

The many-body problem in quantum mechanics

So far we have dealt with a single particle only. The wave function for a single particle is a function of time, spatial coordinates, and, possibly spin:

$$\Psi = \Psi(\vec{r}, \vec{s}, t) = \begin{pmatrix} \Psi_{\uparrow}(\vec{r}, t) \\ \Psi_{\downarrow}(\vec{r}, t) \end{pmatrix} \quad (\text{assuming spin } 1/2)$$

For a system of N particles things become more complicated. If we ignore spin for the moment, the wave function depends on \vec{r}_i $i=1 \dots N$ and t :

$$\Psi = \Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N, t)$$

For a general case of interacting particles the dependence on \vec{r}_i 's is very nontrivial. The time evolution is still governed by the Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

Here the Hamiltonian for the whole system is:

$$\hat{H} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i} + V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, t) = \sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 + V(\vec{r}_1, \dots, \vec{r}_N, t)$$

The statistical interpretation carries over in the obvious way:

$$|\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, t)|^2 d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N$$

is the probability of finding particle 1 in the element of volume $d\vec{r}_1$ and at the same time particle 2 in the element of volume $d\vec{r}_2$, particle 3 in $d\vec{r}_3$ and so on. This probability is a function of time

Since the probability of finding any particle anywhere must be equal to unity, the normalization condition for the wave function is

$$\int |\Psi(\vec{r}_1, \dots, \vec{r}_N, t)|^2 d\vec{r}_1 \dots d\vec{r}_N = 1$$

If the potential V is time independent (e.g. there is no explicit dependence on t) we can, again, as before, use the separation of variables approach to represent the general solution as

$$\Psi(\vec{r}_1, \dots, \vec{r}_N, t) = \sum_{\mathbf{k}} c_{\mathbf{k}} \Psi_{\mathbf{k}}(\vec{r}_1, \dots, \vec{r}_N) e^{-\frac{iE_{\mathbf{k}}t}{\hbar}}$$

where $\Psi_{\mathbf{k}}$'s are stationary (or partial) solutions that satisfy the time-independent Schrödinger equation

$$\left[-\sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 + V(\vec{r}_1, \dots, \vec{r}_N) \right] \Psi_{\mathbf{k}}(\vec{r}_1, \dots, \vec{r}_N) = E_{\mathbf{k}} \Psi_{\mathbf{k}}(\vec{r}_1, \dots, \vec{r}_N)$$

In most practical applications potential V is a sum of single-particle and pairwise interparticle interactions:

$$V = \underbrace{\sum_{\substack{i,j=1 \\ i>j}}^N V_{ij}(\vec{r}_i, \vec{r}_j)}_{\text{two-body potential}} + \underbrace{\sum_{i=1}^N U_i^{\text{ext}}(\vec{r}_i)}_{\text{external potential}}$$

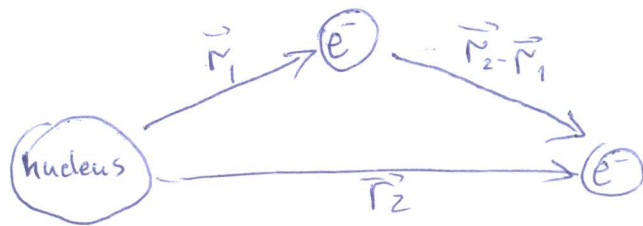
Moreover, oftentimes, V_{ij} is central and depends only on the distance between particles:

$$V_{ij}(\vec{r}_i, \vec{r}_j) = V_{ij}(|\vec{r}_i - \vec{r}_j|) = V_{ij}(r_{ij})$$

The solution of the N -particle Schrödinger equation is, generally, a very difficult task, even in the stationary case. Various numerical approaches have been developed to tackle this problem.

A simple example of a many-body problem in quantum mechanics is the He atom (or He-like ion):

$$\hat{H} = -\frac{\hbar^2}{2m_n} \nabla_n^2 - \frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{|\vec{r}_1 - \vec{r}_n|} - \frac{Ze^2}{|\vec{r}_2 - \vec{r}_n|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$



Here m_n is the mass of the nucleus and m_e is the mass of the electron.

Identical particles

Suppose we have a system of two particles that have the same mass, charge, etc. In other words, suppose the two particles are of exactly the same nature. Now if we suppose particle 1 is in the one-particle state (assume no interaction) $\psi_a(\vec{r})$, and particle 2 is in the state $\psi_b(\vec{r})$. If we ignore spin for the moment then the total wave function is a simple product:

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1) \psi_b(\vec{r}_2)$$

This assumes that we can tell particles apart.

In classical mechanics we can always tell particles apart. In quantum mechanics the situation is fundamentally different. We cannot paint or label particles. We cannot track them as tracking must involve some sort of a measurement that inevitably and unpredictably alter its state. Because of that we cannot be sure that particles switch places. The fact is, all particles of the same nature (e.g. electrons) are utterly identical.

Quantum mechanics neatly accommodates the existence of particles that are indistinguishable in principle. We simply construct a wave function that does not discriminate between particles and is non-committal as to which particle is in which state

$$\Psi_{\pm}(\vec{r}_1, \vec{r}_2) = A [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)]$$

The theory admits two kinds of particles; bosons (the plus sign) and fermions (the minus sign).

Relativistic theory establishes a connection between spin of particles and statistics. It turns out that all fermions have half integer spin and vice versa. All particles with integer spin are bosons.

It follows that two identical fermions cannot occupy the same (single-particle) state. This is because

$$\Psi_{-}(\vec{r}_1, \vec{r}_2) = A [\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_a(\vec{r}_1)] = 0$$

This constitutes the well-known Pauli exclusion principle.

To consider things in a more formal way let us

define the exchange operator (or permutation operator), which interchanges the two particles, or, as they say, interchanges the labels of the two particles:

$$P_{12} f(\vec{r}_1, \vec{r}_2) = f(\vec{r}_2, \vec{r}_1)$$



If \hat{P}_{12} commutes with \hat{H} (which takes place when the particles are identical) the eigenfunctions of \hat{H} can be chosen in such a way that they simultaneously are eigenfunctions of \hat{P}_{12} , and vice versa.

Clearly, $\hat{P}_{12}^2 = \hat{1}$ and the eigenvalues of \hat{P} are ± 1 .

We can sort the solutions of the Schrödinger equation (e.g. eigenfunctions of \hat{H}) into symmetric (eigenvalue $+1$ of \hat{P}_{12}) or antisymmetric (eigenvalue -1) under exchange:

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

The exchange symmetry does not change with time. If a system starts out in a state of particular symmetry, it remains in such state. The new law is that for identical particles the wave function is required to be either symmetric or antisymmetric.

Exchange interaction

The requirement of (anti)symmetry of the wave function for identical particles leads to some important implications. One of them is the Pauli exclusion principle, as we saw it previously. Moreover, some of the implications may occur for macroscopic systems. For example, the well-known Bose-Einstein condensation of bosons at low temperature results from the symmetry of their wave function.

When we talked about systems of bosons or fermions we assumed that the particles do not interact with each other. Strictly speaking this cannot be an absolutely accurate assumption. If particles are in proximity of each other so that their wavefunctions overlap the (anti)symmetry requirement leads to some "effective" "interaction" coming from the indistinguishability of particles. This "interaction", however, is not like what we are used to think about. It cannot be described by a simple function $V(\vec{r}_1, \vec{r}_2)$. The nature of this interaction is more subtle. We will try to understand it using a simple one-dimensional example.

Suppose we have two particles in states $\psi_a(x)$ and $\psi_b(x)$ and let us assume that the states are orthogonal. For distinguishable noninteracting particles the total wave function is

$$\psi(x_1, x_2) = \psi_a(x_1) \psi_b(x_2)$$

For indistinguishable particles, on the other hand,

$$\psi_{\pm}(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_a(x_1) \psi_b(x_2) \pm \psi_b(x_1) \psi_a(x_2))$$

+ for bosons
- for fermions

Let us calculate the expectation value $\langle (x_1 - x_2)^2 \rangle$ for distinguishable particles

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2 \langle x_1 x_2 \rangle$$

$$\langle x_1^2 \rangle = \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_a$$

$$\langle x_2^2 \rangle = \int |\psi_a(x_1)|^2 dx_1 \int x_2^2 |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_b$$

and

$$\langle x_1 x_2 \rangle = \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 = \langle x \rangle_a \langle x \rangle_b$$

Thus

$$\langle (x_1 - x_2)^2 \rangle = \langle x \rangle_a^2 + \langle x \rangle_b^2 - 2 \langle x \rangle_a \langle x \rangle_b$$

Note that the answer is actually independent on which particle is in state ψ_a and which is in state ψ_b .

Now let us compute the same expectation value for the case when particles are identical

$$\begin{aligned} \langle x_i^2 \rangle &= \frac{1}{2} \left(\iint x_i^2 \left[\psi_a(x_1) \psi_b(x_2) \pm \psi_b(x_1) \psi_a(x_2) \right]^2 dx_1 dx_2 \right) = \\ &= \frac{1}{2} \left(\int x_i^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 + \int x_i^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)|^2 dx_2 \right. \\ &\quad \left. \pm \int x_i^2 \psi_a^*(x_1) \psi_b(x_1) dx_1 \int \psi_b^*(x_2) \psi_a(x_2) dx_2 \right. \\ &\quad \left. \pm \int x_i^2 \psi_b^*(x_1) \psi_a(x_1) dx_1 \int \psi_a^*(x_2) \psi_b(x_2) dx_2 \right) = \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0] \\ &= \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b] \end{aligned}$$

Similarly we can obtain $\langle x_2^2 \rangle$:

$$\langle x_2^2 \rangle = \frac{1}{2} (\langle x_2^2 \rangle_b + \langle x_2^2 \rangle_a)$$

$$\langle x_1 x_2 \rangle = \frac{1}{2} \left(\int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 + \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)|^2 dx_2 \right.$$

$$\pm \int x_1 \psi_a^*(x_1) \psi_b(x_1) dx_1 \int x_2 \psi_b^*(x_2) \psi_a(x_2) dx_2$$

$$\pm \int x_1 \psi_b^*(x_1) \psi_a(x_1) dx_1 \int x_2 \psi_a^*(x_2) \psi_b(x_2) dx_2 \Bigg)$$

$$= \frac{1}{2} (\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab}) =$$

$$= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2$$

In the end we get

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2$$

The difference between distinguishable and nondistinguishable particles case is then ($\Delta x \equiv x_1 - x_2$)

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2 |\langle x \rangle_{ab}|^2$$

Identical bosons tend to get somewhat closer together while fermions tend to get farther apart.

If ψ_a and ψ_b are well separated in space so that their overlap ($\int \psi_a^*(x) \psi_b(x) dx$) vanishes then the "exchange" effect disappears.

The tendency of identical particles to get closer or farther apart gives rise to so called exchange forces.