# Rule on filling electrons into single-particle states

## "Pauli Exclusion Principle"

- What is it in QM?
- Related to the symmetry (anti-symmetry) of many-electron wavefunctions under the operation of interchanging the coordinates of indistinguishable particles
- Big ideas that get into many branches of physics
- Pauli exclusion Principle is a by-product

# F. General Requirement on Many-(Indistinguishable)-electron Wavefunction

Key idea

> Many-electron wavefunctions must be anti-symmetric (change sign) with respect to interchanging the coordinates of two electrons

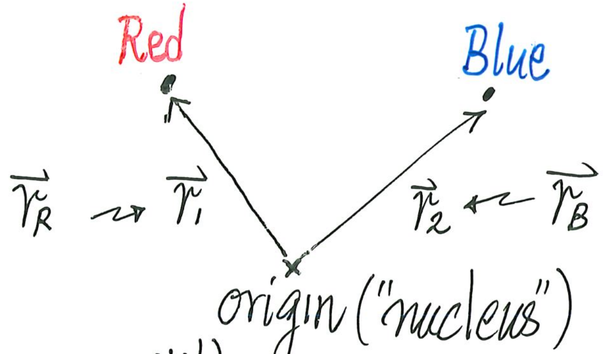
Contexts

- Electrons in an atom, a molecule, $\underbrace{\text{a solid}}_{}$ ~$10^{23}$ electrons in $cm^3$ of solid
- Many-electron systems
- The electrons are identical particles (全同粒子) [contrast to red, green, blue, … balls]
- When electrons "live" in a system, they are indistinguishable (不可分辨的)
  (e.g. the two electrons in a helium atom)
  the ~$10^{23}$ electrons in a piece of metal

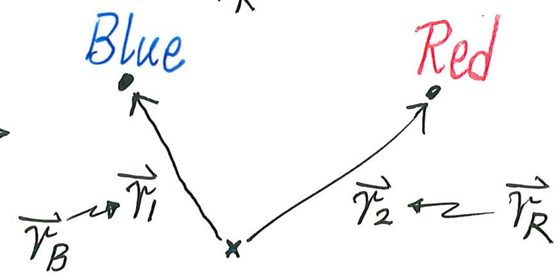
# How does indistinguishability affect the form of many-electron wavefunction?

- Two distinguishable particles (red ball, blue ball)

General 2-particle wavefunction $\psi^{(dist.)}(\underbrace{\text{red ball coordinates}}_{\vec{r}_R}, \underbrace{\text{blue ball coordinates}}_{\vec{r}_B})$




← interchange two particles →




Two different situations

$\psi^{(dist.)}(\vec{r}_R = \vec{r}_1, \vec{r}_B = \vec{r}_2)$

OR

$\psi^{(dist.)}(\vec{r}_1, \vec{r}_2)$

$\psi^{(dist.)}(\vec{r}_R = \vec{r}_2, \vec{r}_B = \vec{r}_1)$

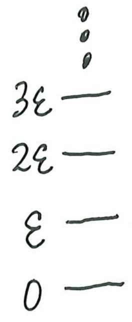
OR

$\psi^{(dist.)}(\vec{r}_2, \vec{r}_1)$

$\Downarrow$

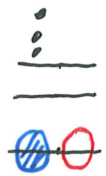
Impose NO requirement on form of $\psi^{(dist.)}(\vec{r}_R, \vec{r}_B)$

## Aside: Connection to statistical physics




Two distinguishable particles 
to fill into the single-particle states

(a) Total energy = 0, how many ways to achieve this?

1 way only 

(b) Total energy = 2ε, how many ways to achieve this?

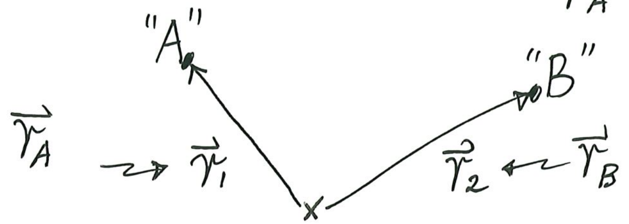

different situations

In statistical physics, Total energy = 2ε [marcostate]

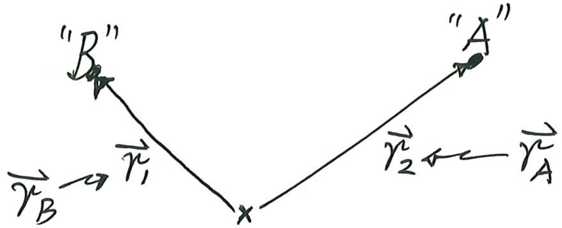
\# ways [# microstates given a macrostate]

- Very different for <u>two indistinguishable particles</u> (call them $\overbrace{A \ \& \ B}^{\text{identical otherwise}}$)

$$\psi(\underbrace{\text{particle A coordinates}}_{\vec{r}_A}, \underbrace{\text{particle B coordinates}}_{\vec{r}_B})$$




← interchange two particles →




$\psi(\vec{r}_A = \vec{r}_1, \vec{r}_B = \vec{r}_2)$

OR

$\psi(\vec{r}_1, \vec{r}_2)$

a value for the function

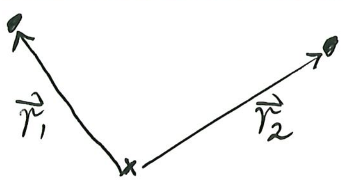
For <u>indistinguishable</u> particles, <u>same</u> physical <u>situation</u>

$\psi(\vec{r}_A = \vec{r}_2, \vec{r}_B = \vec{r}_1)$

OR

$\psi(\vec{r}_2, \vec{r}_1)$ ← "another" value of function $\psi$

<u>Same situation</u>




Key idea

impose <u>relation between</u> $\psi(\vec{r}_1, \vec{r}_2)$ & $\psi(\vec{r}_2, \vec{r}_1)$

The situation is:

"$\underbrace{\text{One particle}}$ takes on $\vec{r}_1$ and $\underbrace{\text{the other}}$ takes on $\vec{r}_2$"

[but can't tell which particle is which] ($\because$ indistinguishable)

- Following notations in standard textbooks:

$$\psi(1,2) \qquad \text{versus} \qquad \psi(2,1)$$

1 refers to one particle; 2 refers to the other particle

Question becomes: Restriction on $\underbrace{\psi(1,2)}_{\text{Note: wavefunction}}$ due to indistinguishability of two particles?

- Born's interpretation of wavefunction in QM

  related to $|\psi|^2$ (not $\psi$ itself)

$$\boxed{|\psi(1,2)|^2 = |\psi(2,1)|^2} \tag{27}$$

- For 2 indistinguishable particles, both sides refer to the probability density of finding one particle at "1" and the other particle at "2"

- Eq. (27) is the restriction imposed due to indistinguish particles

- Eq. (27) is about $|\psi|^2$ ("Exchange symmetry")

- Eq. (27) is the Key Result (must understand)

- Argument works for general many-particle wavefunctions [don't need to invoke single-particle states up to now]

# Possible Consequences of $|\psi(1,2)|^2 = |\psi(2,1)|^2$

(i) $\underbrace{\psi(1,2) = \psi(2,1)}$ (28) ← Work for Bosons†

Wavefunction is symmetric w.r.t. interchanging two particles

- A general statement for many-boson wavefunctions

(ii) $\underbrace{\psi(1,2) = -\psi(2,1)}$ (29) ← Work for Fermions† (electrons)

Wavefunction is Anti-symmetric (change sign) w.r.t. interchanging two particles

- A general statement for many-fermion wavefunctions

$\boxed{\text{Nature made only these two choices}^{\dagger}}$

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† All particles have either integer spins or half-integer spin. All spin $1/2, 3/2, 5/2, \cdots$ particles are fermions. All spin $0, 1, 2, \cdots$ particles are bosons.

Electron has $s = 1/2$ (spin-half)

$\Rightarrow$ Electrons are fermions (must obey (29))

Key Concept

$$\boxed{\text{Many-electron Wavefunction must be anti-symmetric w.r.t. interchanging two particles}} \quad (30)$$

- Applicable to all cases: electrons in atom (He, C, Na, U, ...)
  electrons in molecule ($H_2$, $CO_2$, $H_2O$, $C_6H_6$, ...)
  electrons in solid (metals, insulators, semiconductors, ...)
- Eq. (30) must be satisfied
  - true for general $\psi(1,2)$ or $\underbrace{\psi(1,2,\cdots,N)}_{N\text{-electron}}$
  - even if general $\psi$ is approximated by product of single-particle states (e.g. Hartree or Hartree-Fock)

Next Question: How to enforce (30) in terms of electrons occupying single-particle states?

[Ans: Pauli Exclusion Principle]

Extension/Further Reading (Optional)

- See chapter on "Identical Particles" in standard textbooks
- Relation between spin and "statistics" (fermions OR bosons) has a deeper root in quantum field theory