

Quantum Mechanics Lecture 6
Electron Spin Resonance; Pauli Equation; Zeeman effect

Basic notions of Electron Spin Resonance.

Consider a sample containing unpaired electrons which exert no forces on each other. Each electron has spin $1/2$ and an associated magnetic moment

$$\vec{M} = -g\mu_B\hat{S}/\hbar, \quad (1)$$

where $\mu_B = e\hbar/2m_e = 5.79 \cdot 10^{-4} \text{ eV T}^{-1}$ is the Bohr magneton, $\hat{S} = \hbar\vec{\sigma}/2$ is the electron spin operator with $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ and g is the Landé g -factor.

When the electron is in a magnetic field \vec{B} the interaction between the magnetic moment and \vec{B} gives rise to an energy

$$U = -\vec{M} \cdot \vec{B} = g\mu_B m_s B \quad (2)$$

where $m_s = \pm 1/2$ is the electron spin projection quantum number. The energy difference between the two levels is therefore

$$E = \delta U = g\mu_B B. \quad (3)$$

According to Boltzmann statistics the lower level is more highly populated if there is only the constant magnetic field. If in addition a magnetic field of high frequency ν (radio frequency or microwave frequency) is applied, then this oscillating field will induce transitions between the energy levels, provided that the frequency is tuned to satisfy the **resonance condition**

$$h\nu = E = g\mu_B B. \quad (4)$$

This will increase the population of the upper energy level and hence result in absorption of energy from the r.f. field if there are mechanisms of energy dissipation other than spontaneous and stimulated transitions back into the lower level. Such mechanisms are called **relaxation processes**. Dissipation *via* the thermal vibrations of the crystal lattice is called spin-lattice relaxation; another relaxation process results from the spin-spin interaction between unpaired electrons.

Quantum mechanics of the spin flip mechanism.

The quantum mechanics of the spin flip mechanism was first worked out by I. I. Rabi [1], who also applied the method to measure the magnetic moments of atomic nuclei [2]; it was this work for which Rabi was awarded the Nobel prize in Physics in 1944 [3]. The following derivation follows closely the one given in Ref. [1].

Consider an electron whose only degree of freedom is its spin. Its state of motion in a magnetic field $\vec{B} = (B_x, B_y, B_z)$ is then described by the Schrödinger equation

$$\begin{aligned} i\hbar\dot{\chi}(t) &= -\vec{M} \cdot \vec{B}\chi(t) \\ &= \frac{g}{2}\mu_B \begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix} \chi(t), \end{aligned} \quad (5)$$

where we have substituted \vec{M} from Eq. (1) and made use of the explicit form of the Pauli matrices,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (6)$$

Since the Hamiltonian of our system is a 2×2 matrix, the wave function must be a column matrix of two components:

$$\chi(t) = \begin{pmatrix} a(t) \\ b(t) \end{pmatrix}$$

Let the magnetic field consist of the superposition of a strong constant field B_0 in the z direction: $B_z = B_0$, and a gyrating much weaker field perpendicular to the z axis:

$$B_x = B_1 \cos \omega t, \quad B_y = B_1 \sin \omega t$$

Let us also define

$$\omega_0 = \frac{g}{2} \frac{\mu_B}{\hbar} B_0, \quad \omega_1 = \frac{g}{2} \frac{\mu_B}{\hbar} B_1$$

With these definitions Eq. (5) can be cast into the form

$$\dot{a} = -i\omega_0 a - i\omega_1 b e^{-i\omega t} \quad (7.a)$$

$$\dot{b} = i\omega_0 b - i\omega_1 a e^{i\omega t} \quad (7.b)$$

Suppose that at time $t = 0$ the electron occupies the lower energy level, which corresponds to its spin pointing in the negative z direction (“spin down”). We want to find the probability that at time $t > 0$ its spin points in the positive z direction (“spin up”) under the influence of the gyrating field. Mathematically this means that at $t = 0$ we have

$$\chi(0) = \begin{pmatrix} a(0) \\ b(0) \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (8)$$

The probability for spin-up at $t > 0$ is given by

$$P_{\uparrow} = |a(t)|^2. \quad (9)$$

Thus our task is to find $a(t)$ from Eqs. (7.a,7.b), *i.e.* we must eliminate b from the equation. This is accomplished in three steps: first we differentiate Eq. (7.a) w.r.t. time; this produces a term proportional to \dot{b} in the equation which we express in the second step in terms of a and b from Eq. (7.b). In the last step we express this remaining b in terms of a and \dot{a} from Eq. (7.a):

$$b = \frac{i}{\omega_1} (\dot{a} + i\omega_0 a) e^{i\omega t}. \quad (10)$$

As a result the factors $e^{-i\omega t}$ cancel and we end up with a second-order differential equation with constant coefficients for a :

$$\ddot{a} + i\omega \dot{a} + (\omega_1^2 + \omega_0^2 - \omega\omega_0) a = 0. \quad (11)$$

This equation has solutions of the form $a = e^{i\lambda t}$. Substituting, we get the characteristic equation

$$\lambda^2 + \omega\lambda - (\omega_1^2 + \omega_0^2 - \omega\omega_0) = 0,$$

whose roots are

$$\lambda_{\pm} = -\frac{\omega}{2} \pm \sqrt{\omega_1^2 + \left(\omega_0 - \frac{\omega}{2}\right)^2}.$$

The general solution is

$$a = c_1 e^{i\lambda_+ t} + c_2 e^{i\lambda_- t}$$

and hence with Eq. (10)

$$b = -\frac{1}{\omega_1} \left[c_1 (\lambda_+ + \omega_0) e^{i\lambda_+ t} + c_2 (\lambda_- + \omega_0) e^{i\lambda_- t} \right] e^{i\omega t},$$

where c_1 and c_2 are integration constants to be determined from the initial conditions (8). The first one of these, $a(0) = 0$, yields $c_2 = -c_1$, and hence we get from the second one $c_1 = -\frac{\omega_1}{2\delta}$,

where $\delta = \sqrt{\omega_1^2 + \left(\omega_0 - \frac{\omega}{2}\right)^2}$, hence

$$a = -i \frac{\omega_1}{\delta} e^{-i\omega t/2} \sin \delta t$$

and finally the probability (9):

$$P_{\uparrow} = |a(t)|^2 = \frac{\omega_1^2}{\omega_1^2 + \left(\omega_0 - \frac{\omega}{2}\right)^2} \sin^2 \delta t. \quad (12)$$

Averaged over time the sine-square factor is $1/2$. If we assume that all the energy absorbed from the oscillating r.f. field is instantly dissipated through relaxation processes, then the absorbed energy is proportional to

$$\frac{\omega_1^2}{\omega_1^2 + \left(\omega_0 - \frac{\omega}{2}\right)^2},$$

which is small (because of the choice $\omega_1 \ll \omega, \omega_0$) unless $\omega \approx 2\omega_0$. At $\omega = 2\omega_0$ the probability has a sharp maximum. Such a maximum is referred to as a *resonance*. We also note that the condition $\omega = 2\omega_0$ is identical with the resonance condition (4), *i.e.* our result is consistent with the preliminary discussion in section 1.

It is interesting to note that a magnetic field gyrating in the opposite direction to that chosen above does not give rise to a resonance. Indeed, the opposite sense of gyration can be expressed formally by changing the sign of ω in Eqs. (7.a) and (7.b). This results in replacing ω by $-\omega$ in Eq. (12), *i.e.* no resonance occurs.

In ESR experiments it is usual to apply linearly polarised oscillating fields. A linearly polarised field can be understood as the superposition of two fields gyrating in opposite directions. From the preceding derivation we see that only one component of the linearly polarised field gives rise to the resonance effect.

Pauli Equation.

The Pauli equation is the equation for the electron with spin. Its charge is $-e$, its mass is m_e , its spin is $\vec{S} = \frac{1}{2}\hbar\vec{\sigma}$, and its magnetic moment is

$$\vec{M} = -2\mu_B\vec{S}$$

where μ_B is the Bohr magneton.

In a magnetic field \vec{B} , the magnetic moment gives rise to an energy

$$-\vec{M} \cdot \vec{B} = \mu_B \vec{\sigma} \cdot \vec{B}$$

and we note that this is a 2×2 matrix.

The Hamiltonian is now

$$\hat{H} = \frac{1}{2m_e} (\hat{p} + e\vec{A})^2 - eV + U + \mu_B \vec{\sigma} \cdot \vec{B}$$

To make sense mathematically, the first three terms are understood to be multiplied into the unit 2×2 matrix.

The wave function must now be a column matrix: we write

$$\Psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

and hence the Pauli equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \tag{13}$$

In evaluating $(\hat{p} - e\vec{A})^2$ we must remember the fundamental commutation relations. We have

$$(\hat{p} - e\vec{A})^2 = (\hat{p}_x - eA_x)^2 + (\hat{p}_y - eA_y)^2 + (\hat{p}_z - eA_z)^2$$

and

$$\begin{aligned} (\hat{p}_x - eA_x)^2 &= (\hat{p}_x - eA_x)(\hat{p}_x - eA_x) \\ &= \hat{p}_x^2 - e(A_x\hat{p}_x + \hat{p}_xA_x) + e^2 A_x^2 \end{aligned}$$

hence

$$(\hat{p} - e\vec{A})^2 = \hat{p}^2 - e\vec{A} \cdot \hat{p} + i\hbar e \nabla \cdot \vec{A} + e^2 A^2$$

The term proportional to A^2 is negligibly small except in certain stars with gigantic magnetic fields. In applications to atomic, nuclear and solid state physics this term can be safely neglected.

Splitting of spectral lines in a magnetic field (*Zeeman effect*)

Consider the atom in a constant homogeneous magnetic field $\vec{B} = (0, 0, B)$. The vector potential can be chosen as

$$\vec{A} = \frac{1}{2}B(-y, x, 0)$$

Then, omitting the term proportional to A^2 and dropping the potential U , we get

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}_0 \Psi + \frac{1}{2} \frac{\mu_B}{\hbar} B (\hat{L}_z + \hbar \sigma_z) \Psi$$

where

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e} \nabla^2 + V(r)$$

and

$$\hat{L}_z = -i\hbar(x\partial_y - y\partial_x)$$

is the z component of the orbital angular momentum operator.

For stationary states we have

$$\Psi(\mathbf{r}, t) = \Psi(\mathbf{r}) e^{-iEt/\hbar}$$

and hence

$$\hat{H}_0 \Psi(\mathbf{r}) + \mu_B B (\hat{L}_z + \sigma_z) \Psi(\mathbf{r}) = E \Psi(\mathbf{r})$$

Without the spin term, the equation breaks up into two identical equations for ψ_1 and ψ_2 . But with

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

we have two equations which are slightly different:

$$\begin{aligned} \hat{H}_0 \psi_1 + \frac{\mu_B}{\hbar} B (\hat{L}_z + \hbar) \psi_1 &= E \psi_1 \\ \hat{H}_0 \psi_2 + \frac{\mu_B}{\hbar} B (\hat{L}_z - \hbar) \psi_2 &= E \psi_2 \end{aligned}$$

Substituting for $\psi_{1,2}$ the hydrogen wave function, we get

$$E_{nm}^{(\pm)} = E_n + \mu_B B (m \pm 1)$$

where m is the orbital magnetic quantum number. Thus the energy eigenvalues now depend not only on the principal quantum number n but also on the magnetic quantum number m . Moreover, the s term ($\ell = 0, m = 0$) is also split by the interaction of the magnetic moment of the electron with the magnetic field.

The splitting of the p term ($\ell = 1, m = 0, \pm 1$) is into three levels for each spin orientation. Corresponding to the increased number of energy levels one observes also more spectral lines.

However, not all transitions between the sublevels are allowed but only transitions for which m remains unchanged or changes by $+1$ or -1 and m_s does not change. These **selection rules** find their explanation at a more advanced level of quantum mechanics.

Thus, taking account of the selection rules, the spectral lines corresponding to transitions between the $1s$ and the $2p$ levels are split into three lines by the magnetic field as shown in the figure. This is the **normal Zeeman effect**.

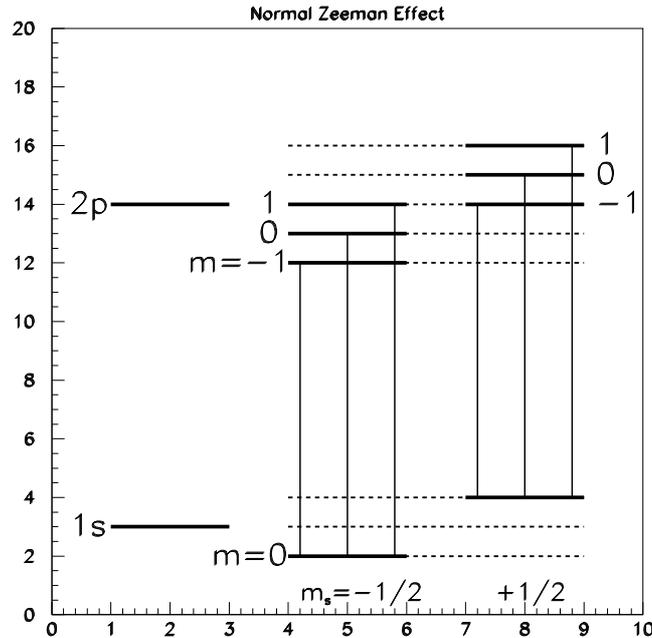


Figure 1: Splitting of 1s and 2p levels in magnetic field

Identical particles.

Identical particles are particles which have the same mass, charge, spin and possibly other properties. Examples are electrons, protons, α particles.

The description of systems of identical particles is different in classical mechanics and in quantum mechanics.

In classical mechanics, to solve the equations of motion, the positions and velocities of all particles must be precisely given at an initial instant of time. At that moment we can therefore distinguish the particles by their positions and velocities. We can for instance number the particles: particle 1, particle 2, *etc.*, particle N . By solving the equations of motion we get the trajectories of all particles. Each particle has its trajectory by which we can tell its position at a later time. We can therefore number the trajectories with the corresponding particle numbers. In this way identical particles can be distinguished in classical mechanics at all times.

In quantum mechanics the situation is different. Here we cannot assign definite positions and velocities to the particles at any time. By Heisenberg's uncertainty principle, the uncertainties of coordinates Δx and momenta Δp_x are related by the inequality

$$\Delta x \Delta p_x \geq h$$

where h is Planck's constant. We can only assign wave functions $\psi(x, t)$ to the particles such that $|\psi(x, t)|^2 dx$ is the probability of finding the particle at time t between x and $x + dx$, and similarly in three dimensions.

If we have two particles we may be able to prepare them such that initially the wave function of one of them is nonzero in a region of space A and the other wave function is nonzero in B , where A and B do not overlap.

If the wave function is localised in space, one says that it represents a **wave packet**. So the situation just described is one where the wave packets of the two particles do not overlap.

In the course of time the wave packets spread and sooner or later they will overlap. Then it is impossible to tell which particle we observe in the overlap region, the one that was initially in A or the one that was in B .

This discussion leads to the general notion of the *indistinguishability* of identical particles. We shall now see how this principle is realised in the mathematical formulation of the quantum mechanics of systems of particles.

Consider a system of two electrons. We can write their Hamiltonian in the following form (ignoring spin for the moment):

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 + V(\mathbf{r}_1) + V(\mathbf{r}_2) + V(|\mathbf{r}_1 - \mathbf{r}_2|)$$

where $\nabla_1 = (\partial/\partial x_1, \partial/\partial y_1, \partial/\partial z_1)$ and similarly for ∇_2 . This Hamiltonian is unchanged if we exchange the coordinates of the electrons, thus

$$\hat{H}(\mathbf{r}_2, \mathbf{r}_1) = \hat{H}(\mathbf{r}_1, \mathbf{r}_2)$$

If we include the electron spins into their sets of coordinates, we can write for instance $q_1 = (x_1, y_1, z_1, m_{s1})$ for the set of coordinates of electron 1, and similarly for electron 2. Then the indistinguishability of electrons means that

$$\hat{H}(q_2, q_1) = \hat{H}(q_1, q_2) \quad (14)$$

Now let us define an operator that exchanges the two electrons:

$$\hat{P}(1, 2)f(q_1, q_2) = f(q_2, q_1) \quad (15)$$

where $f(q_1, q_2)$ is any function of the coordinates q_1 and q_2 , which can be an ordinary function or an operator, like $\hat{H}(q_1, q_2)$.

The operator $\hat{P}(1, 2)$ is linear:

$$\hat{P}(1, 2)[f(q_1, q_2) + g(q_1, q_2)] = \hat{P}(1, 2)f(q_1, q_2) + \hat{P}(1, 2)g(q_1, q_2)$$

and

$$\hat{P}(1, 2)(cf(q_1, q_2)) = c\hat{P}(1, 2)f(q_1, q_2)$$

where c is any complex constant.

If we apply $\hat{P}(1, 2)$ to $f(q_2, q_1)$, then we get back to $f(q_1, q_2)$; therefore

$$\hat{P}^2(1, 2)f(q_1, q_2) = f(q_1, q_2)$$

Now let us write an eigenvalue equation for $\hat{P}(1, 2)$:

$$\hat{P}(1, 2)f(q_1, q_2) = \lambda f(q_1, q_2) \quad (16)$$

then

$$\hat{P}(1, 2)^2 f(q_1, q_2) = \lambda^2 f(q_1, q_2)$$

and hence $\lambda^2 = 1$ or $\lambda = \pm 1$. Thus $\hat{P}(1, 2)$ has only real eigenvalues; it is therefore hermitian, *i.e.* an observable.

$\hat{P}(1, 2)$ commutes with the Hamiltonian $\hat{H}(q_1, q_2)$; indeed:

$$\hat{P}(1, 2)\hat{H}(q_1, q_2)f(q_1, q_2) = \hat{H}(q_2, q_1)\hat{P}(1, 2)f(q_1, q_2)$$

and hence by virtue of Eq. (14) we have

$$\left[\hat{P}(1, 2)\hat{H}(q_1, q_2) - \hat{H}(q_1, q_2)\hat{P}(1, 2) \right] f(q_1, q_2) = 0$$

which we write as an operator equation in the usual notation:

$$[\hat{P}(1, 2), \hat{H}(q_1, q_2)] = 0$$

On general grounds we know that an observable that commutes with the Hamiltonian is a conserved observable.

We need a physical interpretation of the property represented by $\hat{P}(1, 2)$. This can be found if we consider the definition of \hat{P} , Eq. (15), with the eigenvalue equation (16), in which we set $\lambda = \pm 1$ and understand the function $f(q_1, q_2)$ to be an eigenfunction ψ of \hat{H} :

$$\hat{P}(1, 2)\psi(q_1, q_2) = \psi(q_2, q_1) = \pm\psi(q_1, q_2)$$

This means that the wave function of the two-particle system is either symmetric or anti-symmetric under interchange of the two electrons. Since \hat{P} is conserved, this property persists in time; we could therefore have written everywhere $\psi(q_1, q_2, t)$ instead of the time-independent wave function.

Moreover, the two-electron system can be described only by either a symmetric or an anti-symmetric wave function. To see this let us denote the symmetric wave function by ψ^S and the anti-symmetric wave function by ψ^A . Then, if the two-electron system could be in either state, then it could also be in a state given by a superposition of ψ^A and ψ^S

$$\psi = a\psi^A + b\psi^S$$

but this unsymmetric state is not an eigenstate of \hat{P} , so it cannot be a wave function of the two-electron system.

So far I have always called the particle **electron**. But the argument did not make use of any specific property of the electron. We can therefore equally apply our reasoning to other sets of identical particles, protons, π^+ mesons, α particles and so on.

Particles, whose two-particle wave function is symmetric, are called **bosons**; particles, whose two-particle wave function is anti-symmetric, are called **fermions**.

The decision whether electrons are fermions or bosons can come only from experiment. The answer is that electrons are fermions. More generally, all particles of spin 1/2 are fermions. All particles with spins 0 or 1 are bosons. The antiparticles of spin-1/2 fermions are spin-1/2 fermions, and the antiparticles of spin-0 (or of spin 1) bosons are spin 0 (or spin 1) bosons.

We can show that two identical fermions cannot be in the same state. Indeed, consider the two-electron wave function $\psi(q_1, q_2)$. Since electrons are fermions, we have

$$\psi(q_2, q_1) = -\psi(q_1, q_2)$$

For the two electrons to be in the same state we have to put $q_2 = q_1$, and then we get

$$\psi(q_1, q_1) = 0$$

in other words this state does not exist. This result is essentially the statement of the **Pauli exclusion principle**.

Obviously no such principle applies to bosons.

Our results, obtained for two-particle systems, can be easily extended to systems of N identical particles. In that case we write the Hamiltonian in the general form of

$$\hat{H}(q_1, \dots, q_j, \dots, q_k, \dots, q_N, t)$$

and similarly for the wave function. In particular, we conclude that the wave function of a system of N identical fermions is antisymmetric under the exchange of any two particles:

$$\begin{aligned} &\psi(q_1, \dots, q_j, \dots, q_k, \dots, q_N, t) \\ &= -\psi(q_1, \dots, q_k, \dots, q_j, \dots, q_N, t) \end{aligned}$$

where the ellipses stand for coordinates unchanged under the transformation.

Another extension of our discussion is to composite systems containing nonidentical particles. A simple system of this kind is the hydrogen atom, which consists of a proton and an electron. Its wave function is therefore a function of the coordinates and spins of the proton and the electron. The question we want to answer is whether the hydrogen atom is a fermion, a boson or neither. To find this answer we must consider two hydrogen atoms. Its wave function depends on the coordinates of both protons, Q_1 and Q_2 , and of both electrons, q_1 and q_2 , which again are supposed to include the spins as well as the spatial coordinates:

$$\psi = \psi(Q_1, Q_2, q_1, q_2)$$

Now since the electrons are fermions, we have

$$\psi(Q_1, Q_2, q_2, q_1) = -\psi(Q_1, Q_2, q_1, q_2)$$

and since the protons are fermions we have

$$\psi(Q_2, Q_1, q_1, q_2) = -\psi(Q_1, Q_2, q_1, q_2)$$

But to exchange the two hydrogen atoms we must exchange both electrons and protons, and that means that the wave function of the two-hydrogen atom system is symmetric:

$$\psi(Q_2, Q_1, q_2, q_1) = \psi(Q_1, Q_2, q_1, q_2)$$

i.e. the hydrogen atom is a boson.

Similarly we can show that the α particle is a boson: it consists of two protons and two neutrons, and applying the same reasoning as above we get the result. In fact, the total spin of the hydrogen atom is known to be zero, which is another way of seeing that it is a boson.

Moreover, it also follows by extension that all microscopic particles, simple or composite, are either fermions or bosons, and there are no particles which are neither.

The structure of atoms.

From the Rutherford experiment it is known that atoms consist of a nucleus of positive charge surrounded by an electron cloud. To solve the Schrödinger equation for an atom of several electrons poses great computational difficulties. Even in the simplest case beyond the hydrogen atom, namely helium, one has to resort to some method of approximate solution, perturbation theory or the variational principle, to find good agreement with observed spectra.

However, we can make a number of statements concerning the structure of atoms without solving the Schrödinger equation, just on the strength of the Pauli exclusion principle.

Recall that the physical state of a particle can be described not only by its coordinates but by other sets of variables. In the case of a single particle we can specify its energy E , total angular momentum \hat{L}^2 and projection of angular momentum \hat{L}_z . If the particle is in a bound state, then the energy is quantised and we write E_n for the n th energy level. Then it is convenient to characterise the state of the particle by the quantum numbers n , ℓ and m . If the

particle has a non-zero spin, then the complete description of its state must include the spin magnetic quantum number m_s .

Thus the state of an electron is described by the set of quantum numbers n , ℓ , m and $m_s = \pm 1/2$. Then we can express the exclusion principle by saying that no two electrons can have the same set of these four quantum numbers.

Of course, we should be careful with this statement. We must remember that the wave functions of the two electrons have a certain spatial extension. The exclusion principle applies of course only to electrons whose wave functions have a significant amount of overlap, not if they are separated by a macroscopic distance.

Now consider an atom of atomic number Z . We may ask how the Z electrons are distributed in the atom. We shall answer this question in terms of the sets of quantum numbers (n, ℓ, m, m_s) of each of the electrons. Such a set of quantum numbers is called **orbital**. Recall that $n = 1, 2, 3, \dots$, $\ell = 0, 1, 2, \dots, n - 1$, and $m = 0, \pm 1, \dots, \pm \ell$. Thus in the ground state we can have two electrons: one with orbital $(1, 0, 0, +1/2)$ and the other with orbital $(1, 0, 0, -1/2)$. This is called the *K* shell. The next higher shell is the *L* shell with $n = 2$. It is a simple exercise in counting to see that there can be eight electrons in the *L* shell, 18 electrons in the *M* shell ($n = 3$) *etc.*

Consider the oxygen atom. Its atomic number is $Z = 8$. In the ground state it has two electrons in the *K* shell and 6 in the *L* shell. Thus the *L* shell is not completely filled. This gap in the *L* shell determines the chemical affinity of oxygen.

To specify the electronic structure of the elements, one uses the following notation for the orbitals:

put first the **principle quantum number** n , followed by the conventional symbol for the **azimuthal quantum number** ℓ :

$$s, p, d, f, \dots \text{ for } \ell = 0, 1, 2, 3, \dots,$$

and a superscript for the number of electrons in the shell.

Thus the electronic structure of hydrogen is $1s$, that of helium is $1s^2$, and that of oxygen is $1s^2 2s^2 2p^4$.

Without the Pauli exclusion principle there would be none of this structure. Instead all electrons would be in the *K* shell with mean radius $\langle r \rangle_{n=1, \ell=0} = 3a/2Z$ and hence all atoms would be much smaller than they actually are. But much more important, the elements would have nothing like the chemical properties we know, and as a consequence we would not exist.

Identifying the β^- particle.

The discovery of radioactivity was made roughly at the same time as the discovery of the electron. One type of radioactive emission, β rays, were soon found to consist of negatively charged particles. The study of the properties showed that the β^- particles had properties very similar to those of the electrons. However, the experimental errors in the determination of their masses could not completely rule out the possibility that they were different if very similar particles. Then in 1948, Maurice Goldhaber and his wife found a way to demonstrate conclusively that the β^- particle was identical to the electron. Their experiment was a beautiful application of the exclusion principle.

They exposed a piece of lead to β^- particles from a radioactive source. If the β^- particles were not identical with electrons, then the β^- should get captured by a lead atom and make transitions between the shells all the way down to the *K* shell. Each transition had to be accompanied by the emission of a photon of x-ray wave length. This x-ray spectrum is easily

calculable and quite comfortably observable. On the other hand, if the β^- particle were identical with the electron, then the Pauli exclusion principle would not allow it to enter the atom. Not surprisingly, none of the x-ray signal was observed. The β^- particle was conclusively demonstrated to be identical with the electron.

References

- [1] I. I. Rabi, "Space Quantization in a Gyating Magnetic Field", Phys. Rev. **51** (1937) 652.
- [2] I. I. Rabi *et al.*, Phys. Rev. **55** (1939) 526.
- [3] The citation of the Nobel Prize award to I. I. Rabi reads:
"for his resonance method for recording the magnetic properties of atomic nuclei."
(*"Nobel Lectures in Physics"*, 1942-1962, Elsevier, 1964)
E. Hulthén in his presentation of Rabi's work observes:
"By this method Rabi has literally established radio relations with the most subtile particles of matter, with the world of the electron and of the atomic nucleus."