ll 1$ one find again the depletion region (show!).
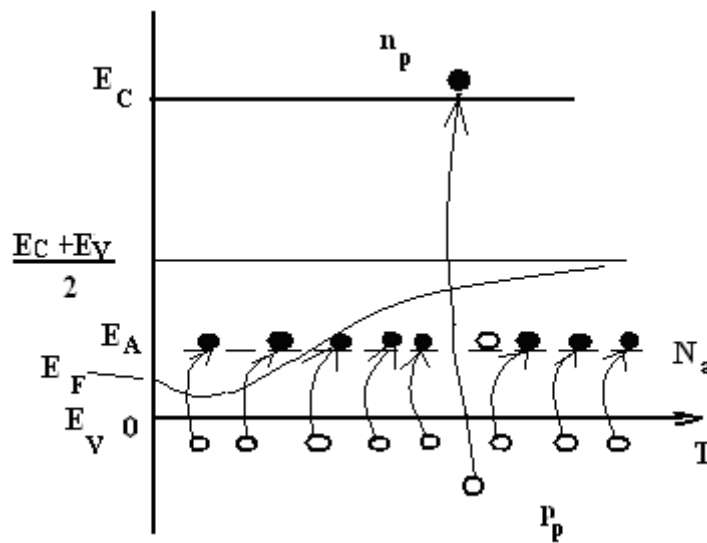
Finally, if $\frac{4n_i^2}{N_D^2} \gg 1$ the donor impurities are overtaken by the intrinsic generation

The majority carrier concentration as function of $1/T$ is given below:

*b2) Type- p semiconductors.*

Impurities from the III$^{rd}$ group e.g. *Al, Ga*. Extra levels in the gap close to $E_V$ as in the drawing below:



$N_a^-$ is the concentration of ionized acceptors, i.e. states filled with electrons. They obey a Fermi-Dirac statistics (up to a factor 2 in front of the exp):

$$N_a^- = \frac{N_a}{2\exp\left[\dfrac{E_A - E_F}{k_B T}\right] + 1}$$

The *neutrality condition* is $\boxed{n_p + N_a^- = p_p}$. Neglecting $n_p$

one finds the dependence $E_F(T)$ as in the figure above. The analytic results are obtained analogous to the case of the *n*-type scond. E.g. (QM2.55) becomes:

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$$E_F = E_A - kT \left\{ \frac{1}{4} \left( -1 + \sqrt{1 + \frac{8N_A}{N_V} \exp\left[ \frac{E_A - E_V}{kT} \right]} \right) \right\} \qquad \text{(QM2.57)}$$

E. g. for high $T$ $N_A^- = N_A$ and $n_i \gg N_A$:

$$E_F = E_A - kT \ln \left\{ \frac{N_A}{2N_V} \left( 1 + \sqrt{1 + \frac{4N_C N_V}{N_A^2} \exp\left[ -\frac{E_g}{kT} \right]} \right) \right\}$$

$$p_p = \frac{N_A}{2} \left( 1 + \sqrt{1 + \frac{4n_i^2}{N_A^2}} \right)$$