3.1.1 The Space of Wave Function

A wave function for $N$ spinless particles

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

with

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

(unit norm)

$\mathbf{x}_i = (x_{i1}, x_{i2}, x_{i3}) \in \mathbb{R}^3$ for $i=1,\ldots,N$

$i$-th particle

$$\mathbf{x} := (x_1, \ldots, x_N) \in \mathbb{R}^3 \times \cdots \times \mathbb{R}^3 = \mathbb{R}^{3N}$$

$$d\mathbf{x} := dx_1 \cdots dx_N$$

@ one function of $N$ variables

cf. $N$ functions of one variable

determinantal functions

$\rightarrow$ Hartree and Hartree-Fock theories
\[ |\psi(x)|^2 = \prod_{i=1}^{N} |\psi(x_1, \ldots, x_N)|^2 \]

Probability density for finding particle 1 at \(x_1\), ..., particle \(N\) at \(x_N\).

Single or one-particle density (total electron density)

\[ \mathcal{Q}_\psi(x) = \prod_{i=1}^{N} \mathcal{Q}_{\psi_i}(x_i), \quad x \in \mathbb{R}^3 \]

where

\[ \mathcal{Q}_{\psi_i}(x_i) = \int_{\mathbb{R}^3(N-1)} |\psi(x_1, \ldots, x_{i-1}, x_i, x_{i+1}, \ldots, x_N)|^2 \]

Probability density of finding particle \(i\) at \(x_i\)

\[ \int_{\mathbb{R}^3} \mathcal{Q}_\psi(x) \, dx = \int_{\mathbb{R}^3} \prod_{i=1}^{N} |\psi(x_1, \ldots, x_N)|^2 \, dx = 1 \]

\[ \int_{\mathbb{R}^3} \mathcal{Q}_\psi(x) \, dx \, dx_1 \ldots \, dx_N \]

\[ = \int_{\mathbb{R}^3} |\psi(x)|^2 \, dx = 1 \]

\[ \int_{\mathbb{R}^3} \mathcal{Q}_\psi(x) \, dx = \prod_{i=1}^{N} \int_{\mathbb{R}^3} \mathcal{Q}_{\psi_i}(x_i) \, dx_i = N \]

Charge density

\[ \mathcal{Q}_\psi(x) = \prod_{i=1}^{N} \mathcal{Q}_{\psi_i}(x_i) \]

Electric charge of \(i\)th particle

\[ \mathcal{Q}_{\psi_i}(x_i) = e_i \mathcal{Q}_{\psi_i}(x_i) \]

where \(e_i\) is the electric charge of the \(i\)th particle.
Kinetic energy

- non-relativistic QM

\[ \Psi \in H^1(\mathbb{R}^{3N}) \]
\[ \Leftrightarrow \Psi \in L^2(\mathbb{R}^{3N}) \text{ and } \nabla \Psi = (\nabla_{x_1} \Psi, \ldots, \nabla_{x_N} \Psi) \]
\[ \nabla_{x_i} \Psi \in L^2(\mathbb{R}^{3N}) \]
\[ \text{in the sense of distribution} \]
\[ T \Psi = \sum_{i=1}^{N} T_{\Psi_i} \]
where \[ T_{\Psi_i} = \frac{1}{2m_i} \int_{\mathbb{R}^{3N}} |(\nabla_{x_i} \Psi)(x)|^2 \, dx \]
\[ m_i \text{ mass of } i\text{th particle} \]

- relativistic QM

\[ \Psi \in H^{1/2}(\mathbb{R}^{3N}) \]
\[ T \Psi = \sum_{\mathbf{k} \in \mathbb{R}^{3N}} \sqrt{2m^2_c + m^2_i - m_i} |c \hat{\Phi}(\mathbf{k})|^2 \, d\mathbf{k} \]
where \[ \mathbf{k} = (k_1, \ldots, k_N) \in \mathbb{R}^{3N} \]
\[ \hat{\Phi}(\mathbf{k}) = \int_{\mathbb{R}^{3N}} \Psi(x) \exp(-2\pi i \mathbf{x} \cdot \mathbf{k}) \, dx \]
\[ \text{Fourier-transform of } \Psi \]
\[ \frac{1}{2} \sum_{j=1}^{N} m_j |\mathbf{k}_j| \]

Potential energy

\[ V \Psi = \int_{\mathbb{R}^{3N}} V(x) |\Psi(x)|^2 \, dx \]
\[ \text{where } V : \mathbb{R}^{3N} \to \mathbb{R} \text{ total potential energy} \]

(See also Vc on p-13)
31.2 Spin

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

$\sigma \in \{1, 2, \ldots, 2\}$ spin state

$g$ electrons: $\sigma = 1$ or $2$ ($\sigma = +\frac{1}{2} \hbar$ or $-\frac{1}{2} \hbar$)

fermion to bosons correspondence $g = N$?

Pauli principle

$i$-th particle has $g_i$ spin state

$\Psi(\alpha_1, \sigma_1, \ldots, \alpha_N, \sigma_N) \in H^1(\mathbb{R}^{3N})$

$1 \leq \sigma_i \leq g_i$ for $i = 1, \ldots, N$

$C^2$-valued function $Q := \prod_{i=1}^{N} g_i$

$\Psi \in H^1(\mathbb{R}^{3N}; C^2) \cong \bigotimes_{i=1}^{N} H^1(\mathbb{R}^3; C^{g_i})$

(isomorphic)
\[ \begin{aligned}
\sigma &:= (\sigma_1, ..., \sigma_N) \rightarrow \psi(\vec{x}, \sigma) \\
\frac{\sigma}{\sigma_i} &:= \frac{q_1}{\sigma_i} \cdots \frac{q_N}{\sigma_i} \\
\sigma &:= \sigma_1 \cdots \sigma_N \quad \sigma_i = 1 \quad \sigma_N = 1
\end{aligned} \]

Another convenient notation

\[ \begin{aligned}
\vec{z}_i &= (\vec{z}_i, \sigma_i) \quad \text{and} \quad \vec{z} = (\vec{z}_1, ..., \vec{z}_N) \\
\int f(\vec{z}_i) \, d\vec{z}_i &= \frac{q_i}{\sigma_i} \int f(\vec{x}_i, \sigma_i) \, d\vec{x}_i
\end{aligned} \]

\[ \begin{aligned}
\psi(\vec{z}) &= \psi(\vec{z}_1, ..., \vec{z}_N) \\
\| \psi \|_2^2 &= \frac{q_i}{\sigma_i} \int_{\mathbb{R}^{3N}} |\psi(\vec{x}, \sigma)|^2 \, d\vec{x}
\end{aligned} \]

\[ \begin{aligned}
&= \int \psi(\vec{z})^2 \, d\vec{z} = 1. \\
&\text{(normalization condition)}
\end{aligned} \]
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 \( \sigma = \{1, \ldots, 2\} \)

kind of particle

Exchange of any pair of particle

\[ \ldots \quad \circ \quad \bigcirc \quad \bigcirc \quad \circ \quad \ldots \]

\( \bullet \) \( j \)

\( \bullet \) \( i \)

\\

@ Bosons (total symmetry)

\( \text{e.g. } \pi^+, \ldots \rightarrow \text{Bose-Einstein} \)

\[ \Psi(\ldots, Z_i, \ldots, Z_j, \ldots) = \Psi(\ldots, Z_j, \ldots, Z_i, \ldots) \]

@ Fermions (total anti-symmetry)

\( \text{e.g. } e, \ldots \rightarrow \text{Fermi-Dirac} \)

\[ \Psi(\ldots, Z_i, \ldots, Z_j, \ldots) = -\Psi(\ldots, Z_j, \ldots, Z_i, \ldots) \]

\( \rightarrow \) Pauli exclusion principle

\[ \Psi = 0 \text{ if } Z_i = Z_j \] (same quantum state)
Example (symmetric function)
\[ \psi(z) = \prod_{i=1}^{N} u(z_i) = u(z_1) \cdots u(z_N) \]
where \( u \in L^2(\mathbb{R}^3; \mathbb{C}) \) and \( u(z_N) \)

Example (antisymmetric function)
Slater determinant
\[ \psi(z) = (N!)^{-1/2} \det \{ u_i(z_j) \}_{i,j=1}^{N} \]
\[ = \frac{1}{\sqrt{N!}} \left| \begin{array}{ccc}
  u_1(z_1) & \cdots & u_1(z_N) \\
  \vdots & \ddots & \vdots \\
  u_N(z_1) & \cdots & u_N(z_N)
\end{array} \right| \\
= \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} \text{sgn}(\sigma) \prod_{i=1}^{N} u_i(z_{\sigma(i)}) \\
\text{where } u_i \in L^2(\mathbb{R}^3; \mathbb{C}) \text{ for } i = 1, \ldots, N \\
\text{with } (u_j, u_k) = \int u_j(z) u_k(z) dz = \delta_{jk} \\
\text{Then } \psi \text{ is antisymmetric and normalized}
\]
\[ \text{(1)} \quad \text{antisymmetric} \]
\[ \text{(2)} \quad \text{normalized} \]
\[ \text{sgn}(\sigma) = \begin{cases} +1 & \text{if } \sigma \text{ is evenperm} \\
-1 & \text{if } \sigma \text{ is odd} \end{cases} \]
\[ \delta_{jk} = \begin{cases} 1 & j = k \\
0 & \text{otherwise} \end{cases} \]
Proof (1) antisymmetric

\[
\Psi(z_1, \ldots, z_k, \ldots, z_j, \ldots, z_N)
= \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \text{sgn}(\pi(1) \ldots \pi(k) \ldots \pi(N)) \\
\times \psi(z_{\pi(1)}) \ldots \psi(z_{\pi(k)}) \ldots \psi(z_{\pi(N)})
\]

\[\pi(j) = k, \quad \pi(k) = j\]

\[
= \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \text{sgn}[(j, k)(\ldots, \frac{j}{j}, \frac{k}{k})] \psi(z_{j}) \psi(z_{k})
\]

\[
= -\frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \text{sgn}[(\ldots, \frac{j}{j}, \frac{k}{k})] \psi(z_{\pi^{-1}(j)}) \psi(z_{\pi^{-1}(k)})
\]

\[\pi' = (j, k) \pi, \quad \pi'(j) = j, \quad \pi'(k) = k\]

\[
= -\psi(z_1, \ldots, z_j, \ldots, z_k, \ldots, z_N) \quad \Box
\]
(2) normalized

\[ \Psi(z) = \frac{1}{\sqrt{N!}} \sum_{j=1}^{N} \mathcal{E}_j \mathcal{E}_C \mathcal{E}_N \Psi_j(z_{\tau(j)}) \]

\[ \| \Psi \|^2 = \int \overline{\Psi(z)} \Psi(z) \, dz \]

\[ = \frac{1}{N!} \sum_{j=1}^{N} \mathcal{E}_j \mathcal{E}_C \mathcal{E}_N \int \sum_{j=1}^{N} \overline{\Psi_j(z_{\tau(j)})} \Psi_k(z_{\tau(k)}) \, dz \]

\[ \quad = \int \mathcal{E}_j \mathcal{E}_C \mathcal{E}_N \Psi_j(z_{\tau(j)}) \Psi_k(z_{\tau(k)}) \, dz \]

\[ = \int \mathcal{E}_j \mathcal{E}_C \mathcal{E}_N \Psi_j(z_{\tau(j)}) \Psi_{\tau(j)}(z_{\tau(j)}) \, dz \]

\[ = \int \mathcal{E}_j \mathcal{E}_C \mathcal{E}_N \left( \Psi_{\tau^{-1}(j)}, \Psi_{\tau^{-1}(j)} \right) \]

Here, \( \tau^{-1}(j) = \pi^{-1}(j) \) for \( j = 1, \ldots, N \)

\[ \tau^{-1} = \pi^{-1} \iff \tau = \pi \]

\[ \| \Psi \|^2 = \frac{1}{N!} \sum_{j=1}^{N} \mathcal{E}_j \mathcal{E}_C \mathcal{E}_N \Psi_j(z_{\tau(j)}) \Psi_j(z_{\tau(j)}) \]

\[ \iff (SN) = N! \]
antisymmetric tensor product

\( \bigwedge^N \mathbb{L}^2(\mathbb{R}^3; \mathbb{C}^2) \subset \mathbb{L}^2(\mathbb{R}^{8N}; \mathbb{C}^{2N}) \)

subspace of all antisymmetric functions

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

\( \Rightarrow \) \( \forall N \) possible

\( \{ \psi(z) \} \) forms an orthonormal basis

for \( \bigwedge^N \mathbb{L}^2(\mathbb{R}^3; \mathbb{C}^2) \)

---

bosons \( \text{ odd number } \frac{\nu}{2} \text{ of spin state } \)

\( \left( \frac{\nu-1}{2} \text{ is an integer } \right) \)

fermions \( \text{ even number } \frac{\nu}{2} \text{ of spin state } \)

\( \left( \frac{\nu-1}{2} \text{ is } \frac{1}{2}, \frac{3}{2}, \text{ etc. } \right) \)

spinless fermion (academic \( \nu=1 \) fermion)

\( \nu=2 \) fermion with \( \Psi = 0 \) unless \( \nu=1 \).

\( \nu=1 \) boson “we shall only consider”

generalization!
3.1.3.1 The case $q \geq N$

$H : \text{not depend on spin}$

$H \otimes I$ in $L^2(\mathbb{R}^qN; \mathbb{C}^qN) \cong L^2(\mathbb{R}^qN) \otimes \mathbb{C}^qN$

$I : \text{identity in } \mathbb{C}^qN$

$q \geq N$ fermionic system

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

Claim

$\forall \phi(\alpha_1, ..., \alpha_N) \text{ taken}$

$\psi(z_1, ..., z_N) = \frac{1}{\sqrt{N!}} \sum_{\sigma} A[\phi(\alpha_1, ..., \alpha_N)] f_{\sigma}(\sigma)$

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

antisymmetrizer

$A[\chi(z_1, ..., z_N)] = \sum_{\sigma \in S_N} \epsilon_\sigma \chi(z_{\sigma(1)}, ..., z_{\sigma(N)})$

(1) $\psi$ is antisymmetric in $L^2(\mathbb{R}^qN; \mathbb{C}^qN)$

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

(1) \[ z_i = (\alpha_i, \sigma_i) \quad 1 \leq \sigma_i \leq \varepsilon = N \]

\[ \psi(\ldots, z_k, \ldots, z_j, \ldots) = \frac{1}{\sqrt{\varepsilon!}} \sum_{\pi \in \pi_N} \varepsilon_{\pi} \phi(\ldots, \pi(k), \ldots, \pi(y), \ldots) \cdot f_j(\pi(k)) \cdot f_k(\pi(y)) \ldots \]

\[ = \frac{1}{\sqrt{\varepsilon!}} \sum_{\pi \in \pi_N} \varepsilon_{\pi} \phi(\ldots, \pi(k), \ldots, \pi(y), \ldots) \cdot f_j(\pi(k)) \cdot f_k(\pi(y)) \ldots \]

\[ = -\psi(\ldots, z_j, \ldots, z_k, \ldots) \]
Revised proof for (1)

Lemma

Antisymmetrizer is total antisymmetric, i.e.

\[ A[\mathbf{X}(\ldots, z_k, \ldots, z_j, \ldots)] = - A[\mathbf{X}(\ldots, z_j, \ldots, z_k, \ldots)] \]

::: \[ A[\mathbf{X}(\ldots, z_k - z_j, \ldots)] \]

\[
\begin{align*}
\sum_{\pi \in S_N} & \varepsilon_{\pi} \mathbf{X}(z_{\pi(1)}, \ldots, z_{\pi(j)}, \ldots, z_{\pi(N)}) \\
\pi' &= (j \ k) \pi \\
\pi'(j) &= \pi(k) \\
\pi'(k) &= \pi(j) \\
\varepsilon_{\pi'} &= -\varepsilon_{\pi} \\
&= \sum_{\pi \in S_N} (-\varepsilon_{\pi}) \mathbf{X}(z_{\pi(1)}, \ldots, z_{\pi(j)}, \ldots, z_{\pi(k)}, \ldots, z_{\pi(N)}) \\
&= - A[\mathbf{X}(\ldots, z_j, \ldots, z_k, \ldots)]
\end{align*}
\]

Using Lemma above with

\[ X(z_1, \ldots, z_N) = \phi(x_1, \ldots, x_N) f_1(\alpha_1) \cdots f_N(\alpha_N) \]

where \( z_j = (x_j, \alpha_j) \) for \( j = 1, \ldots, N \)
(2) $\|\psi\|_2^2 = \int \overline{\psi(z)} \psi(z) \, dz$

$\overline{\psi(z)} \psi(z) = \frac{1}{N!} \left\{ \frac{\sum_{\prod \sigma_i} e^{i \phi(\cdots \chi(\cdots \cdots) \prod f_j(\sigma_{\pi(i)})}}{\prod \sigma_i} \prod \overline{f_k(\sigma_{\pi(k)})} \right\}$

$= \frac{1}{N!} \sum_{\prod \sigma_i} \frac{e^{i \phi(\cdots \chi(\cdots \cdots) \cdots \chi(\cdots \cdots) \cdots \phi(\cdots \chi(\cdots \cdots) \cdots \chi(\cdots \cdots) \cdots) \cdots \cdots) \cdots}}{\prod \sigma_i} \prod \overline{f_k(\sigma_{\pi(k)})}$

$\prod f_j(\sigma_{\pi(j)}) \prod \overline{f_k(\sigma_{\pi(k)})} = 1$

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

$\sigma_{\pi(y)} = \sigma_{\pi'(y)}$ for all $y = 1, \ldots, N$

$\iff \Pi = \Pi'\equiv N!$

$= \frac{1}{N!} \sum_{\prod \sigma_i} \frac{e^{i \phi(\cdots \chi(\cdots \cdots) \cdots \chi(\cdots \cdots) \cdots \phi(\cdots \chi(\cdots \cdots) \cdots \chi(\cdots \cdots) \cdots) \cdots \cdots) \cdots}}{\Pi = \Pi'} \prod f_j(\sigma_{\pi(y)})^2$

$\|\psi\|_2^2 = \frac{1}{N!} \frac{2}{\pi} \frac{1}{\Pi} \int \phi(\cdots \chi(\cdots \cdots) \cdots) \overline{f_j(\sigma_{\pi(y)})}^2 \, dx \cdot \prod f_j(\sigma_{\pi(y)})^2$

$= \|\phi\|_2^2 \cdot \frac{1}{N!} \frac{2}{\pi} \frac{1}{\Pi} \frac{1}{N!} \sum_{\prod \sigma_i} \prod f_j(\sigma_{\pi(y)})^2 = \|\phi\|_2^2$