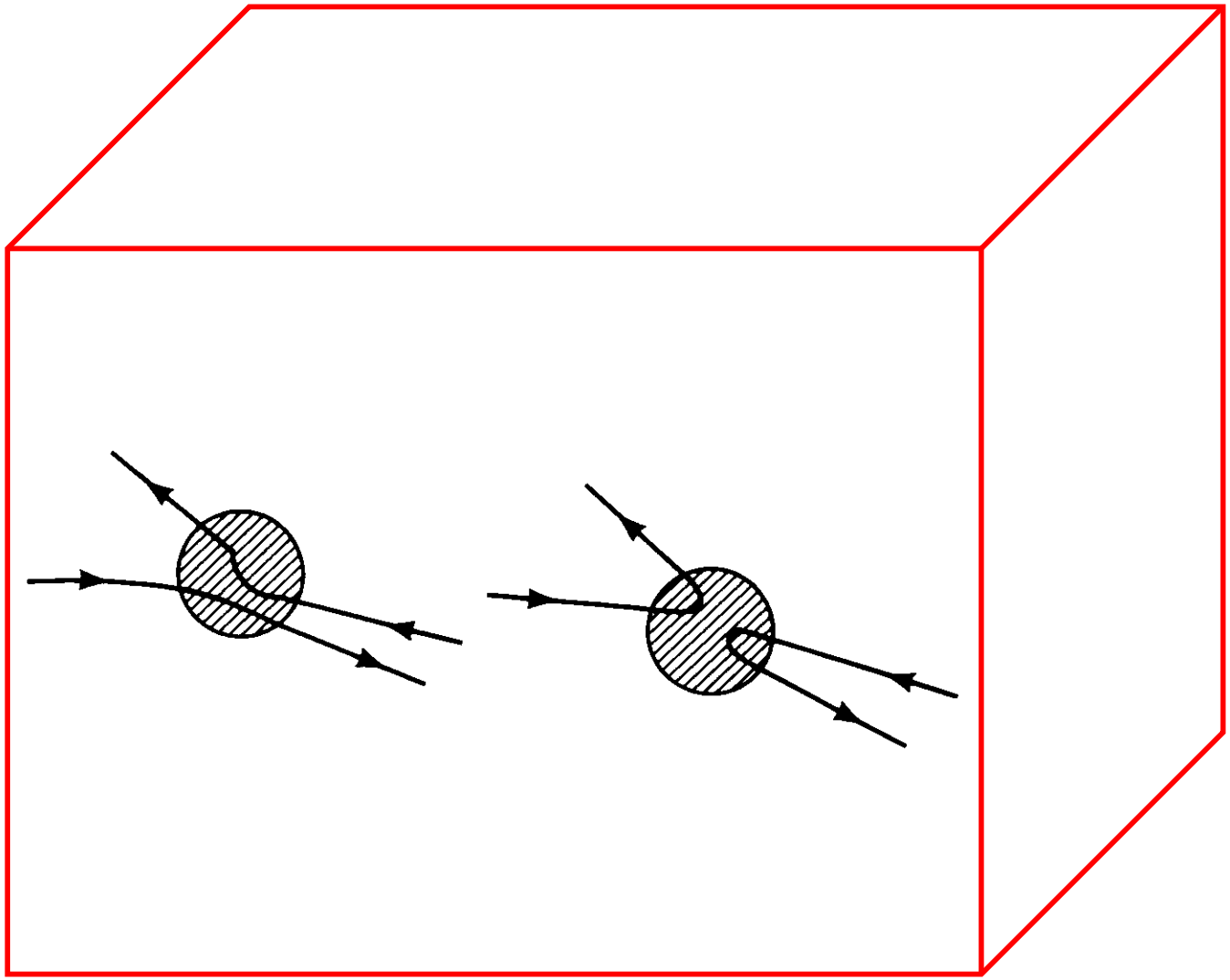
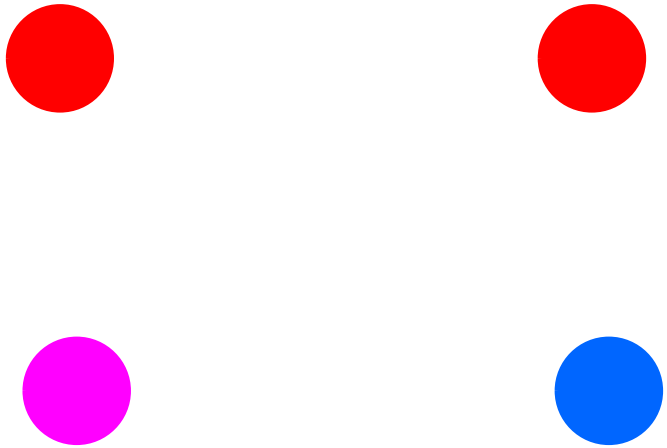
Identical Particles

Consider N identical particles confined in a hard box.



Two different paths, (a) and (b), of a two-electron system, in which we cannot assert even in principle through which of the paths the electrons pass.

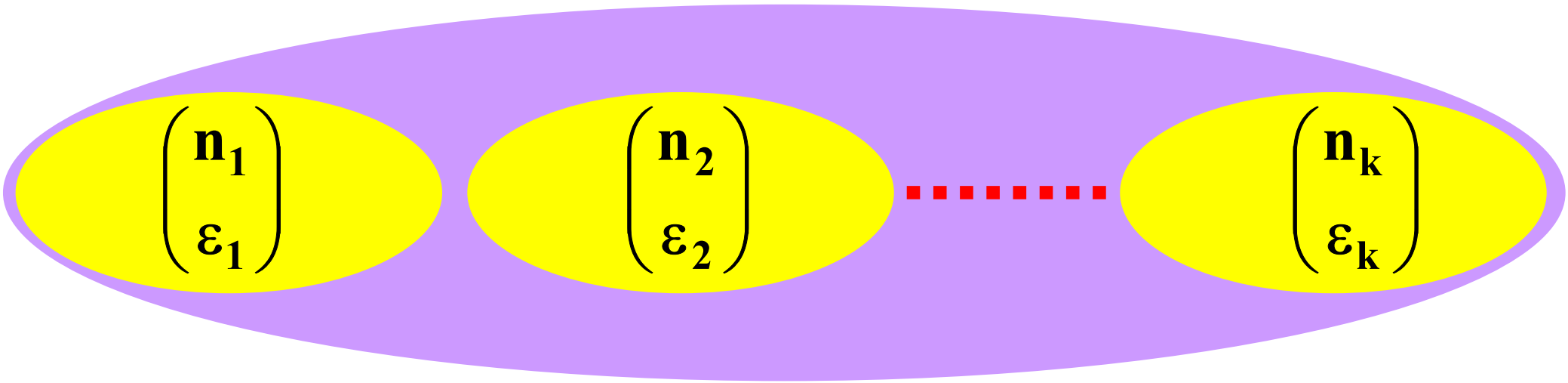
In quantum mechanics the particles constituting the given system are not only identical but also indistinguishable.



accordingly, it is unphysical to label them as No. 1, No. 2, No. 3, etc., and to speak of their being individually in the various single-particle states ε_i.

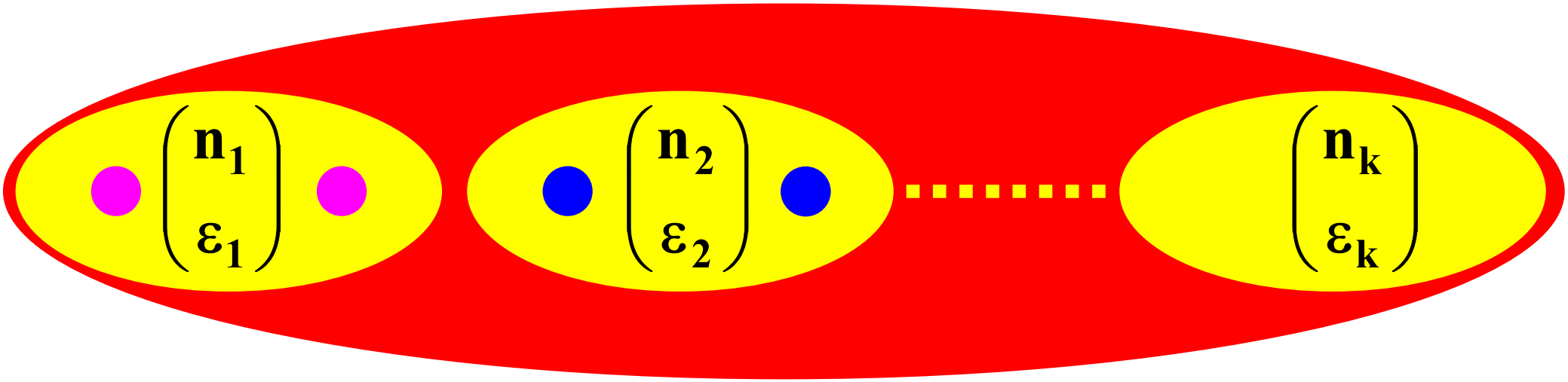
All we can sensibly speak of is their distribution over the states ε_i by numbers, e.g. n_1 particles being in the state ε_1, n_2 in the state ε_2, and so on.

$$\mathbf{E} = \sum_{\mathbf{i}} \mathbf{n_i \varepsilon_i}$$



Thus, the correct way of specifying a microstate of the system is through the distribution numbers $\{n_i\}$, and not through the statement as to "which particle is in which state".

To elaborate the point, we may say that if we consider two microstates which differ from one another merely in an interchange of two particles in different energy states,



then according to our original mode of counting we would regard these microstates as distinct; in view of the indistinguishability of the particles, however, these microstates are not distinct (for, physically, there exists no way of distinguishing between them).

$$C(m,n) = \binom{n}{m} = \frac{n!}{m!(n-m)!}$$

ترکیب که در آن نظم یا ترتیب اهمیت ندارد.

تمایزناپذیری ذرات

مکانیک کوانتمی

$$P(m,n) = (n)_m = \frac{n!}{(n-m)!}$$

ترتیب که در آن نظم یا ترتیب اهمیت دارد.

تمایزپذیری ذرات

مکانیک کلاسیک

به چند طریق می توان دو تا از سه تا عدد 3و2و1 را کنار هم نوشت؟

1, 2, 3

1 $\begin{Bmatrix} 1 & 2 & 1 \\ 2 & 1 & 2 \end{Bmatrix}$

2 $\begin{Bmatrix} 1 & 3 & 3 \\ 3 & 1 & 4 \end{Bmatrix}$

3 $\begin{Bmatrix} 2 & 3 & 5 \\ 3 & 2 & 6 \end{Bmatrix}$

$$C(m,n) = \binom{n}{m} = C(2,3) = \binom{3}{2} = \frac{3!}{2!(3-2)!} = 3$$

تمایز ناپذیر

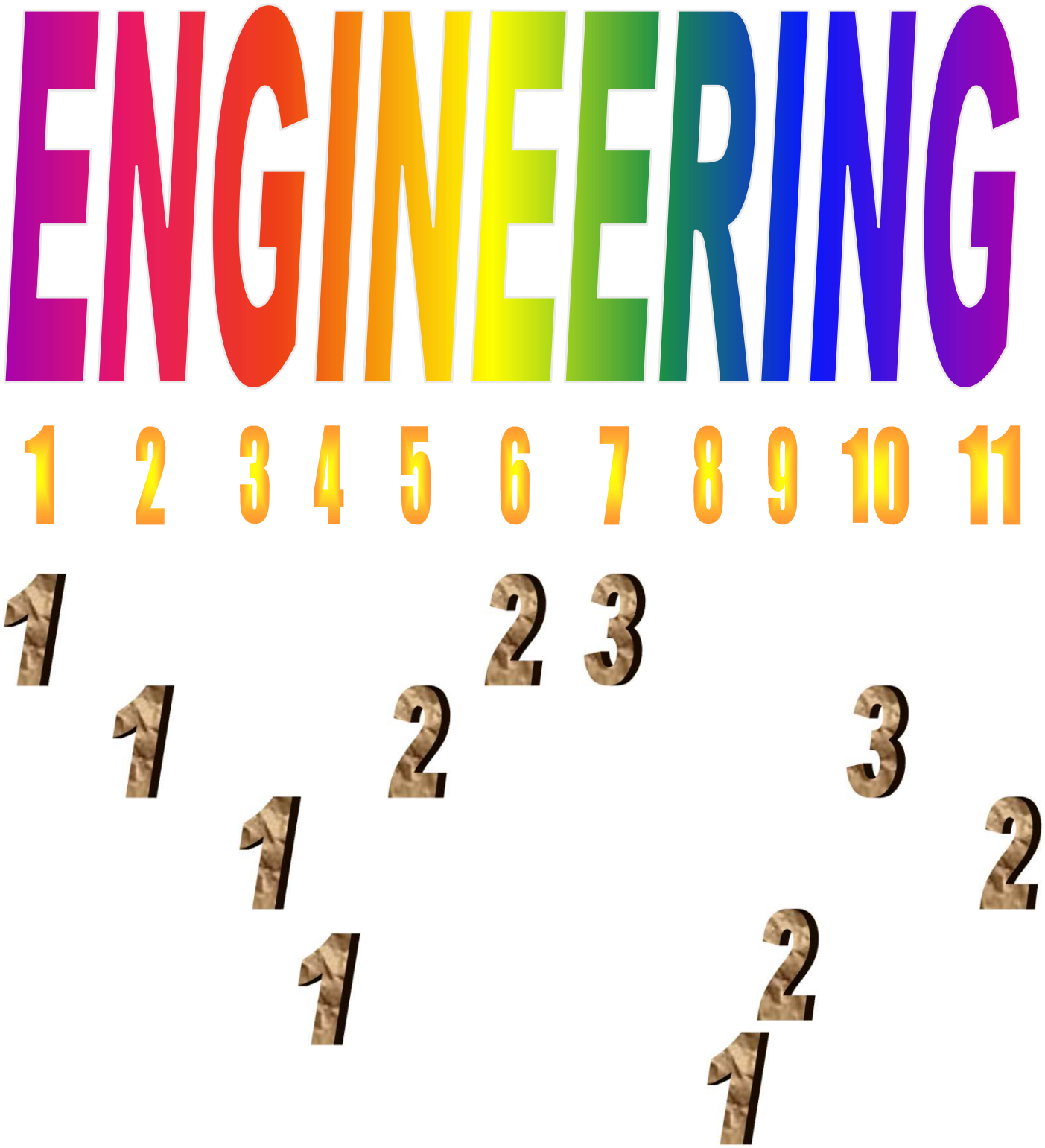
$$P(m,n) = (n)_m = P(2,3) = (3)_2 = \frac{3!}{(3-2)!} = 6$$

تمایز پذیر

تعداد حالتهایی که می توان N شیی را که شامل n_1 شیی از یک نـــوع n_2 شیی از یک نوع دیگر و ... n_k شیی از نوع دیگر هستند را کنار هـــم نوشت:

$$\begin{pmatrix} \{n_1\} & \{n_2\} & \dots & \{n_k\} \\ n_1 + n_2 + \dots + n_k = N \end{pmatrix} \qquad \begin{pmatrix} E = \sum_i n_i \varepsilon_i \\ N = \sum_i n_i \end{pmatrix}$$

$$\frac{N!}{n_1!\, n_2! \dots n_k!}$$


ENGINEERING
1 2 3 4 5 6 7 8 9 10 11
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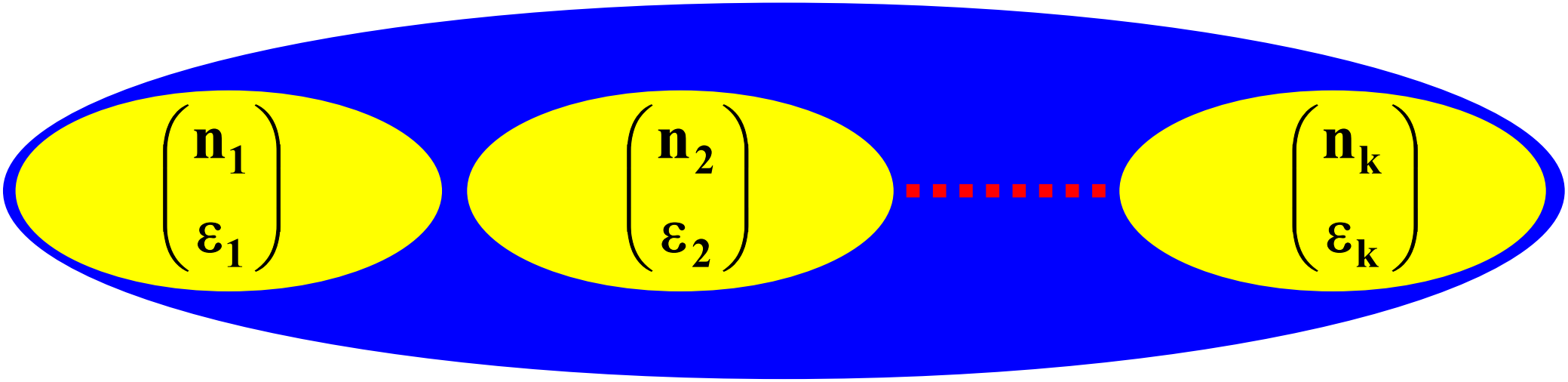
1

$$\frac{11!}{3!3!2!2!1!} = 277200$$



$$\begin{pmatrix} E = \sum_i n_i \varepsilon_i \\ N = \sum_i n_i \end{pmatrix}$$

$$\frac{N!}{n_1! n_2! \ldots n_k!}$$

Systems composed of indistinguishable particles

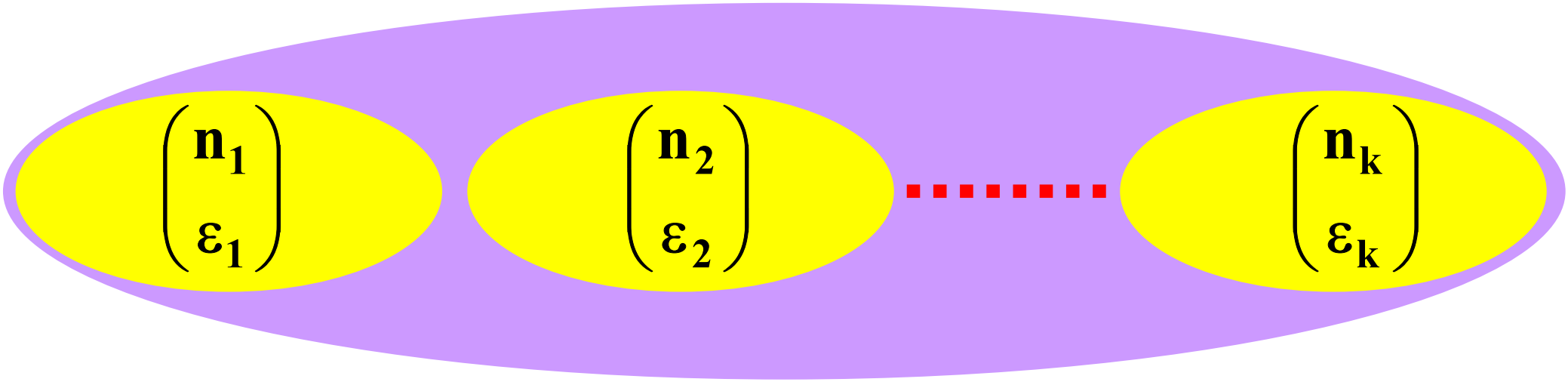
We shall now formulate the quantum-mechanical description of a system of N identical particles. To fix ideas, we consider a gas of *non-interacting* particles; the findings of this study will be of considerable relevance to other systems as well.

$$H\Psi_E(q_1, q_2, \ldots, q_N) = E\Psi_E(q_1, q_2, \ldots, q_N)$$

$$\Psi_E(q_1, q_2, \ldots, q_N) = \prod_{i=1}^{N} U_{\varepsilon_i}(q_i)$$

$$HU_{\varepsilon_i}(q_i) = \varepsilon_i U_{\varepsilon_i}(q_i)$$

$$\sum_i n_i = N \qquad \sum_i n_i \varepsilon_i = E$$

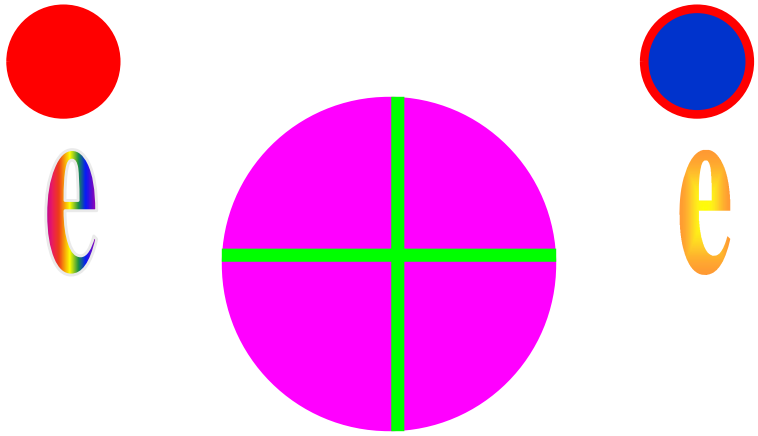


$$\Psi_E(q_1, q_2, \ldots, q_N) = \prod_{i=1}^{N} U_{\varepsilon_i}(q_i)$$

$$= \prod_{i=1}^{n_1} U_1(m) \prod_{i=n_1+1}^{n_1+n_2} U_2(m) \prod_{i=n_1+n_2+1}^{n_1+n_2+n_3} U_3(m) \ldots$$

We would like to be all the electrons in quantum mechanics indistinguishable.

How can we do it?



$$H = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} + V(x_1, x_2)$$

$$H(1,2) = H(2,1)$$

$$H(1,2)\Psi_E(1,2) = E\Psi_E(1,2)$$

$$H(2,1)\Psi_E(2,1) = E\Psi_E(2,1)$$

$$P\Psi_E(1,2) = \Psi_E(2,1)$$

$$H(1,2)\Psi_E(2,1) = E\Psi_E(2,1)$$

$$H(1,2)P\Psi_E(1,2) = EP\Psi_E(1,2)$$

$$H(1,2)P\Psi_E(1,2) = PE\Psi_E(1,2)$$

$$H(1,2)P\Psi_E(1,2) = PH\Psi_E(1,2)$$

$$HP = PH \Rightarrow [H, P] = 0$$

Permutation is conserved

$$[H, P] = 0$$

P and H have common eigenstates

$$P\Psi(1,2) = \lambda\Psi(1,2)$$

$$P^2\Psi(1,2) = \lambda P\Psi(1,2)$$

$$\Psi(1,2) = \lambda^2\Psi(1,2)$$

$$\lambda = \pm 1$$

Bosons

Fermions

Always we can separate a wavefunction into symmetric and asymmetric parts

For two particles we have

$$\Psi(1,2)=\frac{1}{2}\big(\Psi(1,2)+\Psi(2,1)\big)+\frac{1}{2}\big(\Psi(1,2)-\Psi(2,1)\big)$$

$$\Psi(1,2)=\frac{1}{2}\sqrt{2}\Psi^{(S)}(1,2)+\frac{1}{2}\sqrt{2}\Psi^{(A)}(1,2)$$

$$\Psi(1,2)=\frac{\sqrt{2}}{2}\left\{\Psi^{(S)}(1,2)+\Psi^{(A)}(1,2)\right\}$$

For three particles we can write

$$\Psi^{(S)}(1,2,3)=\frac{1}{\sqrt{6}}\left[\Psi(1,2,3)+\Psi(2,1,3)+\Psi(2,3,1)+\Psi(3,2,1)+\Psi(3,1,2)+\Psi(1,3,2)\right]$$

$$\Psi^{(A)}(1,2,3)=\frac{1}{\sqrt{6}}\left[\Psi(1,2,3)-\Psi(2,1,3)+\Psi(2,3,1)-\Psi(3,2,1)+\Psi(3,1,2)-\Psi(1,3,2)\right]$$

For non-interacting particles

$$\Psi^{(A)}(1,2)=\frac{1}{\sqrt{2}}\left[\Psi_{\varepsilon_1}(1)\Psi_{\varepsilon_2}(2)-\Psi_{\varepsilon_1}(2)\Psi_{\varepsilon_2}(1)\right]$$

$$\Psi^{(S)}(1,2)=\frac{1}{\sqrt{2}}\left[\Psi_{\varepsilon_1}(1)\Psi_{\varepsilon_2}(2)+\Psi_{\varepsilon_1}(2)\Psi_{\varepsilon_2}(1)\right]$$

$$\Psi^{(A)}(1,2,\ldots,N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\Psi_{\varepsilon_1}(1) & \Psi_{\varepsilon_1}(2) & \ldots & \Psi_{\varepsilon_1}(N)\\ \Psi_{\varepsilon_2}(1) & \Psi_{\varepsilon_2}(2) & \ldots & \Psi_{\varepsilon_2}(N)\\ \ldots & \ldots & \ldots & \ldots\\ \Psi_{\varepsilon_N}(1) & \Psi_{\varepsilon_N}(2) & & \Psi_{\varepsilon_N}(N)\end{vmatrix}_{N\times N}$$

$$\Psi^{(A)}(1,2,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_{\varepsilon_1}(1) & \Psi_{\varepsilon_1}(2) & \ldots & \Psi_{\varepsilon_1}(N) \\ \Psi_{\varepsilon_2}(1) & \Psi_{\varepsilon_2}(2) & \ldots & \Psi_{\varepsilon_2}(N) \\ \ldots & \ldots & \ldots & \ldots \\ \Psi_{\varepsilon_N}(1) & \Psi_{\varepsilon_N}(2) & & \Psi_{\varepsilon_N}(N) \end{vmatrix}_{N\times N}$$

$$= -\frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_{\varepsilon_1}(2) & \Psi_{\varepsilon_1}(1) & \ldots & \Psi_{\varepsilon_1}(N) \\ \Psi_{\varepsilon_2}(2) & \Psi_{\varepsilon_2}(1) & \ldots & \Psi_{\varepsilon_2}(N) \\ \ldots & \ldots & \ldots & \ldots \\ \Psi_{\varepsilon_N}(2) & \Psi_{\varepsilon_N}(1) & & \Psi_{\varepsilon_N}(N) \end{vmatrix}_{N\times N}$$

Antisymmetric property is satisfied.

$$\Psi^{(A)}(1,2,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_{\varepsilon_1}(1) & \Psi_{\varepsilon_1}(2) & \ldots & \Psi_{\varepsilon_1}(N) \\ \Psi_{\varepsilon_2}(1) & \Psi_{\varepsilon_2}(2) & \ldots & \Psi_{\varepsilon_2}(N) \\ \ldots & \ldots & \ldots & \ldots \\ \Psi_{\varepsilon_N}(1) & \Psi_{\varepsilon_N}(2) & & \Psi_{\varepsilon_N}(N) \end{vmatrix}_{N\times N}$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_{\varepsilon_1}(1) & \Psi_{\varepsilon_1}(2) & \ldots & \Psi_{\varepsilon_1}(N) \\ \Psi_{\varepsilon_1}(1) & \Psi_{\varepsilon_1}(2) & \ldots & \Psi_{\varepsilon_1}(N) \\ \ldots & \ldots & \ldots & \ldots \\ \Psi_{\varepsilon_N}(1) & \Psi_{\varepsilon_N}(2) & & \Psi_{\varepsilon_N}(N) \end{vmatrix}_{N\times N} = 0$$

Pauli's exclusion principle is also satisfied.

Regardless of spin in each state only one electron can be found

The state ket for the two particles can be written in product form,

$$|k'\rangle|k''\rangle \perp |k''\rangle|k'\rangle$$

$$H|k'\rangle|k''\rangle = E|k'\rangle|k''\rangle$$

$$H|k''\rangle|k'\rangle = E|k''\rangle|k'\rangle$$

$$H(c_1|k''\rangle|k'\rangle + c_2|k''\rangle|k'\rangle) = E(c_1|k''\rangle|k'\rangle + c_2|k''\rangle|k'\rangle)$$

This is known as exchange degeneracy.

$$P_{12}|k'\rangle|k''\rangle = |k''\rangle|k'\rangle$$

$$P_{21} = P_{12} \quad \text{and} \quad P_{12}^2 = 1$$

Prove that P_{12} must change the particle labels of observables:

$$A_1|a'\rangle|a''\rangle = a'|a'\rangle|a''\rangle$$

$$A_2|a'\rangle|a''\rangle = a''|a'\rangle|a''\rangle$$

$$P_{12}A_1P_{12}^{-1}P_{12}|a'\rangle|a''\rangle = a'P_{12}|a'\rangle|a''\rangle$$

$$= P_{12}A_1P_{12}^{-1}|a''\rangle|a'\rangle = a'|a''\rangle|a'\rangle$$

$$P_{12}A_1P_{12}^{-1} = A_2$$

Let us now consider the Hamiltonian of a system of two identical particles. The observables, such as momentum and position operators, must necessarily appear symmetrically in the Hamiltonian—for example,

$$H = \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} + V_{\text{pair}}(|\mathbf{x}_1 - \mathbf{x}_2|) + V_{\text{ext}}(\mathbf{x}_1) + V_{\text{ext}}(\mathbf{x}_2). \tag{6.1.9}$$

Here we have separated the mutual interaction between the two particles from their interaction with some other external potential. Clearly, we have

$$P_{12} H P_{12}^{-1} = H \tag{6.1.10}$$

for H made up of observables for two identical particles. Because P_{12} commutes with H, we can say that P_{12} is a constant of the motion. The eigenvalues of P_{12} allowed are $+1$ and -1 because of (6.1.5). It therefore follows that if the two-particle state ket is symmetric (antisymmetric) to start with, it remains so at all times.

$$|k'k''\rangle_+ \equiv \frac{1}{\sqrt{2}}\big(|k'\rangle|k''\rangle + |k''\rangle|k'\rangle\big)$$

$$|k'k''\rangle_- \equiv \frac{1}{\sqrt{2}}\big(|k'\rangle|k''\rangle - |k''\rangle|k'\rangle\big)$$

$$S_{12} \equiv \tfrac{1}{2}(1 + P_{12}), \qquad A_{12} \equiv \tfrac{1}{2}(1 - P_{12})$$

$$\begin{Bmatrix} S_{12} \\ A_{12} \end{Bmatrix} \big[c_1|k'\rangle|k''\rangle + c_2|k''\rangle|k'\rangle\big]$$

$$= \tfrac{1}{2}\big(c_1|k'\rangle|k''\rangle + c_2|k''\rangle|k'\rangle\big) \pm \tfrac{1}{2}\big(c_1|k''\rangle|k'\rangle + c_2|k'\rangle|k''\rangle\big)$$

$$= \frac{c_1 \pm c_2}{2}\big(|k'\rangle|k''\rangle \pm |k''\rangle|k'\rangle\big)$$

$$P_{ij}|k'\rangle|k''\rangle\cdots|k^{i}\rangle|k^{i+1}\rangle\cdots|k^{j}\rangle\cdots$$

$$=|k'\rangle|k''\rangle\cdots|k^{j}\rangle|k^{i+1}\rangle\cdots|k^{i}\rangle\ldots.$$

$$P_{ij}^{2}=1$$

$$\left[P_{ij},P_{kl}\right]\neq 0$$

$$|k'k''k'''\rangle_{\pm}\equiv\frac{1}{\sqrt{6}}\{|k'\rangle|k''\rangle|k'''\rangle\pm|k''\rangle|k'\rangle|k'''\rangle$$

$$+|k''\rangle|k'''\rangle|k'\rangle\pm|k'''\rangle|k''\rangle|k'\rangle$$

$$+|k'''\rangle|k'\rangle|k''\rangle\pm|k'\rangle|k'''\rangle|k''\rangle\}.$$

These are both simultaneous eigenkets of P_{12}, P_{23} and P_{13}.

$$P_{123}\left(|k'\rangle|k''\rangle|k'''\rangle\right) = |k''\rangle|k'''\rangle|k'\rangle$$

Note that $P_{123} = P_{12}P_{13}$ because

$$P_{12}P_{13}\left(|k'\rangle|k''\rangle|k'''\rangle\right) = P_{12}\left(|k'''\rangle|k''\rangle|k'\rangle\right) = |k''\rangle|k'''\rangle|k'\rangle$$

$$|k'k'k''\rangle_{+} = \frac{1}{\sqrt{3}}\left(|k'\rangle|k'\rangle|k''\rangle + |k'\rangle|k''\rangle|k'\rangle + |k''\rangle|k'\rangle|k'\rangle\right)$$

Normalization factor $\sqrt{\dfrac{N_1!N_2!\cdots N_n!}{N!}} = \sqrt{2!/3!}$

where N is the total number of particles and N_i the number of times $|k^{(i)}\rangle$ occurs.

SYMMETRIZATION POSTULATE

So far we have not discussed whether nature takes advantage of totally symmetrical or totally antisymmetrical states. It turns out that systems containing N identical particles are either totally symmetrical under the interchange of any pair, in which case the particles are said to satisfy **Bose-Einstein** (B-E) **statistics**, hence known as **bosons**, or totally antisymmetrical, in which case the particles are said to satisfy **Fermi-Dirac** (F-D) **statistics**, hence known as **fermions**. Thus

$$P_{ij}|N \text{ identical bosons}\rangle = +|N \text{ identical bosons}\rangle$$

$$P_{ij}|N \text{ identical fermions}\rangle = -|N \text{ identical fermions}\rangle$$

Half-integer spin particles are fermions;

Integer spin particles are bosons.

To illustrate the dramatic differences between fermions and bosons, let us consider two particles, each of which can occupy only two states, characterized by k' and k''. For a system of two fermions, we have no choice; there is only one possibility:

$$\frac{1}{\sqrt{2}}\left(|k'\rangle|k''\rangle - |k''\rangle|k'\rangle\right)$$

For bosons there are three states possible:

$$|k'\rangle|k'\rangle, \qquad |k''\rangle|k''\rangle, \qquad \frac{1}{\sqrt{2}}\left(|k'\rangle|k''\rangle + |k''\rangle|k'\rangle\right)$$

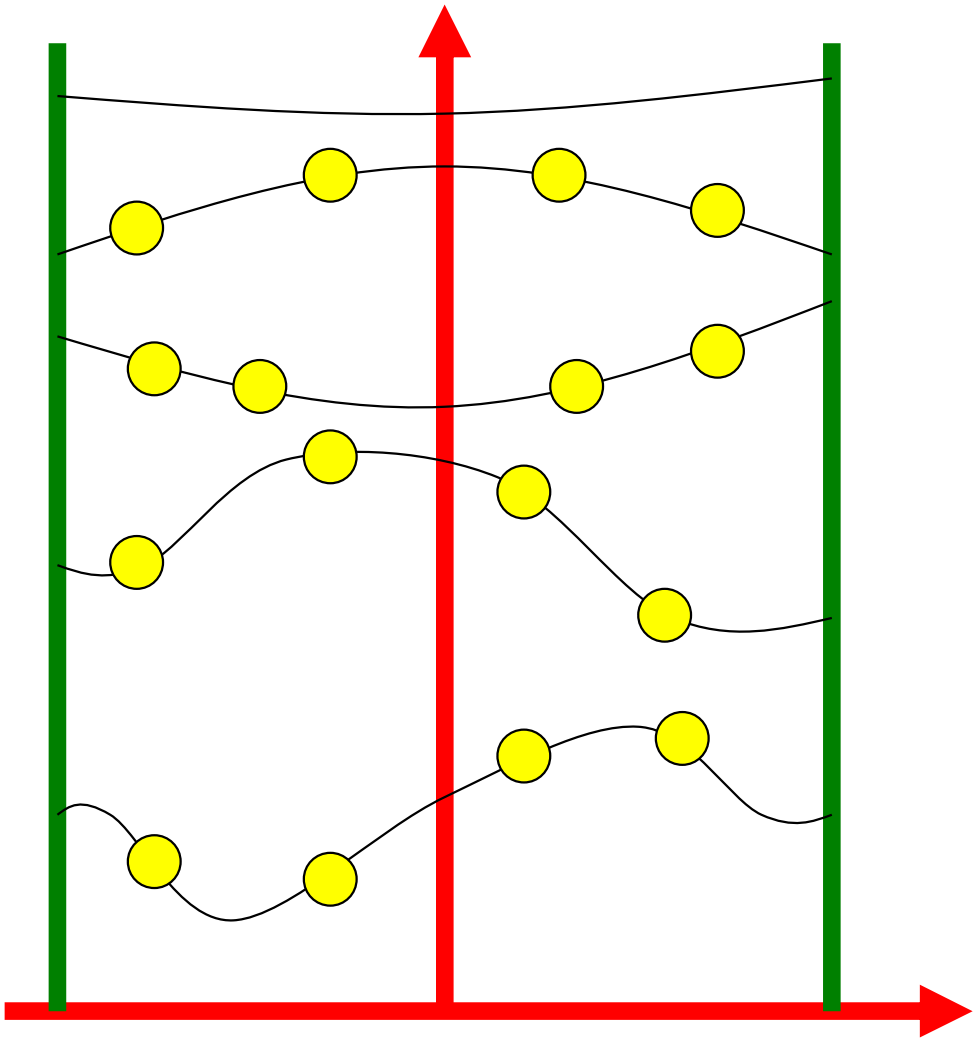
In contrast, for "classical" particles satisfying Maxwell-Boltzmann (M-B) statistics with no restriction on symmetry, we have altogether four independent states:

$$|k'\rangle|k''\rangle, \qquad |k''\rangle|k'\rangle, \qquad |k'\rangle|k'\rangle, \qquad |k''\rangle|k''\rangle$$

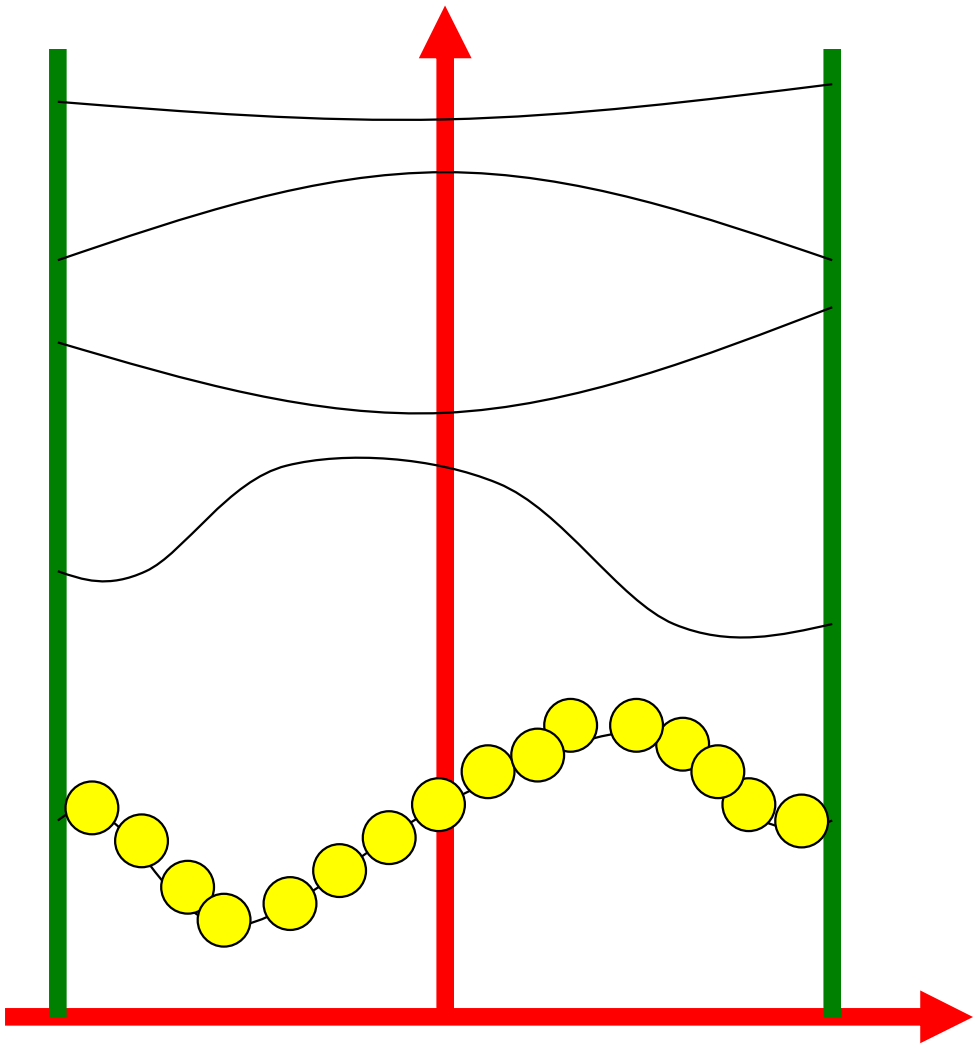
We see that in the fermion case it is impossible for both particles to occupy the same state. In the boson case, for two out of the three allowed kets, both particles occupy the same state. In the classical (M-B) statistics case, both particles occupy the same state for two out of the four allowed kets. In this sense fermions are the least sociable; they avoid each other to make sure that they are not in the same state; in contrast, bosons are the most sociable, they really love to be in the same state, even more so than classical particles obeying M-B statistics.

The difference between fermions and bosons show up most dramatically at low temperatures; a system made up of bosons, such as liquid ^{4}He, exhibits a tendency for all particles to get down to the same ground state at extremely low temperatures. This is known as **Bose-Einstein condensation**, a feature not shared by a system made up of fermions.

چگالش بوز انشتین یعنی هنگامی که می خواهیم زوجهای کوپر را بچینیم باید مانند بوزونها با آنها رفتار کنیم و همه را در حالت زمینه در پایین ترین تراز انرژی قرار دهیم:



$T > T_c$



$T < T_c$

TWO-ELECTRON SYSTEM

Let us now consider specifically a two-electron system. The eigenvalue of the permutation operator is necessarily -1. Suppose the base kets we use may be specified by $\mathbf{x}_1$, $\mathbf{x}_2$, m_{s1}, and m_{s2}, where m_{s1} and m_{s2} stand for the spin-magnetic quantum numbers of electron 1 and electron 2, respectively.

We can express the wave function for a two-electron system as a linear combination of the state ket with eigenbras of $\mathbf{x}_1$, $\mathbf{x}_2$, m_{s1}, and m_{s2} as follows:

$$\psi = \sum_{m_{s1}} \sum_{m_{s2}} C(m_{s1}, m_{s2}) \langle \mathbf{x}_1, m_{s1}; \mathbf{x}_2, m_{s2} | \alpha \rangle$$

If the Hamiltonian commutes with $\mathbf{S}_{\text{tot}}^2$,

$$\left[\mathbf{S}_{\text{tot}}^2, H\right] = 0,$$

then the energy eigenfunction is expected to be an eigenfunction of $\mathbf{S}_{\text{tot}}^2$, and if ψ is written as

$$\psi = \phi(\mathbf{x}_1, \mathbf{x}_2)\chi,$$

then the spin function χ is expected to be one of the following:

$$\chi(m_{s1}, m_{s2}) = \begin{cases} \chi_{++} \\ \dfrac{1}{\sqrt{2}}(\chi_{+-} + \chi_{-+}) \\ \chi_{--} \end{cases} \quad \text{triplet (symmetrical)}$$

$$\frac{1}{\sqrt{2}}(\chi_{+-} - \chi_{-+}) \qquad \text{singlet (antisymmetrical)},$$

where χ_{+-} corresponds to $\chi(m_{s1} = \frac{1}{2},\ m_{s2} = -\frac{1}{2})$. Notice that the triplet spin functions are all symmetrical; this is reasonable because the ladder operator $S_{1-} + S_{2-}$ commutes with P_{12} and the $|+\rangle|+\rangle$ state is even under P_{12}.

We note

$$\langle \mathbf{x}_1, m_{s1}; \mathbf{x}_2, m_{s2} | P_{12} | \alpha \rangle = \langle \mathbf{x}_2, m_{s2}; \mathbf{x}_1, m_{s1} | \alpha \rangle .$$

Fermi-Dirac statistics thus requires

$$\langle \mathbf{x}_1, m_{s1}; \mathbf{x}_2, m_{s2} | \alpha \rangle = - \langle \mathbf{x}_2, m_{s2}; \mathbf{x}_1, m_{s1} | \alpha \rangle .$$

Clearly, P_{12} can be written as

$$P_{12} = P_{12}^{(\text{space})} P_{12}^{(\text{spin})}$$

where $P_{12}^{(\text{space})}$ just interchanges the position coordinate, while $P_{12}^{(\text{spin})}$ just interchanges the spin states. It is amusing that we can express $P_{12}^{(\text{spin})}$ as

$$P_{12}^{(\text{spin})} = \frac{1}{2}\left(1 + \frac{4}{\hbar^2}\mathbf{S}_1 \cdot \mathbf{S}_2\right),$$

which follows because

$$\mathbf{S}_1 \cdot \mathbf{S}_2 = \begin{cases} \dfrac{\hbar^2}{4} & (\text{triplet}) \\ \dfrac{-3\hbar^2}{4} & (\text{singlet}) \end{cases}$$

$$\mathbf{S}_1 \cdot \mathbf{S}_2 = \tfrac{1}{2}(\mathbf{S}^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2)$$

$$= \frac{\hbar^2}{2}(s(s+1) - 3/4 - 3/4)$$

$$= \frac{\hbar^2}{2}(s(s+1) - 3/2)$$

$$(\text{triplet}) \quad = \frac{\hbar^2}{2}(2 - 3/2) = \frac{\hbar^2}{4}; \qquad \text{for} \quad s = 1$$

$$(\text{singlet}) \quad = \frac{\hbar^2}{2}(0 - 3/2) = \frac{-3\hbar^2}{4}; \quad \text{for} \quad s = 0$$

If the space part of the wave function is symmetrical (antisymmetrical) the spin part must be antisymmetrical (symmetrical).

As a result, the spin triplet state has to be combined with an antisymmetrical space function and the spin singlet state has to be combined with a space symmetrical function.

The space part of the wave function $\phi(\mathbf{x}_1, \mathbf{x}_2)$ provides the usual probabilistic interpretation. The probability for finding electron 1 in a volume element d^3x_1 centered around $\mathbf{x}_1$ and electron 2 in a volume element d^3x_2 is

$$|\phi(\mathbf{x}_1, \mathbf{x}_2)|^2 d^3x_1 d^3x_2$$

To see the meaning of this more closely, let us consider the specific case where the mutual interaction between the two electrons [for example, $V_{\text{pair}}(|\mathbf{x}_1-\mathbf{x}_2|),\mathbf{S}_1\cdot\mathbf{S}_2]$ can be ignored. If there is no spin dependence, the wave equation for the energy eigenfunction ψ [see (6.1.9)],

$$\left[\frac{-\hbar^2}{2m}\nabla_1^2-\frac{\hbar^2}{2m}\nabla_2^2+V_{\text{ext}}(\mathbf{x}_1)+V_{\text{ext}}(\mathbf{x}_2)\right]\psi=E\psi, \qquad (6.3.13)$$

is now separable. We have a solution of the form $\omega_A(\mathbf{x}_1)\omega_B(\mathbf{x}_2)$ times the spin function. With no spin dependence $\mathbf{S}_{\text{tot}}^2$ necessarily (and trivially) commutes with H, so the spin part must be a triplet or a singlet, which have definite symmetry properties under $P_{12}^{(\text{spin})}$. The space part must then be written as a symmetrical and antisymmetrical combination of $\omega_A(\mathbf{x}_1)\omega_B(\mathbf{x}_2)$ and $\omega_A(\mathbf{x}_2)\omega_B(\mathbf{x}_1)$:

$$\phi(\mathbf{x}_1,\mathbf{x}_2)=\frac{1}{\sqrt{2}}\left[\omega_A(\mathbf{x}_1)\omega_B(\mathbf{x}_2)\pm\omega_A(\mathbf{x}_2)\omega_B(\mathbf{x}_1)\right] \qquad (6.3.14)$$

where the upper sign is for a spin singlet and the lower is for a spin triplet.

The probability of observing electron 1 in d^3x_1 around $\mathbf{x}_1$ and electron 2 in d^3x_2 around $\mathbf{x}_2$ is given by

$$\tfrac{1}{2}\Big\{|\omega_A(\mathbf{x}_1)|^2|\omega_B(\mathbf{x}_2)|^2+|\omega_A(\mathbf{x}_2)|^2|\omega_B(\mathbf{x}_1)|^2 \pm 2\,\mathrm{Re}\big[\omega_A(\mathbf{x}_1)\omega_B(\mathbf{x}_2)\omega_A^*(\mathbf{x}_2)\omega_B^*(\mathbf{x}_1)\big]\Big\}d^3x_1d^3x_2. \tag{6.3.15}$$

The last term in the curly bracket is known as the **exchange density**.

We immediately see that when the electrons are in a spin-triplet state, the probability of finding the second electron at the same point in space vanishes. Put another way, the electrons tend to avoid each other when their spins are in a triplet state. In contrast, when their spins are in a singlet state, there is enhanced probability of finding them at the same point in space because of the presence of the exchange density.

Clearly, the question of identity is important only when the exchange density is nonnegligible or when there is substantial overlap between function ω_A and function ω_B. To see this point clearly, let us take the extreme case where $|\omega_A(\mathbf{x})|^2$ (where $\mathbf{x}$ may refer to $\mathbf{x}_1$ or $\mathbf{x}_2$) is big only in region A and $|\omega_B(\mathbf{x})|^2$ is big only in region B such that the two regions are widely separated. Now choose d^3x_1 in region A and d^3x_2 in region B; see Figure 6.2. The only important term then is just the first term in (6.3.15),

$$|\omega_A(\mathbf{x}_1)|^2|\omega_B(\mathbf{x}_2)|^2, \tag{6.3.16}$$

which is nothing more than the joint probability density expected for classical particles. In this connection, recall that classical particles are necessarily well localized and the question of identity simply does not arise. Thus the exchange-density term is unimportant if regions A and B do not overlap. There is no need to antisymmetrize if the electrons are far apart and the overlap is negligible. This is quite gratifying. We never have to worry about the question of antisymmetrization with 10 billion electrons, nor is it necessary to take into account the antisymmetrization requirement between an electron in Los Angeles and an electron in Beijing.

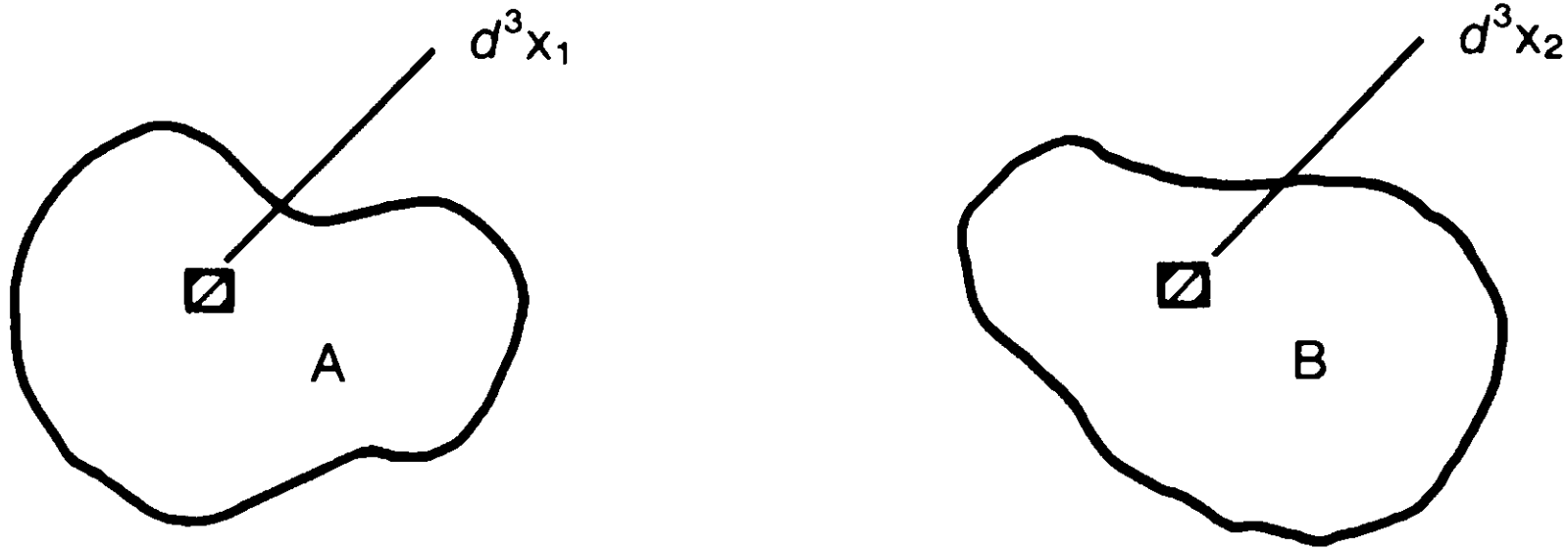
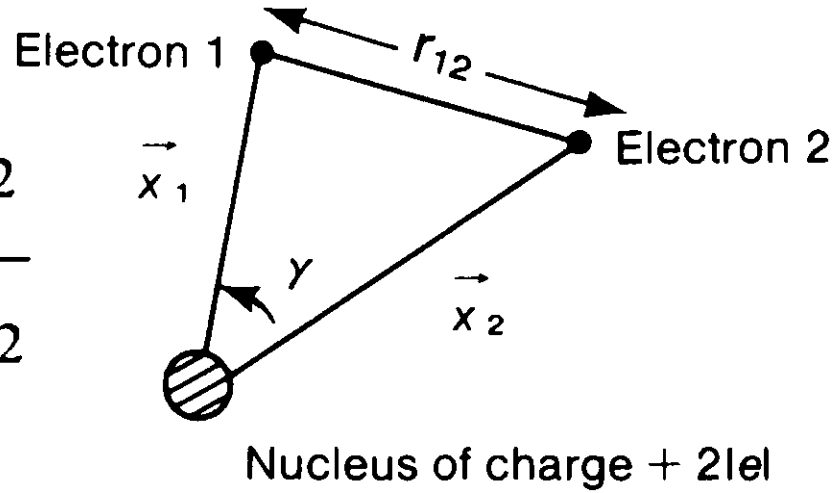


FIGURE 6.2. Two widely separated regions A and B; $|\omega_A(\mathbf{x})|^2$ is large in region A while $|\omega_B(\mathbf{x})|^2$ is large in region B.

THE HELIUM ATOM

$$H = \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$



The space part of the wave function for the important case where one of the electrons is in the ground state and the other in an excited state characterized by (nlm) is

$$\phi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \left[\psi_{100}(\mathbf{x}_1) \psi_{nlm}(\mathbf{x}_2) \pm \psi_{100}(\mathbf{x}_2) \psi_{nlm}(\mathbf{x}_1) \right]$$

where the upper (lower) sign is for the spin singlet (triplet).

For the ground state, we need a special treatment. Here the configuration is characterized by $(1s)^2$, that is, both electrons in $n=1$, $l=0$.

The space function must then necessarily be symmetric and only the spin singlet function is allowed. So we have

$$\psi_{100}(\mathbf{x}_1)\psi_{100}(\mathbf{x}_2)\chi_{\text{singlet}} = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}\chi \tag{6.4.3}$$

with $Z=2$. Not surprisingly, this "unperturbed" wave function gives

$$E = 2\times 4\left(-\frac{e^2}{2a_0}\right) \tag{6.4.4}$$

for the ground-state energy, which is about 30% bigger than the experimental value.

This is just the starting point of our investigation because in obtaining the above form (6.4.3), we have completely ignored the last term in (6.4.1) that describes the interaction between the two electrons. One way to approach the problem of obtaining a better energy value is to apply first-order perturbation theory using (6.4.3) as the unperturbed wave function and e^2/r_{12} as the perturbation. We obtain

$$\Delta_{(1s)^2} = \left\langle \frac{e^2}{r_{12}} \right\rangle_{(1s)^2} = \int\int \frac{Z^6}{\pi^2 a_0^6} e^{-2Z(r_1+r_2)/a_0} \frac{e^2}{r_{12}} d^3x_1 d^3x_2. \quad (6.4.5)$$

To carry out the indicated integration we first note

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\gamma}} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l(\cos\gamma), \quad (6.4.6)$$

where $r_>$ ($r_<$) is the larger (smaller) of r_1 and r_2 and γ is the angle between $\mathbf{x}_1$ and $\mathbf{x}_2$. The angular integration is easily performed by expressing $P_l(\cos\gamma)$ in terms of $Y_l^m(\theta_1, \phi_1)$ and $Y_l^m(\theta_2, \phi_2)$ using the addition theorem of spherical harmonics:

$$P_l(\cos\gamma) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_l^{m*}(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2). \quad (6.4.7)$$

The angular integration is now trivial:

$$\int Y_l^m(\theta_i, \phi_i)\, d\Omega_i = \frac{1}{\sqrt{4\pi}}(4\pi)\delta_{l0}\delta_{m0}. \tag{6.4.8}$$

The radial integration is elementary (but involves tedious algebra!); it leads to

$$\int_0^\infty \left[\int_0^{r_1} \frac{1}{r_1} e^{-(2Z/a_0)(r_1+r_2)} r_2^2\, dr_2 + \int_{r_1}^\infty \frac{1}{r_2} e^{-(2Z/a_0)(r_1+r_2)} r_2^2\, dr_2 \right] r_1^2\, dr_1$$

$$= \frac{5}{128} \frac{a_0^5}{Z^5}. \tag{6.4.9}$$

Combining everything, we have (for $Z = 2$)

$$\Delta_{(1s)^2} = \left(\frac{Z^6 e^2}{\pi^2 a_0^6}\right) 4\pi (\sqrt{4\pi})^2 \left(\frac{5}{128}\right)\left(\frac{a_0^5}{Z^5}\right)$$

$$= \left(\frac{5}{2}\right)\left(\frac{e^2}{2a_0}\right). \tag{6.4.10}$$

Adding this energy shift to (6.4.4), we have

$$E_{\text{cal}} = \left(-8 + \frac{5}{2}\right)\left(\frac{e^2}{2a_0}\right) \simeq -74.8 \text{ eV}. \tag{6.4.11}$$

Compare this with the experimental value,

$$E_{\text{exp}} = -78.8 \text{ eV}. \tag{6.4.12}$$

This is not bad, but we can do better! We propose to use the variational method with Z, which we call Z_{eff}, as a variational parameter. The physical reason for this choice is that the effective Z seen by one of the electrons is smaller than 2 because the positive charge of 2 units at the origin (see Figure 6.3) is "screened" by the negatively charged cloud of the other electron; in other words, the other electron tends to neutralize the positive charge due to the helium nucleus at the center. For the normalized trial function we use

$$\langle \mathbf{x}_1, \mathbf{x}_2 | \tilde{0} \rangle = \left(\frac{Z_{\text{eff}}^3}{\pi a_0^3} \right) e^{-Z_{\text{eff}}(r_1 + r_2)/a_0}. \tag{6.4.13}$$

From this we obtain

$$\begin{aligned} \overline{H} &= \left\langle \tilde{0} \left| \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} \right| \tilde{0} \right\rangle - \left\langle \tilde{0} \left| \frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} \right| \tilde{0} \right\rangle + \left\langle \tilde{0} \left| \frac{e^2}{r_{12}} \right| \tilde{0} \right\rangle \\ &= \left(2\frac{Z_{\text{eff}}^2}{2} - 2ZZ_{\text{eff}} + \frac{5}{8}Z_{\text{eff}} \right) \left(\frac{e^2}{a_0} \right). \end{aligned} \tag{6.4.14}$$

We easily see that the minimization of $\bar{H}$ is at

$$Z_{\text{eff}} = 2 - \tfrac{5}{16} = 1.6875. \tag{6.4.15}$$

This is smaller than 2, as anticipated. Using this value for Z_{eff} we get

$$E_{\text{cal}} = -77.5 \text{ eV}, \tag{6.4.16}$$

which is already very close considering the crudeness of the trial wave function.

Let us briefly consider excited states. This is more interesting from the point of view of illustrating quantum-mechanical effects due to identity. We consider just $(1s)(nl)$. We write the energy of this state as

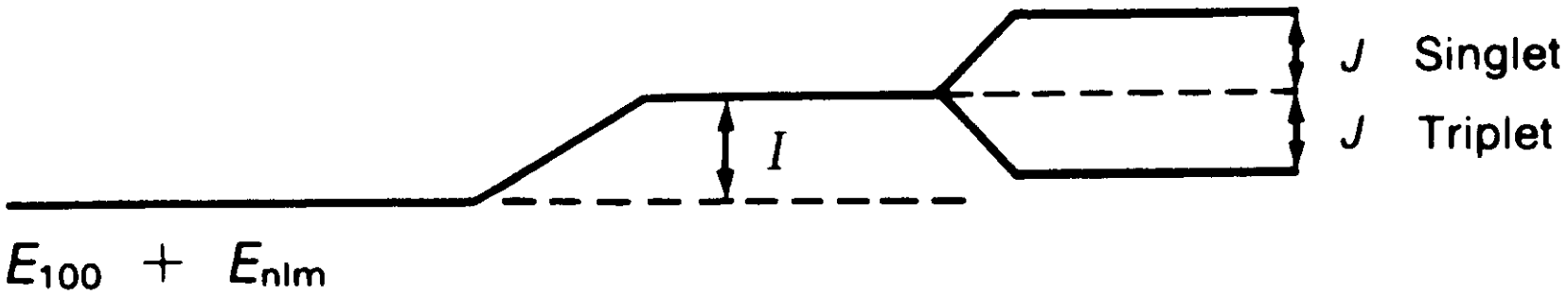
$$E = E_{100} + E_{nlm} + \Delta E. \tag{6.4.17}$$

In first-order perturbation theory, ΔE is obtained by evaluating the expectation value of e^2/r_{12}. We can write

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = I \pm J, \tag{6.4.18}$$

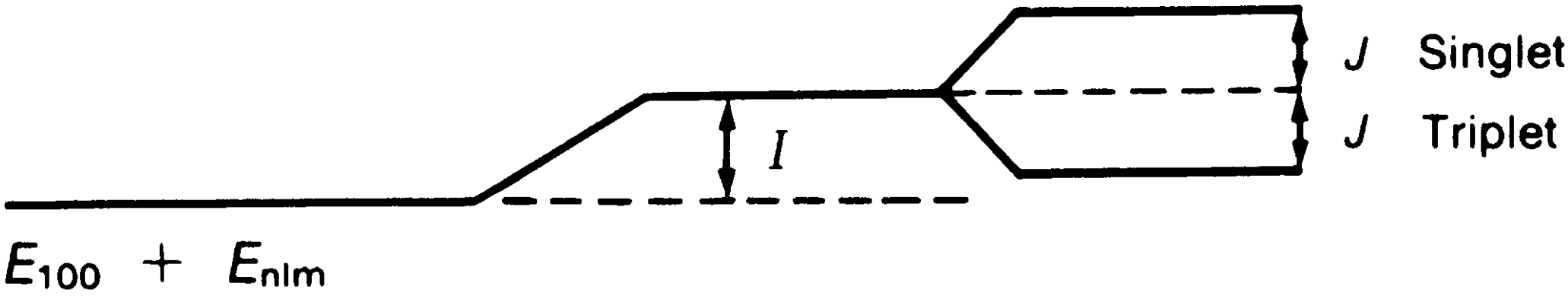
$$I = \int d^3x_1 \int d^3x_2 |\psi_{100}(\mathbf{x}_1)|^2 |\psi_{nlm}(\mathbf{x}_2)|^2 \frac{e^2}{r_{12}},$$

$$J = \int d^3x_1 \int d^3x_2 \psi_{100}(\mathbf{x}_1)\psi_{nlm}(\mathbf{x}_2)\frac{e^2}{r_{12}}\psi^*_{100}(\mathbf{x}_2)\psi^*_{nlm}(\mathbf{x}_1)$$

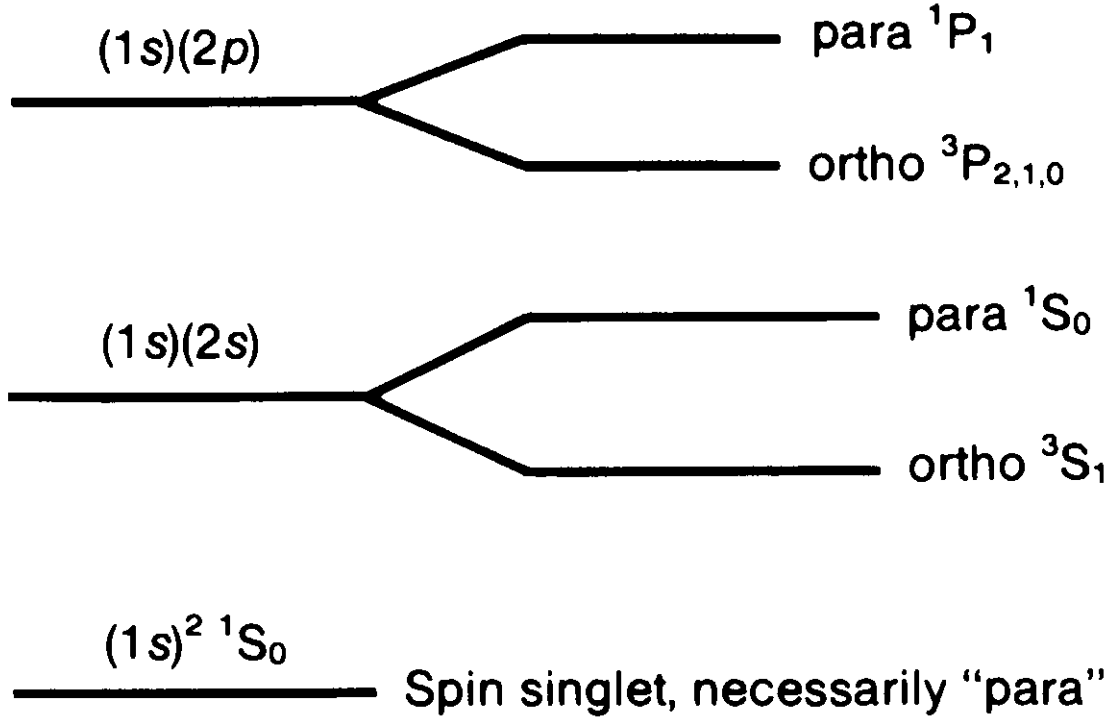


$$\left\langle \frac{e^2}{r_{12}} \right\rangle = I \pm J$$

The upper (lower) sign goes with the spin singlet (triplet) state. Obviously, I is positive; we can also show that J is positive. So the net result is such that for the same configuration, the spin singlet state lies higher, as shown in Figure 6.4.



The physical interpretation for this is as follows: In the singlet case the space function is symmetric and the electrons have a tendency to come close to each other. Therefore, the effect of the electrostatic repulsion is more serious; hence, a higher energy results. In the triplet case, the space function is antisymmetric and the electrons tend to avoid each other. Helium in spin-singlet states is known as **parahelium**, while helium in spin-triplet states is known as **orthohelium**. Each configuration splits into the para state and the ortho state, the para state lying higher. For the ground state only parahelium is possible. See Figure 6.5 for a schematic energy level diagram of the helium atom.

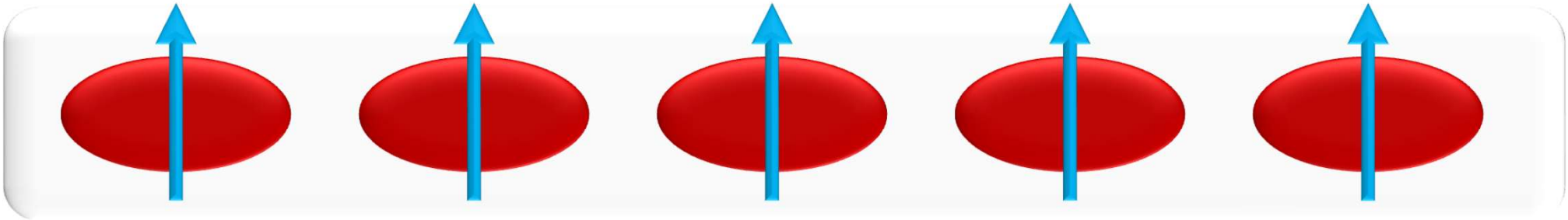


It is very important to recall that the original Hamiltonian is spin-independent because the potential is made up of just three Coulomb terms. There was no $\mathbf{S}_1 \cdot \mathbf{S}_2$-term whatsoever. Yet there is a spin-dependent effect—the electrons with parallel spins have a lower energy—that arises from Fermi-Dirac statistics.

This explanation of the apparent spin dependence of the helium atom energy levels is due to Heisenberg. The physical origin of ferromagnetism—alignment of the electron spins extended over microscopic distances—is also believed to be essentially the same, but the properties of ferromagnets are much harder to calculate quantitatively from first principles.

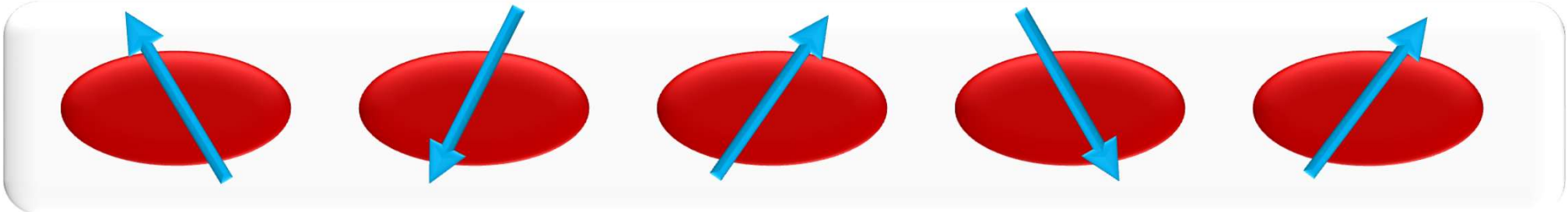
مثبت بودن انرژی تبادلی برای دستگاه های فرومغناطیس سبب می شود که انرژی کل کاهش یابد چون این انرژی با علامت منفی در انرژی کل هارتری-فوک وارد شده است

نکته فوق موید آن است که الکترونها در دستگاه های فرومغناطیس تمایل دارند هم جهت چیده شوند



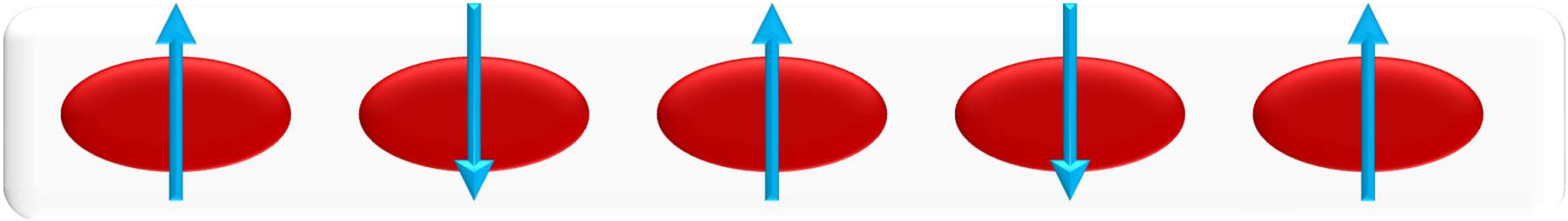
صفر بودن انرژی تبادلی برای دستگاه های پارامغناطیس سبب می شود که انرژی کل بدون تغییر باقی بماند

نکته فوق موید آن است که الکترونها در دستگاه های پارامغناطیس تمایل دارند به صورت تصادفی چیده شوند



منفی بودن انرژی تبادلی برای دستگاه های پادفرومغناطیس سبب می شود که انرژی کل افزایش یابد چون این انرژی با علامت منفی در انرژی کل هارتری-فوک وارد شده است

نکته فوق موید آن است که الکترونها در دستگاه های پادفرومغناطیس تمایل دارند غیر هم جهت چیده شوند



در این صورت انرژی تبادلی برای این دسته از مواد نیز در کل به صورت مثبت وارد می شود تا باز هم انرژی کل کاهش یابد

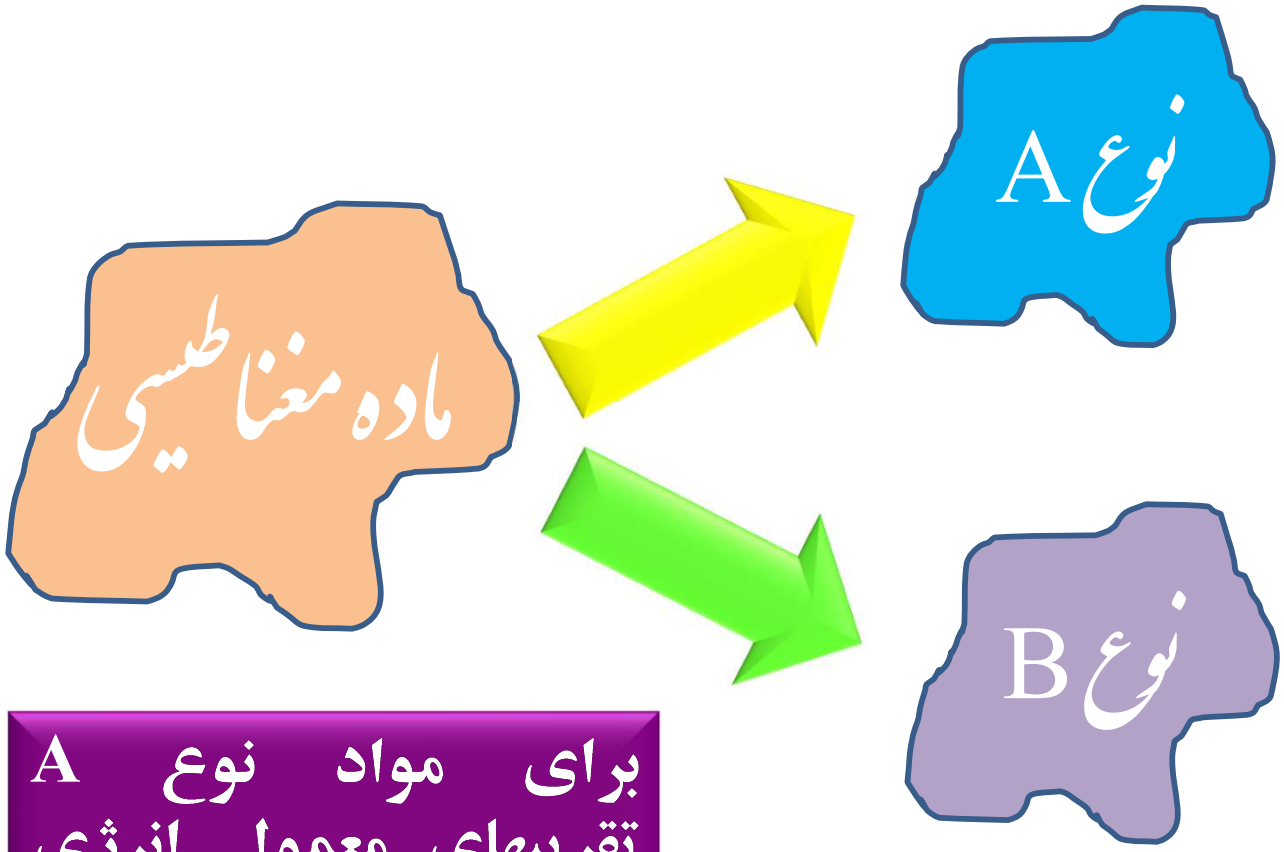
نکته: در مدل هارتری-فوک انتگرال تبادلی برای الکترونهای با اسپینهای پادموازی صفر است

نکته فوق از انتخاب تابع موج به صورت دترمینان اسلیتر ناشی می شود

توجه کنید که این امر کلی نیست

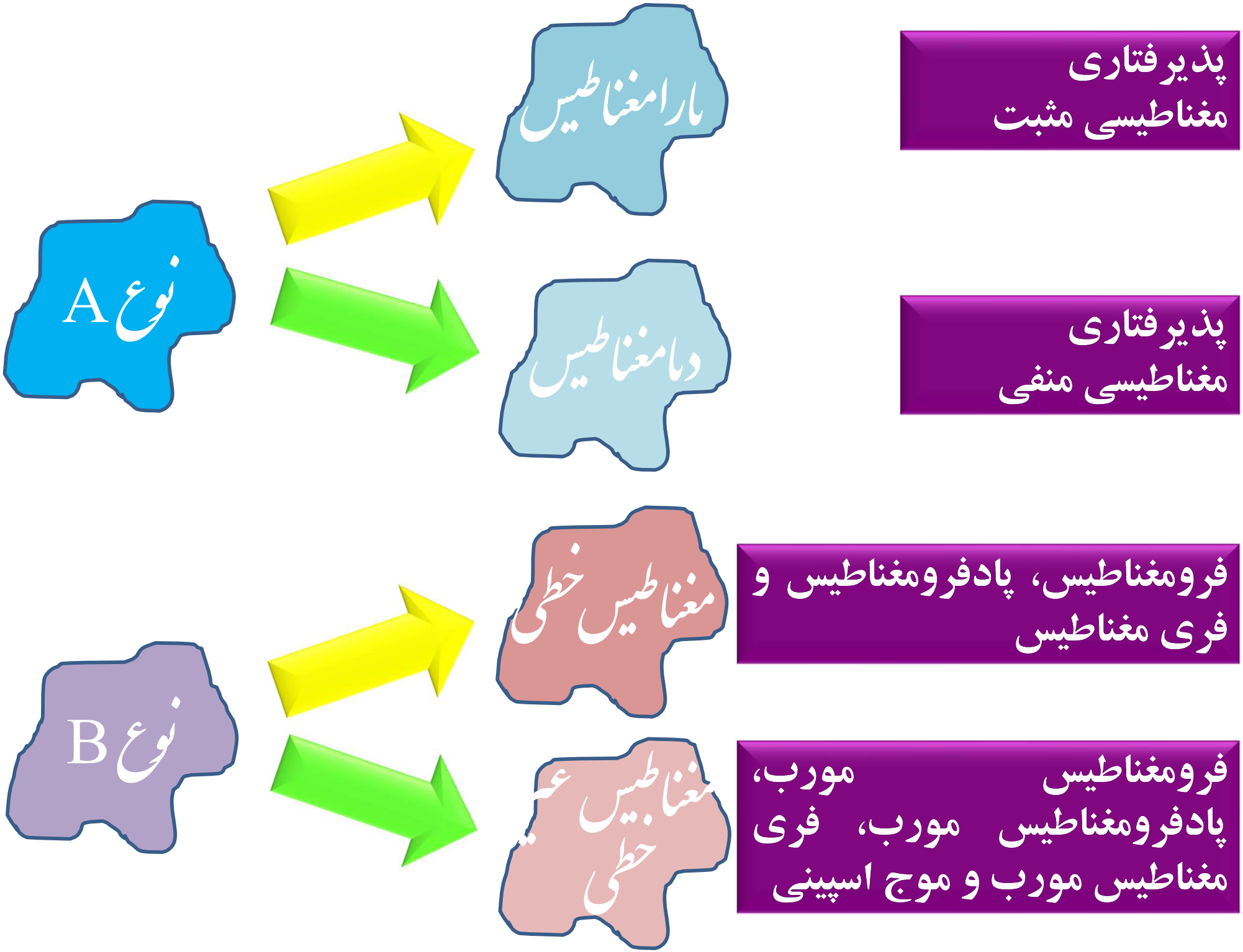
برهمکنش تبادلی–همبستگی

برهمکنش بین اسپینها وجود ندارد و همه ممانهای مغناطیسی به طور مستقل از یکدیگر عمل می کنند

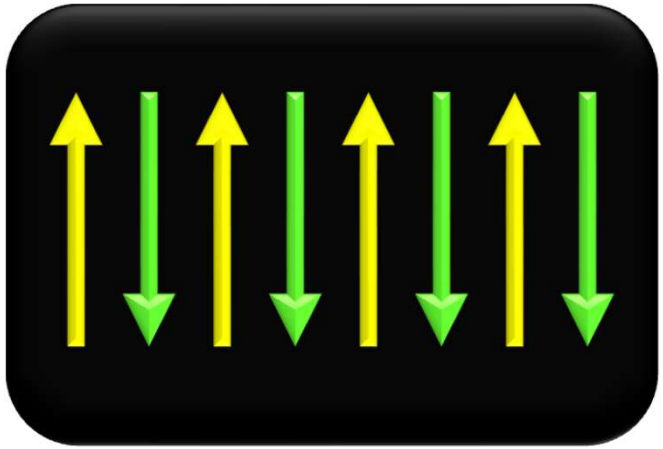


برهمکنش بین اسپینها وجود دارد و ممانهای مغناطیسی با هم جفت می شوند و در نتیجه یک چینش مغناطیسی شکل می گیرد

برای مواد نوع A تقریبهای معمول انرژی تبادلی غالبا مناسب اما برای نوع B گاهی مناسب نیستند


نوع A
نوع B
پارامغناطیس
دیامغناطیس
مغناطیس خطی
پذیرفتاری مغناطیسی مثبت
پذیرفتاری مغناطیسی منفی
فرومغناطیس، پادفرومغناطیس و فری مغناطیس
فرومغناطیس مورب، پادفرومغناطیس مورب، فری مغناطیس مورب و موج اسپینی

مغناطیس خطی



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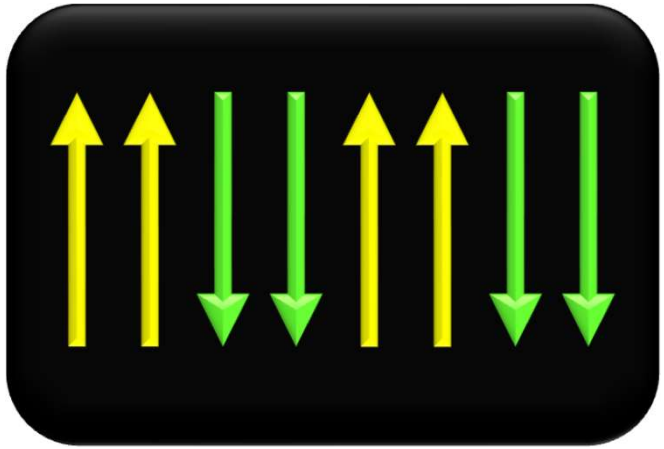

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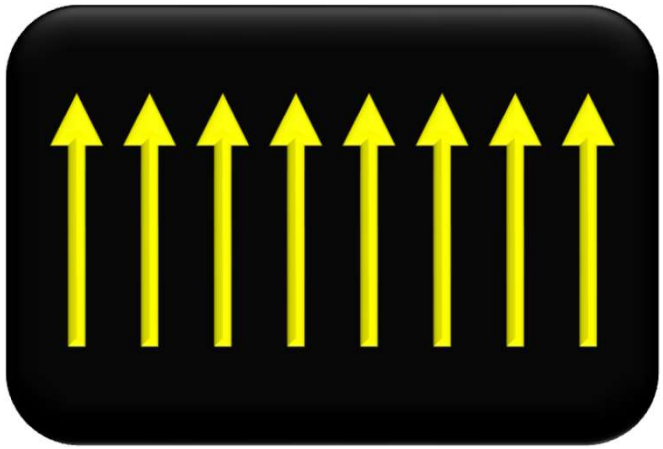

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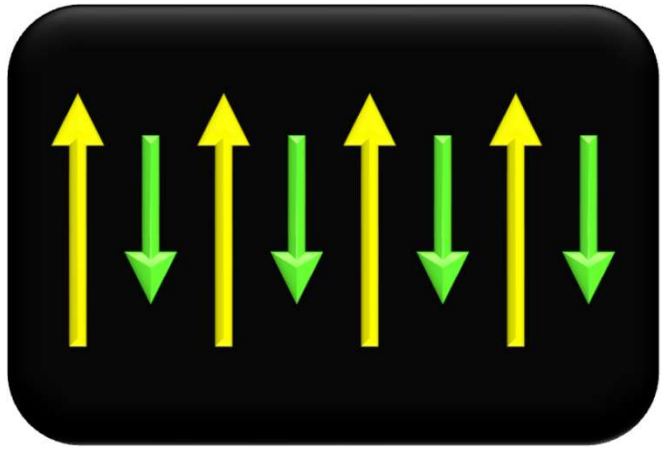
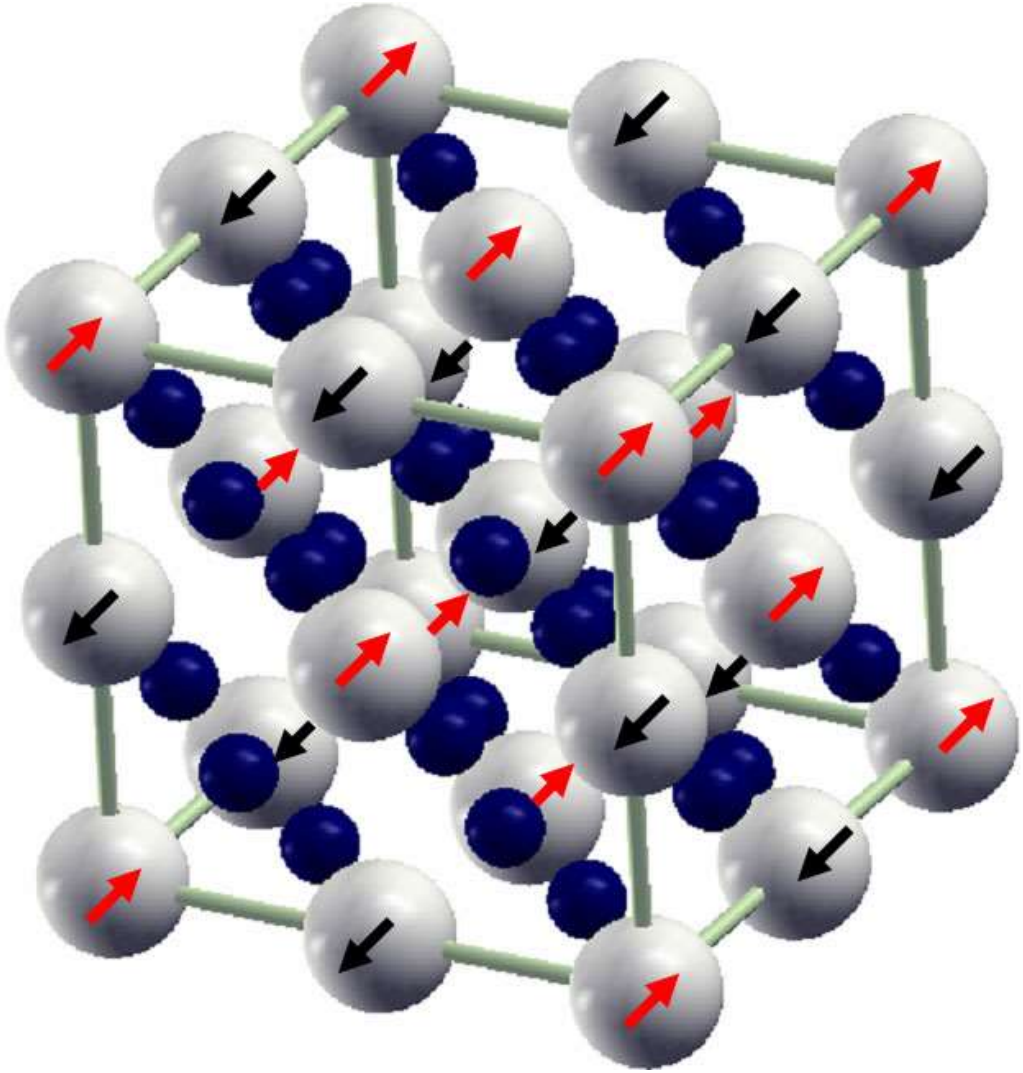
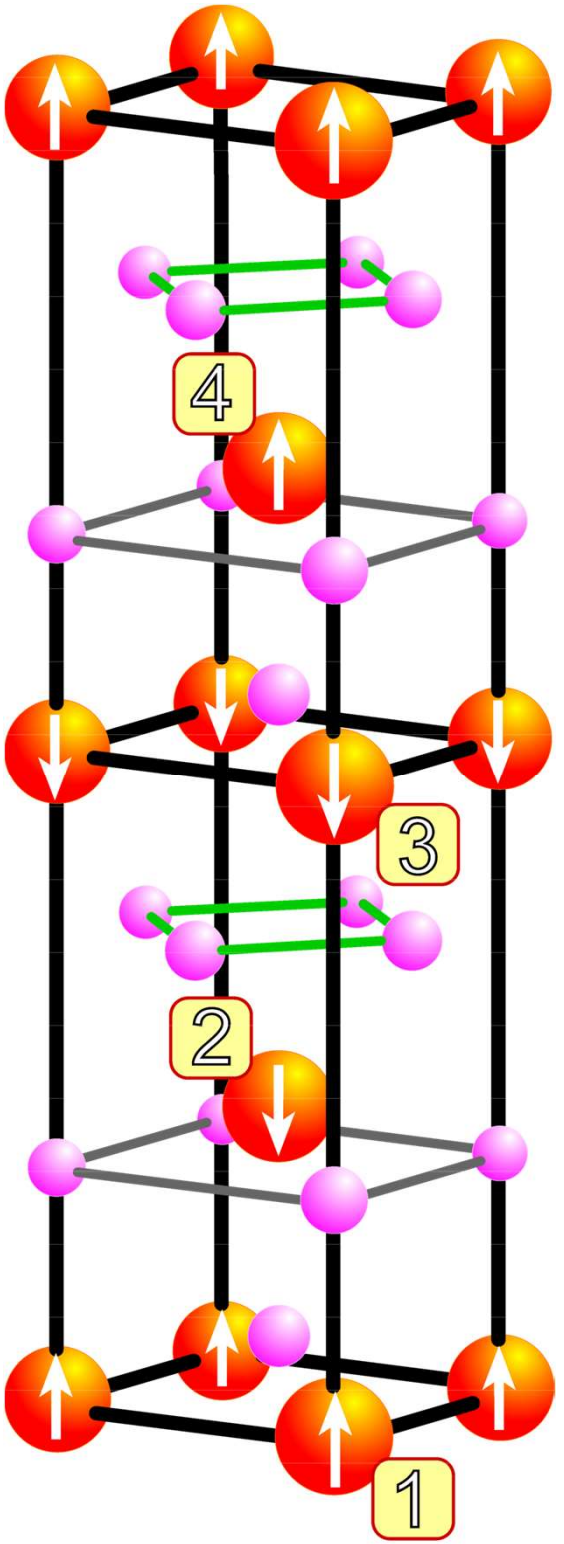
فرومغناطیس



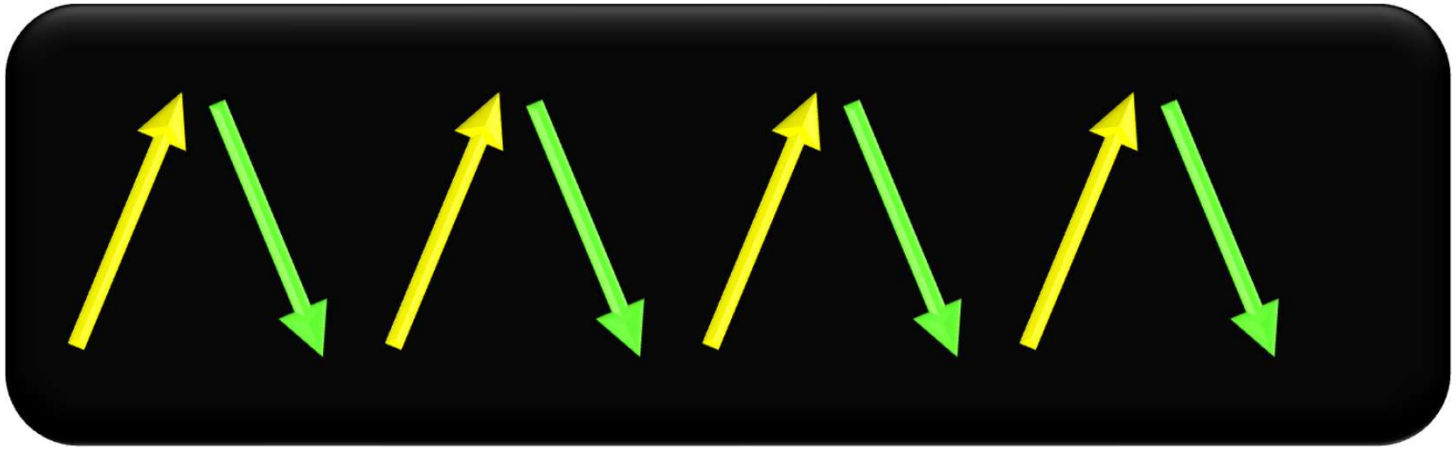
فری مغناطیس

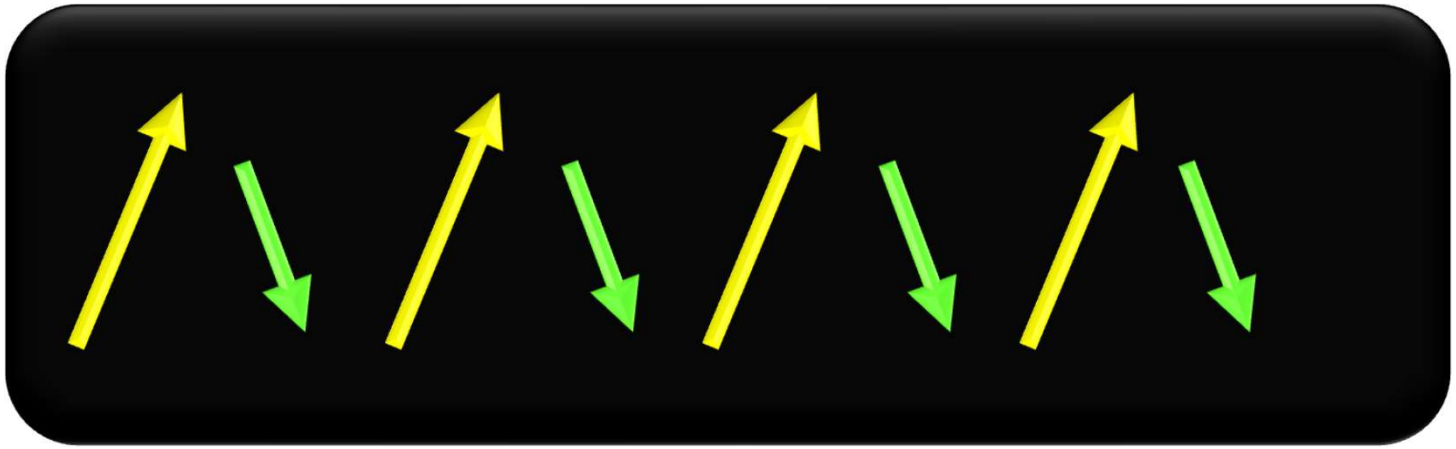
مغناطیس خطی



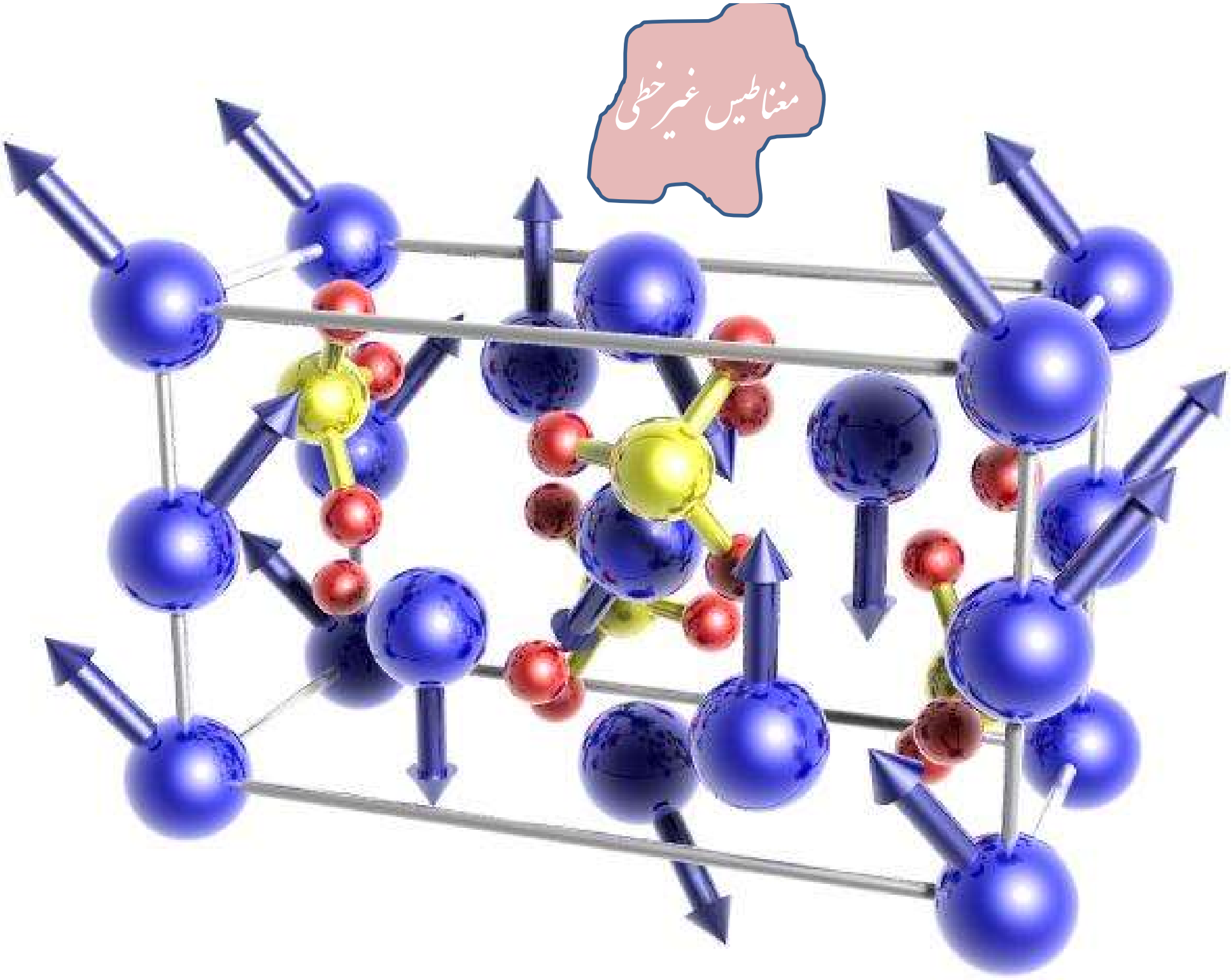


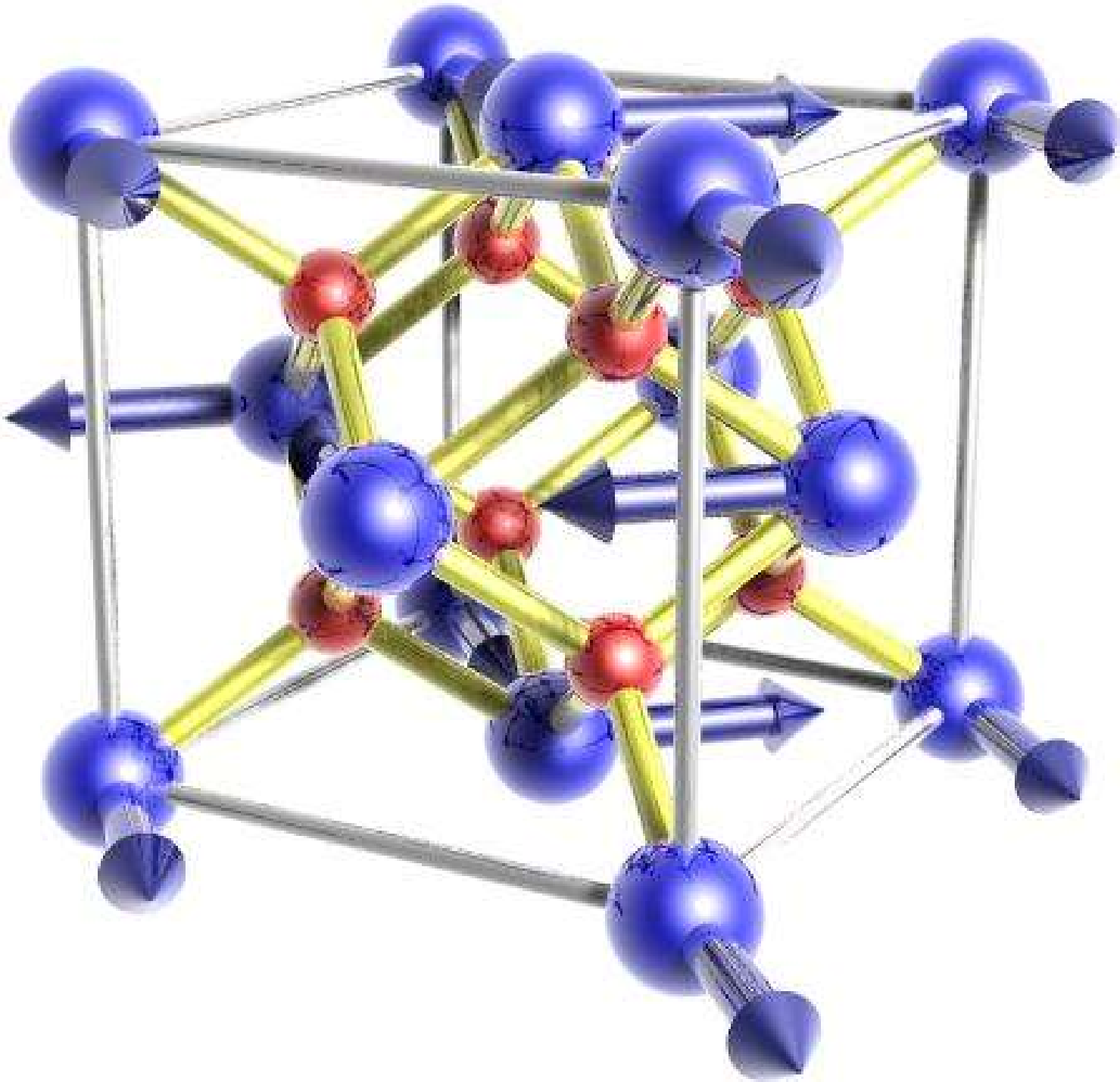
مغناطیس غیر خطی

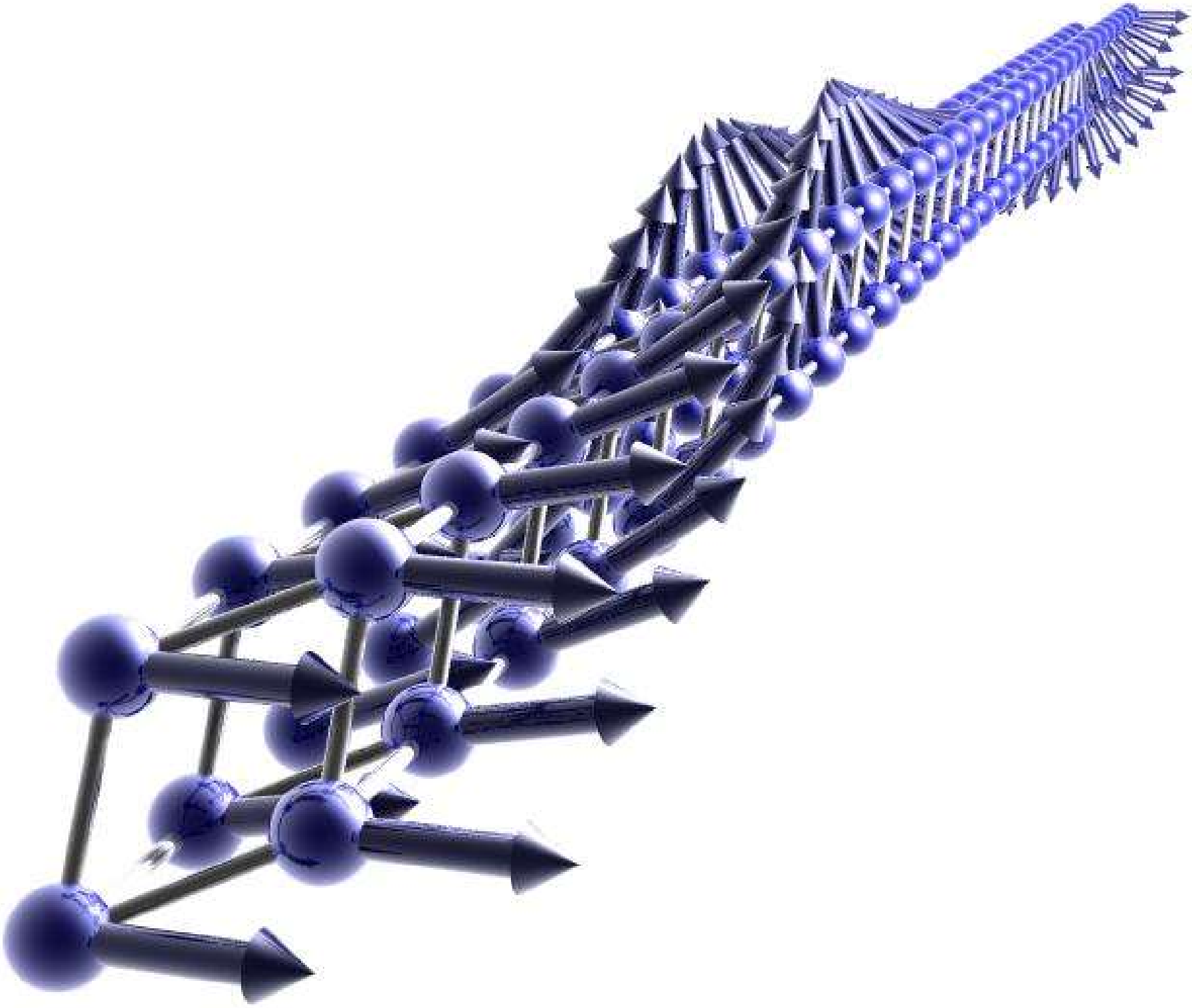




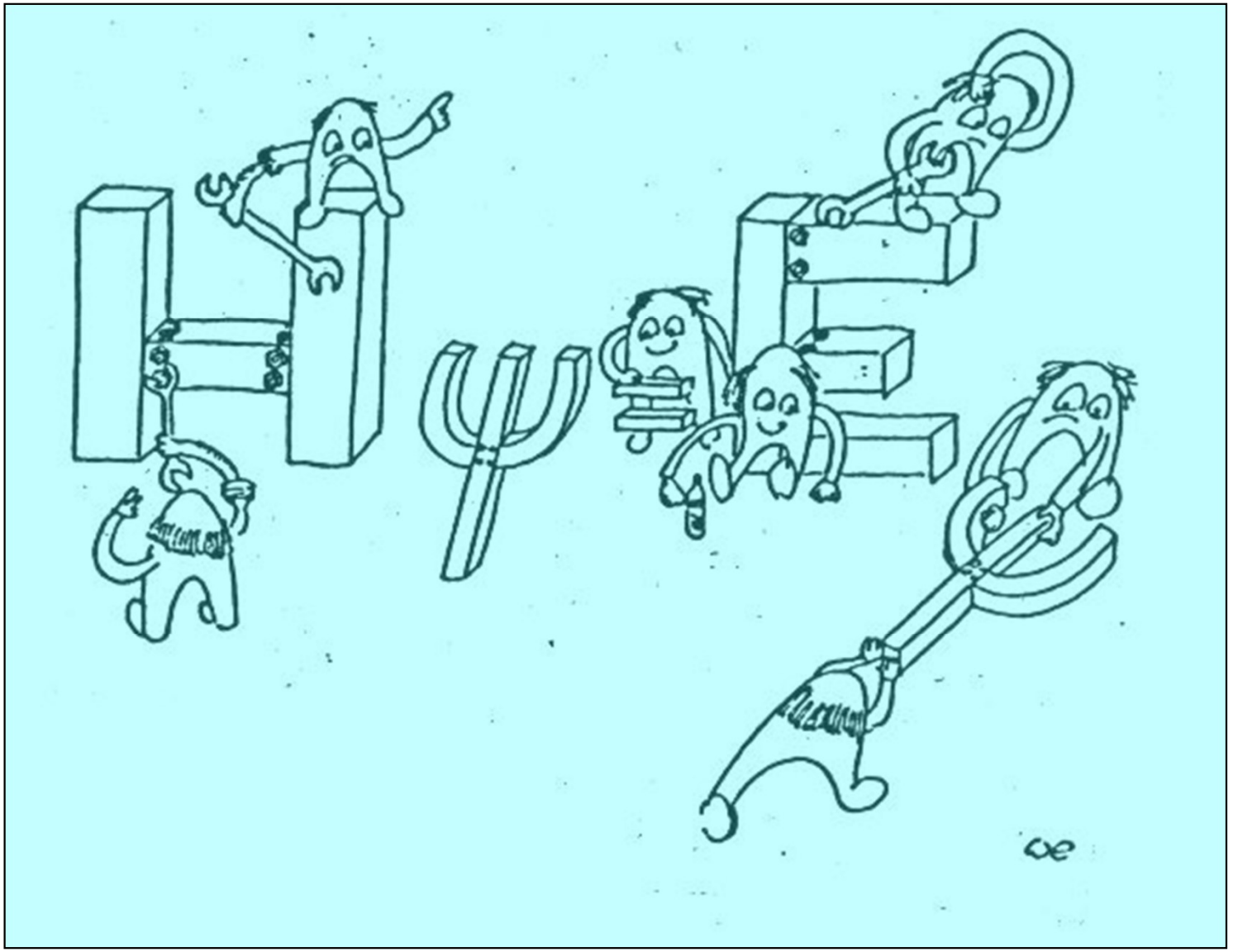
مغناطیس غیر خطی







What is a difference between them?



Why?

$$\begin{pmatrix} H_{11} & 0 \\ 0 & H_{11} \end{pmatrix}$$

Non-Magnetic systems

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \qquad \begin{pmatrix} H_{11} & 0 \\ 0 & H_{22} \end{pmatrix}$$

Magnetic systems

جفت شدگیهای اسپینی در دسته مواد مغناطیسی نوع B اعم از خطی یا غیرخطی طبیعتی کاملا کوانتوم مکانیکی دارند

این جفت شدگیها را برهمکنشهای تبادلی-همبستگی نامند

در روش هارتری این نوع برهمکنشها وجود ندارد

در روش هارتری-فوک به دلیل نوع خاص انتخاب تابع موج به صورت دترمینان اسلیتر فقط برهمکنشهای تبادلی وجود دارد و برهمکنشهایی از نوع همبستگی وجود ندارد


Wolfgang Pauli
(1900-1958)

منشاء برهمکنشهای تبادلی-همبستگی مطابق رابطه زیر از همپوشانی توابع موج الکترونی (شامل هردو بخش فضایی و اسپینی آن) نشات می گیرد

$$J_{ij} = \iint \Phi_i^*(\mathbf{r})\Phi_j^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\Phi_i(\mathbf{r}')\Phi_j(\mathbf{r})d\mathbf{r}\mathbf{r}'$$

این همپوشانیها با رعایت اصل طرد پاولی صورت می پذیرند

$$J_{ij} = \iint \Phi_i^*(\mathbf{r})\Phi_j^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\Phi_i(\mathbf{r}')\Phi_j(\mathbf{r})d\mathbf{r}\mathbf{r}'$$

انتگرال فوق حاصل استفاده از تقریب هارتری-فوک است

یعنی ما حتی از شکل برهمکنش تبادلی-همبستگی هم بی اطلاع هستیم

با این وجود در نظریات دیگر مثلا در نظریه تابعی چگالی هم رابطه فوق را به عنوان تعریف برهمکش تبادلی-همبستگی در نظر می گیریم و آن را تقریب می زنیم

خلاصه این که برهمکنش تبادلی-همبستگی یک برهمکنش علاوه بر برهمکنشهای معمول کولنی است که بواسطه اسپین الکترونی در صورت وجود همپوشانی فضایی به وجود می آید

در دستگاه های فرومغناطیس برهمکنشهای تبادلی-همبستگی بین یونهای همسایه سبب همجهت شدن اسپینها با هم می شود تا انرژی کل کمینه شود

در دستگاه های پادفرومغناطیس برهمکنشهای تبادلی-همبستگی بین یونهای همسایه سبب مختلف الجهت شدن اسپینها با هم می شود تا انرژی کل کمینه شود

در مدلهای ساده و ایده آلی همچون آیزینگ برهمکنش تبادلی-همبستگی بین نزدیکترین همسایگان به صورت ساده زیر در نظر گرفته می شود

$$H = -\sum_{i,j} J_{ij} \mathbf{S}_i . \mathbf{S}_j = -J \sum_{i,j} \mathbf{S}_i . \mathbf{S}_j$$

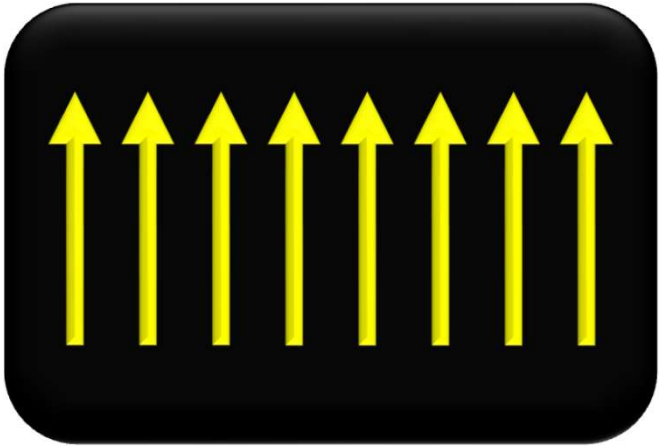
که در آن نه تنها از همه انواع برهمکنشها صرف نظر شده است، بلکه حتی همپوشانی موجود در بخش فضایی تابع موج هم فقط به صورت یک عدد ثابت به عنوان جفت شدگی بین نزدیکترین همسایگان در نظر گرفته شده است

$$H = -\sum_{i,j} J_{ij} \mathbf{S}_i . \mathbf{S}_j = -J \sum_{i,j} \mathbf{S}_i . \mathbf{S}_j$$

فرومغناطیس

$J > 0$

$$H^{\uparrow\uparrow} = -J \sum_{n.n.} \mathbf{S}_i . \mathbf{S}_j < H^{\uparrow\downarrow}$$



پادفرومغناطیس

$J < 0$

$$H^{\uparrow\downarrow} = -J \sum_{n.n.} \mathbf{S}_i . \mathbf{S}_j < H^{\uparrow\uparrow}$$