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Pauli Exclusion Principle

Here we will discus few important concepts of quantum many-body theory because atoms and molecules are many-body systems.

We will mainly ignore the interactions between electrons and only consider their Coulomb repulsion by empirical rules.

Suppose two identical particle system (e.g., two electrons in a Helium atom) and their wavefunction is $\psi(x_1; x_2)$; where x_i is the coordinate of the ith particle, e.g., $x = (r,\sigma)$ with r the spatial position and $\sigma = \uparrow,\downarrow$ the spin of the particle.

Let ay the exchange operation $\hat{P}$: exchanging the coordinates of the two particles,

$$\hat{P}_{1\leftrightarrow 2}\psi(x_1, x_2) = \psi(x_2, x_1)$$

If we choose ψ(x_1, x_2) as an eigenstate of $\hat{P}_{1\leftrightarrow 2}$ with eigenvalue p; then the eigenequation is

$$\hat{P}_{1\leftrightarrow 2}\psi\left(x_1, x_2\right) = p\psi\left(x_1, x_2\right)$$

Applying $\hat{P}_{1\leftrightarrow 2}$ second time we get back to the original state, i.e.,

$$p^2\psi\left(x_1, x_2\right) = \psi\left(x_1, x_2\right), \quad \text{or } p^2 = 1$$

Therefore, p can only has two values, p = ±1

The quantum particles with p = 1 are referred to as Boson particles, or simply Bosons and the quantum particles with p = -1 are referred to as Fermion particles, or simply Fermions.

A more general analysis shows that with integer spin are always Bosons, and particles with half-odd-integer spins are always Fermions.

For example,
electrons and protons are Fermions, and photons (light quanta) are Bosons; Helium-4 is Boson because its spin is zero, but Helium-3 atom is Fermion with spin 1/2.

For a general quantum many-body wavefunction, the exchange operation is

$$\hat{P}_{n \leftrightarrow m} \psi(\cdots, x_n, \cdots, x_m, \cdots) = \pm \psi(\cdots, x_m, \cdots, x_n, \cdots)$$

where + corresponds to Boson system, and   to Fermion system. This is a exact property of a quantum many-body system.

A general Hamiltonian of N-particle system is

$$\hat{H} = \sum_{i=1}^{N} \hat{H}_i + \hat{V}$$

Where $\hat{V}$ is the interaction potential and usually given by

$$\hat{V} = \frac{1}{2} \sum_{i \neq j}^{N} V(\mathbf{r}_{ij})$$

For example,

$$\hat{V} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}}$$ for helium atom and

$$\hat{V} = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right)$$ for lithium

Now consider the simplest approximation by ignoring $\hat{V}$, (the corresponding wavefunction is the zero-order approximation to the true eigenstate), the Hamiltonian becomes separate

$$\hat{H} \approx \sum_{i=1}^{N} \hat{H}_i$$

and the wavefunction becomes a product of single particle states. In general, we refer to such approximation as the independent-particle approximation. The essence of this approximation is to keep the quantum nature of particles but ignoring their dynamic interactions (later, we will see some corrections due to Coulomb repulsion by empirical Hund's rule).

Assume that we have solved the single-particle Schrodinger equation

$$\hat{H}_1 \Phi_k (x_1) = E_k \Phi_k (x_1)$$

The total wavefunction may be written as (not taking the exchange symmetry into account)

$$\Psi (x_1, x_2, \cdots, x_N) \propto \Phi_{k1} (x_1) \Phi_{k2} (x_2) \cdots \Phi_{kN} (x_N)$$

In order to include this important quantum symmetry, consider first a 2-particle system, N = 2

For Bosons,

$$\psi_B (x_1, x_2) = \frac{1}{\sqrt{2}} \left[\varphi_{n_1}(x_1)\varphi_{n_2}(x_2) + \varphi_{n_1}(x_2)\varphi_{n_2}(x_1) \right]$$

and for Fermions,

$$\psi_F (x_1, x_2) = \frac{1}{\sqrt{2}} \left[\varphi_{n_1}(x_1)\varphi_{n_2}(x_2) - \varphi_{n_1}(x_2)\varphi_{n_2}(x_1) \right]$$

so that $\psi_B(x_1, x_2) = \psi_B(x_2, x_1)$ for Bosons and $\psi_F(x_1, x_2) = -\psi_F(x_2, x_1)$ for Fermions.

One can also construct a symmetric wavefunction for two Bosons by a single wavefunction as

$$\psi_B(x_1, x_2) = \varphi_{n_1}(x_1)\varphi_{n_1}(x_2), \text{ or } \varphi_{n_2}(x_1)\varphi_{n_2}(x_2).$$

Extending to N-particle system, for the Fermions, we can write the wavefunction as a determinant, called Slater determinant,

$$\psi(x_1, \cdots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{n_1}(x_1) & \varphi_{n_1}(x_2) & \cdots & \varphi_{n_1}(x_N) \\ \varphi_{n_2}(x_1) & \varphi_{n_2}(x_2) & \cdots & \varphi_{n_2}(x_N) \\ \cdots & & & \\ \varphi_{n_N}(x_1) & \varphi_{n_N}(x_2) & \cdots & \varphi_{n_N}(x_N) \end{vmatrix}.$$

Notice that if $k_1 = k_2$, $\psi_F(x_2, x_1) = 0$, but not $\psi_B(x_1, x_2)$. This indicates that two Fermions cannot occupy the same state, but it two bosons are allowed to occupy the same state. It can be extended to a more general statements:

1) A state can only be occupied by at most a single Fermion

2) But it can be occupied by any number of Bosons

The first above statement is Pauli exclusion principle.

The second statement is the property that leads to the so-called Bose-Einstein condensation of bosons at low temperature.

As active ingredients in atoms and molecules are electrons which are fermions, we will mainly use Pauli principle.

It is obvious that in the independent particle approximation (e.g., ignoring particle interactions), the ground state of an N-electron system is given by the Slater determinant constructed from the lowest N single particle states.

For atoms, these single particles states are naturally the eigenstates of hydrogen like atoms as we discussed previously. For molecules, these single particle states are constructed by a linear combinations of atomic states at different nuclear congurations.

Sometimes it is convenient to separate total wavefunction as discussed above into product of spatial and spin parts of wavefunctions, namely

$$\Psi(x_1, \cdots, x_N) = \psi(\mathbf{r_1}, \cdots, \mathbf{r_N})\chi(\sigma_1, \cdots, \sigma_N).$$

Hence, if spin wavefunction χ is antisymmetric, the spatial wavefucntion ψ must be symmetric in order for the total wavefunction $\mathbf{\psi}$ to be antisymmetric, vice versa.

Now we apply this simple analysis to atoms, the elements on the periodical table, where the identical fermions are electrons with spin -1/2. We will qualitatively discuss the ground states of the atoms.

By solving the Schrodinger equation of hydrogenlike atoms in the previous section, we know the electron's states in an atom can be characterized by four quantum numbers (n, l, m, m_s):

n - principle quantum number specified main energy levels (shells),

l - (orbital) angular momentum quantum number,

m - (orbital) magnetic quantum number and

m_s - spin magnetic quantum number.

We extend this to many-electron's state ignoring the interactions, spin-orbit couplings, etc., by using the independent-particle approximation. Using notation

l = 0 → s state; 1 → p state; 2 → d state ---

Noticing m and m_s are degenerate quantum numbers, we conclude that *s* shell can take up to two electrons (single orbital with m = 0 but one electron with spin up m_s = 1/2, the other electron with spin down ms = -1/2); *p* shell can take up to 6 electrons (three states specied by m = 1, 0,-1, each can take one electron with spin up and one electron with spin down); *d* shell can take up to 10 electrons (5 states
with m = 2, 1, 0, -1, -2, each can take two electrons), etc. These energy levels are ordered as,

orbitals (shells) :	1*s*	2*s*	2*p*	3*s*	3*p*	4*s*	3*d*	4*p*	5*s*	···
electron no. :	2	4	10	12	18	20	30	36	38	···

In the above table, we also list total possible maximal number of electrons

In this independent-particle picture, the way each electron of an atom occupies a particular hydrogen state is called **electron configuration**. As we are mainly interested in the ground state, the electron conguration of an atom is given by filling these hydrogen orbitals from the lowest, in the ordered series as

$$(1s)(2s)(2p)(3s)(3p)(4s)(3d)(4p)(5s)\cdots.$$

We notice that a given electron configuration will not uniquely determine some basic properties (such as total angular momentum, spins etc.) of the corresponding atom. More information can be specied by using the so called atomic spectral term (or atomic term) to represent states of an atoms.

Some correction to independent-particle approximation for the ground-state atomic term due to Coulomb repulsion will be considered by the empirical rules.

Atomic spectral terms:

We use notation $^{(2S+1)}L_J$ to denote a particular atomic state where S is its total spin, L is its total orbital angular momentum and J the total angular momentum (spins and orbitals). We use capital Latin letters for each value of orbital quantum number as

$$L = \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 10 \quad \cdots$$
$$\quad\quad S \quad P \quad D \quad F \quad G \quad H \quad I \quad K \quad L \quad M \quad N \quad \cdots$$

For example, $^2P_{3/2}$ denotes levels with L = 1; S = 1/2 and J = 3/2. The difference in energy between atomic levels having different L and S but the same electron configuration is due to repulsive Coulomb interaction between electrons. These energy differences are small

We have the following empirical Hund's rules (F. Hund, 1925) concerning relative position of levels with the same configuration but different L and S:

(i) For a given shell (configuration), the term with greatest possible value of S gives the lowest energy;
(ii) The greatest possible value of L (for this S) has the lowest energy;
(iii) For half or less than half filling shell, J = │L-S│ gives lowest energy; For more than half-filling shell, J = L + S gives lowest energy.

The origin of the first rule is obvious: the largest total spin corresponds to symmetric (parallel) spin wavefunction and antisymmetric orbital wavefunction, the later reduces electron-electron repulsive interaction energy.

Example 1. Helium (Z = 2) has a simple conguration $(1s)^2$. Hence S = 0 and L = 0. The ground state term is $^1S_0$ with J = 0.

Example 2. Carbon (Z = 6) has electron configuration as $(1s)^2(2s)^2(2p)^2$. There are three p orbitals with m = 1, 0,-1 as l = 1. Two electrons with both spin equal to 1/2 (corresponding to total largest spin S = 1) are in orbital m = 1, 0 with total maximal M = 1+0 =1, corresponding to L = 1. Hence the ground state term is $^3P_0$. It is less than half-filling, J = $\left|L - S\right|$ = 0.
The other two possible terms are ^1S and ^1D. They correspond to higher energies. Do you know how to obtain these
terms? Hint: Use symmetry argument.

Reference:

1) Molecular Quantum mechanics, Atkins and Friedman, 4th edition

2) Physical Chemistry by K. L. Kapoor

3) Physical Chemistry by Levine