Real-World Quantum Mechanics

The Many-Body Problem

1) System of $N$ interacting particles

$$\hat{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m_i} + \sum_{i<j} V(|\vec{r}_i - \vec{r}_j|)$$

$$+ \sum_{i=1}^{N} V_{\text{ext}}(\vec{r}_i)$$

$$\Psi_N = \Psi_N(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t)$$
\textbf{Schrödinger equation}:

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

\textbf{Example}: The atom (ion)

\[ \hat{H} = \frac{\vec{p}_1^2}{2m_1} + \frac{\vec{p}_2^2}{2m_2} + \frac{\vec{p}_2^2}{2m_2} - \frac{Ze^2}{|\vec{r}_1 - \vec{r}_N|} - \frac{Ze^2}{|\vec{r}_2 - \vec{r}_N|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \]

\textbf{2) Identical particles}

In the He atom, the two electrons have exactly the same mass, charge, etc. The Hamiltonian is unchanged if we interchange the two particles.

\[ \vec{r}_1 \leftrightarrow \vec{r}_2, \quad \vec{p}_1 \leftrightarrow \vec{p}_2. \]
We can define an exchange operator

\[ \hat{P}_{12} \psi(..., r_1, r_2, ...) = \psi(..., r_2, r_1, ...) \]

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

Thus the eigenfunctions of \( \hat{H} \) can be chosen as eigenfunctions of \( \hat{P}_{12} \) and vice versa.

What does this mean? Is it just academic? After all, we can tell electron 1 apart from electron 2, can't we? No!

Unless the two electrons are sufficiently far apart that their
Wavefunctions don't overlap, there is no way to be sure which of the two electrons is which, thanks to the uncertainty principle which prevent us from following their individual trajectories.

3) Eigenvalues and eigenfunctions of $\hat{P}_{12}$

$$\hat{P}_{12} \Psi(r_1, r_2, +) = \Psi(r_2, r_1, +)$$

$$(\hat{P}_{12})^2 \Psi(r_1, r_2, +) = 0$$

$$\Rightarrow \hat{P}_{12}^2 = \mathbb{1} \Rightarrow \text{eigenvalues} \lambda = \pm 1$$
4) Separable Systems

Suppose

\[ \hat{\mathcal{H}} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} + V(\vec{r}_1) + V(\vec{r}_2). \]

\[ = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2 \]

Then

\[ \Psi(\vec{r}_1, \vec{r}_2, t) = \psi_1(\vec{r}_1) \psi_2(\vec{r}_2) \]

\[ H_1 \psi_1 = E_1 \psi_1, \quad H_2 \psi_2 = E_2 \psi_2 \]

is a solution of time-dependent Schrödinger equation. However, \( \Psi \) is not an eigenfunction of \( \hat{p}_{12} \).
Symmetric \text{ and antisymmetric functions (dropping trivial } t\text{-dependence)}

\[ \Psi_\pm (\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left[ \Psi_1(\vec{r}_1) \Psi_2(\vec{r}_2) \pm \Psi_1(\vec{r}_2) \Psi_2(\vec{r}_1) \right] \]

\[ \hat{P}_{12} \Psi_\pm = \pm \Psi_\pm \]

\[ \Psi_\pm \] are also energy eigenstates of \( \hat{H} \), with eigenvalue \( E_1 \pm E_2 \).

Which should we choose?

5) Fermions and bosons

Depending on their spin, systems of identical particles are either symmetric under
particle exchange (bosons) or L

- antisymmetric (fermions):
  spin-statistics theorem (relativity + QM)

<table>
<thead>
<tr>
<th>Type of particle</th>
<th>intrinsic spin</th>
<th>Symmetry under $\hat{P}_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>boson</td>
<td>integer</td>
<td>+</td>
</tr>
<tr>
<td>fermion</td>
<td>half-odd integer</td>
<td>-</td>
</tr>
</tbody>
</table>

Examples of fermions:
- electrons, proton, neutron, neutrino, quark, atom with half-odd integer total angular momentum

Examples of bosons:
- photon, gluon, $W^\pm$, $Z$, phonon, atom with integer total angular momentum
6) Pauli principle

Two fermions of the same species cannot have the same wavefunction — they cannot occupy the same quantum state.

Proof: Suppose each occupied some state, with wavefunction \( \psi(\vec{r}) \).

Then

\[
\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left[ \psi(\vec{r}_1) \psi(\vec{r}_2) - \psi(\vec{r}_2) \psi(\vec{r}_1) \right] = 0.
\]

⇒ not allowed state (unnormalizable)
Example: Electrons in a 1D box.

\[ \begin{array}{c}
E_3 \\
E_2 \\
E_1 \\
\end{array} \]

\[ \begin{array}{cc}
\uparrow & \downarrow \\
\uparrow & \downarrow \\
\uparrow & \downarrow \\
\end{array} \]

7) Periodic table of the Elements

Mean-field picture of atoms.
The notation used to describe the electronic configuration of atoms and ions is discussed in all textbooks of introductory atomic physics. The letters s, p, d, ... signify electrons having orbital angular momentum 0, 1, 2, ... in units of ħ; the number to the left of the letter denotes the principal quantum number of one orbital, and the superscript to the right denotes the number of electrons in the orbit.