Wavefunction of Many Electrons: Fermion System

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Particles That Obey Quantum Mechanics Are Indistinguishable

Theoretically, particles that obey classical mechanics are distinguishable from other particles, and detected its movement despite that the system are consisted of many particles of the same kind. For the particles that obey quantum mechanics have completely different situations; they eventually become indistinguishable even if each particle are kept far apart at certain time to avoid the wavefunctions from piling up. This is because the wavefunction expand and gradually lying on top of the other one. In order to describe this situation, we consider for a system of N number particles of the same kind. The particle coordinates r_i and the spin coordinates σ_i are arranged to

$$\xi_i = (\mathbf{r}_i, \sigma_i), i = 1, 2 \cdots N$$
 (1)

The Hamiltonian of the system is defined as a function of $\xi_1 \sim \xi_N$ yet, in general, it remains unchanged in respect to the arbitrary coordinate interchanges. Thus, the operator P_{ij} that interchanges the coordinates ξ_i and ξ_j is written as:

$$P_{ij}H(\xi_1, \dots \xi_i \dots \xi_j \dots, \xi_N)$$

$$=H(\xi_1, \dots \xi_j \dots \xi_i \dots, \xi_N)P_{ij}$$

$$=H(\xi_1, \dots \xi_i \dots \xi_j \dots, \xi_N)P_{ij}$$
(2)

(2) represents the commutability of the Hamiltonian with P_{ij} then we can define the state of N particles to be the eigenstate of P_{ij} . Now, we investigate the eigenstate of P_{ij} .

For the simplification, we write the wavefunction for the eigenstate with two electrons to be:

$$\Psi_a(\xi_1, \xi_2) \tag{3}$$

The subscript a specifies the eigenstate. To operate theoperator P_{12} to the above, one obtains $P_{12}\Psi_a(\xi_1,\xi_2)=\Psi_a(\xi_2,\xi_1)$. Here, we take $\Psi_a(\xi_1,\xi_2)$ as the eigenstate of P_{ij} , and P_a as its eigenvalue, and then we can write the equation:

$$P_{12}\Psi_a(\xi_1, \xi_2) = \Psi_a(\xi_2, \xi_1) = p_a\Psi_a(\xi_1, \xi_2)$$
 (4)

If P_{12} is operated again, ξ_1 and ξ_2 may be interchanged twice at the initial wavedunction, thus goes back to the initial wavefunction:

$$P_{12}^2 \Psi_a(\xi_1, \xi_2) = p_a P_{12} \Psi_a(\xi_1, \xi_2) = p_a^2 \Psi_a(\xi_1, \xi_2) = \Psi_a(\xi_1, \xi_2)$$
 (5)

From (5), square of the eigenvalue
$$p_a$$
 is gained $p_a^2 = 1$, therefore:
 $p_a = \pm 1$ (6)

In general, (6) is also given for N particles so, the particles that obey quantum mechanics are expressed in the wavefunctions of either symmetric ($P_a=1$) or antisymmetric ($P_a=-1$). The sign remains the same when the coordinates of two particles are interchanged (symmetry), and the sign changes when the coordinates are interchanged (antisymmetric).

As (2) shows, a Hamiltonian and the interchange operator P_{ij} are commutative thus conservation of symmetric property for the wavefunction can be established. This is established regardless of any existence of interactions among particles. All quantum mechanical particles have the state either p=+1 or p=-1 in coordinate interchange of particles, and have no mixed state. Moreover, the choice of the state: p=+1 or p=-1 depends upon the charectericies of the particles and not depending on the state of the particles. The particles that are expressed in the symmetric wavefunction are called bosons, while those particles expressed in antisymmetric wavefunction are called fermions. Bosons obey Bose-Einstein statistics, and fermions obey Fermi-Dirac statistics. Fermions are commonly known as particles with half odd integer spin such as electron, neutron, proton, etc., and bosons are known as particles with integer spin such as photon. It is possible to draw a logical explanation of this fact within the frame of relativistic quantum mechanics.

Symmetric Wavefunction and Antisymmetric Wavefunction

Now let us go deep on the wavefunctions for many particles. For simplification, we suppose there are two particles in the central force potential with no interaction between the particles, and no spin-orbit interaction. The Hamiltonian then be given as:

$$H = \frac{1}{2m} \mathbf{p}_1^2 + V(r_1) + \frac{1}{2m} \mathbf{p}_2^2 + V(r_2)$$
(7)

The Hamiltonian is completely separated in terms of the coordinates hence we suppose the wavefunctions to form the separation of variables, also:

$$\Psi_a(\xi_1, \xi_2) = \psi_1(\xi_1)\psi_2(\xi_2) \tag{8}$$

When (8) is substituted into the two particles Schrodinger's equations, we obtain:

$$H\Psi_a(\xi_1, \xi_2) = E_a \Psi_a(\xi_1, \xi_2)$$
(9)

$$\psi_{2}(\xi_{2})\left\{\frac{1}{2m}\boldsymbol{p}_{1}^{2}+V(r_{1})\right\}\psi_{1}(\xi_{1})+\psi_{1}(\xi_{1})\left\{\frac{1}{2m}\boldsymbol{p}_{2}^{2}+V(r_{2})\right\}\psi_{2}(\xi_{2})$$

$$=E_{a}\psi_{1}(\xi_{1})\psi_{2}(\xi_{2})$$
(10)

Divided each side by $\psi_1\psi_2$ then:

$$E_a = \frac{1}{\psi_1(\xi_1)} \left\{ \frac{1}{2m} \boldsymbol{p}_1^2 + V(r_1) \right\} \psi_1(\xi_1) + \frac{1}{\psi_2(\xi_2)} \left\{ \frac{1}{2m} \boldsymbol{p}_2^2 + V(r_2) \right\} \psi_2(\xi_2)$$

The right side first term and the second term should be consisted of ξ_1 and ξ_2 respectively that the invariables in each term must have no ξ_1 or ξ_2 . We write the invariables E_1, E_2 for each, the equations can be reformed to:

$$\{\frac{1}{2m}\mathbf{p}_{1}^{2} + V(r_{1})\}\psi_{1}(\xi_{1}) = E_{1}\psi_{1}(\xi_{1})$$

$$\{\frac{1}{2m}\mathbf{p}_{2}^{2} + V(r_{2})\}\psi_{2}(\xi_{2}) = E_{2}\psi_{2}(\xi_{2})$$

$$E_{a} = E_{1} + E_{2}$$
(11)

The two-particle wavefuntion can be written out based on the solution of single particle Schrodinger's equations, however we notice that this wavefunction is not the generalized form of eigenstate for the interchanging particles coordinates.

$$P_{12}\Psi_a(\xi_1, \xi_2) = P_{12}\psi_1(\xi_1)\psi_2(\xi_2) = \psi_1(\xi_2)\psi_2(\xi_1)$$
 (12)

Let us consider the following:

$$\Psi_b(\xi_1, \xi_2) = \psi_2(\xi_1)\psi_1(\xi_2) \tag{13}$$

This equation should have the same eigenenergy E_a and should satisfy the eigenfunction below:

$$H\Psi_b(\xi_1, \xi_2) = E_a \Psi_b(\xi_1, \xi_2)$$
 (14)

Even if we take the linear combination of Ψ_a and Ψ_b :

$$\Psi(\xi_1, \xi_2) = a\Psi_a(\xi_1, \xi_2) + b\Psi_b(\xi_1, \xi_2)$$

$$= a\psi_1(\xi_1)\psi_2(\xi_2) + b\psi_2(\xi_1)\psi_1(\xi_2)$$
(15)

The equation above remains the eigenfunction, which has the eigenenergy E_a with an identical Hamiltonian.

Next, we consider the possibility for forming the eigenfunction of the particles operator P_{12} in such form of wavefunctions above:

$$\begin{split} P_{12}\{a\psi_1(\xi_1)\psi_2(\xi_2) + b\psi_2(\xi_1)\psi_1(\xi_2)\} \\ &= \{a\psi_1(\xi_2)\psi_2(\xi_1) + b\psi_2(\xi_2)\psi_1(\xi_1)\} \\ &= \pm \{a\psi_1(\xi_1)\psi_2(\xi_2) + b\psi_2(\xi_1)\psi_1(\xi_2)\} \end{split}$$

So,

$$a = b$$
 $(p = +1)$, $orall a = -b$ $(p = -1)$ (16)

On the one hand, if the wavefunction of ψ_1 and ψ_2 stays the same, we should be careful that the wavefunction corresponding to p=-1 do not appear. While on the other hand, ψ_1 and ψ_2 has different wavefunctions, they orthogonalize to be:

$$\sum_{\sigma} \int d\mathbf{r} \psi_i(\xi)^* \psi_j(\xi) = \delta_{ij}$$
(17)

For example,

$$\psi_i(\xi) = \phi_n(\mathbf{r})\alpha(\sigma) \, \sharp \, \mathcal{T} \, i \sharp \psi_j(\xi) = \phi_m(\mathbf{r})\beta(\sigma)$$

$$\int d\mathbf{r} \phi_n(\mathbf{r})^* \phi_m(\mathbf{r}) = \delta_{nm} \qquad (18)$$

The subscripts i,j specify the state that wavefunctions represent as well as the conditions of orbit, and the spin for the wavefunction all at the same time. The single particle wavefunction (17) is orthonormalized and the two particles wavefunction is

normalized to be 1 then we must take $a = 1/\sqrt{2}$:

$$\Psi(\xi_1, \xi_2) = \frac{1}{\sqrt{2}} \{ \psi_1(\xi_1) \psi_2(\xi_2) \pm \psi_2(\xi_1) \psi_1(\xi_2) \}$$
(± correspond to $p = \pm 1$ {bosons and fermions}) (19)

Actually, normalization can be verified in following:

$$\begin{split} &\sum_{\sigma_{1}\sigma_{2}} \int d\mathbf{r}_{1} d\mathbf{r}_{2} \Psi(\xi_{1}, \xi_{2})^{*} \Psi(\xi_{1}, \xi_{2}) \\ &= \frac{1}{2} \sum_{\sigma_{1}\sigma_{2}} \int d\mathbf{r}_{1} d\mathbf{r}_{2} \{ |\psi_{1}(\xi_{1})\psi_{2}(\xi_{2})|^{2} + |\psi_{2}(\xi_{1})\psi_{1}(\xi_{2})|^{2} \\ &\quad \pm \psi_{1}(\xi_{1})^{*} \psi_{2}(\xi_{2})^{*} \psi_{2}(\xi_{1}) \psi_{1}(\xi_{2}) \pm \psi_{2}(\xi_{1})^{*} \psi_{1}(\xi_{2})^{*} \psi_{1}(\xi_{1}) \psi_{2}(\xi_{2})] \\ &= \frac{1}{2} \sum_{\sigma_{1}} \int d\mathbf{r}_{1} |\psi_{1}(\xi_{1})|^{2} \sum_{\sigma_{2}} \int d\mathbf{r}_{2} |\psi_{1}(\xi_{1})|^{2} \\ &\quad + \frac{1}{2} \sum_{\sigma_{1}} \int d\mathbf{r}_{1} |\psi_{2}(\xi_{1})|^{2} \sum_{\sigma_{2}} \int d\mathbf{r}_{2} |\psi_{1}(\xi_{1})|^{2} \\ &\quad \pm \frac{1}{2} \sum_{\sigma_{1}} \int d\mathbf{r}_{1} \psi_{1}(\xi_{1})^{*} \psi_{2}(\xi_{1}) \sum_{\sigma_{2}} \int d\mathbf{r}_{2} \psi_{2}(\xi_{2})^{*} \psi_{1}(\xi_{2}) \\ &\quad \pm \frac{1}{2} \sum_{\sigma_{1}} \int d\mathbf{r}_{1} \psi_{2}(\xi_{1})^{*} \psi_{1}(\xi_{1}) \sum_{\sigma_{2}} \int d\mathbf{r}_{2} \psi_{1}(\xi_{2})^{*} \psi_{2}(\xi_{2}) \\ &\quad = \frac{1}{2} \cdot 1 \cdot 1 + \frac{1}{2} \cdot 1 \cdot 1 \pm \frac{1}{2} \cdot 0 \cdot 0 \pm \frac{1}{2} \cdot 0 \cdot 0 = 1 \end{split}$$

The antisymmetric wavefunction in (19) can be expressed with determinant:

$$\Psi_{Fermi}(\xi_1, \xi_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(\xi_1) & \psi_1(\xi_2) \\ \psi_2(\xi_1) & \psi_2(\xi_2) \end{vmatrix}$$
(20)

The rows in the determinant are corresponding to the state of the particles, and the columns are corresponding to the particles coordinates. The two-particle eigenstate taking the eigenstate in regard with the replacement of particle coordinates may be expressed with the linear combination of 2! two-particle wavefunction. This antisymmetric property corresponds to the characteristics of the determinant.

According to the discussions above, we also verified for the general case; N particles involve the interactions as long as the single particle wavefunction is determined, then it becomes directly applicable. Using the orthonormalized single particle wavefunction $\{\psi_i(\xi)\}$, the state for the N particles can be expressed as:

Bosons:

$$\Psi(\xi_1, \dots, \xi_n) = \frac{1}{\sqrt{N!}} \sum_{P} \psi_1(\xi_{P1}) \psi_2(\xi_{P2}) \dots \psi_N(\xi_{PN}) ,$$

Fermions:

$$\Psi(\xi_{1}, \dots, \xi_{n}) = \frac{1}{\sqrt{N!}} \sum_{P} sgn(P)\psi_{1}(\xi_{P1})\psi_{2}(\xi_{P2}) \dots \psi_{N}(\xi_{PN})$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{1}(\xi_{1}) & \psi_{1}(\xi_{2}) & \dots & \psi_{1}(\xi_{N}) \\ \psi_{2}(\xi_{1}) & \psi_{2}(\xi_{2}) & \dots & \psi_{2}(\xi_{N}) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{N}(\xi_{1}) & \psi_{N}(\xi_{2}) & \dots & \psi_{N}(\xi_{N}) \end{vmatrix}$$
(21)

A determinant wavefunction for the fermions is called a Slater determinant. The sum P is concerned with the permutation numbers $1 \sim N$. The permutation for n numbers is consisted of n! all together thus we have normalization constant $1/\sqrt{N!}$. The permutation P implies conducting rearrangement in regard with the particle coordinates in below:

$$P: (1, 2, 3, \dots, N) \to (P1, P2, \dots, PN)$$

sgn(P) is the value for ± 1 ; an even permutation takes +1 while an odd permutation takes -1. In this way, we have obtained the wavefunction that satisfies the symmetric property for composite particles yet the procedures of determining single particle wavefunction should be considered separately.

Let us study the meaning of N-fermion wavefunction and its expression in the second equation of (21). Among the single particle wavefunctions for N particles $\psi_1 \sim \psi_N$, suppose ψ_1 and ψ_2 are identical. Based on the essential characteristics that when two

rows become exactly the same, the value for the permutation turns 0, the second equation in (21) identitically becomes zero. To put in other words, a single particle state does not hold the property for no more than single fermion. This is called the Pauli exclusion principle. For bosons, the same restriction cannot be derived from the first equation (21) so, there exists no restrictions for the particles probability, and the single particle quantum state is capable of holding as much identical particles as possible.

Property of Many-Particle Wavefunction

The square of the absolute value for single particle wavefunction $|\psi(\xi)|^2$ refers to the probability to figure out a particle in certain spatial coordinates r, and spin coordinates $\sigma = \pm 1$. For N particles:

$$P_N(\xi_1, \xi_2, \dots \xi_N) = |\Psi(\xi_1, \xi_2, \dots \xi_N)|^2$$
(22)

It is the probability of finding out N particles in $\xi_1 = (r_1, \sigma_1), \xi_2, \dots \xi_N$. If we can determine N-1particles within N particles then what is left out should be the probability for the single particle. In order to show a logic in this verification,

$$P_1(\xi) = \sum_{\sigma_2 \cdots \sigma_N} \int d\mathbf{r}_2 \cdots d\mathbf{r}_N P_N(\xi, \xi_2, \cdots \xi_N)$$
(23)

(23) is the probability of figuring out the left out single particle in ξ ,

$$P_2(\xi_1, \xi_2) = \sum_{\sigma_3 \cdots \sigma_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N P_N(\xi_1, \xi_2, \cdots \xi_N)$$
(24)

(24) is the probability of figuring out two particles in ξ_1, ξ_2 . To write out the equation in regard to N=2:

$$P_{2}(\xi_{1}, \xi_{2}) = \frac{1}{2} \{ |\psi_{1}(\xi_{1})|^{2} |\psi_{2}(\xi_{2})|^{2} + |\psi_{2}(\xi_{1})|^{2} |\psi_{1}(\xi_{2})|^{2} - \psi_{1}(\xi_{1})^{*} \psi_{2}(\xi_{1}) \cdot \psi_{2}(\xi_{2})^{*} \psi_{1}(\xi_{2}) - \psi_{2}(\xi_{1})^{*} \psi_{1}(\xi_{1}) \cdot \psi_{1}(\xi_{2})^{*} \psi_{2}(\xi_{2}) \}$$

$$(25)$$

Then conduct summation and integration, then with (17),

$$P_1(\xi) = \sum_{\sigma_2} \int d\mathbf{r}_2 P_2(\xi, \xi_2) = \frac{1}{2} \{ |\psi_1(\xi)|^2 + |\psi_2(\xi)|^2 \}$$
(26)

(26) represents the particle density when the particles are equally filled up in both states ψ_1 and ψ_2 .

$$\psi_1(\xi) = \phi_1(\mathbf{r})\alpha(\sigma)$$
, $\psi_2(\xi) = \phi_2(\mathbf{r})\alpha(\sigma)$ (27a)

Then,

$$P_{1}(\xi) = \frac{1}{2} \{ |\phi_{1}(\mathbf{r})|^{2} + |\phi_{2}(\mathbf{r})|^{2} \} |\alpha(\sigma)|^{2}$$

$$\sum_{\sigma} P_{1}(\xi) = \frac{1}{2} \{ |\phi_{1}(\mathbf{r})|^{2} + |\phi_{2}(\mathbf{r})|^{2} \}$$
(27b)

If

$$\psi_1(\xi) = \phi_1(\mathbf{r})\alpha(\sigma)$$
, $\psi_2(\xi) = \phi_2(\mathbf{r})\beta(\sigma)$ (28a)

Then,

$$P_{1}(\xi) = \frac{1}{2} \{ |\phi_{1}(\mathbf{r})|^{2} |\alpha(\sigma)|^{2} + |\phi_{2}(\mathbf{r})|^{2} |\beta(\sigma)|^{2} \}$$

$$\sum_{\sigma} P_{1}(\xi) = \frac{1}{2} \{ |\phi_{1}(\mathbf{r})|^{2} + |\phi_{2}(\mathbf{r})|^{2} \}$$
(28b)

In the examples above (27)~(28), the two states have different spin densities, however, the two share the same particle density.

Now, we study the two-particle density $P_2(\xi_1, \xi_2)$ when (27a) and (28a). Using (25), we can directly calculate the density. When we have the same spin in two states:

$$(27a) \rightarrow \sum_{\sigma_1 \sigma_2} P_2(\xi_1, \xi_2) = \frac{1}{2} \{ |\phi_1(\mathbf{r}_1)|^2 |\phi_2(\mathbf{r}_2)|^2 + |\phi_2(\mathbf{r}_1)|^2 |\phi_1(\mathbf{r}_2)|^2 - \phi_1(\mathbf{r}_1)^* \phi_2(\mathbf{r}_1) \cdot \phi_2(\mathbf{r}_2)^* \phi_1(\mathbf{r}_2) - \phi_2(\mathbf{r}_1)^* \phi_1(\mathbf{r}_1) \cdot \phi_1(\mathbf{r}_2)^* \phi_2(\mathbf{r}_2) \}$$

$$(29a)$$

The density for different spins in two states on the other hand becomes:

$$(28a) \rightarrow \sum_{\sigma_1 \sigma_2} P_2(\xi_1, \xi_2) = \frac{1}{2} \{ |\phi_1(\mathbf{r}_1)|^2 |\phi_2(\mathbf{r}_2)|^2 + |\phi_2(\mathbf{r}_1)|^2 |\phi_1(\mathbf{r}_2)|^2$$
(29b)

This is because $\sum_{\sigma} {\psi_1}^*(\xi) \psi_2(\xi) = 0$ when (28a). The difference between (29a) and (29b):

$$-\phi_1(\mathbf{r}_1)^*\phi_2(\mathbf{r}_1)\cdot\phi_2(\mathbf{r}_2)^*\phi_1(\mathbf{r}_2) - \phi_2(\mathbf{r}_1)^*\phi_1(\mathbf{r}_1)\cdot\phi_1(\mathbf{r}_2)^*\phi_2(\mathbf{r}_2)\}$$

$$= -2Re\{\phi_1(\mathbf{r}_1)^*\phi_2(\mathbf{r}_1)\cdot\phi_2(\mathbf{r}_2)^*\phi_1(\mathbf{r}_2)\}$$

In the region $r_1 \simeq r_2$:

$$\phi_1(\mathbf{r}_1)^*\phi_1(\mathbf{r}_2) \simeq |\phi_1(\mathbf{r}_1)|^2$$

Therefore, the density difference makes negative contribution. In the space, two particles in the same spins have greater repellence of each other in comparison with the two in the different spins. This clearly shows the existence of the Pauli exclusion principle acting on among fermions in space and nothing else.

In the case of N fermions, let us calculate the probability of two particles. We take the sum of spin coordinates and integrals of the spatial coordinates for $N\sim2$ particles from ξ_3 to ξ_N . Based on the definition of the determinant, we can put the permutation (21) to the wavefunction instead of the coordinates hence,

$$P_{2}(\xi_{1}, \xi_{2}) = \sum_{\sigma_{3} \cdots \sigma_{N}} \int \cdots \int d\mathbf{r}_{3} \cdots d\mathbf{r}_{N} |\Psi(\xi_{1}, \xi_{2}, \xi_{3} \cdots \xi_{N})|^{2}$$

$$= \sum_{\sigma_{3} \cdots \sigma_{N}} \int \cdots \int d\mathbf{r}_{3} \cdots d\mathbf{r}_{N} \frac{1}{N!} \sum_{P} \sum_{Q} sgn(P)sgn(Q)$$

$$\psi_{P1}(\xi_{1})^{*} \psi_{Q1}(\xi_{1}) \cdot \psi_{P2}(\xi_{2})^{*} \psi_{Q2}(\xi_{2}) \cdots \psi_{PN}(\xi_{N})^{*} \psi_{QN}(\xi_{N}). \tag{30}$$

According to the orthonormalization conditions (17),

$$P3 = Q3, P4 = Q4, \cdots PN = QN$$
 (31)

A set of state consisted of $N\sim2$ particles should agree with the corresponding state as is shown in (31). For the rest of the first two sets may be either,

$$P1 = Q1, P2 = Q2; (sgn(P) = sgn(Q))$$
 (32a)

Or,

$$P1 = Q2, P2 = Q1; (sgn(P) = -sgn(Q))$$
 (32b)

We find P1 has N ways to choose from 1 to N, and P2 has N-1 ways, as there are N(N-1) ways all together. We do not need to distinguish the rest of the permutations as long as we conduct integrations and summations in terms of $\xi_3 \sim \xi_N$. Here, we write out the permutation P1 for 1 as P1 then obtain the following:

$$\begin{split} P_2(\xi_1, \xi_2) &= \frac{1}{N(N-1)} \sum_{p_1=1}^{N} \sum_{p_2=1}^{N} \sum_{(p_2 \neq p_1)}^{N} \\ \{|\psi_{p_1}(\xi_1)|^2 |\psi_{p_2}(\xi_2)|^2 - \psi_{p_1}(\xi_1)^* \psi_{p_2}(\xi_1) \cdot \psi_{p_2}(\xi_2)^* \psi_{p_1}(\xi_2) \}_{(33)} \end{split}$$

This is the generalization of two-particle density that corresponds to (25). In addition, by conducting the integrations and summations on ξ_2 then, with (17) we have:

$$P_1(\xi_1) = \sum_{\sigma_2} \int d\mathbf{r}_2 P_2(\xi_1, \xi_2) = \frac{1}{N} \sum_{p_1=1}^{N} |\psi_{p_1}(\xi_1)|^2$$
(34)

Summarizing, we find equal allocation of probability to figure out the single particle.