3.1.1 The Space of Wave Function

A <u>wave function</u> for N spinless particles

$$\psi : \mathbb{R}^{3N} \to \mathbb{C} \quad \text{in } L^2(\mathbb{R}^{3N}) \cong \bigotimes^N L^2(\mathbb{R}^3)$$

with $$\|\psi\|_2^2 = \int_{\mathbb{R}^{3N}} |\psi(x_1, \dots, x_N)|^2 \, dx_1 \cdots dx_N = 1$$

(unit norm)

spatial coordinate

$$x_i = (x_i^1, x_i^2, x_i^3) \in \mathbb{R}^3 \quad \text{for } i = 1, \dots, N$$

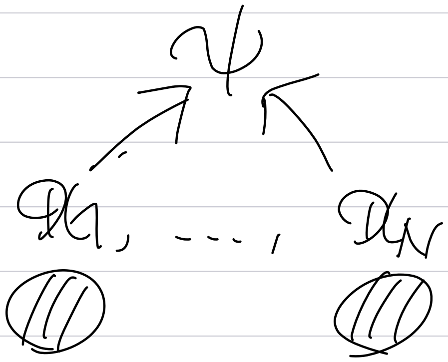
ith particle

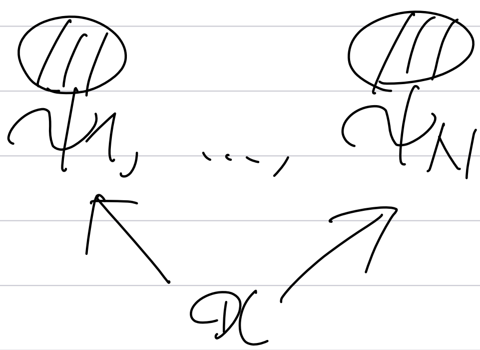
$$\underline{X} := (x_1, \dots, x_N) \in \mathbb{R}^3 \times \cdots \times \mathbb{R}^3 = \mathbb{R}^{3N}$$

$$d\underline{X} := dx_1 \cdots dx_N$$

@ one function of N variables

cf. N functions of one variable





determinantal functions

→ Hartree and <u>Hartree-Fock theories</u>

$|\psi(\underline{X})|^2 = |\psi(x_1, \ldots, x_N)|^2$

probability density for finding particle 1 at x_1, $\ldots$, particle N at x_N.

Single or one-particle density (total electron density)

$$\rho_\psi(x) = \sum_{i=1}^{N} \rho_\psi^i(x), \qquad x \in \mathbb{R}^3$$

where

$$\rho_\psi^i(x) = \int_{\mathbb{R}^{3(N-1)}} |\psi(x_1, \ldots, x_{i-1}, x, x_{i+1}, \ldots, x_N)|^2 \, dx_1 \cdots \widehat{dx_i} \cdots dx_N$$

probability density of finding particle i at x

$\uparrow$ omitted

$$\int_{\mathbb{R}^3} \rho_\psi^i(x)\, dx = \int_{\mathbb{R}^3}\int_{\mathbb{R}^{3(N-1)}} |\psi(\ldots, x, \ldots)|^2 \, dx_1 \cdots \widehat{dx_i} \cdots dx_N \, dx_i$$

$$= \int_{\mathbb{R}^{3N}} |\psi(\underline{X})|^2 d\underline{X} = 1.$$

$$\int_{\mathbb{R}^3} \rho_\psi(x)\, dx = \sum_{i=1}^{N} \int_{\mathbb{R}^3} \rho_\psi^i(x)\, dx = N.$$

Charge density

$e_1 \quad \cdots \quad e_N$

$$Q_\psi(x) = \sum_{i=1}^{N} Q_\psi^i(x)$$

where $Q_\psi^i(x) = e_i \rho_\psi^i(x)$

electric charge of ith particle

Kinetic energy

- non-relativistic QM

$$\psi \in H^1(\mathbb{R}^{3N})$$

$$\Leftrightarrow \psi \in L^2(\mathbb{R}^{3N}) \text{ and } \nabla\psi = (\nabla_{x_1}\psi, \cdots, \nabla_{x_N}\psi)$$

$$\nabla_{x_i}\psi \in L^2(\mathbb{R}^{3N})$$

in the sense of distribution

$$T_\psi = \sum_{i=1}^{N} T_\psi^i$$

where $T_\psi^i = \frac{1}{2m_i}\int_{\mathbb{R}^{3N}} |(\nabla_{x_i}\psi)(X)|^2 \, dX.$

m_i ← mass of ith particle

- relativistic QM

$$\psi \in H^{1/2}(\mathbb{R}^{3N})$$

$$T_\psi^i = \int_{\mathbb{R}^{3N}} \left(\sqrt{(2\pi|k_i|)^2 + m_i^2} - m_i\right) |\hat{\psi}(\underline{\mathbb{K}})|^2 \, d\underline{\mathbb{K}}$$

where $\underline{\mathbb{K}} = (k_1, \ldots, k_N) \in \mathbb{R}^{3N}$

$$\hat{\psi}(\underline{\mathbb{K}}) = \int_{\mathbb{R}^{3N}} \psi(X) \exp(-2\pi i \underbrace{X \cdot \mathbb{K}}_{= \sum_{j=1}^{N} x_j \cdot k_j}) \, d\underline{X}$$

Fourier transform of ψ

Potential energy

$$V_\psi = \int_{\mathbb{R}^{3N}} V(\underline{X}) |\psi(\underline{X})|^2 \, d\underline{X}$$

(See also V_c on p-13)

where $V: \mathbb{R}^{3N} \to \mathbb{R}$ total potential energy

3.1.2 Spin

spin, isospin, flavor, etc. (internal degree of freedom)

$\sigma \in \{1, 2, \dots, q\}$ q spin state

@ electrons : $\sigma = 1$ or 2 $\left(\leftarrow \sigma = +\frac{1}{2}\hbar \text{ or } -\frac{1}{2}\hbar\right)$

$\{1, 2\}$

fermion to bosons $q = N$?

Bosons will be seen to correspond to $q = N$

Pauli principle

i^{th} particle has q_i spin state $\overbrace{\underset{q_1}{(\,)} \cdots \underset{q_N}{(\,)}}^{N \text{ particles}}$

$\psi(x_1, \sigma_1, \dots, x_N, \sigma_N) \in H^1(\mathbb{R}^{3N})$

$1 \le \sigma_i \le q_i$ for $i = 1, \dots, N$

$\downarrow$

$\mathbb{C}^Q$-valued function $Q := \prod_{i=1}^{N} q_i$

$$\psi \in H^1(\mathbb{R}^{3N}; \mathbb{C}^Q) \cong \bigotimes_{i=1}^{N} H^1(\mathbb{R}^3; \mathbb{C}^{q_i})$$

(isomorphic)

$$\begin{cases} \underline{\sigma} := (\sigma_1, \dots, \sigma_N) \longrightarrow \psi(\underline{X}, \underline{\sigma}) \\ \sum_{\underline{\sigma}} := \sum_{\sigma_1=1}^{q_1} \cdots \sum_{\sigma_N=1}^{q_N} \end{cases}$$

Another convenient notation

$$z_i = (x_i, \sigma_i) \text{ and } \underline{z} = (z_1, \dots, z_N)$$

$$\int f(z_i)\, dz_i := \sum_{\sigma_i=1}^{q_i} \int_{\mathbb{R}^3} f(x_i, \sigma_i)\, dx_i$$

$$\Rightarrow \quad \psi(\underline{z}) = \psi(z_1, \dots, z_N)$$

$$\|\psi\|_2^2 := \sum_{\underline{\sigma}} \int_{\mathbb{R}^{3N}} |\psi(\underline{X}, \underline{\sigma})|^2\, dX$$

$$= \int |\psi(\underline{z})|^2\, dz = 1.$$

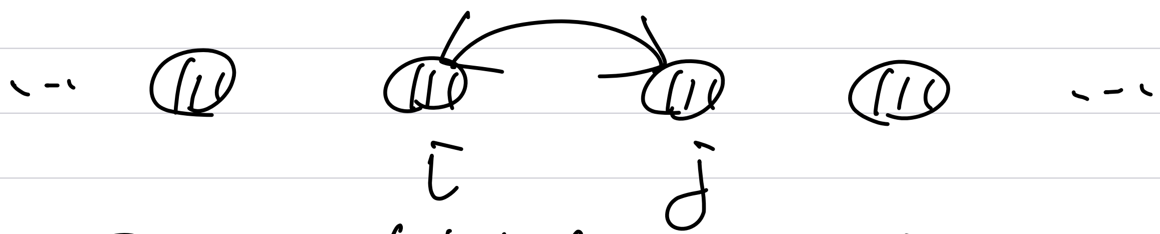
(normalization condition)

3.1.3 Bosons and Fermions
(The Pauli Exclusion Principle)

$z_j = (x_j, \sigma_j)$ space-spin variable of j^{th} particle

point $x_j \in \mathbb{R}^3$ and point $\sigma = \{1, \dots, \underline{q}\}$
kind of particle

Exchange of any pair of particle



@ Bosons (total symmetry)
eg. $\pi^+, \cdots \longrightarrow$ Bose-Einstein

$$\psi(\dots, z_i, \dots, z_j, \dots) = \psi(\dots, z_j, \dots, z_i, \dots)$$

@ Fermions (total antisymmetry)
eg. $e^-, \cdots \longrightarrow$ Fermi-Dirac

$$\psi(\dots, z_i, \dots, z_j, \dots) = -\psi(\dots, z_j, \dots, z_i, \dots)$$

$\longrightarrow$ Pauli exclusion principle

$$\psi = 0 \text{ if } z_i = z_j$$

(same quantum state)

Example (symmetric function)

$$\psi(\underline{z}) = \prod_{i=1}^{N} u(z_i) = u(z_1)\cdots\boxed{u(z_i)}\cdots\boxed{u(z_j)}\cdots u(z_N)$$

where $u \in L^2(\mathbb{R}^3; \mathbb{C}^q)$

simple!

Example (antisymmetric function)

Slater determinant

$$\psi(\underline{z}) = (N!)^{-1/2} \det\{u_i(z_j)\}_{i,j=1}^{N}$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(z_1) & \cdots & u_1(z_N) \\ \vdots & \ddots & \vdots \\ u_N(z_1) & \cdots & u_N(z_N) \end{vmatrix}$$

$$= \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \underbrace{\boxed{\varepsilon_\pi}}_{\mathrm{sgn}(\pi)} \prod_{i=1}^{N} u_i(z_{\pi(i)})$$

where $u_i \in L^2(\mathbb{R}^3; \mathbb{C}^q)$ for $i = 1, \ldots, N$

with $(u_j, u_k) = \int \overline{u_j(z)}\, u_k(z)\, dz = \delta_{jk}$

Then ψ is (1) antisymmetric and (2) normalized

$$\varepsilon_\pi = \mathrm{sgn}(\pi) = \begin{cases} +1 & \pi \text{ is even perm.} \\ -1 & \text{odd} \end{cases}$$

$$\delta_{jk} = \begin{cases} 1 & j = k \\ 0 & \text{otherwise} \end{cases}$$

Proof

(1) antisymmetric

$$\psi(z_1, \ldots, z_K, \ldots, z_J, \ldots, z_N)$$

$$= \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \mathrm{sgn}\begin{pmatrix} 1 & \cdots & j & \cdots & k & \cdots & N \\ \pi(1) & \cdots & K & \cdots & J & \cdots & \pi(N) \end{pmatrix}$$

$$\times u_1(z_{\pi(1)}) \cdots u_j(z_K) \cdots u_k(z_J) \cdots u_N(z_{\pi(N)})$$

$\pi(j) = K, \quad \pi(k) = J$

$$= \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \mathrm{sgn}\left[(J\ K) \begin{pmatrix} \cdots j \cdots k \\ J \quad K \end{pmatrix} \right] \cdots u_j(z_J) \cdots u_k(z_K)$$

$$= -\frac{1}{\sqrt{N!}} \sum_{\pi' \in S_N} \mathrm{sgn}\begin{pmatrix} \cdots j \cdots k \cdots \\ \cdots J \cdots K \cdots \end{pmatrix} \cdots u_j(z_{\pi'(j)}) \cdots u_k(z_{\pi'(k)}) \cdots$$

$\pi' = (J\ K)\pi$

$\pi'(j) = J, \quad \pi'(k) = K$

$$= -\psi(z_1, \ldots, z_J, \ldots z_K, \ldots, z_N) \qquad //$$

(2) normalized

$$\psi(\underline{z}) = \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \varepsilon_\pi \prod_{j=1}^{N} u_j(z_{\pi(j)})$$

$$\|\psi\|_2^2 = \int \overline{\psi(\underline{z})}\, \psi(\underline{z})\, d\underline{z}$$

$$= \frac{1}{N!} \sum_{\pi \in S_N} \sum_{\pi' \in S_N} \varepsilon_\pi \varepsilon_{\pi'} \underbrace{\int \overline{\prod_{j=1}^{N} u_j(z_{\pi(j)})} \prod_{k=1}^{N} u_k(z_{\pi'(k)})\, d\underline{z}}_{= I}$$

$$I = \int \overline{\prod_{J=1}^{N} u_{\pi^{-1}(J)}(z_J)} \prod_{K=1}^{N} u_{\pi'^{-1}(K)}(z_K)\, d\underline{z}$$

$$= \int \prod_{J=1}^{N} \overline{u_{\pi^{-1}(J)}(z_J)}\, u_{\pi'^{-1}(J)}(z_J)\, d\underline{z}$$

$$= \prod_{J=1}^{N} \int \overline{u_{\pi^{-1}(J)}(z_J)}\, u_{\pi'^{-1}(J)}(z_J)\, dz_J$$

$$= \prod_{J=1}^{N} \left(u_{\pi^{-1}(J)},\ u_{\pi'^{-1}(J)} \right)$$

Here, $\pi^{-1}(J) = \pi'^{-1}(J)$ for $J = 1, \dots, N$

$$\pi^{-1} = \pi'^{-1} \iff \pi = \pi'$$

$$\therefore \|\psi\|_2^2 = \frac{1}{N!} \sum_{\substack{\pi \in S_N \\ (\pi' = \pi)}} \varepsilon_\pi^2 \prod_{j=1}^{N} (u_j, u_j) = 1 \quad // \quad (\because |S_N| = N!)$$

antisymmetric tensor product

$\bigwedge^N L^2(\mathbb{R}^3; \mathbb{C}^q) \subseteq L^2(\mathbb{R}^{3N}; \mathbb{C}^{qN})$

subspace of all antisymmetric functions

@ $\{u_i(z)\}_{i=1}^{\infty}$ forms a basis for $L^2(\mathbb{R}^3; \mathbb{C}^q)$

$\Rightarrow$ $\forall N$ possible

$\psi(\underline{z})$ forms an orthonormal basis for $\bigwedge^N L^2(\mathbb{R}^3; \mathbb{C}^q)$

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bosons: odd number q of spin state ($\frac{q-1}{2}$ is an integer)

fermions: even number q of spin state ($\frac{q-1}{2}$ is $1/2$, $3/2$, etc.)

spinless fermion (academic $q=1$ fermion)

$q=2$ fermion with $\psi = 0$ unless $\forall \sigma_j = 1$.

$q=1$ boson "we shall only consider"

$\downarrow$

generalization!

3.1.3.1 The case $q \geq N$

H : not depend on spin

$\downarrow$

$H \otimes I$ in $L^2(\mathbb{R}^{3N}; \mathbb{C}^{q^N}) \simeq L^2(\mathbb{R}^{3N}) \otimes \mathbb{C}^{q^N}$

I : identity in $\mathbb{C}^{q^N}$

$q \geq N$ fermionic system

$\Rightarrow$ " $q=1$ without any symmetry restrictions on the wave functions."

Claim

$^{\forall}\phi(x_1, \dots, x_N)$ taken

$$\psi(z_1, \dots, z_N) = \frac{1}{\sqrt{N!}} \mathcal{A}[\phi(x_1, \dots, x_N) f_1(\sigma_1) \cdots f_N(\sigma_N)]$$

where $f_j(\sigma) = \begin{cases} 1 & \sigma = i \\ 0 & \text{otherwise} \end{cases}$

antisymmetrizer

$$\mathcal{A}[\chi(z_1, \dots, z_N)] = \sum_{\pi \in S_N} \varepsilon_\pi \chi(z_{\pi(1)}, \dots, z_{\pi(N)})$$

(1) ψ is antisymmetric in $L^2(\mathbb{R}^{3N}; \mathbb{C}^{q^N})$

(2) $\|\psi\|_2 = \|\phi\|_2$

Proof.

(1) $z_i = (x_i, \sigma_i)$ $\quad 1 \le \sigma_i \le q = N$

$$\psi(\cdots, z_k, \cdots, z_j, \cdots)$$

$$= \frac{1}{\sqrt{N!}} \mathcal{A}[\phi(\cdots, x_k, \cdots, x_j, \cdots) \cdots f_j(\sigma_k) \cdots f_k(\sigma_j) \cdots$$

$$= \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \varepsilon_\pi \phi(\cdots x_{\pi(k)} \cdots x_{\pi(j)} \cdots) \cdots f_j(\sigma_{\pi(k)}) \cdots f_k(\sigma_{\pi(j)}) \cdots$$

$\pi \to \pi'$ $\left(\begin{array}{l} \pi' = (j\ k)\pi \\ \pi'(j) = \pi(k) \\ \pi'(k) = \pi(j) \\ \varepsilon_{\pi'} = -\varepsilon_\pi \end{array} \right.$

$$= \frac{1}{\sqrt{N!}} \sum_{\pi' \in S_N} \varepsilon_{\pi'} \phi(\cdots x_{\pi'(k)} \cdots x_{\pi'(j)} \cdots) \cdots f_j(\sigma_{\pi'(k)}) \cdots f_k(\sigma_{\pi'(j)}) \cdots$$

$$= -\frac{1}{\sqrt{N!}} \sum_{\pi' \in S_N} (-\varepsilon_\pi) \phi(\cdots x_{\pi(j)} \cdots x_{\pi(k)} \cdots) \cdots f_j(\sigma_{\pi(j)}) \cdots f_k(\sigma_{\pi(k)}) \cdots$$

$\pi' \to \pi$

$$= -\psi(\cdots, z_j, \cdots, z_k, \cdots) \quad //$$

Revised proof for (1)

Lemma

Antisymmetrizer is total antisymmetric,

i.e.

$$\mathcal{A}[\mathcal{X}(\cdots, z_k, \cdots, z_j, \cdots)] = -\mathcal{A}[\mathcal{X}(\cdots, z_j, \cdots, z_k, \cdots)]$$

$\because$) $\mathcal{A}[\mathcal{X}(\cdots z_k \cdots z_j \cdots)]$

$$= \sum_{\pi \in S_N} \varepsilon_{\pi'} \mathcal{X}(z_{\pi'(1)}, \ldots, z_{\pi'(k)}, \ldots, z_{\pi'(j)}, \ldots, z_{\pi'(N)})$$

$\pi' = (j\ k)\pi$

$\pi'(j) = \pi(k)$ $\quad \pi'(i) = \pi(i)$

$\pi'(k) = \pi(j)$ $\quad i \neq j, i \neq k$

$\varepsilon_{\pi'} = -\varepsilon_\pi$

$$= \sum_{\pi \in S_N} (-\varepsilon_\pi) \mathcal{X}(z_{\pi(1)}, \ldots, z_{\pi(j)}, \ldots, z_{\pi(k)}, \ldots, z_{\pi(N)})$$

$$= -\mathcal{A}[\mathcal{X}(\cdots z_j \cdots z_k \cdots)] \ //$$

Using Lemma above with

$$\mathcal{X}(z_1, \ldots, z_N) = \phi(x_1, \ldots, x_N) f_1(\sigma_1) \cdots f_N(\sigma_N)$$

where $z_j = (x_j, \sigma_j)$ for $j = 1, \ldots, N$ //

(2) $\|\psi\|_2^2 = \int \overline{\psi(\underline{z})}\psi(\underline{z})\, d\underline{z}$

$\overline{\psi(\underline{z})}\psi(\underline{z})$

$$= \frac{1}{N!}\left\{\sum_{\pi\in S_N} \varepsilon_\pi \overline{\phi(\cdots x_{\pi(i)}\cdots)}\prod_j f_j(\sigma_{\pi(j)})\right\} \times \left\{\sum_{\pi'\in S_N} \varepsilon_{\pi'}\phi(\cdots x_{\pi'(i)}\cdots)\prod_k f_k(\sigma_{\pi'(k)})\right\}$$

$$= \frac{1}{N!}\sum_{\pi}\sum_{\pi'} \varepsilon_\pi\varepsilon_{\pi'}\overline{\phi(\cdots, x_{\pi(i)}\cdots)}\phi(\cdots x_{\pi'(i)}\cdots) \times \prod_j f_j(\sigma_{\pi(j)})\prod_k f_k(\sigma_{\pi'(k)})$$

$$\prod_j f_j(\sigma_{\pi(j)}) f_j(\sigma_{\pi'(j)}) = 1$$

if $j = \sigma_{\pi(j)}$ and $j = \sigma_{\pi'(j)}$

$\sigma_{\pi(j)} = \sigma_{\pi'(j)}$ for $\forall j = 1, \cdots, N$

$\Longleftrightarrow \pi = \pi'$

$$= \frac{1}{N!}\sum_{\substack{\pi\in S_N\\(\pi'=\pi)}} \varepsilon_\pi^2 |\phi(\cdots x_{\pi(i)}\cdots)|^2 \prod_j f_j(\sigma_{\pi(j)})^2$$

$$\therefore \|\psi\|_2^2 = \frac{1}{N!}\sum_\pi \int |\phi(\cdots x_{\pi(i)}\cdots)|^2 d\underline{X} \cdot \underbrace{\boxed{\prod_j f_j(\sigma_{\pi(j)})^2}}_{=1}$$

$$= \|\phi\|_2^2 \cdot \frac{1}{N!}\sum_\pi 1 = \|\phi\|_2^2 \quad //$$