Physics 481: Quantum Mechanics II

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Lecture III
Combining more than two identical particles to form a symmetrized state under the interchange of any pair of identical particles:

Suppose we have three particles, each in one of the single-particle states $\psi_a$, $\psi_b$, or $\psi_c$. (We will consider the case when each particle is in a different state. In problem 5.33, you will consider all possibilities.)

If the particles are distinguishable, then the state of the system can be

$$\psi(1, 2, 3) = \psi_a(1)\psi_b(2)\psi_c(3)$$

or $$\psi(2, 1, 3) = \psi_a(2)\psi_b(1)\psi_c(3)$$

or $$\psi(2, 3, 1) = \psi_a(2)\psi_b(3)\psi_c(1)$$

or $$\psi(1, 3, 2) = \psi_a(1)\psi_b(3)\psi_c(2)$$

or $$\psi(3, 1, 2) = \psi_a(3)\psi_b(1)\psi_c(2)$$

or $$\psi(3, 2, 1) = \psi_a(3)\psi_b(2)\psi_c(1)$$

I have adopted the convention that we keep the states in the same order $a$, $b$, $c$ and the order of the numbers in the argument of $\psi$ tells us which particle is in each of the three states. There are $3! = 6$ different states.
For three particles, the **symmetric** state is just the sum of these six states

\[ \psi_S = \frac{1}{\sqrt{3!}} [\psi(1, 2, 3) + \psi(2, 3, 1) + \psi(3, 1, 2) + \psi(1, 3, 2) + \psi(2, 1, 3) + \psi(3, 2, 1)]. \]

Symmetrization requires that all six terms be included.

How do we form the **antisymmetric** state? Again, all \(3! = 6\) terms must be present but each term that is an **odd** permutation of \(\psi(1, 2, 3) = \psi_a(1)\psi_b(2)\psi_c(3)\) must have a **negative** sign in front and each term which is an **even** permutation of \(\psi(1, 2, 3)\) must have a positive sign:

\[ \psi_A = \frac{1}{\sqrt{3!}} [\psi(1, 2, 3) + \psi(2, 3, 1) + \psi(3, 1, 2) - \psi(1, 3, 2) - \psi(2, 1, 3) - \psi(3, 2, 1)]. \]

In this way, one exchange of a pair will introduce a negative sign (e.g. under \(1 \leftrightarrow 2\), \(\psi_A \rightarrow -\psi_A\)).
Aside: Definition of even and odd permutation of \((1, 2, 3, \ldots, N)\) —

Even permutation \(\Rightarrow\) an even \# of exchanges of pairs of indices will return order to \((1, 2, 3, \ldots, N)\);
Odd permutation \(\Rightarrow\) an odd \# of exchanges of pairs of indices will return order to \((1, 2, 3, \ldots, N)\).

Now let’s generalize to \(N\) particles in \(N\) distinct states \(\psi_i\). For \(N\) distinguishable particles, there will be \(N!\) different allowed states, each of which is an even or odd permutation of \(\psi(1, 2, 3, \ldots, N) = \psi_a(1)\psi_b(2) \ldots \psi_p(N)\). Let \(P_\alpha\) be a permutation operator associated with a system of \(N\) particles; \(\alpha\) represents an arbitrary permutation of the \(N\) integers: \(\alpha = 1, 2, \ldots, N!\) (i.e., there are \(N!\) distinct permutations).
Define

\[ \epsilon_\alpha = +1 \text{ if } P_\alpha \text{ is an even permutation,} \]
\[ \epsilon_\alpha = -1 \text{ if } P_\alpha \text{ is an odd permutation.} \]

Then

\[ \psi_S = \frac{1}{\sqrt{N!}} \sum_{\alpha=1}^{N!} P_\alpha \psi_a(1)\psi_b(2) \ldots \psi_p(N) \]

is a symmetric state, and

\[ \psi_A = \frac{1}{\sqrt{N!}} \sum_{\alpha=1}^{N!} \epsilon_\alpha P_\alpha \psi_a(1)\psi_b(2) \ldots \psi_p(N) \]

is an antisymmetric state, under the interchange of any two particles.

(If the individual states \( \psi_i \) are orthonormal, then \( \psi_{S,A} \) is normalized.)

Note that if any two of the states coincide (e.g. \( \psi_a = \psi_b \)), then \( \psi_A = 0 \) (Pauli’s exclusion principle again.).
Slater Determinant

A convenient way to find the antisymmetric state $\psi_A$ is through the following determinant:

$$
\psi_A = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_a(1) & \psi_b(1) & \psi_c(1) & \cdots & \psi_p(1) \\
\psi_a(2) & \psi_b(2) & \psi_c(2) & \cdots & \psi_p(2) \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\psi_a(N) & \psi_b(N) & \psi_c(N) & \cdots & \psi_p(N)
\end{vmatrix}
$$

This is a convenient way to get the signs right. Note that if two states coincide, two rows will be identical and the determinant will be zero.
Parity and Symmetry under Interchange for identical particles in a state with orbital angular momentum quantum number $l$:

Last semester, we defined the parity of a one-dimensional eigenfunction as the quantity that describes the behavior of the eigenfunction when the sign of the coordinate is changed:
If $\psi(-x) = +\psi(x) \Rightarrow$ parity is even;
if $\psi(-x) = -\psi(x) \Rightarrow$ parity is odd.

The definition can immediately be extended to three dimensions. That is, wave functions satisfying the relation $\psi(-x, -y, -z) = \psi(x, y, z)$ are said to be of even parity and wave functions satisfying $\psi(-x, -y, -z) = -\psi(x, y, z)$ are said to be of odd parity.
All eigenfunctions that are bound state solutions to T.I.S.E.’s for a potential that can be written as $V(r)$, like the Coulomb potential, have definite parities, either even or odd.

Why? Since the potential has the same value at $(x, y, z)$ and $(-x, -y, -z)$, the probability densities $\psi^*\psi$ should also have the same value at $(x, y, z)$ and $(-x, -y, -z)$. Therefore, $\psi(x, y, z) = \pm \psi(-x, -y, -z)$ or $\psi(\vec{r}) = \pm \psi(-\vec{r})$.

For example, the solutions to the Hydrogen atom $\psi_{nlm}$ all have definite parity.
The figure below shows that when the signs of the rectangular coordinates are changed, the behavior of the spherical polar coordinates is $r \rightarrow r$, $\theta \rightarrow \pi - \theta$, $\phi \rightarrow \pi + \phi$.

The part of the solution to the Hydrogen atom that depends on $\theta$ and $\phi$ is $Y_{l}^{m}(\theta, \phi)$ (i.e., the spherical harmonics). Inspection of the spherical harmonics in Table 4.3, page 139 in Griffith reveals that

$$Y_{l}^{m}(\pi - \theta, \pi + \phi) = (-1)^{l}Y_{l}^{m}(\theta, \phi).$$
Therefore,

\[ P\psi_{nlm}(r, \theta, \phi) = \psi_{nlm}(r, \pi - \theta, \pi + \phi) = (-1)^l \psi_{nlm}(r, \theta, \phi). \]

So, the parity of the wave function is determined by \((-1)^l\). The parity is **even** if the orbital angular momentum quantum number \(l\) is even; and **odd** if \(l\) is odd. This is true for all eigenfunctions of any spherically symmetric potential \(V(r)\).
Now, for a system of two particles, the **parity** and **symmetry** under interchange of the two particles of the spatial wave function are the **same**, because reflecting the wave function through the origin interchanges the two particles. For example, if $\vec{r}$ is defined as the vector pointing from particle 1 to particle 2, then $\vec{r} \rightarrow -\vec{r}$ when the particles are interchanged:

\[ \begin{array}{c}
1 \\
\vec{r} \\
2 \\
\end{array} \quad \begin{array}{c}
2 \\
\rightarrow \\
1 \\
\end{array} \quad \begin{array}{c}
1 \\
\rightarrow -\vec{r} \\
2 \\
\end{array} \]

$\vec{r} \rightarrow -\vec{r}$ is equivalent to interchanging particles.

So the spatial part of the wave function for two particles with $V = V(r)$ is symmetric under interchange of the two particles if $l$ is even, and antisymmetric under interchange if $l$ is odd.