

Contents: Symmetry / Anti-Symmetry wave function

Form of 2-particle wavefunction $\Psi(r_1; r_2) = ?$

Try: $\Psi(r_1; r_2) = \Psi_{n_1}(r_1)\Psi_{n_2}(r_2)$ (Eq. I)

Gives wrong answer for two electrons confined to He atom if particle-particle interaction is neglected.

How to do better? Realized that at the microscopic level it is impossible to distinguish between the two electrons. What does this imply? Eq. I is ruled out.

For two particles, we have two choices:

$$\Psi(r_1; r_2) = \Psi(r_2; r_1) \quad (\text{Eq. II})$$

OR

$$\Psi(r_1; r_2) = -\Psi(r_2; r_1) \quad (\text{Eq. III})$$

Symmetry / Anti-Symmetry wave function

What are acceptable forms for the 2-particle wavefunction consistent with indistinguishable particles?

One possibility is

$$\Psi_s(r_1; r_2) = \frac{1}{\sqrt{2}} [\Psi_n(r_1)\Psi_m(r_2) + \Psi_n(r_2)\Psi_m(r_1)]$$

this automatically makes $\Psi_s(r_1; r_2) = +\Psi_s(r_2; r_1)$

The
"exchange"
term

Another possibility is

$$\Psi_a(r_1; r_2) = \frac{1}{\sqrt{2}} [\Psi_n(r_1)\Psi_m(r_2) - \Psi_n(r_2)\Psi_m(r_1)]$$

this automatically makes $\Psi_a(r_1; r_2) = -\Psi_a(r_2; r_1)$

Numerically speaking, the minus sign doesn't matter much since ultimately you calculate $|\Psi|^2$

Any wavefunction is said to be asymmetric under particle exchange if the wavefunction flips sign when the particles are interchanged

Symmetry / Anti-Symmetry wave function

What are the consequences of these wavefunctions?

Focus on calculating the probability to find both particles in the same quantum state w . There are three cases to consider:

Case I: Two distinguishable (identical) particles in same quantum state w

$$\Psi_D(r_1, r_2) = \Psi_n(r_1)\Psi_m(r_2)|_{n=m=w} = \Psi_w(r_1)\Psi_w(r_2)$$

$$\text{Probability Density} \propto \Psi_w(r_1)\Psi_w(r_2)\Psi_w^*(r_1)\Psi_w^*(r_2) dV_1 dV_2$$

Symmetry / Anti-Symmetry wave function

Case II: Two indistinguishable (identical) particles described by symmetric wavefunction in same quantum state w

$$\begin{aligned}\Psi_s(r_1; r_2) &= \frac{1}{\sqrt{2}} [\Psi_n(r_1)\Psi_m(r_2) + \Psi_n(r_2)\Psi_m(r_1)] \Big|_{n=m=w} \\ &= \frac{1}{\sqrt{2}} [\Psi_w(r_1)\Psi_w(r_2) + \Psi_w(r_2)\Psi_w(r_1)] \\ &= \frac{2}{\sqrt{2}} [\Psi_w(r_1)\Psi_w(r_2)] = \sqrt{2} [\Psi_w(r_1)\Psi_w(r_2)]\end{aligned}$$

$$\begin{aligned}\text{Probability Density} &\propto \Psi_s(r_1; r_2)\Psi_s^*(r_1; r_2) dV_1 dV_2 \\ &= \textcircled{2} \times \Psi_w(r_1)\Psi_w(r_2)\Psi_w^*(r_1)\Psi_w^*(r_2) dV_1 dV_2\end{aligned}$$

Symmetry / Anti-Symmetry wave function

Case III: Two indistinguishable (identical) particles described by antisymmetric wavefunction in same quantum state w

$$\begin{aligned}\Psi_a(r_1; r_2) &= \frac{1}{\sqrt{2}} [\Psi_n(r_1)\Psi_m(r_2) - \Psi_n(r_2)\Psi_m(r_1)] \Big|_{n=m=w} \\ &= \frac{1}{\sqrt{2}} [\Psi_w(r_1)\Psi_w(r_2) - \Psi_w(r_2)\Psi_w(r_1)] \\ &= 0\end{aligned}$$

$$\text{Probability Density} \propto \Psi_a(r_1; r_2)\Psi_a^*(r_1; r_2) dV_1 dV_2 = 0$$

Symmetry / Anti-Symmetry wave function

Which wavefunction Ψ_s or Ψ_a should we choose for electrons?

Pauli's exclusion principle helps us decide - since for electrons in atoms, two electrons **are never found** in the same quantum state.

Pauli exclusion implies that Ψ_a is the correct choice for electrons since if $n=m$ (i.e. if we insist that two electrons have the same quantum state), we have:

$$\begin{aligned}\Psi_a(r_1; r_2) &= \frac{1}{\sqrt{2}} [\Psi_n(r_1)\Psi_m(r_2) - \Psi_n(r_2)\Psi_m(r_1)]_{if\ n=m} \\ &= \frac{1}{\sqrt{2}} [\Psi_n(r_1)\Psi_n(r_2) - \Psi_n(r_2)\Psi_n(r_1)] \equiv 0\end{aligned}$$

Writing Ψ_a is just an elegant (and equivalent) way to express the Pauli exclusion principle!

Symmetry / Anti-Symmetry wave function

This discussion implies that there are fundamentally two different types of quantum particles

Bosons:
$$\Psi_s(r_1; r_2) = \frac{1}{\sqrt{2}} [\Psi_n(r_1)\Psi_m(r_2) + \Psi_n(r_2)\Psi_m(r_1)]$$

$$\Psi_s(r_1; r_2) = \Psi_s(r_2; r_1)$$

Bosons have enhanced probability of being in the same quantum state.

Fermions:
$$\Psi_a(r_1; r_2) = \frac{1}{\sqrt{2}} [\Psi_n(r_1)\Psi_m(r_2) - \Psi_n(r_2)\Psi_m(r_1)]$$

$$\Psi_a(r_1; r_2) = -\Psi_a(r_2; r_1)$$

Fermions have zero probability of being in the same quantum state.

Symmetry / Anti-Symmetry wave function

To guarantee that no two particles have the same quantum state, make sure the wavefunction is **anti-symmetric** under the exchange of any two particles. If the two states happen to be the same, the wavefunction will automatically become ZERO.

Hence,the Slater determinant:

$$\Psi_a(r_1; r_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \Psi_n(r_1) & \Psi_m(r_1) \\ \Psi_n(r_2) & \Psi_m(r_2) \end{vmatrix}$$

↑ Quantum state n ↑ Quantum state m

← Coordinates for particle 1
← Coordinates for particle 2

Important implication: Ψ_a says that either of the two indistinguishable particles are equally likely to be found in either state.

School of Basic and Applied Science

Course Code :MSCP 6002

Course Name: ATOMIC AND MOLECULAR PHYSICS

References:

1. Raj Kumar, Atomic and Molecular Spectra: Laser, Kedear Nath Publication, Meerut, 2015
2. Arthur Beiser, Concepts of Modern Physics, 6th ed., McGraw Hill, New Delhi, 2008.
3. Harvey Elliott White, Introduction to Atomic Spectra, McGraw Hill, 1963.
4. G M Barrow, Introduction to molecular spectroscopy, Tata McGraw Hill, Japan, 1962.
5. Internet
6. <https://www.youtube.com/watch?v=Yexx6IJXeEM>

GALGOTIAS
UNIVERSITY