2. Identical Particles

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AQM

Lorenzo

Tosi

As first extension of QM 1, we will deal with **MANY PARTICLE SYSTEMS** and see how this can help us to understand **Atoms with $Z > 1$**

$\Rightarrow$ we will focus on Helium, $Z = 2$, and then generalize to the whole **PERIODIC TABLE** in the exercise sessions.

The delicate issue that differentiates QM from CM is the treatment of <u>**IDENTICAL PARTICLES**</u>

From 1 to N particles, QM formalism is obvious to generalize

$|\psi(1, \dots, N)\rangle$ state vector

$$\langle x_1 \dots x_N | \psi(1, \dots, N)\rangle = \psi(x_1, \dots, x_N)$$

$$i\hbar \frac{\partial \psi(x_1 \dots, x_N)}{\partial t} = H\, \psi(x_1, \dots, x_n)$$

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(x_1, \dots, x_N)$$

$$= -\hbar^2 \sum_{i=1}^{N} \frac{1}{2m_i} \frac{\partial}{\partial x_i^2} + V(x_1, \dots, x_N)$$

↑ in coordinate space

If particles are different, nothing special happens

INSTEAD:

There is overwhelming experimental evidence that, if particles are IDENTICAL, then they must be INDISTINGUISHABLE

- Atoms & molecular spectra
- Ideal gases [GIBBS PARADOX]
- Photons in LASERS
- Elementary particles in collider experiments

...

We will see some elementary examples here

We start considering system that contains

TWO IDENTICAL PARTICLES [NO SPIN !]

$\psi(x_1, x_2)$ wave function, amplitude to find

$\parallel$

$\psi(1, 2)$ first particle at x_1, second at x_2

What is $\psi(2, 1)$ $\Rightarrow$ amplitude to find first

at x_2, second at x_1

If particle are identical & indistinguishable

they must represent SAME PHYSICS

$\Rightarrow$ still $\psi(1,2) \neq \psi(2, 1)$

but $|\psi(1,2)|^2 = |\psi(2,1)|^2$

$\Rightarrow \psi(1,2) = e^{i\phi}\, \psi(2, 1)$!

this equation must be true $\forall\ x_1, x_2$, so ϕ is independent of x_1, x_2 !

$\Rightarrow$ if we swap arguments we get $e^{i\phi}$, whatever the arguments

$$\psi(1,2) = e^{i\phi}\,\psi(2,1) \underset{\substack{\uparrow \\ \text{swapping again}}}{=} e^{2i\phi}\,\psi(1,2)$$

$$\Rightarrow e^{2i\phi} = 1 \Rightarrow \phi = n\pi \quad n \in \mathbb{Z}$$

wave function must be either

- symmetric if n EVEN
- antisymmetric if n ODD

Now let's add extra degree of freedom

$\Rightarrow$ SPIN

same thing but now $\psi_{\sigma_1 \sigma_2}(1,2)$

SPIN PARTICLE @ 1 SPIN PARTICLE @ 2

Again $\psi_{\sigma_2 \sigma_1}(2,1) = e^{i\phi}\, \psi_{\sigma_1 \sigma_2}(1,2)$

$$\Rightarrow \quad \psi_{\sigma_1 \sigma_2}(1,2) = e^{2i\phi}\, \psi_{\sigma_1 \sigma_2}(1,2)$$

$$\phi = n\pi \qquad n \in \mathbb{Z}$$

Now it is again matter of EXPERIMENTAL EVIDENCE

that n ODD for FERMIONS spin $= \frac{1}{2}, \frac{3}{2}, \ldots$

n EVEN for BOSONS spin $= 0, 1, 2, \ldots$

Notice that while in QM this is experimental evidence, in RELATIVISTIC QUANTUM FIELD THEORY this can be PROVED !

Now consider system of 2 particles with Hamiltonian $H(1,2)$

Hamiltonian for indistinguishable particles must be also symmetric

$$H(1,2) = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V(1,2)$$

of course same mass!

$$H(1,2) = H(2,1)$$

these might include spin

- $H(1,2)\,\psi_{\sigma_1\sigma_2}(1,2) = E\,\psi_{\sigma_1\sigma_2}(1,2) \qquad (1)$

- $H(2,1)\,\psi_{\sigma_2\sigma_1}(2,1) = E\,\psi_{\sigma_2\sigma_1}(2,1) \qquad (2)$

introduce EXCHANGE OPERATOR P_{12}

$$P_{12}\,\psi_{\sigma_1\sigma_2}(1,2) = \psi_{\sigma_2\sigma_1}(2,1)$$

then eq (2) becomes

$$H(1,2) \quad P_{12} \, \psi_{\sigma_1\sigma_2}(1,2) = E \, P_{12} \, \psi_{\sigma_1\sigma_2}(1,2)$$

$$\{ \overset{\parallel}{H(2,1)} \}$$

$$= P_{12} \, H(1,2) \, \psi_{\sigma_1\sigma_2}(1,2)$$

$$\Rightarrow \left[H(1,2), P_{12} \right] = 0$$

P_{12} is a constant of the motion

moreover $[P_{12}]^2 = 1$

so $P_{12} = \pm 1$ eigenvalues; Eigenstates are

$$\begin{cases} \psi^{(S)}(1,2) = \dfrac{1}{N_{2S}} \left[\psi(1,2) + \psi(2,1) \right] \\[2ex] \psi^{(A)}(1,2) = \dfrac{1}{N_{2A}} \left[\psi(1,2) - \psi(2,1) \right] \end{cases}$$

ALL LABELS INCLUDING SPIN σ_i

Since P_{12} is const of the motion, a state that is symmetric at some time, will always remain symmetric, and similarly for an antisymmetric one!

it's easy to work out generalization to more particles, FOR 3 PARTICLES:

$$\psi^{(A)}(1,2,3) = \frac{1}{N_{3A}}\Big[\psi(1,2,3) - \psi(2,1,3) + \psi(2,3,1) - \psi(3,2,1) + \psi(3,1,2) - \psi(1,3,2)\Big]$$

Antisymm w.r.t. swapping ANY PAIR of indices

While IN PRINCIPLE mixed statistics could exist, they are EXPERIMENTALLY EXCLUDED in QM

this is part of the

<u>PAULI EXCLUSION PRINCIPLE</u>

PAULI EXCLUSION PRINCIPLE

- Systems consisting of N identical particles of half-odd-integer spin are described by antisymmetric wave functions and called FERMIONS
- Systems consisting of N identical particles of integer spin are described by symmetric wave functions and called BOSONS
- Mixed statistics are not allowed !

First clear consequence $\Rightarrow$ there is ZERO PROBABILITY of finding 2 FERMIONS in same state

$$\psi_{\sigma_1\sigma_2}(1,2) = -\psi_{\sigma_2\sigma_1}(2,1) \qquad \text{if} \quad \begin{array}{l} 1=2 \\ \sigma_1=\sigma_2=\sigma \end{array}$$

$$\Rightarrow \quad \psi_{\sigma\sigma}(1,1) = 0 \; !$$

since $\psi_{\sigma\sigma}(x_1, x_2)$ must be a continuous function

↑ SAME SPIN

it must be zero in some neighbourhood of

$x_1 = x_2$! $\Rightarrow$ Fermions with same spin avoid each other !

Condition on wave functions ψ can be rephrased for states.

Let $\{|n\rangle\}$ be complete set of states for SINGLE FERMION

$|\psi\rangle$ state of PAIR of FERMIONS can be expanded

$$|\psi\rangle = \sum_{n,m} a_{n,m} |n\rangle|m\rangle$$

$$\langle x_1\, x_2 ; \sigma_1\, \sigma_2 | \psi\rangle = \psi_{\sigma_1\sigma_2}(1, 2) \text{ above}$$

$$\psi_{\sigma_1\sigma_2}(1,2) = \sum_{n,m} a_{n,m} \langle x_1,\sigma_1|n\rangle\langle x_2,\sigma_2|m\rangle$$

now swap $x_1,\sigma_1 \Leftrightarrow x_2,\sigma_2$ and add two expr

$$0 = \sum_{n,m}\Big[a_{n,m}\langle x_1\sigma_1|n\rangle\langle x_2,\sigma_2|m\rangle$$

$$+ \underset{\substack{\uparrow \\ \text{rename } n,m}}{a_{n,m}} \langle x_2\sigma_2|n\rangle\langle x_1\sigma_1|m\rangle\Big]$$

$$= \sum_{n,m} \langle x_1\sigma_1|n\rangle\langle x_2,\sigma_2|m\rangle\left[a_{n,m} + a_{m,n}\right]$$

$$= \langle x_1 x_2; \sigma_1\sigma_2| \underbrace{\sum_{n,m} |n\rangle|m\rangle\left(a_{n,m} + a_{m,n}\right)}_{=0}$$

since $|n\rangle$ are linearly independent

$$\Rightarrow \boxed{a_{n,m} + a_{m,n} = 0}$$

$a_{n,m} = -a_{m,n}$

or $\boxed{a_{n,n} = 0}$

$$\psi = \sum_{n,m} a_{n,m} |n\rangle |m\rangle$$

zero probability to find two fermions in same state $|n\rangle$

THE TWO-PARTICLE PROBLEM

Consider a system of two particles in $D=3$

$$H = \frac{\vec{P}_1^2}{2m_1} + \frac{\vec{P}_2^2}{2m_2} + V(\vec{r}_1, \vec{r}_2) \; ; \quad \psi(1,2) = \underset{\text{spins}}{\chi_{12}} \; \underset{\text{coordinates}}{\psi(r_1, r_2)}$$

Focus on $\psi(r_1, r_2)$ for now :

Define $\vec{P} = \vec{p}_1 + \vec{p}_2 \qquad \vec{r} = \vec{r}_1 - \vec{r}_2$

$$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2} \qquad \text{C.o.M coordinate}$$

$[P_i, R_j] = -i\hbar\, \delta_{ij}$ $\quad \vec{R}$ conjugate to total mom.

momentum conjugate to $\vec{r}$ is $\vec{p} = \dfrac{m_2 \vec{p}_1 - m_1 \vec{p}_2}{m_1+m_2}$

$$\begin{cases} \vec{p}_1 = \vec{p} + \dfrac{m_1}{m_1+m_2} \vec{P} \\ \vec{p}_2 = -\vec{p} + \dfrac{m_2}{m_1+m_2} \vec{P} \end{cases} \Rightarrow \frac{\vec{p}_1^{\,2}}{2m_1} + \frac{\vec{p}_2^{\,2}}{2m_2} = \frac{\vec{P}^2}{2M} + \frac{\vec{p}^{\,2}}{2\mu}$$

$$\begin{cases} M = m_1 + m_2 \\ \mu = \dfrac{m_1 m_2}{m_1+m_2} \end{cases}$$

so

$$H = \frac{\vec{P}^2}{2M} + \frac{\vec{p}^{\,2}}{2\mu} + V(\vec{r}, \vec{R}) \; ; \; \underline{\psi(\vec{r}, \vec{R}) \text{ too}}$$

if H unchanged under a translation, i.e.

$\vec{r}_i \to \vec{r}_i + \vec{X} \Rightarrow V(\vec{r})$

↑ only on relative coordinates

$\Rightarrow$ TOTAL MOMENTUM $\vec{P}$ is CONSERVED !

now if particles are identical $m_1 = m_2$

$$\vec{p} = \frac{\vec{p}_1 - \vec{p}_2}{2} \qquad \mu = \frac{m}{2} \ ; \ M = 2m$$

if we interchange $1 \Leftrightarrow 2$ $\quad V(\vec{r}) = V(-\vec{r})$

but particles are identical, system must fulfil the same equation $\Rightarrow V(\vec{r}) \equiv V(r)$

modulus only

Schrödinger Eq becomes

$$\left[\frac{\vec{p}_{op}^{\,2}}{2\mu} + \frac{\vec{P}_{op}^{\,2}}{2M} + V(r) \right] \psi(\vec{r}, \vec{R}) = E \, \psi(\vec{r}, \vec{R})$$

indep of $\vec{R}$

$$\psi(\vec{r}, \vec{R}) = e^{i \vec{P} \cdot \vec{R} / \hbar} \, u(\vec{r})$$

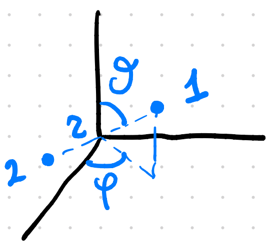
with

$$\left[\frac{\vec{p}_{op}^{\,2}}{2\mu} + V(r)\right] u(\vec{r}) = \left(E - \frac{P^2}{2M}\right) u(\vec{r})$$

central potential

$$u(\vec{r}) = R_{n,\ell}(r)\, Y_{\ell,m}(\vartheta,\varphi)$$

spherical harmonics



swapping $1 \Leftrightarrow 2$ means $\begin{cases} r \to r \\ \vartheta \to \pi - \vartheta \\ \varphi \to \varphi + \pi \end{cases}$

$$Y_{\ell,m}(\vartheta,\varphi) \to (-1)^{\ell}\, Y_{\ell,m}(\vartheta,\varphi)$$ Like PARITY!

Now let's look at the spin part

$$\psi(1,2) = R_{nl}(r)\, Y_{l,m}(\theta,\varphi)\, \underbrace{\chi_{12}}_{\text{spin part}}$$

1. two spins in singlet state

$$\chi_{12}^{[S]} = \frac{1}{\sqrt{2}}\left(\chi_+^{(1)}\chi_-^{(2)} - \chi_-^{(1)}\chi_+^{(2)}\right)$$

Antisymmetric under $1 \Leftrightarrow 2$

2. two spins in triplet state

$$\chi_{12}^{[T]} = \begin{cases} \chi_+^{(1)}\chi_+^{(2)} & +1 \\ \frac{1}{\sqrt{2}}\left[\chi_+^{(1)}\chi_-^{(2)} + \chi_-^{(1)}\chi_+^{(2)}\right] & 0 \\ \chi_-^{(1)}\chi_-^{(2)} & -1 \end{cases}$$

symmetric under exchange $1 \Leftrightarrow 2$

Pauli Exclusion Principle applies to TOTAL WAVE FUNCTION!

$\Rightarrow$ if two particles are FERMIONS (Electrons)

$\psi(1,2)$ must be antisymmetric

$\Rightarrow$ Spin singlet states must have $l = 0, 2, 4, \ldots$

Spin triplet states must have $l = 1, 3, 5, \ldots$

DO WE ALWAYS NEED TO ANTISYMMETRIZE?

Do we need to care if we consider two electrons very far away? Do we need to antisymmetrize every electron in the Universe?

take two "free" fermions $\psi_a(x_1)$ $\psi_b(x_2)$

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

OR

$$= \frac{1}{N}\left[\psi_a(x_1)\,\psi_b(x_2) - \psi_a(x_2)\,\psi_b(x_1)\right]$$

correlated (antisymmetric)

all labels $\{E, \sigma, \dots\}$

by squaring you can see that

$$N^2 = 2\left(1 - \left|\int dx\, \psi_a^*(x)\,\psi_b(x)\right|^2\right)$$

where we used normalization of $\psi_a(x_1)$ & $\psi_b(x_2)$

QUESTION IS

is there a difference if we try to compute the probability that particle with labels "a" is in some region R?

(does this depend on whether I antisymmetrized?)

1. uncorrelated

$$P(R) = \int_R dx \underbrace{\int dy}_{\text{"EVERYWHERE"}} |\psi_a(x)|^2 |\psi_b(y)|^2$$

$$= \int_R dx\, |\psi_a(x)|^2$$

integrated everywhere normalized to 1

2. correlated 4 terms

$$P(R) = \frac{1}{N^2} \int_R dx\, |\psi_a(x)|^2 \overbrace{\underbrace{\int}_{\text{"EVERYWHERE"}} dy\, |\psi_b(y)|^2}^{1}$$

$$+ \frac{1}{N^2} \int_R dy\, |\psi_a(y)|^2 \underbrace{\underbrace{\int}_{\text{"EVERYWHERE"}} dx\, |\psi_b(x)|^2}_{1}$$

$$- \frac{1}{N^2} \int_R dx \int_R dy \Big[\psi_a^*(x)\psi_b(x)\psi_b^*(y)\psi_a(y)$$

$$+ \psi_b^*(x)\psi_a(x)\psi_a^*(y)\psi_b(y) \Big]$$

$$P(R) = \frac{2}{N^2} \int_R dx\, |\psi_a(x)|^2$$

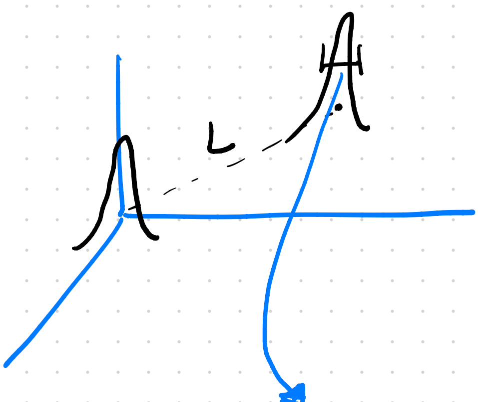
$$- \frac{2}{N^2} \int_R dx \int_R dy\; \underbrace{\psi_a^*(x)\, \psi_b(x)\, \psi_b^*(y)\, \psi_a(y)}$$

$\neq 0$ only if two wave functions overlap over R

Say now $\psi_a(x) \sim C\, e^{-\beta^2 x^2}$

$\psi_b(x) \sim C\, e^{-\beta^2 (x-L)^2}$

$D = 1$ for simplicity



two electrons gaussian centred at distance "L"

$\frac{1}{\beta} \sim$ variance, "width" overlap integral becomes

$$\left| \int_R dx \left[\psi_a^*(x)\, \psi_b(x) \right] \right|^2$$

$$\sim \int_R dx\, e^{-\beta^2 (x^2 + (x-L)^2)} \quad \propto \quad e^{-\frac{\beta^2 L^2}{2}}$$

Also implies

$N \simeq 2 +$ small corrections $\Leftarrow$ decreases exponentially with distance !

when $L \gg \frac{1}{\beta}$ it can be easily ignored !

result is the same what

PAULI PRINCIPLE must be taken into account for electrons bound in same ATOM or MOLECULE

$\Rightarrow$ often it can be neglected even in LATTICES when $L \sim$ several Angstroms !