

Identical particles
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In classical mechanics, identical particles (such as electrons) do not lose their "individuality", despite the identity of their physical properties. In quantum mechanics, the situation is entirely different. Because of the Heisenberg's principle of uncertainty, the concept of the path of an electron ceases to have any meaning. Thus, there is in principle no possibility of separately following each of a number of similar particles and thereby distinguishing them. In quantum mechanics, identical particles entirely lose their individuality. The principle of the in-distinguishability of similar particles plays a fundamental part in the quantum theory of system composed of identical particles. Here we start to consider a system of only two particles. Because of the identity of the particles, the states of the system obtained from each other by interchanging the two particles must be completely equivalent physically.

1 System of particles 1 and 2

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

$$|\psi_a\rangle = |k'\rangle_1 |k''\rangle_2 \quad |\psi_b\rangle = |k''\rangle_1 |k'\rangle_2$$

Even though the two particles are indistinguishable, mathematically $|\psi_a\rangle$ and $|\psi_b\rangle$ are distinct kets for $|k'\rangle \neq |k''\rangle$. In fact we have $\langle\psi_a|\psi_b\rangle = 0$. Suppose we make a measurement on the two particle system.

$|k'\rangle$: state of one particle and $|k''\rangle$: state of the other particle.

We do not know a priori whether the state ket is $|\psi_a\rangle = |k'\rangle_1 |k''\rangle_2$ or $|\psi_b\rangle = |k''\rangle_1 |k'\rangle_2$ or -for that matter- any linear combination of the two: $c_a |\psi_a\rangle + c_b |\psi_b\rangle$.

2 Exchange degeneracy

A specification of the eigenvalue of a complete set of observables does not completely determine the state ket.

Mathematics of permutation symmetry:

$$\hat{P}_{12} |\psi_a\rangle = \hat{P}_{12} |k'\rangle_1 |k''\rangle_2 = |k''\rangle_1 |k'\rangle_2 = |\psi_b\rangle.$$

Clearly

$$\hat{P}_{21} = \hat{P}_{12}, \quad \text{and} \quad \hat{P}_{12}^2 = 1.$$

Under \hat{P}_{12} , particle 1 having $|k'\rangle$ becomes particle 1 having $|k''\rangle$; particle 2 having $|k''\rangle$ becomes particle 1 having $|k'\rangle$. In other words, it has the effect of interchanging 1 and 2.

((Note))

Matrix element of $\hat{P}_{21} = \hat{P}_{12}$ in terms of $|\psi_a\rangle = |k'\rangle_1 |k''\rangle_2$ and $|\psi_b\rangle = |k''\rangle_1 |k'\rangle_2$

$$\hat{P}_{12}|\psi_a\rangle = \hat{P}_{12}|k'\rangle_1 |k''\rangle_2 = |k''\rangle_1 |k'\rangle_2 = |\psi_b\rangle,$$

$$\hat{P}_{12}|\psi_b\rangle = \hat{P}_{12}|k''\rangle_1 |k'\rangle_2 = |k'\rangle_1 |k''\rangle_2 = |\psi_a\rangle.$$

Matrix element of $\hat{P}_{21} = \hat{P}_{12}$

$$\hat{P}_{12} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

or

$$\begin{array}{cc} & |\psi_a\rangle & |\psi_b\rangle \\ \langle\psi_a| & 0 & 1 \\ \langle\psi_b| & 1 & 0 \end{array}$$

Eigensystem[\hat{P}_{12}]

$\lambda = 1$ (symmetric):

$$\hat{P}_{12}|\psi_{symm}\rangle = |\psi_{symm}\rangle$$

$$|\psi_{symm}\rangle = \frac{1}{\sqrt{2}}(|k'\rangle_1 |k''\rangle_2 + |k''\rangle_1 |k'\rangle_2) = \frac{1}{\sqrt{2}}(\hat{1} + \hat{P}_{12})|k'\rangle_1 |k''\rangle_2$$

where the symmetrizer is defined by

$$\hat{S} = \frac{1}{\sqrt{2}}(\hat{1} + \hat{P}_{12})$$

$\lambda = -1$ (anti-symmetric)

$$\hat{P}_{12}|\psi_{anti}\rangle = -|\psi_{anti}\rangle$$

$$|\psi_{anti}\rangle = \frac{1}{\sqrt{2}}(|k'\rangle_1 |k''\rangle_2 - |k''\rangle_1 |k'\rangle_2) = \frac{1}{\sqrt{2}}(\hat{1} - \hat{P}_{12})|k'\rangle_1 |k''\rangle_2$$

where the antisymmetrizer is defined by

$$\hat{A} = \frac{1}{\sqrt{2}}(\hat{1} - \hat{P}_{12})$$

Our consideration can be extended to a system made up of many identical particles. A transposition is a permutation which simply exchange the role of two of the particles, without touching others.

$$\hat{P}_{ij} |k'\rangle_1 |k''\rangle_2 \dots |k^i\rangle_i |k^{i+1}\rangle_{i+1} \dots |k^j\rangle_j \dots = |k'\rangle_1 |k''\rangle_2 \dots |k^j\rangle_i |k^{i+1}\rangle_{i+1} \dots |k^i\rangle_j \dots$$

The **transposition operators** \hat{P}_{ij} are Hermitian ($\hat{P}_{ij}^+ = \hat{P}_{ij}$)

$$\hat{P}_{ij}^2 = 1$$

So that \hat{P}_{ij} is an unitary operator. The allowed eigenvalues of \hat{P}_{ij} are ± 1 . It is important to note, however, that in general

$$[\hat{P}_{ij}, \hat{P}_{kl}] \neq 0.$$

(i) The first example

Now we consider a **permutation operator** \hat{P}_{123} for

$$\hat{P}_{123} |k'\rangle_1 |k''\rangle_2 |k'''\rangle_3 = |k'\rangle_2 |k''\rangle_3 |k'''\rangle_1 = |k'''\rangle_1 |k'\rangle_2 |k''\rangle_3$$

for the system of 3 identical particles ($|k'\rangle_1 |k''\rangle_2 |k'''\rangle_3$)

$$P_{123} = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix}$$

This means replacement of $1 \rightarrow 2, 2 \rightarrow 3, 3 \rightarrow 1$.

$$P_{123} = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} \begin{pmatrix} 2 & 1 & 3 \\ 2 & 3 & 1 \end{pmatrix} = P_{12} P_{13}$$

Quantum mechanically this is not correct. The correct one is

$$\hat{P}_{123} = \hat{P}_{13} \hat{P}_{12}$$

(ii) The second example

$$P_{123} = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} \begin{pmatrix} 1 & 3 & 2 \\ 2 & 3 & 1 \end{pmatrix} = P_{23} P_{12}$$

or quantum mechanically

$$\hat{P}_{123} = \hat{P}_{12} \hat{P}_{23}$$

(iii) The third example

$$P_{132} = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} \begin{pmatrix} 3 & 2 & 1 \\ 3 & 1 & 2 \end{pmatrix} = P_{13} P_{12}$$

or quantum mechanically

$$\hat{P}_{132} = \hat{P}_{12} \hat{P}_{13}$$

((Proof))

$$\hat{P}_{12} \hat{P}_{13} |k'\rangle_1 |k''\rangle_2 |k'''\rangle_3 = \hat{P}_{12} |k'''\rangle_1 |k''\rangle_2 |k'\rangle_3 = |k''\rangle_1 |k'''\rangle_2 |k'\rangle_3$$

and

$$\hat{P}_{132} |k'\rangle_1 |k''\rangle_2 |k'''\rangle_3 = |k'\rangle_3 |k''\rangle_1 |k'''\rangle_2 = |k''\rangle_1 |k'''\rangle_2 |k'\rangle_3$$

Therefore we have $\hat{P}_{132} = \hat{P}_{12} \hat{P}_{13}$.

Any permutation operators can be broken into a product of transposition operators.

$$\hat{P}_{132} = \hat{P}_{23} \hat{P}_{12} = \hat{P}_{13} \hat{P}_{23} = \hat{P}_{12} \hat{P}_{13} = \hat{P}_{23} \hat{P}_{12} \hat{P}_{23}^2 = \dots$$

The decomposition is not unique. However, for a given permutation, it can be shown that the parity of the number of transposition into which it can be broken down is always the same: it is called the **parity of the permutation**.

$$\hat{P}_{132} = \hat{P}_{23} \hat{P}_{12} = \hat{P}_{13} \hat{P}_{23} = \hat{P}_{12} \hat{P}_{13} = \hat{P}_{23} \hat{P}_{12} \hat{P}_{23}^2 \quad \text{even permutation}$$

$$\hat{P}_{123} = \hat{P}_{12} \hat{P}_{23} = \hat{P}_{13} \hat{P}_{12} : \quad \text{even permutation}$$

$$\hat{P}_{23} \quad \text{odd permutation}$$

$$\hat{P}_{12} \quad \text{odd permutation}$$

$$\hat{P}_{31} \quad \text{odd permutation}$$

((Note))

$$\hat{P}_{132} = \hat{P}_{321} = \hat{P}_{213}$$

3 Symmetrizer and antisymmetrizer

Now we consider the two Hermitian operators

$$\hat{S} = \frac{1}{N!} \sum_{\alpha} \hat{P}_{\alpha} : \text{symmetrizer}$$

$$\hat{A} = \frac{1}{N!} \sum_{\alpha} \varepsilon_{\alpha} \hat{P}_{\alpha} : \text{antisymmetrizer}$$

where $\varepsilon_{\alpha} = 1$ if \hat{P}_{α} is an even permutation and $\varepsilon_{\alpha} = -1$ if \hat{P}_{α} is an odd permutation.

$$\hat{S}^+ = \hat{S} \text{ and } \hat{A}^+ = \hat{A}.$$

((Theorem-1))

If \hat{P}_{α_0} is an arbitrary permutation operator, we have

$$\begin{aligned} \hat{P}_{\alpha_0} \hat{S} &= \hat{S} \hat{P}_{\alpha_0} = \hat{S} \\ \hat{P}_{\alpha_0} \hat{A} &= \hat{A} \hat{P}_{\alpha_0} = \varepsilon_{\alpha_0} \hat{A} \end{aligned} \quad (1)$$

((Proof))

This is due to the fact that

$$\hat{P}_{\alpha_0} \hat{P}_{\alpha} = \hat{P}_{\beta}$$

such that

$$\varepsilon_{\beta} = \varepsilon_{\alpha_0} \varepsilon_{\alpha}$$

or

$$\varepsilon_{\alpha_0} \varepsilon_{\beta} = \varepsilon_{\alpha_0}^2 \varepsilon_{\alpha} = \varepsilon_{\alpha}$$

$$\hat{P}_{\alpha_0} \hat{S} = \frac{1}{N!} \sum_{\alpha} \hat{P}_{\alpha_0} \hat{P}_{\alpha} = \frac{1}{N!} \sum_{\alpha} \hat{P}_{\beta} = \hat{S}$$

$$\hat{P}_{\alpha_0} \hat{A} = \frac{1}{N!} \sum_{\alpha} \varepsilon_{\alpha} \hat{P}_{\alpha_0} \hat{P}_{\alpha} = \frac{1}{N!} \sum_{\alpha} \varepsilon_{\alpha_0} \varepsilon_{\beta} \hat{P}_{\beta} = \varepsilon_{\alpha_0} \hat{A}$$

From Eq.(1) we see the following theorem

((Theorem-2))

$$\hat{S}^2 = \hat{S}$$

$$\hat{A}^2 = \hat{A}$$

and

$$\hat{A} \hat{S} = \hat{S} \hat{A} = 0$$

((Proof))

$$\hat{S}^2 = \frac{1}{N!} \sum_{\alpha} \hat{P}_{\alpha} \hat{S} = \frac{1}{N!} \sum_{\alpha} \hat{S} = \hat{S}$$

$$\hat{A}^2 = \frac{1}{N!} \sum_{\alpha} \varepsilon_{\alpha} \hat{P}_{\alpha} \hat{A} = \frac{1}{N!} \sum_{\alpha} \varepsilon_{\alpha}^2 \hat{A} = \hat{A}$$

$$\hat{A} \hat{S} = \hat{A} = \frac{1}{N!} \sum_{\alpha} \varepsilon_{\alpha} \hat{P}_{\alpha} \hat{S} = \frac{1}{N!} \hat{S} \sum_{\alpha} \varepsilon_{\alpha} = 0$$

since half the ε_{α} are equal to 1 and half the ε_{α} equal to -1. \hat{S} and \hat{A} are therefore projectors. Their action on any ket $|\psi\rangle$ of the state space yields a completely symmetric or completely antisymmetric ket.

$$\hat{P}_{\alpha_0} \hat{S} |\psi\rangle = \hat{S} |\psi\rangle$$

$$\hat{P}_{\alpha_0} \hat{A} |\psi\rangle = \varepsilon_{\alpha_0} \hat{A} |\psi\rangle$$

$$|\psi_S\rangle = \hat{S} |\psi\rangle$$

$$|\psi_A\rangle = \hat{A} |\psi\rangle$$

((Example))

For $N = 3$,

$$\hat{S} = \frac{1}{6} [\hat{1} + \hat{P}_{12} + \hat{P}_{23} + \hat{P}_{31} + \hat{P}_{123} + \hat{P}_{132}]$$

and

$$\hat{A} = \frac{1}{6} [\hat{1} - \hat{P}_{12} - \hat{P}_{23} - \hat{P}_{31} + \hat{P}_{123} + \hat{P}_{132}]$$

where

$$\hat{P}_{123} = \hat{P}_{12} \hat{P}_{23}, \quad \hat{P}_{132} = \hat{P}_{12} \hat{P}_{13}$$

$$\hat{S} + \hat{A} = \frac{1}{3} (\hat{1} + \hat{P}_{123} + \hat{P}_{132}) \neq \hat{1}$$

4 Symmetrization postulate

The system containing N identical particles are either totally symmetrical under the interchange of any pair (**boson**), or totally antisymmetrical under the interchange of any pair (**fermion**).

$$\hat{P}_{ij}|\psi_{N,B}\rangle = |\psi_{N,B}\rangle,$$

$$\hat{P}_{ij}|\psi_{N,F}\rangle = -|\psi_{N,F}\rangle,$$

where $|\psi_{N,B}\rangle$ is the eigenket of N identical boson systems and $|\psi_{N,F}\rangle$ is the eigenket of N identical fermion systems.

((**Note**)) It is an empirical fact that a mixed symmetry does not occur.

Even more remarkable is that there is a connection between the spin of a particle and the statistics obeyed by it:

Half-integer spin particles are fermion, while integer-spin particles are bosons.

5 Pauli exclusion principle

Wolfgang Ernst Pauli (April 25, 1900 – December 15, 1958) was an Austrian theoretical physicist and one of the pioneers of quantum physics. In 1945, after being nominated by Albert Einstein, he received the Nobel Prize in Physics for his "decisive contribution through his discovery of a new law of Nature, the exclusion principle or Pauli principle," involving spin theory, underpinning the structure of matter and the whole of chemistry.



http://en.wikipedia.org/wiki/Wolfgang_Pauli

Electron is a fermion. No two electrons can occupy the same state. We discuss the fundamental difference between fermions and bosons. Let us consider two particles. Each of which can occupy only two states $|k'\rangle$ and $|k''\rangle$.

For a system of two fermions, we have no choice

$$\frac{1}{\sqrt{2}}[|k'\rangle_1|k''\rangle_2 - |k''\rangle_1|k'\rangle_2] = \frac{1}{\sqrt{2}} \begin{vmatrix} |k'\rangle_1 & |k'\rangle_2 \\ |k''\rangle_1 & |k''\rangle_2 \end{vmatrix}$$

For bosons, there are three states.

$$|k'\rangle_1 |k'\rangle_2,$$

$$|k''\rangle_1 |k''\rangle_2,$$

$$\frac{1}{\sqrt{2}}(|k'\rangle_1 |k''\rangle_2 + |k''\rangle_1 |k'\rangle_2).$$

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

$$|k'\rangle_1 |k''\rangle_2, |k''\rangle_1 |k'\rangle_2, |k'\rangle_1 |k'\rangle_2 \text{ and } |k''\rangle_1 |k''\rangle_2$$

We see that in the fermion case, it is impossible for both particles to occupy the same state.

6 Transformation of observables by permutation

For simplicity, we consider a specific case where the two particle state ket is completely specified by the eigenvalues of a single observable \hat{A} for each of the particle.

$$\hat{A}_1 |a'\rangle_1 |a''\rangle_2 = a' |a'\rangle_1 |a''\rangle_2$$

and

$$\hat{A}_2 |a'\rangle_1 |a''\rangle_2 = a'' |a'\rangle_1 |a''\rangle_2$$

Since

$$\hat{P}_{12} \hat{A}_1 \hat{P}_{12}^{-1} \hat{P}_{12} |a'\rangle_1 |a''\rangle_2 = \hat{P}_{12} \hat{A}_1 \hat{P}_{12}^{-1} |a''\rangle_1 |a'\rangle_2$$

or

$$\begin{aligned} \hat{P}_{12} \hat{A}_1 \hat{P}_{12}^{-1} \hat{P}_{12} |a'\rangle_1 |a''\rangle_2 &= \hat{P}_{12} \hat{A}_1 |a'\rangle_1 |a''\rangle_2 \\ &= a' \hat{P}_{12} |a'\rangle_1 |a''\rangle_2 \\ &= a' |a''\rangle_1 |a'\rangle_2 = \hat{A}_2 |a''\rangle_1 |a'\rangle_2 = \hat{A}_2 \hat{P}_{12} |a'\rangle_1 |a''\rangle_2 \end{aligned}$$

we obtain

$$\hat{P}_{12} \hat{A}_1 \hat{P}_{12}^{-1} = \hat{A}_2.$$

Similarly, we have

$$\hat{P}_{21} \hat{A}_2 \hat{P}_{21}^{-1} = \hat{A}_1.$$

It follows that \hat{P}_{12} must change the particle label of observables.

There are also observables, such as $\hat{A}_1 + \hat{B}_2$, $\hat{A}_1\hat{B}_2$, which involve both indices simultaneously.

$$\hat{P}_{12}(\hat{A}_1 + \hat{B}_2)\hat{P}_{12}^{-1} = \hat{A}_2 + \hat{B}_1$$

$$\hat{P}_{12}\hat{A}_1\hat{B}_2\hat{P}_{12}^{-1} = \hat{P}_{12}\hat{A}_1\hat{P}_{12}^{-1}\hat{P}_{12}\hat{B}_2\hat{P}_{12}^{-1} = \hat{A}_2\hat{B}_1$$

These results can be generalized to all observables which can be expressed in terms of observables which can be expressed in terms of observables of the type of \hat{A}_1 and \hat{B}_2 , to be denoted by $\hat{O}(1,2)$.

$$\hat{P}_{12}\hat{O}(1,2)\hat{P}_{12}^{-1} = \hat{O}(2,1)$$

where $\hat{O}(2,1)$ is the observable obtained from $\hat{O}(1,2)$ by exchanging indices 1 and 2 throughout.

$\hat{O}_s(1,2)$ is said to be symmetric if

$$\hat{O}_s(1,2) = \hat{O}_s(2,1)$$

or

$$[\hat{O}_s(1,2), \hat{P}_{12}] = 0$$

Symbolic observables commute with the permutation operator.

In general. the observables $\hat{O}_s(1,2,3,\dots,N)$ which are completely symmetric under exchange of indices 1, 2, ..., N commute with all the transposition operators, and with all the permutation operators

7 Example

Let us now consider a Hamiltonian of a system of two identical particles.

$$\hat{H} = \frac{1}{2m}\hat{\mathbf{p}}_1^2 + \frac{1}{2m}\hat{\mathbf{p}}_2^2 + V_{pair}(|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|) + V_{ext}(\hat{\mathbf{r}}_1) + V_{ext}(\hat{\mathbf{r}}_2)$$

Clearly we have

$$\hat{P}_{12}\hat{H}\hat{P}_{12}^{-1} = \hat{H}$$

or

$$[\hat{P}_{12}, \hat{H}] = 0$$

\hat{P}_{12} is a constant of the motion. Since $\hat{P}_{12}^2 = 1$, the eigenvalue of \hat{P}_{12} allowed are ± 1 .

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

$$\hat{P}_{12}|\psi\rangle = \lambda|\psi\rangle$$

$$\hat{P}_{12}^2 |\psi\rangle = \lambda \hat{P}_{12} |\psi\rangle = \lambda^2 |\psi\rangle = |\psi\rangle$$

or

$$\lambda = \pm 1.$$

It therefore follows that if the two-particle state ket is symmetric (antisymmetric) to start with, it remains so at all times.

(i) $N = 2$ case

We can define the symmetrizer and antisymmetrizer as follows.

$$\hat{S} = \frac{1}{2}(1 + \hat{P}_{12}) \quad \hat{A} = \frac{1}{2}(1 - \hat{P}_{12})$$

$$\hat{S} + \hat{A} = \hat{1}$$

$$\hat{S}^2 = \frac{1}{2}(\hat{1} + \hat{P}_{12}) \frac{1}{2}(\hat{1} + \hat{P}_{12}) = \frac{1}{4}(\hat{1} + 2\hat{P}_{12} + \hat{1}) = \frac{1}{2}(\hat{1} + \hat{P}_{12}) = \hat{S}$$

$$\hat{A}^2 = \frac{1}{2}(\hat{1} - \hat{P}_{12}) \frac{1}{2}(\hat{1} - \hat{P}_{12}) = \frac{1}{4}(\hat{1} - 2\hat{P}_{12} + \hat{1}) = \frac{1}{2}(\hat{1} - \hat{P}_{12}) = \hat{A}$$

Then we have

$$|\psi_S\rangle = \frac{1}{\sqrt{2}}(|k'\rangle_1 |k''\rangle_2 + |k''\rangle_1 |k'\rangle_2)$$

and

$$|\psi_A\rangle = \frac{1}{\sqrt{2}}(|k'\rangle_1 |k''\rangle_2 - |k''\rangle_1 |k'\rangle_2)$$

where

$$\hat{S}|k'\rangle_1 |k''\rangle_2 = \frac{1}{2}(1 + \hat{P}_{12})|k'\rangle_1 |k''\rangle_2 = \frac{1}{2}(|k'\rangle_1 |k''\rangle_2 + |k''\rangle_1 |k'\rangle_2)$$

$$\hat{A}|k'\rangle_1 |k''\rangle_2 = \frac{1}{2}(1 - \hat{P}_{12})|k'\rangle_1 |k''\rangle_2 = \frac{1}{2}(|k'\rangle_1 |k''\rangle_2 - |k''\rangle_1 |k'\rangle_2)$$

(ii) $N = 3$ Cases

$$\hat{S} = \frac{1}{6}(1 + \hat{P}_{12} + \hat{P}_{23} + \hat{P}_{31} + \hat{P}_{123} + \hat{P}_{132})$$

$$\hat{A} = \frac{1}{6}(1 - \hat{P}_{12} - \hat{P}_{23} - \hat{P}_{31} + \hat{P}_{123} + \hat{P}_{132})$$

$$\hat{S} + \hat{A} = \frac{1}{3}(1 + \hat{P}_{123} + \hat{P}_{132}) \neq 1$$

$$\hat{A}|k'\rangle_1|k''\rangle_2|k'''\rangle_3 = \frac{1}{3!} \begin{vmatrix} |k'\rangle_1 & |k''\rangle_1 & |k'''\rangle_1 \\ |k'\rangle_2 & |k''\rangle_2 & |k'''\rangle_2 \\ |k'\rangle_3 & |k''\rangle_3 & |k'''\rangle_3 \end{vmatrix}$$

Slater determinant

$\hat{A}|k'\rangle_1|k''\rangle_2|k'''\rangle_3$ is zero if two of individual states coincide. We obtain Pauli's exclusion principle.

8 Generalized method (Tomonaga)

We now consider a system consisting of many spins.

$$\hat{S} = \hat{S}_1 + \hat{S}_2 + \hat{S}_3 + \dots + \hat{S}_N$$

$$\hat{S} \cdot \hat{S} = (\hat{S}_1 + \hat{S}_2 + \hat{S}_3 + \dots + \hat{S}_N) \cdot (\hat{S}_1 + \hat{S}_2 + \hat{S}_3 + \dots + \hat{S}_N)$$

or

$$\hat{S}^2 = \sum_{n=1}^N \hat{S}_n^2 + 2 \sum_{n < n'} (\hat{S}_n \cdot \hat{S}_{n'}) = \frac{\hbar^2}{4} \sum_{n=1}^N \hat{\sigma}_n^2 + \frac{1}{2} \hbar^2 \sum_{n < n'} (\hat{\sigma}_n \cdot \hat{\sigma}_{n'})$$

or

$$\frac{\hat{S}^2}{\hbar^2} = \frac{3N}{4} \hat{1} + \frac{1}{2} \sum_{n < n'} (\hat{\sigma}_n \cdot \hat{\sigma}_{n'})$$

Here we define an operator

$$\hat{O} = \frac{2}{N(N-1)} \sum_{n < n'} \hat{P}_{nn'}$$

\hat{O} is Hermitian and $[\hat{P}, \hat{O}] = 0$. We assume that

$$\hat{P}_{nn'} = \frac{1}{2} (\hat{1} + \hat{\sigma}_n \cdot \hat{\sigma}_{n'}) \quad (\text{Dirac exchange interaction})$$

$$\hat{O} = \frac{2}{N(N-1)} \sum_{n < n'} \frac{1}{2} (\hat{1} + \hat{\sigma}_n \cdot \hat{\sigma}_{n'}) = \frac{2}{N(N-1)} \left[\frac{1}{2} \frac{N(N-1)}{2} \hat{1} + \frac{1}{2} \sum_{n < n'} \hat{\sigma}_n \cdot \hat{\sigma}_{n'} \right]$$

or

$$\hat{O} = \frac{1}{2}[\hat{1} + \frac{2}{N(N-1)} \sum_{n < n'} \hat{\sigma}_n \cdot \hat{\sigma}_{n'}]$$

Using the relation,

$$\frac{\hat{S}^2}{\hbar^2} = \frac{3N}{4} \hat{1} + \frac{1}{2} \sum_{n < n'} (\hat{\sigma}_n \cdot \hat{\sigma}_{n'}),$$

we get

$$\hat{O} = \frac{1}{2}[\hat{1} + \frac{2}{N(N-1)} (\frac{2}{\hbar^2} \hat{S}^2 - \frac{3N}{2})] = \frac{1}{2}[\frac{N-4}{(N-1)} \hat{1} + \frac{4}{N(N-1)} \frac{1}{\hbar^2} \hat{S}^2]$$

$[\hat{S}^2, \hat{O}] = 0$. When the eigenvalue of \hat{S}^2 is given by $\hbar^2 S(S+1)$, the eigenvalue of \hat{O} is equal to

$$\chi = \frac{1}{2}[\frac{N-4}{(N-1)} + \frac{4S(S+1)}{N(N-1)}]$$

The eigenvalue of $\hat{O}, (\chi)$, specifies the symmetry.

(i) For $N = 2$,

$$D_{1/2} \times D_{1/2} = D_1 + D_0$$

$$\chi = \frac{1}{2}[-2 + 2S(S+1)] = -1 + S(S+1)$$

When $S = 1$, $\chi = 1$ (symmetric).

When $S = 0$, $\chi = -1$ (anti-symmetric).

(ii) For $N = 3$,

$$D_{1/2} \times D_{1/2} \times D_{1/2} = D_{3/2} + 2 D_{1/2}$$

$$\chi = \frac{1}{2}[-\frac{1}{2} + \frac{2}{3} S(S+1)]$$

When $S = 3/2$, $\chi = 1$ (symmetric).

When $S = 1/2$, $\chi = 0$.

(iii) For $N = 4$,

$$D_{1/2} \times D_{1/2} \times D_{1/2} \times D_{1/2} = D_2 + 3D_1 + 2D_0$$

$$\chi = \frac{S(S+1)}{6}$$

For $S = 2$, $\chi = 1$ (symmetric).
 For $S = 1$, $\chi = 1/3$.
 For $S = 0$, $\chi = 0$.

9. Summary: fermion and boson

The Hamiltonian H of the system (in the absence of a magnetic field) does not contain the spin operators, and hence, when it is applied to the wave function, it has no effect on the spin variables. The wave function of the system of particles can be written in the form of product,

$$|\psi\rangle = |\psi_{space}\rangle |\chi_{spin}\rangle,$$

where $|\psi_{space}\rangle$ depends only on the coordinate of the particles and $|\chi_{spin}\rangle$ only on their spins. $|\psi\rangle = |\psi_{space}\rangle |\chi_{spin}\rangle$ should be anti-symmetric since electrons are fermions.

The system containing N identical particles are either totally symmetrical under the interchange of any pair (**boson**), or totally antisymmetrical under the interchange of any pair (**fermion**).

$$\hat{P}_{ij} |\psi_{N,B}\rangle = |\psi_{N,B}\rangle,$$

$$\hat{P}_{ij} |\psi_{N,F}\rangle = -|\psi_{N,F}\rangle,$$

where $|\psi_{N,B}\rangle$ is the eigenket of N identical boson systems and $|\psi_{N,F}\rangle$ is the eigenket of N identical fermion systems.

((Note)) It is an empirical fact that a mixed symmetry does not occur.

Even more remarkable is that there is a connection between the spin of a particle and the statistics obeyed by it:

Half-integer spin particles are fermion, obeying the Fermi-Dirac statistic, while integer-spin particles are bosons, obeying the Bose-Einstein statistics.

10. Ground state for systems with many electrons

We construct the form of wavefunctions for the system with two, three, four, and five electrons (identical particles, **fermion**) using the Slater determinant. We assume that each electron has spin states

$$|\alpha\rangle = |+\rangle, \quad |\beta\rangle = |-\rangle.$$

We also assume the orbital state: $|a\rangle = |n=1\rangle$, $|b\rangle = |n=2\rangle$, $|c\rangle = |n=3\rangle$..., where n is the principal quantum number. It is reasonable to consider that the ground state can be expressed by electrons occupied by

$$|a\rangle|\alpha\rangle, \quad |a\rangle|\beta\rangle$$

taking into account of the Pauli's exclusion principle. For the system with three electrons, the ground state can be expressed by

$$|a\rangle|\alpha\rangle, \quad |a\rangle|\beta\rangle, \quad |b\rangle|\alpha\rangle$$

For the system with the four electrons, the ground state can be expressed by

$$|a\rangle|\alpha\rangle, \quad |a\rangle|\beta\rangle, \quad |b\rangle|\alpha\rangle, \quad |b\rangle|\beta\rangle$$

For the system with the five electrons, the ground state can be expressed by

$$|a\rangle|\alpha\rangle, \quad |a\rangle|\beta\rangle, \quad |b\rangle|\alpha\rangle, \quad |b\rangle|\beta\rangle, \quad |c\rangle|\alpha\rangle$$

(a) Two particles state

For the two states,

$$|a\alpha\rangle = |a\rangle|\alpha\rangle, \text{ and } |a\beta\rangle = |a\rangle|\beta\rangle$$

we have the Slater determinant

$$|\psi\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} a_1\alpha_1 & a_1\beta_1 \\ a_2\alpha_2 & a_2\beta_2 \end{vmatrix} = \frac{1}{\sqrt{2}} a_1 a_2 (\alpha_1 \beta_2 - \beta_1 \alpha_2)$$

where index 1, 2 denotes the particle 1 and particle 2. Clearly, the state vector is antisymmetric under the exchange of two particles.

(b) Three particles state

For the three states,

$$|a\alpha\rangle = |a\rangle|\alpha\rangle, |a\beta\rangle = |a\rangle|\beta\rangle, \text{ and } |b\alpha\rangle = |b\rangle|\alpha\rangle$$

we have the Slater determinant

$$\begin{aligned} |\psi\rangle &= \frac{1}{\sqrt{6}} \begin{vmatrix} a_1\alpha_1 & a_1\beta_1 & b_1\alpha_1 \\ a_2\alpha_2 & a_2\beta_2 & b_2\alpha_2 \\ a_3\alpha_3 & a_3\beta_3 & b_3\alpha_3 \end{vmatrix} \\ &= \frac{1}{\sqrt{6}} [a_2 a_3 (\alpha_2 \beta_3 - \beta_2 \alpha_3) b_1 \alpha_1 + a_1 a_3 (\beta_1 \alpha_3 - \alpha_1 \beta_3) b_2 \alpha_2 + a_1 a_2 (\alpha_1 \beta_2 - \beta_1 \alpha_2) b_3 \alpha_3] \end{aligned}$$

This state vector is antisymmetric under the exchange between any two particles (such that $1 \rightarrow 2$).

(c) Four particle state

For the four states,

$$|a\alpha\rangle = |a\rangle|\alpha\rangle, |a\beta\rangle = |a\rangle|\beta\rangle, |b\alpha\rangle = |b\rangle|\alpha\rangle, \text{ and } |b\beta\rangle = |b\rangle|\beta\rangle$$

we have the Slater determinant

$$\begin{aligned} |\psi\rangle &= \frac{1}{\sqrt{24}} \begin{vmatrix} a_1\alpha_1 & a_1\beta_1 & b_1\alpha_1 & b_1\beta_1 \\ a_2\alpha_2 & a_2\beta_2 & b_2\alpha_2 & b_2\beta_2 \\ a_3\alpha_3 & a_3\beta_3 & b_3\alpha_3 & b_3\beta_3 \\ a_4\alpha_4 & a_4\beta_4 & b_4\alpha_4 & b_4\beta_4 \end{vmatrix} \\ &= b_1b_2(\alpha_1\beta_2 - \beta_1\alpha_2)a_3a_4(\alpha_3\beta_4 - \beta_3\alpha_4) \\ &\quad + b_2b_3(\alpha_2\beta_3 - \beta_2\alpha_3)a_1a_4(\alpha_1\beta_4 - \beta_1\alpha_4) \\ &\quad + b_2b_4(\alpha_2\beta_4 - \beta_2\alpha_4)a_1a_4(\alpha_1\beta_4 - \beta_1\alpha_4) \\ &\quad - b_1b_3(\alpha_1\beta_3 - \beta_1\alpha_3)a_2a_4(\alpha_2\beta_4 - \beta_2\alpha_4) \\ &\quad + b_1b_4(\alpha_1\beta_4 - \beta_1\alpha_4)a_2a_3(\alpha_2\beta_3 - \beta_2\alpha_3) \\ &\quad + b_3b_4(\alpha_3\beta_4 - \beta_3\alpha_4)a_1a_2(\alpha_1\beta_2 - \beta_1\alpha_2) \end{aligned}$$

This state vector is antisymmetric under the exchange between any two particles (such that $1 \rightarrow 2$), but symmetric under the two types exchange (such that $1 \rightarrow 2$ and $3 \rightarrow 4$)

(d) Five particle state

For the five states

$$|a\alpha\rangle = |a\rangle|\alpha\rangle, |a\beta\rangle = |a\rangle|\beta\rangle, |b\alpha\rangle = |b\rangle|\alpha\rangle, |b\beta\rangle = |b\rangle|\beta\rangle, |c\alpha\rangle = |c\rangle|\alpha\rangle$$

we have the Slater determinant

$$\begin{aligned} |\psi\rangle &= \frac{1}{\sqrt{120}} \begin{vmatrix} a_1\alpha_1 & a_1\beta_1 & b_1\alpha_1 & b_1\beta_1 & c_1\alpha_1 \\ a_2\alpha_2 & a_2\beta_2 & b_2\alpha_2 & b_2\beta_2 & c_2\alpha_2 \\ a_3\alpha_3 & a_3\beta_3 & b_3\alpha_3 & b_3\beta_3 & c_3\alpha_3 \\ a_4\alpha_4 & a_4\beta_4 & b_4\alpha_4 & b_4\beta_4 & c_4\alpha_4 \\ a_5\alpha_5 & a_5\beta_5 & b_5\alpha_5 & b_5\beta_5 & c_5\alpha_5 \end{vmatrix} \\ &= \frac{1}{\sqrt{120}} [a_1a_2(\alpha_1\beta_2 - \beta_1\alpha_2)b_3b_4(\alpha_3\beta_4 - \beta_4\alpha_3)c_5\alpha_5 + \dots] \end{aligned}$$

((Mathematica))

$$\text{Clear["Global`*"]}; \mathbf{A1} = \begin{pmatrix} a1 \alpha1 & a1 \beta1 \\ a2 \alpha2 & a2 \beta2 \end{pmatrix};$$

Det[A1] // FullSimplify

$$a1 a2 (-\alpha2 \beta1 + \alpha1 \beta2)$$

$$\mathbf{B1} = \begin{pmatrix} a1 \alpha1 & a1 \beta1 & b1 \alpha1 \\ a2 \alpha2 & a2 \beta2 & b2 \alpha2 \\ a3 \alpha3 & a3 \beta3 & b3 \alpha3 \end{pmatrix};$$

Det[B1] // FullSimplify

$$a1 (a3 b2 - a2 b3) \alpha2 \alpha3 \beta1 + \\ a2 (-a3 b1 + a1 b3) \alpha1 \alpha3 \beta2 + a3 (a2 b1 - a1 b2) \alpha1 \alpha2 \beta3$$

$$\mathbf{C1} = \begin{pmatrix} a1 \alpha1 & a1 \beta1 & b1 \alpha1 & b1 \beta1 \\ a2 \alpha2 & a2 \beta2 & b2 \alpha2 & b2 \beta2 \\ a3 \alpha3 & a3 \beta3 & b3 \alpha3 & b3 \beta3 \\ a4 \alpha4 & a4 \beta4 & b4 \alpha4 & b4 \beta4 \end{pmatrix};$$

Det[C1] // FullSimplify

$$b2 (a3 a4 b1 (\alpha2 \beta1 - \alpha1 \beta2) (\alpha4 \beta3 - \alpha3 \beta4) + \\ a1 (a4 b3 (\alpha3 \beta2 - \alpha2 \beta3) (\alpha4 \beta1 - \alpha1 \beta4) - \\ a3 b4 (\alpha3 \beta1 - \alpha1 \beta3) (\alpha4 \beta2 - \alpha2 \beta4)) + \\ a2 (-a4 b1 b3 (\alpha3 \beta1 - \alpha1 \beta3) (\alpha4 \beta2 - \alpha2 \beta4) + \\ b4 (a3 b1 (\alpha3 \beta2 - \alpha2 \beta3) (\alpha4 \beta1 - \alpha1 \beta4) + \\ a1 b3 (\alpha2 \beta1 - \alpha1 \beta2) (\alpha4 \beta3 - \alpha3 \beta4)))$$

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APPENDIX: $|r\rangle$

((Townsend textbook))

1. Formula-1

For a symmetric spatial state under the exchange of two particles, we have

$$\begin{aligned} |\psi_s\rangle &= \int d\mathbf{r}' \int d\mathbf{r}'' |\mathbf{r}', \mathbf{r}''; S\rangle \langle \mathbf{r}', \mathbf{r}''; S | \psi_s \rangle \\ &= \int d\mathbf{r}' \int d\mathbf{r}'' \hat{S} |\mathbf{r}', \mathbf{r}''\rangle \langle \mathbf{r}', \mathbf{r}'' | \hat{S} | \psi_s \rangle \\ &= \int d\mathbf{r}' \int d\mathbf{r}'' |\mathbf{r}', \mathbf{r}''\rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_s \rangle \end{aligned}$$

and for an anti-symmetric spatial state under the exchange of two particles, we have

$$\begin{aligned} |\psi_A\rangle &= \int d\mathbf{r}' \int d\mathbf{r}'' |\mathbf{r}', \mathbf{r}''; A\rangle \langle \mathbf{r}', \mathbf{r}''; A | \psi_A \rangle \\ &= \int d\mathbf{r}' \int d\mathbf{r}'' \hat{A} |\mathbf{r}', \mathbf{r}''\rangle \langle \mathbf{r}', \mathbf{r}'' | \hat{A} | \psi_A \rangle \\ &= \int d\mathbf{r}' \int d\mathbf{r}'' |\mathbf{r}', \mathbf{r}''\rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_A \rangle \end{aligned}$$

where

$$|\mathbf{r}', \mathbf{r}''\rangle = |\mathbf{r}'\rangle_1 |\mathbf{r}''\rangle_2$$

$$\hat{S} = \frac{1}{2}(\hat{1} + \hat{P}_{12}), \quad \hat{A} = \frac{1}{2}(\hat{1} - \hat{P}_{12})$$

((Proof))

$$\begin{aligned} |\psi_s\rangle &= \int d\mathbf{r}' \int d\mathbf{r}'' |\mathbf{r}', \mathbf{r}''; S\rangle \langle \mathbf{r}', \mathbf{r}''; S | \psi_s \rangle \\ &= \int d\mathbf{r}' \int d\mathbf{r}'' \hat{S} |\mathbf{r}', \mathbf{r}''\rangle \langle \mathbf{r}', \mathbf{r}'' | \hat{S} | \psi_s \rangle \\ &= \int d\mathbf{r}' \int d\mathbf{r}'' \frac{1}{2}(\hat{1} + \hat{P}_{12}) |\mathbf{r}', \mathbf{r}''\rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_s \rangle \\ &= \frac{1}{2} \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{1} + \hat{P}_{12}) |\mathbf{r}', \mathbf{r}''\rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_s \rangle \\ &= \frac{1}{2} \int d\mathbf{r}' \int d\mathbf{r}'' (|\mathbf{r}', \mathbf{r}''\rangle + |\mathbf{r}'', \mathbf{r}'\rangle) \langle \mathbf{r}', \mathbf{r}'' | \psi_s \rangle \\ &= \frac{1}{2} \int d\mathbf{r}' \int d\mathbf{r}'' (|\mathbf{r}', \mathbf{r}''\rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_s \rangle + |\mathbf{r}'', \mathbf{r}'\rangle \langle \mathbf{r}', \mathbf{r}'' | \hat{P}_{12} | \psi_s \rangle) \\ &= \frac{1}{2} \int d\mathbf{r}' \int d\mathbf{r}'' (|\mathbf{r}', \mathbf{r}''\rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_s \rangle + |\mathbf{r}'', \mathbf{r}'\rangle \langle \mathbf{r}'', \mathbf{r}' | \psi_s \rangle) \\ &= \int d\mathbf{r}' \int d\mathbf{r}'' |\mathbf{r}', \mathbf{r}''\rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_s \rangle \end{aligned}$$

where

$$\hat{S}^2 |\psi\rangle = \hat{S} |\psi_s\rangle = \hat{S} |\psi\rangle = |\psi_s\rangle$$

$$\hat{S} |\psi_s\rangle = |\psi_s\rangle,$$

$$\langle \mathbf{r}', \mathbf{r}'' | \psi_S \rangle = \langle \mathbf{r}', \mathbf{r}'' | \hat{P}_{12} | \psi_S \rangle = \langle \mathbf{r}'', \mathbf{r}' | \psi_S \rangle.$$

$$\hat{P}_{12} | \psi_S \rangle = | \psi_S \rangle$$

Similarly,

$$\begin{aligned} | \psi_A \rangle &= \int d\mathbf{r}' \int d\mathbf{r}'' \hat{A} | \mathbf{r}', \mathbf{r}''; A \rangle \langle \mathbf{r}', \mathbf{r}''; A | \psi_A \rangle \\ &= \int d\mathbf{r}' \int d\mathbf{r}'' \hat{A} | \mathbf{r}', \mathbf{r}'' \rangle \langle \mathbf{r}', \mathbf{r}'' | \hat{A} | \psi_A \rangle \\ &= \frac{1}{2} \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{1} - \hat{P}_{12}) | \mathbf{r}', \mathbf{r}'' \rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_A \rangle \\ &= \frac{1}{2} \int d\mathbf{r}' \int d\mathbf{r}'' (| \mathbf{r}', \mathbf{r}'' \rangle - | \mathbf{r}'', \mathbf{r}' \rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_A \rangle) \\ &= \frac{1}{2} \int d\mathbf{r}' \int d\mathbf{r}'' (| \mathbf{r}', \mathbf{r}'' \rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_A \rangle - | \mathbf{r}'', \mathbf{r}' \rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_A \rangle) \\ &= \frac{1}{2} \int d\mathbf{r}' \int d\mathbf{r}'' (| \mathbf{r}', \mathbf{r}'' \rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_A \rangle + | \mathbf{r}'', \mathbf{r}' \rangle \langle \mathbf{r}', \mathbf{r}'' | \hat{P}_{12} | \psi_A \rangle) \\ &= \frac{1}{2} \int d\mathbf{r}' \int d\mathbf{r}'' (| \mathbf{r}', \mathbf{r}'' \rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_A \rangle + | \mathbf{r}'', \mathbf{r}' \rangle \langle \mathbf{r}'', \mathbf{r}' | \psi_A \rangle) \\ &= \int d\mathbf{r}' \int d\mathbf{r}'' | \mathbf{r}', \mathbf{r}'' \rangle \langle \mathbf{r}', \mathbf{r}'' | \psi_A \rangle \end{aligned}$$

where

$$\hat{A}^2 | \psi \rangle = \hat{A} | \psi_A \rangle = \hat{A} | \psi \rangle = | \psi_A \rangle$$

$$\langle \mathbf{r}', \mathbf{r}'' | \psi_A \rangle = -\langle \mathbf{r}', \mathbf{r}'' | \hat{P}_{12} | \psi_A \rangle = -\langle \mathbf{r}'', \mathbf{r}' | \psi_A \rangle$$

$$\hat{P}_{12} | \psi_A \rangle = -| \psi_A \rangle$$

2. Formula-2: symmetric case

$$| k', k''; S \rangle = \frac{1}{2} (\hat{1} + \hat{P}_{12}) | k' \rangle_1 | k'' \rangle_2 = \hat{S} | k', k'' \rangle$$

$$| x', x''; S \rangle = \frac{1}{2} (1 + \hat{P}_{12}) | x' \rangle_1 | x'' \rangle_2 = \hat{S} | x', x'' \rangle$$

$$\begin{aligned}
\langle x', x''; S | k', k''; S \rangle &= \langle x', x'' | \hat{S}^+ | k', k''; S \rangle \\
&= \langle x', x'' | \hat{S} | k', k''; S \rangle \\
&= \langle x', x'' | k', k''; S \rangle \\
&= \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} [\langle x' | k' \rangle \langle x'' | k'' \rangle + \langle x' | k'' \rangle \langle x'' | k' \rangle]
\end{aligned}$$

or

$$\begin{aligned}
\sqrt{2} \langle x', x''; S | k', k''; S \rangle &= \psi_S(x', x'') \\
&= \frac{1}{\sqrt{2}} [\langle x' | k' \rangle \langle x'' | k'' \rangle + \langle x' | k'' \rangle \langle x'' | k' \rangle]
\end{aligned}$$

3. Formula-3: antisymmetric case

$$\begin{aligned}
|k', k''; A\rangle &= \frac{1}{2} (\hat{1} - \hat{P}_{12}) [|k'\rangle_1 |k''\rangle_2] = \hat{A} |k', k''\rangle \\
\langle x', x''; A | k', k''; A \rangle &= \langle x', x'' | \hat{A}^+ | k', k''; A \rangle \\
&= \langle x', x'' | \hat{A} | k', k''; A \rangle \\
&= \langle x', x'' | \hat{A}^2 | k', k'' \rangle \\
&= \langle x', x'' | \hat{A} | k', k'' \rangle \\
&= \langle x', x'' | k', k''; A \rangle \\
&= \frac{1}{2} [\langle x' | k' \rangle \langle x'' | k'' \rangle - \langle x' | k'' \rangle \langle x'' | k' \rangle] \\
&= \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} [\langle x' | k' \rangle \langle x'' | k'' \rangle - \langle x' | k'' \rangle \langle x'' | k' \rangle]
\end{aligned}$$

or

$$\begin{aligned}
\sqrt{2} \langle x', x''; A | k', k''; A \rangle &= \psi_A(x', x'') \\
&= \frac{1}{\sqrt{2}} \begin{vmatrix} \langle x' | k' \rangle & \langle x' | k'' \rangle \\ \langle x'' | k' \rangle & \langle x'' | k'' \rangle \end{vmatrix}
\end{aligned}$$

4. Inner product for the symmetric and antisymmetric cases

We consider the inner product for the symmetric case

$$\begin{aligned}
\langle x', x''; S | y', y''; S \rangle &= \langle x' x'' | \hat{S}^+ | y', y''; S \rangle \\
&= \langle x' x'' | \hat{S} | y', y''; S \rangle \\
&= \langle x' x'' | \hat{S}^2 | y', y'' \rangle \\
&= \langle x' x'' | \hat{S} | y', y'' \rangle \\
&= \langle x' x'' | y', y''; S \rangle \\
&= \frac{1}{2} [\langle x' | y' \rangle \langle x'' | y'' \rangle + \langle x' | y'' \rangle \langle x'' | y' \rangle] \\
&= \frac{1}{2} [\delta(x' - y') \delta(x'' - y'') + \delta(x' - y'') \delta(x'' - y')]
\end{aligned}$$

where

$$\hat{S}^+ = \hat{S} \quad (\text{Hermitian operator})$$

$$\hat{S}^2 = \hat{S}$$

$$|y', y''; S\rangle = \hat{S} |y', y''\rangle$$

We also consider the inner product for the antisymmetric case,

$$\begin{aligned}
\langle x', x''; A | y', y''; A \rangle &= \langle x' x'' | \hat{A}^+ | y', y''; A \rangle \\
&= \langle x' x'' | \hat{A} | y', y''; A \rangle \\
&= \langle x' x'' | \hat{A}^2 | y', y'' \rangle \\
&= \langle x' x'' | \hat{A} | y', y'' \rangle \\
&= \langle x' x'' | y', y''; A \rangle \\
&= \frac{1}{2} [\langle x' | y' \rangle \langle x'' | y'' \rangle - \langle x' | y'' \rangle \langle x'' | y' \rangle] \\
&= \frac{1}{2} [\delta(x' - y') \delta(x'' - y'') - \delta(x' - y'') \delta(x'' - y')]
\end{aligned}$$

where

$$\hat{A}^+ = \hat{A} \quad (\text{Hermitian operator})$$

$$\hat{A}^2 = \hat{A}$$

$$|y', y''; A\rangle = \hat{A} |y', y''\rangle$$

5. Closure relation

(i) Symmetric case

$$\iint d\mathbf{r} d\mathbf{r}' |\mathbf{r}', \mathbf{r}''; S\rangle \langle \mathbf{r}', \mathbf{r}''; S| = \hat{1} \quad (\text{completeness})$$

((Proof))

$$\begin{aligned} & \int d\mathbf{r}' \int d\mathbf{r}'' \langle \mathbf{s}', \mathbf{s}''; S | \mathbf{r}', \mathbf{r}''; S \rangle \langle \mathbf{r}', \mathbf{r}''; S | \psi_S \rangle \\ &= \int d\mathbf{r}' \int d\mathbf{r}'' \frac{1}{2} [\delta(\mathbf{s}' - \mathbf{r}') \delta(\mathbf{s}'' - \mathbf{r}'') + \delta(\mathbf{s}' - \mathbf{r}'') \delta(\mathbf{s}'' - \mathbf{r}')] \langle \mathbf{r}', \mathbf{r}''; S | \psi_S \rangle \\ &= \frac{1}{2} [\langle \mathbf{s}', \mathbf{s}''; S | \psi_S \rangle + \langle \mathbf{s}'', \mathbf{s}'; S | \psi_S \rangle] \\ &= \langle \mathbf{s}', \mathbf{s}''; S | \psi_S \rangle \end{aligned}$$

since

$$\langle \mathbf{s}', \mathbf{s}''; S | \mathbf{r}', \mathbf{r}''; S \rangle = \frac{1}{2} [\delta(\mathbf{s}' - \mathbf{r}') \delta(\mathbf{s}'' - \mathbf{r}'') + \delta(\mathbf{s}' - \mathbf{r}'') \delta(\mathbf{s}'' - \mathbf{r}')] \langle \mathbf{r}', \mathbf{r}''; S | \psi_S \rangle$$

$$\langle \mathbf{s}', \mathbf{s}''; S | \psi_S \rangle = \langle \mathbf{s}', \mathbf{s}'' | \hat{S}^2 | \psi_S \rangle = \langle \mathbf{s}', \mathbf{s}'' | \hat{S} | \psi_S \rangle = \langle \mathbf{s}', \mathbf{s}'' | \psi_S \rangle$$

$$\langle \mathbf{s}'', \mathbf{s}'; S | \psi_S \rangle = \langle \mathbf{s}'', \mathbf{s}' | \psi_S \rangle = \langle \mathbf{s}', \mathbf{s}'' | \hat{P}_{12} | \psi_S \rangle = \langle \mathbf{s}', \mathbf{s}'' | \psi_S \rangle$$

or

$$\langle \mathbf{s}', \mathbf{s}''; S | \psi_S \rangle = \langle \mathbf{s}'', \mathbf{s}'; S | \psi_S \rangle$$

(ii) **Antisymmetric case**

$$\iint d\mathbf{r} d\mathbf{r}' |\mathbf{r}', \mathbf{r}''; A\rangle \langle \mathbf{r}', \mathbf{r}''; A| = \hat{1} \quad (\text{completeness})$$

((Proof))

$$\begin{aligned} & \int d\mathbf{r}' \int d\mathbf{r}'' \langle \mathbf{s}', \mathbf{s}''; A | \mathbf{r}', \mathbf{r}''; A \rangle \langle \mathbf{r}', \mathbf{r}''; A | \psi_A \rangle \\ &= \int d\mathbf{r}' \int d\mathbf{r}'' \frac{1}{2} [\delta(\mathbf{s}' - \mathbf{r}') \delta(\mathbf{s}'' - \mathbf{r}'') - \delta(\mathbf{s}' - \mathbf{r}'') \delta(\mathbf{s}'' - \mathbf{r}')] \langle \mathbf{r}', \mathbf{r}''; A | \psi_A \rangle \\ &= \frac{1}{2} [\langle \mathbf{s}', \mathbf{s}''; A | \psi_A \rangle - \langle \mathbf{s}'', \mathbf{s}'; A | \psi_A \rangle] \\ &= \langle \mathbf{s}', \mathbf{s}''; A | \psi_A \rangle \end{aligned}$$

since

$$\langle \mathbf{s}', \mathbf{s}''; A | \mathbf{r}', \mathbf{r}''; A \rangle = \frac{1}{2} [\delta(\mathbf{s}' - \mathbf{r}') \delta(\mathbf{s}'' - \mathbf{r}'') - \delta(\mathbf{s}' - \mathbf{r}'') \delta(\mathbf{s}'' - \mathbf{r}')] \langle \mathbf{r}', \mathbf{r}''; A | \psi_A \rangle$$

$$\langle s', s''; A | \psi_A \rangle = \langle s', s'' | \hat{A}^2 | \psi \rangle = \langle s', s'' | \hat{A} | \psi \rangle = \langle s', s'' | \psi_A \rangle$$

$$\langle s'', s'; A | \psi_A \rangle = \langle s'', s' | \psi_A \rangle = \langle s', s'' | \hat{P}_{12} | \psi_A \rangle = -\langle s', s'' | \psi_A \rangle$$

or

$$\langle s'', s'; A | \psi_A \rangle = -\langle s', s''; A | \psi_A \rangle$$

6. Wave function representation (symmetric case)

We have the relation for the symmetric case, such that

$$\langle x', x''; S | \psi_S \rangle = \frac{1}{2} [\langle x', x'' | \psi_S \rangle + \langle x'', x' | \psi_S \rangle]$$

and

$$\langle x', x''; S | \psi_S \rangle = \langle x', x'' | \hat{S}^2 | \psi \rangle = \langle x', x'' | \hat{S} | \psi \rangle = \langle x', x'' | \psi_S \rangle$$

Noting that

$$\langle x', x''; S | \psi_S \rangle = \langle x', x'' | \psi_S \rangle = \langle x'', x' | \hat{P}_{12} | \psi_S \rangle = \langle x'', x' | \psi_S \rangle$$

$$\hat{P}_{12} | \psi_S \rangle = | \psi_S \rangle$$

we get

$$\langle x', x''; S | \psi_S \rangle = \langle x', x'' | \psi_S \rangle = \langle x'', x' | \psi_S \rangle$$

7. Wave function representation (anti-symmetric case)

We have the relation for the anti-symmetric case, such that

$$\langle x', x''; A | \psi_A \rangle = \frac{1}{2} [\langle x', x'' | \psi_A \rangle - \langle x'', x' | \psi_A \rangle]$$

and

$$\langle x', x''; A | \psi_A \rangle = \langle x', x'' | \hat{A}^2 | \psi \rangle = \langle x', x'' | \hat{A} | \psi \rangle = \langle x', x'' | \psi_A \rangle$$

Noting tht

$$\langle x', x''; A | \psi_A \rangle = \langle x', x'' | \psi_A \rangle = \langle x'', x' | \hat{P}_{12} | \psi_A \rangle = -\langle x'', x' | \psi_A \rangle$$

$$\hat{P}_{12} | \psi_A \rangle = -| \psi_A \rangle$$

we have

$$\langle x', x''; A | \psi_A \rangle = \langle x', x'' | \psi_A \rangle = \langle x'', x' | \psi_A \rangle$$

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