

Real-World Quantum Mechanics:

The Many-Body Problem

1) System of N interacting particles

two-body central potential

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

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

external potential

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

Schrödinger equation:

$$\bullet \quad i\hbar \frac{\partial \Psi_N}{\partial t} = \hat{H} \Psi_N$$

Example: He atom (ion)

$$\hat{H} = \frac{\vec{p}_N^2}{2M_N} + \frac{\vec{p}_1^2}{2me} + \frac{\vec{p}_2^2}{2me} - \frac{Ze^2}{|\vec{r}_1 - \vec{r}_N|} \\ - \frac{Ze^2}{|\vec{r}_2 - \vec{r}_N|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

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:

$$\bullet \quad \vec{r}_1 \Leftrightarrow \vec{r}_2, \quad \vec{p}_1 \Leftrightarrow \vec{p}_2$$

We can define an exchange

(3)

● operator

$$\hat{P}_{12} \Psi(\dots, \vec{r}_1, \vec{r}_2, \dots) = \Psi(\dots, \vec{r}_2, \vec{r}_1, \dots)$$

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

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,

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- there is no way to be sure which of the two electrons is which, thanks to the uncertainty principle, which prevents us from following their individual trajectories.

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

$$\hat{P}_{12} \Psi(\vec{r}_1, \vec{r}_2, t) = \Psi(\vec{r}_2, \vec{r}_1, t)$$

$$(\hat{P}_{12})^2 \Psi(\vec{r}_1, \vec{r}_2, t) = \Psi(\vec{r}_1, \vec{r}_2, t)$$

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

(If $\hat{P}_{12} \Psi = \lambda \Psi$ and $\hat{P}_{12}^2 \Psi = \lambda^2 \Psi = \Psi \Rightarrow \lambda = \pm 1$) (5)

4) Separable systems

Suppose
$$\hat{H} = \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} + V(\vec{r}_1) + V(\vec{r}_2)$$

$$= \hat{H}_1 + \hat{H}_2$$

Then
$$\Psi(\vec{r}_1, \vec{r}_2, t) = \psi_1(\vec{r}_1) \psi_2(\vec{r}_2) e^{-i \frac{E_1 + E_2}{\hbar} t}$$

$$H_1 \psi_1 = E_1 \psi_1, H_2 \psi_2 = E_2 \psi_2$$

is a solution of time-dep.

Schrödinger equation. However,

Ψ is not an eigenfunction of

$$\hat{P}_{12}$$

- Symmetric + antisymmetric functions (dropping trivial t-dependence)

$$\Psi_{\pm}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \pm \psi_1(\vec{r}_2)\psi_2(\vec{r}_1)]$$

$$\hat{P}_{12} \Psi_{\pm} = \pm \Psi_{\pm}$$

- Ψ_{\pm} are also energy eigenstates of \hat{H} , with eigenvalue $E_1 + E_2$.
Which should we choose?

5) Fermions and bosons

- Depending on their spin, systems of identical particles are either symmetric under

particle exchange (bosons) or 7

● antisymmetric (fermions) :
Spin-Statistics theorem (relativity + QM)

Type of particle	intrinsic spin	Symmetry under \hat{P}_{12}
boson	integer	+
● fermion	half-odd integer	-

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

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

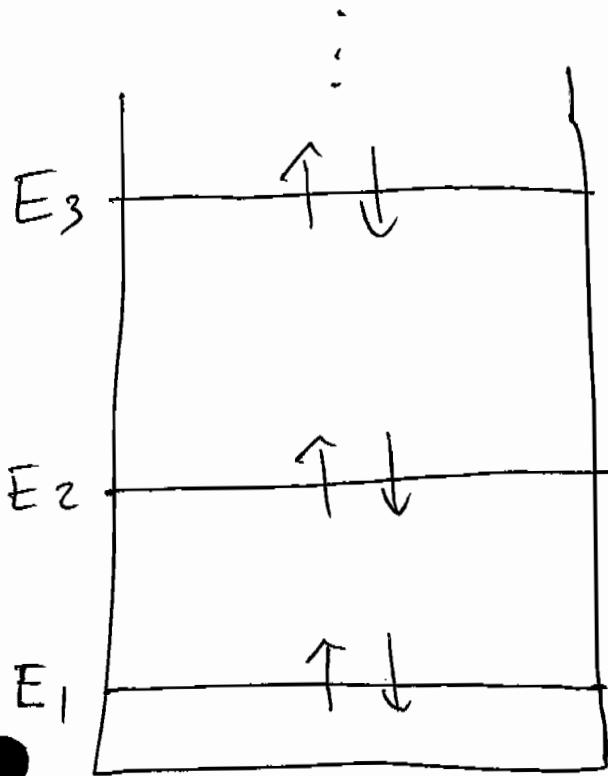
Proof Suppose each occupied some state, with wavefunction $\psi(\vec{r})$.

Then

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

\Rightarrow not allowed state (unnormalizable)

Example Electrons in a 1D box.



7) Periodic table of the Elements

mean-field picture of atoms.

H ¹ 1s	He ² 1s ²
Li ³ 2s	Be ⁴ 2s ²
Na ¹¹ 3s	Mg ¹² 3s ²
K ¹⁹ 4s	Ca ²⁰ 4s ²
Rb ³⁷ 5s	Sr ³⁸ 5s ²
Ce ⁵⁵ 6s	Ba ⁵⁶ 6s ²
Fr ⁸⁷ 7s	Ra ⁸⁸ 7s ²
	B ⁵ 2s ² 2p
	C ⁶ 2s ² 2p ²
	N ⁷ 2s ² 2p ³
	O ⁸ 2s ² 2p ⁴
	F ⁹ 2s ² 2p ⁵
	Ne ¹⁰ 2s ² 2p ⁶
	Al ¹³ 3s ² 3p
	Si ¹⁴ 3s ² 3p ²
	P ¹⁵ 3s ² 3p ³
	S ¹⁶ 3s ² 3p ⁴
	Cl ¹⁷ 3s ² 3p ⁵
	Ar ¹⁸ 3s ² 3p ⁶
	Ga ³¹ 4s ² 4p
	Ge ³² 4s ² 4p ²
	As ³³ 4s ² 4p ³
	Se ³⁴ 4s ² 4p ⁴
	Br ³⁵ 4s ² 4p ⁵
	Kr ³⁶ 4s ² 4p ⁶
	In ⁴⁹ 5s ² 5p
	Sn ⁵⁰ 5s ² 5p ²
	Sb ⁵¹ 5s ² 5p ³
	Te ⁵² 5s ² 5p ⁴
	Xe ⁵⁴ 5s ² 5p ⁶
	Tl ⁸¹ 6s ² 6p
	Pb ⁸² 6s ² 6p ²
	Bi ⁸³ 6s ² 6p ³
	Po ⁸⁴ 6s ² 6p ⁴
	At ⁸⁵ 6s ² 6p ⁵
	Rn ⁸⁶ 6s ² 6p ⁶

Periodic Table, with the Outer Electron Configurations of Neutral Atoms in Their Ground States

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 \hbar ; the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.

Ce ⁵⁸ 4f ²	Pr ⁵⁹ 4f ³	Nd ⁶⁰ 4f ⁴	Pm ⁶¹ 4f ⁵	Sm ⁶² 4f ⁶	Eu ⁶³ 4f ⁷	Gd ⁶⁴ 4f ⁷ 5d	Tb ⁶⁵ 4f ⁹ 5d	Dy ⁶⁶ 4f ¹⁰	Ho ⁶⁷ 4f ¹¹	Er ⁶⁸ 4f ¹²	Tm ⁶⁹ 4f ¹³	Yb ⁷⁰ 4f ¹⁴	Lu ⁷¹ 4f ¹⁴ 5d
Th ⁹⁰ 6d ² 7s ²	Pa ⁹¹ 5f ² 6d	U ⁹² 5f ³ 6d	Np ⁹³ 5f ⁵ 7s ²	Pu ⁹⁴ 5f ⁶ 7s ²	Am ⁹⁵ 5f ⁷ 7s ²	Cm ⁹⁶ 5f ⁷ 6d 7s ²	Bk ⁹⁷ 7s ²	Cf ⁹⁸ 7s ²	Es ⁹⁹ 7s ²	Fm ¹⁰⁰ 7s ²	Md ¹⁰¹ 7s ²	No ¹⁰² 7s ²	Lr ¹⁰³ 7s ²