Lecture notes prepared by Piotr Piecuch for the mini-course on the single-reference many-body perturbation theory offered in the College of Chemistry and Molecular Engineering of Peking University on November 12-14, 2019.

PART I: Introductory material, including molecular electronic Schrödinger equation, Slater determinants, configuration interaction wave function expansions, and elements of second quantization needed in the discussion of the many-body perturbation theory in PART II.

PRELIMINARIES

Introduction: Importance of the electronic Schrödinger equation (as derived from the Born-Oppenheimer approximation).

1) Molecular Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = \mathcal{H}\Psi \quad \text{or} \quad \mathcal{H}\Psi = E\Psi,$$

$$\mathcal{H} = T_e + T_n + V_{ee} + V_{en} + V_{nn},$$

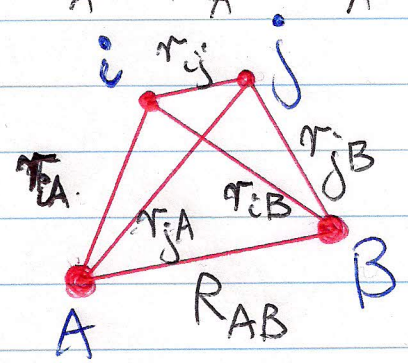
$$T_e = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N} \Delta_i \qquad \left(\Delta_i = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right),$$

$$T_n = -\sum_{A=1}^{N_A} \frac{\hbar^2}{2M_A}\Delta_A \qquad \left(\Delta_A = \frac{\partial^2}{\partial X_A^2} + \frac{\partial^2}{\partial Y_A^2} + \frac{\partial^2}{\partial Z_A^2}\right),$$

$$V_{ee} = \sum_{1=i<j}^{N} \frac{e^2}{r_{ij}},$$

$$V_{en} = -\sum_{i=1}^{N}\sum_{A=1}^{N_A} \frac{Z_A e^2}{r_{iA}}$$

$$V_{nn} = \sum_{1=A<B}^{N_A} \frac{Z_A Z_B e^2}{R_{AB}}$$



$i = 1, \dots, N$

$A = 1, \dots, N_A$

electronic coordinates ($x = (r, \sigma)$)

$$\Psi = \Psi(\underset{\sim}{x}_1, \ldots, \underset{\sim}{x}_N, \underset{\sim}{R}_1, \ldots, \underset{\sim}{R}_{N_A}) \equiv \Psi(\underset{\sim}{X}, \underset{\sim}{R})$$

$$\Psi = \Phi_{\underset{\sim}{R}}(\underset{\sim}{X})\,\chi(\underset{\sim}{R}) \quad (\text{or } \chi(R,t))$$

$$\Phi_{\underset{\sim}{R}}(\underset{\sim}{X}) \equiv \Phi(\underset{\sim}{X}; \underset{\sim}{R})$$

(or $\Psi = \sum_{\mu,k} \Phi_\mu(X;R)\chi_{k,\mu}(R)$ from $R \to 0$ (one μ) $\Phi_\mu(X;R)\chi_{k,\mu}(R)$)

$$H_e \Phi_\mu(\underset{\sim}{X}; \underset{\sim}{R}) = \mathcal{E}_\mu(\underset{\sim}{R})\,\Phi_\mu(\underset{\sim}{X}; \underset{\sim}{R})$$

$$H_e = T_e + V_{ne} + V_{ee}$$

$V_{nn}(\underset{\sim}{R})$ in

$$\left[T_n + V_{nn} + \mathcal{E}_\mu(\underset{\sim}{R})\right]\chi_{k\mu}(\underset{\sim}{R}) = \mathcal{E}_{k\mu}\,\chi_{k\mu}(\underset{\sim}{R})$$

or

$$i\hbar \frac{\partial \chi_\mu(\underset{\sim}{R},t)}{\partial t} = \left[T_n + V_{nn} + \mathcal{E}_\mu(\underset{\sim}{R})\right]\chi_\mu(\underset{\sim}{R},t)$$

must be antisymmetric (Fermions)

$$H_e \Psi_\mu(\underset{\sim}{x}, \underset{\sim}{R}) = \mathcal{E}_\mu(\underset{\sim}{R})\,\Psi_\mu(\underset{\sim}{x}, \underset{\sim}{R})$$

$$H_e = -\frac{\hbar^2}{2m_e}\sum_i \Delta_i - \sum_i \sum_A \frac{Z_A e^2}{r_{Ai}} + \sum_{i<j} \frac{e^2}{r_{ij}}$$

$$H_e = T + V,$$

$$T = \sum_{i=1}^{N} t(i),$$

$$V = \sum_{i<j} v(i,j),$$

(an example of external potential)

where

$$t(i) = -\frac{\hbar^2}{2m_e}\Delta(i) - \sum_{A=1}^{N_A} \frac{Z_A e^2}{r_{Ai}}$$

$$v(i,j) \equiv v(j,i) = \frac{e^2}{r_{ij}}$$

$$t(i) \equiv t(\underset{\sim}{x}_i)$$

$$v(i,j) \equiv v(\underset{\sim}{x}_i, \underset{\sim}{x}_j)$$

Atoms
Hoseill: $\frac{p^2}{2m} + \frac{kx^2}{2}$
$\rightarrow \hbar\omega(N+\frac{1}{2})$
$N = a^\dagger a$
$|E_n\rangle \sim (a^\dagger)^n |0\rangle$

1.1. Many-Fermion Wave Functions & Spaces, Occupation Number Representation

~~Molecular orbital theories~~

Molecular orbital theories (MO)
[Algebraic approximation ⇔ all other many-Fermion methods]

$\Psi \equiv \Psi_\mu$ must be antisymmetric, i.e.,

$$\Psi(x_2, x_1, \ldots, x_N) = -\Psi(x_1, x_2, \ldots, x_N)$$

↑ Fermions

In general,

$$\Psi(x_{P_1}, \ldots, x_{P_N}) = \underbrace{(-1)^P}_{\text{sgn}(P)} \Psi(x_1, \ldots, x_N),$$

where

$$P = \begin{pmatrix} 1 & 2 & \cdots & N \\ P_1 & P_2 & \cdots & P_N \end{pmatrix} \in \mathcal{S}_N.$$

In MO theories (or algebraic approaches), we construct Ψ as follows:

1) Introduce an orthonormal and complete set of 1-particle functions, called spin-orbitals,

$$\chi_p(x) \equiv \langle x | \chi_p \rangle \equiv \langle x | p \rangle, \quad (p = 1, 2, \ldots,)$$

- orth.: $\langle \chi_p | \chi_q \rangle \equiv \langle p | q \rangle = \delta_{pq}$
- complete: $\psi(x) = \sum_{p=1}^{\infty} c_p \chi_p(x)$ or

$$|\psi\rangle = \sum_p c_p |p\rangle ,$$

where

$$c_p = \langle p | \psi \rangle = \int \chi_p^*(x) \psi(x) \, dx$$

(recall that $\langle f | g \rangle = \int f^*(x) g(x) \, dx$).

Usually, (but not necessarily) $\chi_p(\underset{\sim}{x}) = \phi_p(\underset{\sim}{r}) \sigma_p(\sigma)$

σ_p: α or β spin eigenfunction

2). Clearly, any function of $\underline{x}_1, \dots, \underline{x}_N$ has the form,

$$\Psi(x_1, \dots, x_N) = \sum_{p_1 \neq \dots \neq p_N} \alpha_{p_1 \dots p_N} \psi_{p_1}(x_1) \dots \psi_{p_N}(x_N)$$

$$\langle \psi_{p_1} \dots \psi_{p_N} | \Psi \rangle = \int \psi_{p_1}^*(x_1) \dots \psi_{p_N}^*(x_N) \Psi(x_1 \dots x_N)$$

Let us introduce

$$\mathcal{A} = \frac{1}{N!} \sum_{Q \in S_N} (-)^Q \hat{Q}$$

↙ permutation of electronic coordinates

↗ antisymmetrizer (projector on the subspace of antisymmetric functions)

Properties: $\mathcal{A}^2 = \mathcal{A}$, $\mathcal{A}^\dagger = \mathcal{A}$ [prove it in assignment]

[example, $\mathcal{A} = \frac{1}{2!}(\hat{I} - \hat{(12)})$]

$\mathcal{A}|\Psi\rangle = |\Psi\rangle$, thus,

$$|\Psi\rangle = \sum_{p_1 \neq \dots \neq p_N} \alpha_{p_1 \dots p_N} \mathcal{A} \{ \psi_{p_1} \dots \psi_{p_N} \}$$

$$= \sum_{p_1 \neq \dots \neq p_N} \frac{1}{\sqrt{N!}} \alpha_{p_1 \dots p_N} \underbrace{(\sqrt{N!}) \mathcal{A} \{ \psi_{p_1} \dots \psi_{p_N} \}}$$

$|\Phi_{p_1 \dots p_N}\rangle$ or $|\{\psi_{p_1} \dots \psi_{p_N}\}\rangle$ or $|\{p_1 \dots p_N\}\rangle$ ...

$|\psi_{p_1}\rangle \otimes \dots \otimes |\psi_{p_N}\rangle$

$$(1) \quad \boxed{\Psi^{(x_1 \ldots x_N)} \equiv \sum_{p_1 \ldots p_N} D_{p_1 \ldots p_N} \, \Phi_{p_1 \ldots p_N}(x_1, \ldots, x_N)}$$

$$D_{p_1 \ldots p_N} \equiv \frac{1}{\sqrt{N!}} \, d_{p_1 \ldots p_N}$$

$$\Phi_{p_1 \ldots p_N}(x_1, \ldots, x_N) \equiv$$

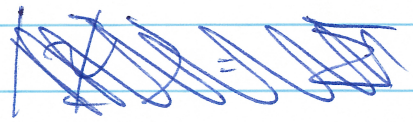
$$\equiv \langle x_1, \ldots, x_N \,|\, \overbrace{\{\psi_{p_1} \ldots \psi_{p_N}\}}^{\{p_1 \ldots p_N\}} \rangle$$

$$= \frac{1}{\sqrt{N!}} \sum_{Q \in S_N} (-1)^Q \psi_{p_1}(x_{Q_1}) \ldots \psi_{p_N}(x_{Q_N})$$

$$= \frac{1}{\sqrt{N!}} \sum_{Q \in S_N} (-1)^Q \psi_{p_{Q_1}}(x_1) \ldots \psi_{p_{Q_N}}(x_N)$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{p_1}(x_1) & \ldots & \psi_{p_N}(x_N) \\ \psi_{p_2}(x_1) & \ldots & \psi_{p_2}(x_N) \\ & \ldots & \\ \psi_{p_N}(x_1) & \ldots & \psi_{p_N}(x_N) \end{vmatrix}$$

Slater det.: ↑ normalized, antisymmetric, orthonormal



e.g.,

$$\Phi_{\beta_1 \beta_2}(x_1, x_2) \equiv \langle x_1, x_2 | \{\psi_{\beta_1} \psi_{\beta_2}\} \rangle$$

$$\equiv \langle x_1, x_2 | \{\beta_1 \beta_2\} \rangle =$$

$$= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{\beta_1}(x_1) & \psi_{\beta_1}(x_2) \\ \psi_{\beta_2}(x_1) & \psi_{\beta_2}(x_2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \left(\psi_{\beta_1}(x_1) \psi_{\beta_2}(x_2) - \right.$$

$$\left. - \psi_{\beta_2}(x_1) \psi_{\beta_1}(x_2) \right)$$

~~Moreover~~ Notice that

$$\Phi_{p_2 p_1 - p_N} = -\Phi_{p_1 p_2 - p_N}, \text{ etc.}$$

Also, $\int \int \psi_{p_1}^*(x_1) \cdots \psi_{p_N}(x_N)^* \Psi(x_1 \cdots x_N)$

$$a_{p_1 \cdots p_N} = \langle \psi_{p_1} \cdots \psi_{p_N} | \Psi \rangle$$

$$= \langle \psi_{p_1} \cdots \psi_{p_N} | \mathcal{A} \Psi \rangle \overset{\text{term-over-rule}}{=}$$

$$= \langle \mathcal{A}(\psi_{p_1} \cdots \psi_{p_N}) | \Psi \rangle$$

$$= \frac{1}{\sqrt{N!}} \langle \{p_1 \cdots p_N\} | \Psi \rangle$$

$$= \frac{1}{\sqrt{N!}} \langle \Phi_{p_1 \cdots p_N} | \Psi \rangle \quad (2)$$

Clearly, $a_{p_2 p_1 \cdots p_N} = -a_{p_1 p_2 \cdots p_N}$, etc.

Going back to (1) [p. 7],

$$|\Psi\rangle = \sum_{\rho_1 - \rho_N} D_{\rho_1 - \rho_N} |\Phi_{\rho_1 - \rho_N}\rangle$$

$$= \sum_{\rho_1 \neq \rho_2 \neq \cdots \neq \rho_N} D_{\rho_1 - \rho_N} |\Phi_{\rho_1 - \rho_N}\rangle$$

$$= \sum_{1 \leq \rho_1 < \rho_2 < \cdots < \rho_N < \infty} \underbrace{[(N!) D_{\rho_1 - \rho_N}]}_{N! \cdot \frac{1}{\sqrt{N!}} \mathcal{A}_{\rho_1 - \rho_N} = \sqrt{N!}\, \mathcal{A}_{\rho_1 - \rho_N} \equiv C_{\rho_1 - \rho_N}} |\Phi_{\rho_1 - \rho_N}\rangle$$

ORDERED CONFIGURATIONS

$$= \sum_{1 \leq \rho_1 < \cdots < \rho_N < \infty} C_{\rho_1 - \rho_N} |\Phi_{\rho_1 - \rho_N}\rangle, \text{ where}$$

$$C_{\rho_1 - \rho_N} = \sqrt{N!}\, \mathcal{A}_{\rho_1 - \rho_N} \overset{(2), \text{p.9.}}{=} \langle \Phi_{\rho_1 - \rho_N} | \Psi \rangle$$

[In agreement with the fact that

$$\langle \Phi_{\rho_1 - \rho_N} | \Phi_{q_1 - q_N} \rangle \overset{\substack{\rho_1 < \cdots < \rho_N \\ q_1 < \cdots < q_N}}{=} \delta_{\rho_1 q_1} - \delta_{\rho_N q_N}]$$

Remark:

Direct proof of orthonormality of Φ's:

$(p_1 < p_2 < \dots < p_N)$
$q_1 < q_2 < \dots < q_N)$

$$\langle \Phi_{p_1 \dots p_N} | \Phi_{q_1 \dots q_N} \rangle =$$

$$= \sqrt{N!}\sqrt{N!} \langle \mathcal{A}(\chi_{p_1} \dots \chi_{p_N}) | \mathcal{A}(\chi_{q_1} \dots \chi_{q_N}) \rangle \qquad \mathcal{A}^2 = \mathcal{A}$$

$$= N! \langle \chi_{p_1} \dots \chi_{p_N} | \mathcal{A}(\chi_{q_1} \dots \chi_{q_N}) \rangle$$

$$= N! \frac{1}{N!} \sum_{Q \in S_N} (-1)^Q \int \chi_{p_1}^*(x_1) \dots \chi_{p_N}^*(x_N)\, \chi_{Q q_1}(x_1) \dots \chi_{Q q_N}(x_N)$$

~~We get a nonzero result.~~

If one or more q's are different from all p's, we obtain zero. If $p_1 = q_1, \dots, p_N = q_N$ we get

$$\sum_Q (-1)^Q \int \chi_{p_1}^*(x_1) \dots \chi_{p_N}^*(x_N)\, \chi_{Q p_1}(x_1) \dots \chi_{Q p_N}(x_N) =$$

$Q = \hat{1}$ only

end of remark

SUMMARY:

$$|\Psi\rangle = \sum_{p_1 < \dots < p_N} c_{p_1 \dots p_N} |\Phi_{p_1 \dots p_N}\rangle$$

$$|\Phi_{p_1 \dots p_N}\rangle = \sqrt{N!}\, \mathcal{A} |\psi_{p_1} \dots \psi_{p_N}\rangle$$

or

$$\langle x_1 \dots x_N | \{p_1 \dots p_N\}\rangle =$$

$$= \frac{1}{\sqrt{N!}} \sum_Q (-1)^Q Q\, \psi_{p_1}(x_1) \dots \psi_{p_N}(x_N)$$

$$c_{p_1 \dots p_N} = -c_{p_2 p_1 \dots p_N} = \dots =$$

$$= \langle \Phi_{p_1 \dots p_N} | \Psi \rangle .$$

$\{|\Phi_{p_1 \ldots p_N}\rangle\}$ — basis of an N-electron Hilbert space $\mathcal{H}_N$ (orthonormal, complete)

Symbolically, if

$$\text{Span}\{|\psi_p\rangle, p=1,\ldots,\infty\} \equiv \mathcal{V}$$

Then,

$$\mathcal{H}_N(\mathcal{F}_N \text{ in Paldus}) =$$

$$= \mathcal{A}\,\mathcal{V}^{\otimes N} \equiv$$

$$\equiv \mathcal{A}\big(\underbrace{\mathcal{V}\otimes \ldots \otimes \mathcal{V}}_{N\text{-times}}\big)$$

$\mathcal{V}^{\otimes N}$ spanned by $|\psi_{p_1}\rangle \otimes \ldots \otimes |\psi_{p_N}\rangle \equiv |\psi_{p_1} \ldots \psi_{p_N}\rangle$

$\mathcal{A}\mathcal{V}^{\otimes N}$ by $|\Phi_{p_1 \ldots p_N}\rangle \equiv \mathcal{A}|\psi_{p_1} \ldots \psi_{p_N}\rangle$

Properties of Φ's (Slater determinants):

$$|\Phi_{p_2 p_1 p_3 \ldots p_N}\rangle = -|\Phi_{p_1 p_2 \ldots p_N}\rangle, \text{ thus,}$$

$$|\Phi_{p_1 p_1 \ldots p_N}\rangle = 0$$

Two electrons cannot occupy the same spin-orbital (Pauli's principle)

Thus, in order to uniquely specify a given ordered configuration, we only need to specify $p_1 \ldots p_N$, or, equivalently which spin-orbital is occupied and which one is not.

Imagine that we order all spin-orbitals,

1 2 3 4 ..... p .....

Then, symbolically,

$$|\{p_1 \dots p_N\}\rangle \iff$$

$$\iff |0 \dots 0|0 \dots 0|0 \dots 1 \dots 1|0 \dots\rangle$$

$$= |n_1 n_2 \dots n_{p_1} \dots n_{p_2} \dots n_{p_N} \dots\rangle$$

(occupation numbers)

where

$$n_1 = 0, \dots, n_{p_1} = 1, \dots n_{p_2} = 1, \dots, n_{p_N} = 1,$$

$$n_{p_i} = 0 \text{ for } i \neq 1, \dots, N; \quad n_{p_i} = 1 \text{ for } i = 1, \dots, N$$

This defines the occupation number representation, and a new space (called the Fock space) spanned by kets

$$|n_1 n_2 \dots n_p \dots\rangle, \quad n_p = \begin{cases} 0 \\ 1 \end{cases}.$$

$\mathcal{H}_N$ then is defined as

$$\text{Span}\left\{ |n_1 \dots n_p \dots\rangle, \ \sum_p n_p = N \right\}.$$

Examples:

$$|\Phi_{1,7,10}\rangle = |\{\psi_1 \psi_2 \psi_7 \psi_{10}\}\rangle \equiv |\{1\,2\,7\,10\}\rangle$$

$$\overset{\text{occ. numbers}}{\underset{\text{rep.}}{\Leftrightarrow}} |\,1\,1\,0\,0\,0\,0\,1\,0\,0\,1\,0\,0\,0 \ldots\rangle$$

(positions: 1, 2, 7, 10)

$$|\Phi_{1,2,3,4}\rangle = |\{\psi_1 \psi_2 \psi_3 \psi_4\}\rangle \equiv |\{1234\}\rangle$$

$$\Leftrightarrow |\,1\,1\,1\,1\,0\,0\,0\,0 \ldots\rangle$$

1.2. Creation and annihilation operators, number operator.

1.3. Anti-commutation relations

In the Fock space of kets $|n_1 \dots n_p \dots\rangle$, all operators are expressed in terms of the basic operators called the annihilation and creation operators. These operators change the particle number, which may seem to be a strange thing to do, but it is very useful to introduce them.

Def: ANNIHILATION OPERATORS

$$X_p \underbrace{|\dots n_p \dots\rangle}_{0 \text{ or } 1} = (-1)^{\sum_{k=1}^{p-1} n_k} n_p |\dots (1-n_p) \dots\rangle$$

X_p are linear.

What is that these operators really do? Since $n_p = 0, 1$, we can simplify our notation by writing

$|\ldots p \ldots\rangle$ if $n_p = 1$ and

$|\ldots \not{p} \ldots\rangle$ if $n_p = 0$.

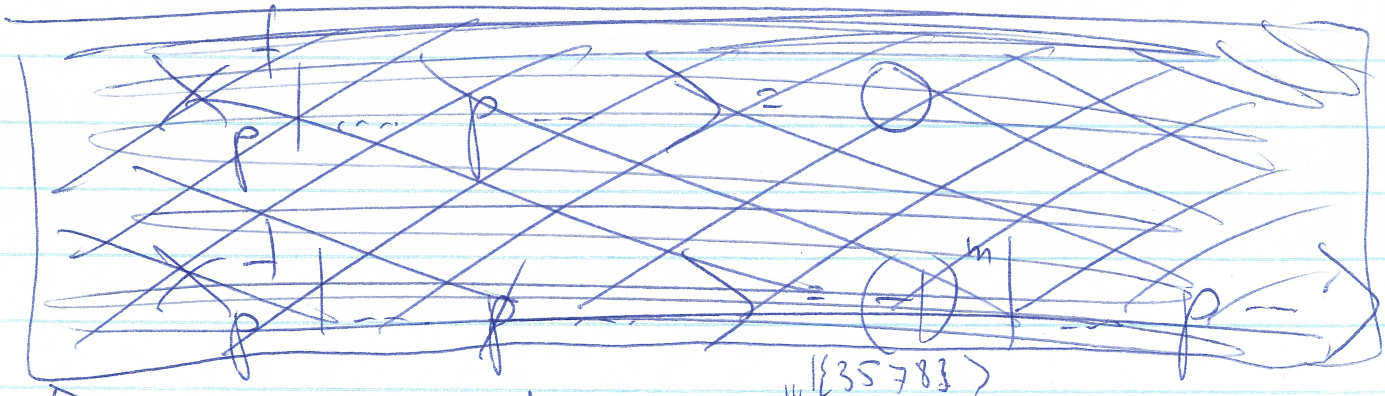
Then, we have

$$X_p |\ldots p \ldots\rangle = (-1)^m |\ldots \not{p} \ldots\rangle$$

$$X_p |\ldots \not{p} \ldots\rangle = 0 ,$$

where

$$m = \sum_{k=1}^{p-1} n_k$$



Examples: $X_3 |00101011100\ldots\rangle =$

$= |00001011100\ldots\rangle \to |\{5783\}\rangle$

$X_5 |00101011100\ldots\rangle =$

$= -|00100011100\ldots\rangle$, etc.

$\hookrightarrow |\{3785\}\rangle$

In the language of configurations $|\Phi_{p_1 \dots p_N}\rangle = |\{p_1 \dots p_N\}\rangle$,

$$X_p |\{p\, p_2 \dots p_N\}\rangle = |\{p_2 \dots p_N\}\rangle$$

$$X_p |\{p_1 p_2 \dots p_N\}\rangle = 0 \text{ if } p \neq p_1, \dots p_N$$

Indeed,

$$X_p |\{p\, p_2 \dots p_N\}\rangle \Leftrightarrow X_p |\underbrace{0 \dots 0}_{m=0}\, 1\, \underbrace{0 \dots}_{p}\, 1\, \underbrace{0 \dots}_{p_2}\, 1\, \underbrace{0 \dots}_{p_N}\rangle$$

$$= |0 \dots 0\, 0\, 0 \dots 1\, 0 \dots 1\, 0 \dots\rangle$$

$$= |\{p_2 \dots p_N\}\rangle$$

If p is not the leftmost occupied spin-orbital, then we use the fact that

$$|\{p_{Q_1} p_{Q_2} \dots p_{Q_N}\}\rangle = (-1)^Q |\{p_1 \dots p_N\}\rangle.$$

For example,

$$X_p |\{p_1 p p_3 \sim p_N\}\rangle = -X_p |\{p p_1 p_3 \sim p_N\}\rangle$$

$$= - |\{p_1 p_3 \sim p_N\}\rangle .$$

This agrees with the fact that in this case,

$$|\{p_1 p p_3 \sim p_N\}\rangle = |0..010..010..010..10\rangle$$

p_1 p p_3 p_N

so that $m = 1$ and

$$X_p |\sim p \sim\rangle = - |\sim p \sim\rangle .$$

Thus,

$$X_3 |\{3578\}\rangle = |\{578\}\rangle$$

(verify: $X_3 |00\textcircled{1}0101100..\rangle = |00\textcircled{0}0101100..\rangle$)

$$X_5 |\{3578\}\rangle = -X_5 |\{53 78\}\rangle$$

$$= - |\{378\}\rangle$$

Verify: $X_5 |0010\textcircled{1}01100..\rangle = -|0010\textcircled{0}01100..\rangle$

Vacuum state:

Among all states $|\dots p \dots\rangle$, there is one where all n_p's equal zero,

$$|0\rangle = |000\dots0\dots0\dots\rangle .$$

As for all (basis) states in the Fock space,

$$\langle 0|0\rangle = 1 .$$

This state spans a zero-particle subspace of space $\mathcal{H}_0$, which is isomorphic with $\mathbb{C}$.

This state is called a free or physical vacuum (or, simply, vacuum) state.

The presence of this state in the formalism is essential for the completeness of the whole theory.

In particular, if

$$|p\rangle = |00\dots0p0\dots0\dots\rangle$$ (a 1-particle state)

we obtain (according to our rules)

$$\chi_p |p\rangle = |0\rangle .$$

We must also have,

$$\chi_p |0\rangle = 0 \quad \forall_p .$$

Creation operators:

Creation operators, $\chi_p^\dagger$, are hermitian adjoints of χ_p. In order to understand how they act, let us note that

$$\chi_p |p\rangle = |0\rangle , \quad \text{so that}$$

$$\langle p | \chi_p^\dagger = \langle 0| , \quad \text{or}$$

$$\langle p | \chi_p^\dagger |0\rangle = \langle 0|0\rangle = 1 .$$

Since $|p\rangle$'s are orthonormal, $\langle p|q\rangle = \delta_{pq}$

$\langle p| \underbrace{X_q^\dagger |0\rangle}_{|q\rangle} = 1$ implies that $X_p^\dagger |0\rangle = |p\rangle$.

$X_p^\dagger$ CREATES a particle in the single-particle state p.

In general,

$$X_p^\dagger |\{p_1 p_2 \cdots p_N\}\rangle =$$

$$= |\{p\, p_1 p_2 \cdots p_N\}\rangle \quad , \text{ if } p < p_1 \leq p_2 \cdots$$

If we want to add a particle to $p_1 < p < p_2$ between p_1 & p_2, we proceed as usual,

$$X_p^\dagger |\{p_1 p_2 \cdots p_N\}\rangle = |\{p\, p_1 p_2 \cdots p_N\}\rangle =$$
$$= -|\{p_1\, p\, p_2 \cdots p_N\}\rangle .$$

If p is among $p_1, \cdots, p_N$, we get zero,

$$a_p^\dagger |\{p p_2 \cdots p_N\}\rangle = |\{p p p_2 \cdots p_N\}\rangle$$
$$= 0 \quad \text{due to antisymmetric property.}$$

In the occupation number representation,

$$a_p^\dagger |\cdots \not{p} \cdots\rangle = (-1)^m |\cdots p \cdots\rangle$$
$$a_p^\dagger |\cdots p \cdots\rangle = 0, \text{ or}$$

$$a_p^\dagger |\cdots n_p \cdots\rangle = (-1)^{\sum_{k=1}^{p-1} n_k} (1-n_p) |\cdots (1-n_p) \cdots\rangle$$

Summary

$$a_p |\cdots n_p \cdots\rangle = (-1)^{\sum_{k=1}^{p-1} n_k} n_p |\cdots (1-n_p) \cdots\rangle$$
$$a_p^\dagger |\cdots n_p \cdots\rangle = (-1)^{\sum_{k=1}^{p-1} n_k} (1-n_p) |\cdots (1-n_p) \cdots\rangle$$
$$a_p |\cdots p \cdots\rangle = (-1)^m |\cdots \not{p} \cdots\rangle$$
$$a_p |\cdots \not{p} \cdots\rangle = 0$$
$$a_p^\dagger |\cdots p \cdots\rangle = 0$$
$$a_p^\dagger |\cdots \not{p} \cdots\rangle = (-1)^m |\cdots p \cdots\rangle.$$

Number operator:

As we can anticipate, all particle-conserving operators must contain the same number of creators & annihilators. An example of such operator is provided by the number operator:

$$N_p = X_p^\dagger X_p \qquad (\text{note, } N_p = N_p^\dagger).$$

Let us see how N_p acts on the left from (*).

$$N_p |\ldots p \ldots\rangle = X_p^\dagger X_p |\overset{m}{\ldots} p \ldots\rangle$$
$$= (-1)^m X_p^\dagger |\ldots \not{p} \ldots\rangle =$$
$$= (-1)^m (-1)^m |\ldots p \ldots\rangle = |\ldots p \ldots\rangle$$

$$N_p |\ldots \not{p} \ldots\rangle = X_p^\dagger X_p |\ldots \not{p} \ldots\rangle$$
$$= 0,$$

Thus,

$$N_p |\ldots n_p \ldots\rangle = n_p |\ldots n_p \ldots\rangle$$

Eigenvalues of N_p are n_p's.

All basis states $|\cdots n_p \cdots\rangle$ are eigenstates of N_p's (diagonalize N_p's). For this reason, we call the representation of ~~many-electron~~ many-body quantum mechanics in $\mathcal{F}$, the occupation number representation (recall, the momentum representation, the energy representation, etc).

We can also define the TOTAL number operator,

$$\hat{N} = \sum_p \chi_p^\dagger \chi_p .$$

Clearly, $\hat{N}|\cdots n_p \cdots\rangle = \left(\sum_{p=1}^{\infty} n_p\right)|\cdots n_p \cdots\rangle$

$\sum_{p=1}^{\infty} n_p$: the number of particles in $|\cdots n_p \cdots\rangle$.

$$\left(\hat{N}|\Phi_{p_1\cdots p_N}\rangle = N|\Phi_{p_1\cdots p_N}\rangle\right).$$

Anti-commutation rules:

We will now prove that

anticomm. ↓

① $\{\chi_p^\dagger, \chi_q\} \equiv \chi_p^\dagger \chi_q + \chi_q \chi_p^\dagger = \delta_{pq}$

② $\{\chi_p, \chi_q\} \equiv \chi_p \chi_q + \chi_q \chi_p = 0$

③ $\{\chi_p^\dagger, \chi_q^\dagger\} \equiv \chi_p^\dagger \chi_q^\dagger + \chi_q^\dagger \chi_p^\dagger = 0$

① :

~~Without a loss of generality, we can~~

There are two cases, $p \neq q$ and $p = q$.

- We begin with $p \neq q$. We will apply $\{\chi_p^\dagger, \chi_q\}$ to basis states in $\mathcal{F}$. ~~The only~~ ~~time we get a nonzero result is when~~

Let us assume that $p < q$ (the case $p > q$ is analyzed in a similar way).
We have four situations:

(i) $\{X_p^\dagger, X_q\} | \cdots p \cdots q \cdots \rangle$

$= X_p^\dagger X_q | \cdots p \cdots q \cdots \rangle + X_q X_p^\dagger | \cdots p \cdots q \cdots \rangle$

$= 0 + X_q (-1)^m | \cdots p \cdots q \cdots \rangle$

$= 0$, where m is the number of occ. states preceding p.

(ii) $\{X_p^\dagger, X_q\} | \overbrace{\cdots}^{m \text{ states}} p \overbrace{\cdots}^{n \text{ levels}} q \cdots \rangle$

$= X_p^\dagger X_q | \cdots p \cdots q \cdots \rangle$

$+ X_q X_p^\dagger | \cdots p \cdots q \cdots \rangle$

$= X_p^\dagger (-1)^{m+n} | \cdots p \cdots q \cdots \rangle$

$+ X_q (-1)^m | \overbrace{\cdots}^{m} p \overbrace{\cdots}^{n} q \cdots \rangle$

$= (-1)^n | \cdots p \cdots q \cdots \rangle$

$+ (-1)^{m+1+n} (-1)^m | \cdots p \cdots q \cdots \rangle$

$= \{(-1)^n + (-1)^{n+1}\} | \cdots p \cdots q \cdots \rangle$

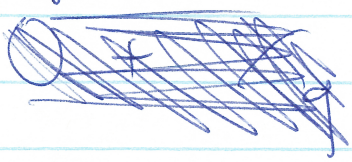
$= 0$, where n is the number of levels between p and q.

(iii) $\{X_p^\dagger, X_q\}\,|\cdots p \cdots q \cdots\rangle$

$= X_p^\dagger X_q\,|\cdots p \cdots q \cdots\rangle$



$+ X_q X_p^\dagger\,|\cdots p \cdots q \cdots\rangle$

$=$  0

(iv) $\{X_p^\dagger, X_q\}\,|\cdots p \cdots q \cdots\rangle$

$= X_p^\dagger X_q\,|\overset{m}{\cdots} p \overset{n}{\cdots} q \cdots\rangle +$

$+ X_q X_p^\dagger\,|\cdots p \cdots q \cdots\rangle =$

$= (-1)^{m+1+n} X_p^\dagger\,|\cdots p \cdots q \cdots\rangle = 0.$

In all four cases, $\{X_p^\dagger, X_q\} = 0$.

Thus, $\{X_p^\dagger, X_q\} = 0$ for $p \neq q$.

- $p = q$. Now, we have two subcases,

(i) $\{X_p^\dagger, X_p\}\,|\cdots p \cdots\rangle$

$$= (\chi_p^\dagger \chi_p + \chi_p \chi_p^\dagger) |\overset{m}{\cdots} p \cdots\rangle$$

$$= (-1)^m \chi_p^\dagger |\cdots p \cdots\rangle + 0 =$$

$$= (-1)^m (-1)^m |\cdots p \cdots\rangle = |\cdots p \cdots\rangle$$

(ii) $\{\chi_p^\dagger, \chi_p\} |\cdots p \cdots\rangle$

$$= \chi_p^\dagger \chi_p |\overset{m}{\cdots} p \cdots\rangle$$

$$+ \chi_p \chi_p^\dagger |\overset{m}{\cdots} p \cdots\rangle = (-1)^m \chi_p^\dagger |\cdots p \cdots\rangle$$

$$= (-1)^m (-1)^m |\cdots p \cdots\rangle = |\cdots p \cdots\rangle$$

In both cases,

$$\{\chi_p^\dagger, \chi_p\} |\rangle = |\rangle .$$

Thus,

$$\{\chi_p^\dagger, \chi_p\} = \mathbb{1} .$$

This means that, in general,

$$\{\chi_p^\dagger, \chi_q\} = \delta_{pq} .$$

assignment

~~①~~ ② & ③ can be analyzed in a similar manner ($p \neq q$, $p = q$; four and two subcases, respectively). As a matter of fact, ③ is a consequence of ② :

$$\{ X_p, X_q \} = 0$$

$$0 = \{ X_p, X_q \}^\dagger = \left(X_p X_q + X_q X_p \right)^\dagger$$

$$= (X_p X_q)^\dagger + (X_q X_p)^\dagger =$$

$$= X_q^\dagger X_p^\dagger + X_p^\dagger X_q^\dagger = \{ X_p^\dagger, X_q^\dagger \}.$$

Interesting consequences of anticommutation rules:

nilpotent

1. $X_p^2 = 0$, $(X_p^\dagger)^2 = 0$.

Indeed,

$$0 = \{X_p, X_p\} = X_p^2 + X_p^2 = 2X_p^2.$$

(also, $X_p X_q = -X_q X_p$, $X_{p_R} - X_{p_N} = (-1)^R (X_{p_1} - X_{p_N})$)

2. $N_p^2 = N_p$ (N_p is idempotent).

$$N_p^2 = (X_p^\dagger X_p)(X_p^\dagger X_p) = X_p^\dagger (X_p X_p^\dagger) X_p$$

$$= X_p^\dagger (1 - X_p^\dagger X_p) X_p = X_p^\dagger X_p$$

$$- (X_p^\dagger)^2 (X_p)^2 = X_p^\dagger X_p = N_p.$$

($(X_p^\dagger)^2 = 0$)

($N_p^\dagger = N_p$ of course)

(also, eigenvalues of N_p only 0 or 1)

3. $[N_p, N_q] = 0$

$$[N_p, N_q] = X_p^\dagger X_p X_q^\dagger X_q -$$

$$- X_q^\dagger X_q X_p^\dagger X_p =$$

$$= \chi_p^\dagger (\delta_{pq} - \chi_q^\dagger \chi_p) \chi_q$$

$$- \chi_q^\dagger (\delta_{pq} - \chi_p^\dagger \chi_q) \chi_p$$

$$= \delta_{pq} \chi_p^\dagger \chi_q - \chi_p^\dagger \chi_q^\dagger \chi_p \chi_q$$

$$- \delta_{pq} \chi_q^\dagger \chi_p + \chi_q^\dagger \chi_p^\dagger \chi_q \chi_p$$

$$= \delta_{pq} (\chi_p^\dagger \chi_p - \chi_p^\dagger \chi_p) = 0.$$

ess.

4. $[\chi_p, N_q] = \delta_{pq} \chi_p$

and $[\chi_p^\dagger, N_q] = -\delta_{pq} \chi_p^\dagger$.

$$[\chi_p, N_q] = \chi_p \chi_q^\dagger \chi_q - \chi_q^\dagger \chi_q \chi_p$$

$$= (\delta_{pq} - \chi_q^\dagger \chi_p) \chi_q - \chi_q^\dagger \chi_q \chi_p$$

$$= \delta_{pq} \chi_q - \chi_q^\dagger \chi_p \chi_q - \chi_q^\dagger \chi_q \chi_p$$

$$= \delta_{pq} \chi_q.$$

(-1)

$$[X_p^+, N_q] = [X_p^+, N_q^+] =$$
$$= [N_q, X_p]^+ = -[X_p, N_q]^+$$
$$= -\delta_{pq} X_p^+ .$$

5. Calculate an overlap of

$$S = \langle \{pq\} | \{rs\} \rangle \equiv \langle \hat{\mathcal{T}}_{pq} | \hat{\mathcal{T}}_{rs} \rangle .$$

Let us assume that $p<q$, $r<s$.

First, what is $|\{pq\}\rangle$, $|\{rs\}\rangle$?

$$|\{pq\}\rangle = X_p^+ |\{q\}\rangle = X_p^+ X_q^+ |0\rangle$$

(in the occ. # rep.:

$$|\{pq\}\rangle = |\overset{m=0}{\sim} \overset{n=0}{\sim} p \sim q \sim \rangle =$$
$$= X_p^+ | \sim p \sim q \sim \rangle =$$
$$= X_p^+ X_q^+ | \sim \underbrace{p \sim q}_{|0\rangle} \sim \rangle).$$

Similarly, $|\{rs\}\rangle = X_r^\dagger X_s^\dagger |0\rangle$.

Thus, (move p to the right)

$$S = \langle 0| X_q \overbrace{X_p X_r^\dagger} X_s^\dagger |0\rangle$$

$$= \langle 0| X_q (\delta_{pr} - X_r^\dagger X_p) X_s^\dagger |0\rangle$$

$$= \delta_{pr} \langle 0| X_q X_s^\dagger |0\rangle$$

$$- \langle 0| X_q X_r^\dagger \overbrace{X_p X_s^\dagger} |0\rangle$$

$$= \langle p|r\rangle \langle q|s\rangle$$

$$- \langle 0| X_q X_r^\dagger (\delta_{ps} - X_s^\dagger X_p)|0\rangle$$

$$= \langle p|r\rangle\langle q|s\rangle -$$

$$- \delta_{ps} \langle 0| X_q X_r^\dagger |0\rangle$$

$$+ \underbrace{\langle 0| X_q X_r^\dagger X_s^\dagger X_p |0\rangle}_{\text{"}0}$$

$$= \langle p|r\rangle\langle q|s\rangle - \langle p|s\rangle\langle q|r\rangle$$

$$= \begin{vmatrix} \langle p|r\rangle & \langle p|s\rangle \\ \langle q|r\rangle & \langle q|s\rangle \end{vmatrix}$$, a well-known result.

1.4. Operators in a second-quantized form:

In order to see how the operators looks like in a second-quantized form, we must learn how the one-body, two-body, etc. operators act on basis states

$$|\{n_1 - n_N\}\rangle \quad \text{or} \quad |1 - - p - \rangle.$$

~~Examples of one~~

One-body operator

1.4. Operators in a second quantized form.

We will be interested in particle-conserving operators describing many-fermion systems.

In general, these operators are sums of their various many-body components:

$$\hat{O} = \sum_{k=0}^{N} \hat{O}_k \,,$$

where each $\hat{O}_k$ is completely symmetric, i.e.,

$$[\hat{O}_k, P] = 0 \,, \quad P \in S_N \,,$$

the k-body operator

$$\hat{O}_k = \sum_{1 \le i_1 < i_2 < \ldots < i_k} \hat{o}_k(x_{i_1}, \ldots, x_{i_k}) \,.$$

Since operators $\hat{O}$ cannot change the symmetry of many-fermion functions,

$$[\hat{O}, R] = 0, \quad \forall R \in S_N \,.$$

This immediately implies that

$$\hat{O}_k(x_{R_{i_1}}, \ldots, x_{R_{i_k}}) = \hat{O}_k(x_{i_1}, \ldots, x_{i_k}).$$

Examples:

- $$\hat{Z} = \sum_{i=1}^{N} z(x_i),$$

atomic units →

$$z(x_i) = -\frac{1}{2}\Delta_i - \sum_{A=1}^{N_A} \frac{Z_A}{r_{Ai}}$$

This is a one-body operator

- $$\hat{V} = \sum_{i<j}^{N} v(i,j) = \sum_{i<j}^{N} v(x_i, x_j)$$

atomic units →

$$v(x_i, x_j) = \frac{1}{r_{ij}}$$

This is a two-body operator.

- $H = Z + V$ → some operators are sums of many-body components

$$\hat{\mu}_x = -\sum_{i=1}^{N} \overset{\text{electron charge}}{e} x_i \rightarrow \text{the } x\text{-component of the electronic dipole moment operator.}$$

We would like to learn how the general operator $\hat{Q}$ or its various $\hat{Q}_k$ components look like in a second-quantized form. In other words, we would like to know what happens when $\hat{Q}_k$ acts on $\overbrace{|\{p_1 \ldots p_N\}\rangle}^{\text{basis kets}}$ or $|\ldots np \ldots\rangle$.

In order to figure this out, we will apply $\hat{Q}_1, \hat{Q}_2, \ldots$ to basis states $|\{p_1 \ldots p_N\}\rangle$.

($\hat{Q}_0$ is a trivial case $\rightarrow \hat{Q}_0 = q_0 \rightarrow$ number).

We will proceed in a few steps (focusing on $\hat{O}_1, \hat{O}_2$):

Step 1 (lemma 1): (What is $|\{\rho_1 - \rho_N\}\rangle$ in terms of $X^\dagger$'s):

$$|\{\rho_1 - \rho_N\}\rangle \equiv X^\dagger_{\rho_1} X^\dagger_{\rho_2} \cdots X^\dagger_{\rho_N} |0\rangle$$

for $\rho_1 < \cdots < \rho_N$.

We have already seen this for $N=2$.
For other N, the argument is very similar:

$$|\{\rho_1 \rho_2 \cdots \rho_N\}\rangle = X^\dagger_{\rho_1} |\{\rho_2 \rho_3 \cdots \rho_N\}\rangle$$
$$= X^\dagger_{\rho_1} X^\dagger_{\rho_2} |\{\rho_3 \cdots \rho_N\}\rangle = \cdots = X^\dagger_{\rho_1} \cdots X^\dagger_{\rho_{N-1}} |\rho_N\rangle$$
$$= X^\dagger_{\rho_1} \cdots X^\dagger_{\rho_N} |0\rangle.$$

Thus, there is an isomorphism between Slater determinants

$$\Phi_{\rho_1 \cdots \rho_N}(x_1, \ldots, x_N) \equiv \langle x_1 \cdots x_N | \{\rho_1 \cdots \rho_N\}\rangle$$

and operator strings $X^\dagger_{\rho_1} \cdots X^\dagger_{\rho_N}$ acting on a vacuum state:

$$\Phi_{\rho_1 \cdots \rho_N}(x_1 \cdots x_N) \Leftrightarrow X^\dagger_{\rho_1} \cdots X^\dagger_{\rho_N} |0\rangle$$
for $\rho_1 < \cdots < \rho_N$.

Step 2 (lemma 2):

Let us consider a determinant

$\Phi_{q_1 \dots q_N}(x_1, \dots, x_N)$ obtained by permuting ordered indices $p_1 < \dots < p_N$ according to permutation:

$R = \begin{pmatrix} p_1 & \dots & p_N \\ q_{(=R)1} & & q_N \end{pmatrix}$ [q's are permuted p's].

Then, there is an isomorphism

$$\Phi_{q_1 \dots q_N}(x_1, \dots, x_N) \Leftrightarrow x^+_{q_1} \dots x^+_{q_N} |0\rangle.$$

Proof:

$$\Phi_{q_1 \dots q_N}(x_1 \dots x_N) = \Phi_{p_{R_1} \dots p_{R_N}}(x_1 \dots x_N)$$

$$= (-1)^R \Phi_{p_1 \dots p_N}(x_1 \dots x_N) \Leftrightarrow$$

$$\Leftrightarrow (-1)^R x^+_{p_1} \dots x^+_{p_N} |0\rangle \quad \begin{matrix} \text{anticomm.} \\ = \\ \text{rules} \end{matrix}$$

$$= x^+_{q_1} \dots x^+_{q_N} |0\rangle, \text{ since}$$

$$x^+_{p_i} x^+_{p_j} = - x^+_{p_j} x^+_{p_i}.$$

Step 3 (Lemma 3):

Let

$$\prod X^\dagger|0\rangle \equiv X^\dagger_{p_1} \cdots X^\dagger_{p_N}|0\rangle$$

$$\prod^{p_i} X^\dagger|0\rangle \equiv X^\dagger_{p_1} \cdots X^\dagger_{p_{i-1}} X^\dagger_{p_{i+1}} \cdots X^\dagger_{p_N}|0\rangle$$

removed $X^\dagger_{p_i}$

We have:

$$X_q \prod X^\dagger|0\rangle = \sum_{i=1}^{N} (-1)^{i-1} \delta_{q p_i} \prod^{p_i} X^\dagger|0\rangle$$

or, explicitly,

$$X_q X^\dagger_{p_1} \cdots X^\dagger_{p_N}|0\rangle = \sum_i (-1)^{i-1} \delta_{q p_i} X^\dagger_{p_1} \cdots X^\dagger_{p_{i-1}} X^\dagger_{p_{i+1}} \times \cdots X^\dagger_{p_N}|0\rangle.$$

Proof: (if none of p_i's equals q, we get zero right away).

Let $p_{k_1} < \cdots < p_{k_S}$ are those indices from among $p_1, \ldots, p_N$ that equal q,

$$p_{k_1} = p_{k_2} = \cdots = p_{k_S} = q.$$

We obtain,

$$X_q X^\dagger_{p_1} \cdots X^\dagger_{p_N} |0\rangle = \overbrace{X_q X^\dagger_{p_1} \cdots X^\dagger_{p_{k_1-1}}}^{k_1-1 \text{ times}} X^\dagger_{p_{k_1}} \cdots X^\dagger_{p_N} |0\rangle$$

$$= (-1)^{k_1-1} X^\dagger_{p_1} \cdots X^\dagger_{p_{k_1-1}} (X_q X^\dagger_{p_{k_1}}) X^\dagger_{p_{k_1+1}} \cdots X^\dagger_{p_N} |0\rangle$$

$$\overset{\text{anticomm.}}{=} (-1)^{k_1-1} X^\dagger_{p_1} \cdots X^\dagger_{p_{k_1-1}} X^\dagger_{p_{k_1+1}} \cdots X^\dagger_{p_N} |0\rangle$$

$$- (-1)^{k_1-1} X^\dagger_{p_1} \cdots X^\dagger_{p_{k_1-1}} X^\dagger_{p_{k_1}} X_q X^\dagger_{p_{k_1+1}} \cdots X^\dagger_{p_N} |0\rangle$$

$$= (-1)^{k_1-1} \prod^{p_{k_1}} X^\dagger |0\rangle$$

$$+ (-1)^{k_1} X^\dagger_{p_1} \cdots X^\dagger_{p_{k_1}} X_q \overbrace{X^\dagger_{p_{k_1+1}} \cdots X^\dagger_{p_{k_2-1}}}^{k_2-k_1-1 \text{ times}} X^\dagger_{p_{k_2}} \cdots X^\dagger_{p_N} |0\rangle$$

$$= (-1)^{k_1-1} \prod^{p_{k_1}} X^\dagger |0\rangle + (-1)^{k_2-1} \times$$

$$\times X^\dagger_{p_1} \cdots X^\dagger_{p_{k_2-1}} X_q X^\dagger_{p_{k_2}} X^\dagger_{p_{k_2+1}} \cdots X^\dagger_{p_N} |0\rangle$$

$$\overset{\text{anticomm. rules}}{=} (-1)^{k_1-1} \prod^{p_{k_1}} \chi^\dagger |0\rangle$$

$$+ (-1)^{k_2-1} \chi^\dagger_{p_1} \cdots \chi^\dagger_{p_{k_2-1}} \chi^\dagger_{p_{k_2+1}} \cdots \chi^\dagger_{p_N} |0\rangle$$

$$- (-1)^{k_2-1} \chi^\dagger_{p_1} \cdots \chi^\dagger_{p_{k_2-1}} \chi^\dagger_{p_{k_2}} \chi^\dagger_{q} \chi^\dagger_{p_{k_2+1}} \cdots \chi^\dagger_{p_N} |0\rangle$$

$$= (-1)^{k_1-1} \prod^{p_{k_1}} \chi^\dagger |0\rangle + (-1)^{k_2-1} \prod^{p_{k_2}} \chi^\dagger |0\rangle$$

$$+ (-1)^{k_2} \chi^\dagger_{p_1} \cdots \chi^\dagger_{p_{k_2}} \chi^\dagger_{q} \chi^\dagger_{p_{k_2}} \cdots \chi^\dagger_{p_N} |0\rangle$$

$$= \cdots = (-1)^{k_1-1} \prod^{p_{k_1}} \chi^\dagger |0\rangle +$$

$$+ (-1)^{k_2-1} \prod^{p_{k_2}} \chi^\dagger |0\rangle + \cdots + (-1)^{k-1} \prod^{p_k} \chi^\dagger |0\rangle$$

$$+ \underbrace{(-1)^N \chi^\dagger_{p_1} \cdots \chi^\dagger_{p_N} \chi^\dagger_{q} |0\rangle}_{\| \; 0}$$

$$= \sum_{m=1}^{5} (-1)^{k_m - 1} \prod^{p_{k_m}} X^\dagger |0\rangle$$

$$= \sum_{i=1}^{N} (-1)^{i-1} \sum_{q_{p_i}} \prod^{p_i} X^\dagger |0\rangle$$

etc.

Step 4 (Lemma 4):

$$X_r X_s \prod X^\dagger |0\rangle =$$

$$= \sum_{i<j}^{N} (-1)^{i+j} \delta_{r p_i} \delta_{s p_j} \prod^{p_i p_j} X^\dagger |0\rangle$$

$$+ \sum_{i>j}^{N} (-1)^{i+j-1} \delta_{r p_i} \delta_{s p_j} \prod^{p_i p_j} X^\dagger |0\rangle,$$

where $\prod^{p_i p_j} X^\dagger |0\rangle = X^\dagger_{p_1} \cdots \not{X}^\dagger_{p_i} \cdots \not{X}^\dagger_{p_j} \cdots X^\dagger_{p_N} |0\rangle$

for $i < j$ and

$\prod^{p_i p_j} X^\dagger |0\rangle = X^\dagger_{p_1} \cdots \not{X}^\dagger_{p_j} \cdots \not{X}^\dagger_{p_i} \cdots X^\dagger_{p_N} |0\rangle$

for $i > j$.

Proof:

$$X_r X_s \prod X^\dagger|0\rangle \overset{\text{Step 3 (Lemma 3)}}{=\!=} X_r \sum_j (-1)^{j-1} \delta_{sp_j} \prod^{p_j} X^\dagger|0\rangle$$

(j: jth place, $(N+1)$th p_j)

$$= \sum_j (-1)^{j-1} \delta_{sp_j} X_r (X^\dagger_{p_1} \cdots X^\dagger_{p_{j-1}} X^\dagger_{p_{j+1}} \cdots X^\dagger_{p_N})|0\rangle$$

$$\overset{\text{lemma 3}}{=\!=} \sum_{j=1}^{N} (-1)^{j-1} \delta_{sp_j} \Big\{ \sum_{i=1}^{j-1} (-1)^{i-1} \delta_{rp_i} \prod^{p_i p_j} X^\dagger|0\rangle$$

$$+ \sum_{i=j+1}^{N} (-1)^{i-2} \delta_{rp_i} \prod^{p_i p_j} X^\dagger|0\rangle \Big\}$$

$$= \sum_{i<j}^{N} (-1)^{i+j} \delta_{rp_i} \delta_{sp_j} \prod^{p_i p_j} X^\dagger|0\rangle$$

$$+ \sum_{i>j}^{N} (-1)^{i+j-1} \delta_{rp_i} \delta_{sp_j} \prod^{p_i p_j} X^\dagger|0\rangle$$

$$\vdots$$

Now, that we know how X_q and $X_r X_s$ act on $\prod X_i^\dagger |0\rangle$ (arbitrary boson state), we can prove the following formulas for the one- and two-body operators:

(I) If $\hat{O}_1 = \sum_{i=1}^{N} \hat{o}_1(x_i)$ is a one-body operator, then

$$\hat{O}_1 = \sum_{pq} \langle p|\hat{o}_1|q\rangle X_p^\dagger X_q$$

$$\left(\langle p|\hat{o}_1|q\rangle = \int \chi_p(\underline{x})^* \hat{o}_1(\underline{x}) \chi_q(\underline{x}) d\underline{x} \right)$$

(II) If $\hat{O}_2 = \sum_{i<j}^{N} \hat{o}_2(x_i, x_j)$ is a two-body operator, then

$$\hat{O}_2 = \frac{1}{2} \sum_{pqrs} \langle pq|\hat{o}_2|rs\rangle X_p^\dagger X_q^\dagger X_s X_r,$$

where

$$\langle pq|\hat{o}_2|rs\rangle = \int \chi_p^*(x_1) \chi_q^*(x_2) \hat{o}_2(x_1 x_2) \times$$

$$\times \psi_r(\underline{x}_1)\,\psi_s(\underline{x}_2)\,d\underline{x}_1\,d\underline{x}_2 \,.$$

Proof:

(I) Let us apply $\hat{Q}_1$ to an arbitrary Bose state $\langle x_1 \dots x_N | \{p_1 \dots p_N\}\rangle \equiv$

$$\equiv \Phi_{p_1 \dots p_N}(x_1, \dots, x_N) =$$

$$= \sqrt{N!}\,\mathcal{A}\left(\psi_{p_1}(x_1)\,\psi_{p_2}(x_2) \dots \psi_{p_N}(x_N)\right):$$

$$\hat{Q}_1\,\Phi_{p_1 \dots p_N}(x_1, \dots, x_N) \equiv$$

$$= \sqrt{N!}\;\hat{Q}_1\,\mathcal{A}\prod_{k=1}^{N}\psi_{p_k}(x_k) \qquad [\hat{Q}_1, \mathcal{A}] = 0 \;(\text{cf. p. 37}) \;=$$

$$= \sqrt{N!}\,\mathcal{A}\sum_{i=1}^{N}\hat{q}_1(x_i)\prod_{k=1}^{N}\psi_{p_k}(x_k)$$

$$= \sqrt{N!}\,\mathcal{A}\sum_{i}\hat{q}_1(x_i)\,\psi_{p_i}(x_i)\prod_{k(\neq i)}\psi_{p_k}(x_k)$$

Clearly (ψ_p's form a complete basis in $\mathcal{V}$),

$$\hat{q}_1(x_i)\,\psi_{p_i}(x_i) = \sum_{p=1}^{\infty} \langle p|\hat{q}_1|p_i\rangle \times \psi_p(x_i),$$

where $\langle p|\hat{q}_1|p_i\rangle = \langle \psi_p|\hat{q}_1|\psi_{p_i}\rangle$.

Thus,

$$\hat{Q}_1\,\Phi_{p_1\cdots p_N}(x_1\cdots x_N) =$$

$$= \sqrt{N!}\,\mathcal{A} \sum_{i,p} \langle p|\hat{q}_1|p_i\rangle\, \psi_p(x_i) \prod_{k(\neq i)} \psi_{p_k}(x_k)$$

$$= \sum_{i,p} \langle p|\hat{q}_1|p_i\rangle\, \sqrt{N!}\,\mathcal{A}\left(\psi_{p_1}(x_1)\cdots\psi_{p_{i-1}}(x_{i-1}) \times \psi_p(x_i)\,\psi_{p_{i+1}}(x_{i+1})\cdots\psi_{p_N}(x_N)\right)$$

$$= \sum_{i,p} \langle p|\hat{q}_1|p_i\rangle\, \Phi_{p_1\cdots p_{i-1}\,p\,p_{i+1}\cdots p_N}(x_1\cdots x_N).$$

Because of the equivalence between (lemma 2 (Step 2))

$\Phi_{q_1 \dots q_N}(x_1 \dots x_N)$ and $X^\dagger_{q_1} \dots X^\dagger_{q_N} |0\rangle$,

for any $q_1, \dots, q_N$, we can write (in the Fock space):

$$\hat{Q}_1 X^\dagger_{p_1} \dots X^\dagger_{p_N} |0\rangle = \sum_{i,p} \langle p | \hat{q}_1 | p_i \rangle \times X^\dagger_{p_1} \dots X^\dagger_{p_{i-1}} X^\dagger_p X^\dagger_{p_{i+1}} \dots X^\dagger_{p_N} |0\rangle$$

($i-1$ times)

or, in a more symbolic (compact) form:

$$\hat{Q}_1 \underbrace{\prod X^\dagger |0\rangle}_{\text{basis state}} = \sum_{i,p} \langle p | \hat{q}_1 | p_i \rangle (-1)^{i-1} X^\dagger_p \times \prod^{p_i} X^\dagger |0\rangle =$$

$$= \sum_{i,p,q} \langle p | \hat{q}_1 | q \rangle (-1)^{i-1} \delta_{q p_i} X^\dagger_p \prod^{p_i} X^\dagger |0\rangle$$

In other words,

$$\hat{O}_1 \left(\prod X^\dagger |0\rangle \right) = \sum_{pq} \langle p | \hat{o}_1 | q \rangle X^\dagger_p \times$$

$$\times \left\{ \sum_i (-1)^{i-1} \delta_{qp_i} \prod^{p_i} X^\dagger |0\rangle \right\} =$$

$$\underset{(\text{step } 3)}{\overset{\text{lemma } 3}{=}} \sum_{pq} \langle p | \hat{o}_1 | q \rangle X^\dagger_p \underbrace{X_q \left(\prod X^\dagger |0\rangle \right)}_{\{\dots\}}$$

Since $\prod X^\dagger |0\rangle$ is an arbitrary basis state, we obtain

$$\hat{O}_1 = \sum_{pq} \langle p | \hat{o}_1 | q \rangle X^\dagger_p X_q .$$

$$\vdots$$

(II) As in the case of $\hat{O}_1$, let us apply $\hat{O}_2$ to $\langle x_1 \dots x_N | \{p_1 \dots p_N\} \rangle \equiv$

$\equiv \Phi_{p_1 \dots p_N}(x_1 \dots x_N)$. We obtain,

$$\hat{O}_2 \, \Phi_{p_1 \cdots p_N}(x_1, \ldots, x_N) = \frac{1}{2} \sum_{i \neq j} \hat{o}_2(x_i, x_j)$$

$$\times \sqrt{N!}\, \mathcal{A}\left(\prod_{k=1}^{N} \chi_{p_k}(x_k) \right), \quad \text{where}$$

we used the fact that

$$\hat{o}_2(x_i, x_j) = \hat{o}_2(x_j, x_i), \text{ so that}$$

$$\hat{O}_2 = \frac{1}{2} \sum_{i \neq j} \hat{o}_2(x_i, x_j).$$

Since $[\hat{O}_2, \mathcal{A}] = 0$, we can write,

$$\hat{O}_2 \, \Phi_{p_1 \cdots p_N}(x_1 \ldots x_N) = \frac{1}{2} \sqrt{N!}\, \mathcal{A} \sum_{i \neq j} \hat{o}_2(x_i, x_j)$$

$$\times \prod_{k=1}^{N} \chi_{p_k}(x_k) = \frac{1}{2} \sqrt{N!}\, \mathcal{A} \sum_{i \neq j} \hat{o}_2(x_i, x_j) \times$$

$$\times \chi_{p_i}(x_i)\, \chi_{p_j}(x_j) \prod_{k(\neq i,j)}^{N} \chi_{p_k}(x_k).$$

Now, from the completeness of $\{\chi_p\}$, we obtain

$$\hat{O}_2(x_i, x_j)\,\psi_{p_i}(x_i)\,\psi_{p_j}(x_j) =$$

$$= \sum_{p,q} \langle pq|\hat{o}_2|p_i p_j\rangle\, \psi_p(x_i)\,\psi_q(x_j).$$

Thus,

$$\hat{O}_2\,\Phi_{p_1\cdots p_N}(x_1\cdots x_N) = \frac{1}{2}\sqrt{N!}\,\mathcal{A} \sum_{i\neq j} \sum_{p,q} \langle pq|\hat{o}_2|p_i p_j\rangle$$

$$\times\ \psi_p(x_i)\,\psi_q(x_j) \prod_{k(\neq i,j)}^{N} \psi_{p_k}(x_k)$$

$$= \frac{1}{2}\sum_{i<j} \sum_{p,q} \langle pq|\hat{o}_2|p_i p_j\rangle$$

$$\sqrt{N!}\,\mathcal{A}\{\psi_{p_1}(x_1)\cdots\psi_{p_{i-1}}(x_{i-1})\,\psi_p(x_i)\,\psi_{p_{i+1}}(x_{i+1})\cdots$$

$$\cdots\psi_{p_{j-1}}(x_{j-1})\,\psi_q(x_j)\,\psi_{p_{j+1}}(x_{j+1})\cdots\psi_{p_N}(x_N)\}$$

$$+\ \frac{1}{2}\sum_{i>j}\sum_{p,q}\langle pq|\hat{o}_2|p_i p_j\rangle\,\sqrt{N!}\,\mathcal{A}\{\psi_{p_1}(x_1)\cdots$$

$$\cdots\psi_{p_{j-1}}(x_{j-1})\,\psi_q(x_j)\,\psi_{p_{j+1}}(x_{j+1})\cdots\psi_{p_{i-1}}(x_{i-1})\,\psi_p(x_i)\,\psi_{p_{i+1}}(x_{i+1})\cdots$$

$\cdots \psi_{p_N}(x_N)\}$. = In other words,

$$\hat{O}_2 \Phi_{p_1 \cdots p_N}(x_1 \cdots x_N) = \frac{1}{2} \sum_{i<j} \sum_{pq} \langle pq|\hat{o}_2|p_i p_j\rangle$$

$$\times \Phi_{p_1 \cdots p_{i-1} p\, p_{i+1} \cdots p_{j-1} q\, p_{j+1} \cdots p_N}(x_1 \cdots x_N)$$

$$+ \frac{1}{2} \sum_{i>j} \sum_{pq} \langle pq|\hat{o}_2|p_i p_j\rangle \times$$

$$\times \Phi_{p_1 \cdots p_{j-1} q\, p_{j+1} \cdots p_{i-1} p\, p_{i+1} \cdots p_N}(x_1 \cdots x_N) .$$

Because of the equivalence of Φ's and $\Pi X^\dagger|0\rangle$, (step or Lemma 2), we can write (in the Fock space),

$$\hat{O}_2 \Pi X^\dagger|0\rangle = \frac{1}{2} \sum_{i<j} \sum_{pq} \langle pq|\hat{o}_2|p_i p_j\rangle \times$$

($i-1$ times) ($j-2$ times)

$$\times X^\dagger_{p_1} \cdots X^\dagger_{p_{i-1}} X^\dagger_p X^\dagger_{p_{i+1}} \cdots X^\dagger_{p_{j-1}} X^\dagger_q X^\dagger_{p_{j+1}} \cdots X^\dagger_{p_N}|0\rangle$$

$$+ \frac{1}{2} \sum_{i>j} \sum_{pq} \langle pq|\hat{o}_2|p_i p_j\rangle \times$$

$$\times X^\dagger_{p_1} \cdots X^\dagger_{p_{j-1}} X^\dagger_q X^\dagger_{p_{j+1}} \cdots X^\dagger_{p_{i-1}} X^\dagger_p X^\dagger_{p_{i+1}} \cdots X^\dagger_{p_N}|0\rangle$$

$$= \frac{1}{2} \sum_{i<j} \sum_{pq} \langle pq|\hat{O}_2|p_i p_j\rangle (-1)^{i+j-2} X_p^\dagger X_q^\dagger$$

$$\times \prod^{p_i p_j} X^\dagger|0\rangle \quad +$$

$$+ \frac{1}{2} \sum_{i<j} \sum_{pq} \langle pq|\hat{O}_2|p_i p_j\rangle (-1)^{j+i-2} X_q^\dagger X_p^\dagger$$

$$\times \prod^{p_i p_j} X^\dagger|0\rangle \,.$$

Since $X_q^\dagger X_p^\dagger = -X_p^\dagger X_q^\dagger$, we obtain,

$$\hat{O}_2 \prod X^\dagger|0\rangle = \frac{1}{2} \sum_{i<j} \sum_{pq} \langle pq|\hat{O}_2|p_i p_j\rangle$$

$$\times (-1)^{i+j-1} X_p^\dagger X_q^\dagger \prod^{p_i p_j} X^\dagger|0\rangle$$

$$+ \frac{1}{2} \sum_{i<j} \sum_{pq} \langle pq|\hat{O}_2|p_i p_j\rangle (-1)^{i+j} X_p^\dagger X_q^\dagger$$

$$\times \prod^{p_i p_j} X^\dagger|0\rangle \quad =$$

$$= \frac{1}{2} \sum_{i<j} \sum_{pq} \sum_{rs} \langle pq|\hat{o}_2|rs\rangle$$

$$\times (-1)^{i+j-1} \delta_{rp_i} \delta_{sp_j} \; X_p^\dagger X_q^\dagger \prod p_i p_j X^\dagger|0\rangle$$

$$+ \frac{1}{2} \sum_{i>j} \sum_{pq} \sum_{rs} \langle pq|\hat{o}_2|rs\rangle (-1)^{i+j}$$

$$\times \delta_{rp_i} \delta_{sp_j} \; X_p^\dagger X_q^\dagger \prod p_i p_j X^\dagger|0\rangle$$

$$= \frac{1}{2} \sum_{pqrs} \langle pq|\hat{o}_2|rs\rangle \; X_p^\dagger X_q^\dagger \; \times$$

$$\times \Big\{ \sum_{i<j} (-1)^{i+j-1} \delta_{rp_i} \delta_{sp_j} \prod p_i p_j X^\dagger|0\rangle$$

$$+ \sum_{i>j} (-1)^{i+j} \delta_{rp_i} \delta_{sp_j} \prod p_i p_j X^\dagger|0\rangle \Big\}$$

$$\overset{\text{lemma 4}}{\underset{(\text{step 4})}{=}} \frac{1}{2} \sum_{pqrs} \langle pq|\hat{o}_2|rs\rangle \; X_p^\dagger X_q^\dagger \; \times$$

$$\times \underbrace{(-X_r X_s)}_{i} \prod X^\dagger|0\rangle \quad =$$

$$X_s X_r$$

$$= \frac{1}{2} \sum_{pqrs} \langle pq|\hat{o}_2|rs\rangle \, X_p^\dagger X_q^\dagger X_s X_r \prod X^\dagger|0\rangle$$

Thus,

$$\hat{O}_2 \prod X^\dagger|0\rangle = \frac{1}{2} \sum_{pq,rs} \langle pq|\hat{o}_2|rs\rangle \times X_p^\dagger X_q^\dagger X_s X_r \prod X^\dagger|0\rangle.$$

Since $\prod X^\dagger|0\rangle$ is an arbitrary basis state in $\mathcal{F}$, we can finally write

$$\hat{O}_2 = \frac{1}{2} \sum_{pqrs} \langle pq|\hat{o}_2|rs\rangle X_p^\dagger X_q^\dagger X_s X_r.$$

∴

SUMMARY:

$\hat{O}_1 = \sum_{i=1}^{N} \hat{o}_1(x_i)$ becomes

$\hat{O}_1 = \sum_{pq} \langle p|\hat{o}_1|q\rangle X_p^\dagger X_q$.

$\hat{O}_2 = \frac{1}{2} \sum_{i \neq j} \hat{o}_2(x_i, x_j)$ becomes

$\hat{O}_2 = \frac{1}{2} \sum_{pqrs} \langle pq|\hat{o}_2|rs\rangle X_p^\dagger X_q^\dagger X_s X_r$.

In general, the first-quantized form of the k-body operator,

$$\hat{O}_k = \sum_{i_1<\dots<i_k} \hat{o}_k(x_{i_1}\dots x_{i_k}) =$$

$$= \frac{1}{k!} \sum_{i_1\neq\dots\neq i_k} \hat{o}_k(x_{i_1}\dots x_{i_k}) \,,$$

is replaced in the language of second quantization by

$$\hat{O}_k = \frac{1}{k!} \sum_{\substack{p_1\dots p_k \\ q_1\dots q_k}} \langle p_1\dots p_k|\hat{o}_k|q_1\dots q_k\rangle$$

$$\times \chi^\dagger_{p_1}\dots\chi^\dagger_{p_k}\chi_{q_k}\dots\chi_{q_1} \,,$$

where

$$\langle p_1\dots p_k|\hat{o}_k|q_1\dots q_k\rangle = \int \varphi^*_{p_1}(x_1)\dots\varphi^*_{p_k}(x_k)$$

$$\times \hat{o}_k\,\varphi_{q_1}(x_1)\dots\varphi_{q_k}(x_k)\,dx_1\dots dx_k \,.$$

Another form (useful for the so-called Hugenholtz diagrams):

$$\hat{O}_k = \left(\frac{1}{k!}\right)^2 \sum_{\substack{p_1 \dots p_k \\ q_1 \dots q_k}} \langle p_k \dots p_k | \hat{o}_k | q_1 \dots q_k \rangle_A \times X^+_{p_1} \dots X^+_{p_k} X_{q_k} \dots X_{q_1} , \quad (\star)$$

where

$$\langle p_1 \dots p_k | \hat{o}_k | q_1 \dots q_k \rangle_A =$$

$$= \sum_{R \in \mathcal{S}_k} (-1)^R \langle p_1 \dots p_k | \hat{o}_k | q_{R_1} \dots q_{R_k} \rangle$$

In particular,

$$\hat{O}_2 = \frac{1}{4} \sum_{pqrs} \langle pq | \hat{o}_2 | rs \rangle_A \times X^+_p X^+_q X_s X_r ,$$

where $\langle pq | \hat{o}_2 | rs \rangle_A = \langle pq | \hat{o}_2 | rs \rangle - \langle pq | \hat{o}_2 | sr \rangle .$

Proof of (★):

$$\left(\frac{1}{k!}\right)^2 \sum_{\substack{p_1 \dots p_k \\ q_1 \dots q_k}} \langle p_1 \dots p_k | \hat{O}_k | q_1 \dots q_k \rangle_A \; X^\dagger_{p_1} \dots X^\dagger_{p_k} X_{q_k} \dots X_{q_1}$$

$$= \left(\frac{1}{k!}\right)^2 \sum_{\substack{p_1 \dots p_k \\ q_1 \dots q_k}} \sum_{R \in S_k} (-1)^R \langle p_k \dots p_k | \hat{O}_k | q_{R_1} \dots q_{R_k} \rangle \quad \text{(permutation of } q_1 \dots q_k\text{)}$$

$$\times X^\dagger_{p_1} \dots X^\dagger_{p_k} X_{q_k} \dots X_{q_1} =$$

$$= \left(\frac{1}{k!}\right)^2 \sum_{R \in S_k} \sum_{\substack{p_1 \dots p_k \\ q_{R_1} \dots q_{R_k}}} \langle p_1 \dots p_k | \hat{O}_k | q_{R_1} \dots q_{R_k} \rangle$$

$$\times X^\dagger_{p_1} \dots X^\dagger_{p_k} X_{q_{R_k}} \dots X_{q_{R_1}}$$, where we used the fact that the signs of $\binom{1 \dots k}{R_1 \dots R_k}$ and $\binom{1 \dots k}{R_1^{-1} \dots R_k^{-1}}$ are identical. Since $q_{R_1}, \dots, q_{R_k}$ for a given R give us all possible values of $q_1, \dots, q_k$, we can write

$$\left(\frac{1}{k!}\right)^2 \sum_{\substack{p_1 \dots p_k \\ q_1 \dots q_k}} \langle p_1 \dots p_k | \hat{q}_k | q_1 \dots q_k \rangle_A \, X^\dagger_{p_1} \dots X^\dagger_{p_k} X_{q_k} \dots X_{q_1}$$

$$= \left(\frac{1}{k!}\right)^2 \sum_{R \in S_k} \sum_{\substack{p_1 \dots p_k \\ q_1 \dots q_k}} \langle p_1 \dots p_k | \hat{o}_k | q_1 \dots q_k \rangle$$

$$\times X^\dagger_{p_1} \dots X^\dagger_{p_k} X_{q_k} \dots X_{q_1} =$$

$$= \left(\frac{1}{k!}\right)^2 \cdot k! \sum_{\substack{p_1 \dots p_k \\ q_1 \dots q_k}} \langle p_1 \dots p_k | \hat{q}_k | q_1 \dots q_k \rangle$$

$$\times X^\dagger_{p_1} \dots X^\dagger_{p_k} X_{q_k} \dots X_{q_1} = \hat{O}_k$$

$\therefore$

Examples: ① The number operator: $N = \sum_p X^\dagger_p X_p$

② The Hamiltonian, $H = Z + V$,

$$Z = \sum_{p,q} \langle p | \hat{z} | q \rangle X^\dagger_p X_q ,$$

$$V = \frac{1}{2} \sum_{pq} \langle pq | v | rs \rangle X^\dagger_p X^\dagger_q X_s X_r$$

$$= \frac{1}{4} \sum_{pqrs} \langle pq | v | rs \rangle_A X^\dagger_p X^\dagger_q X_s X_r .$$

2. Fermi vacuum, normal products, contractions and normal product with contractions (relative to Fermi vacuum)

In the single-reference MBPT, we will be choosing one of the determinants (typically, the determinant that dominates in the wave function) as the zeroth-order state. This state will also serve as the Fermi vacuum, a reference determinant for constructing correlated many-fermion wave functions. We will designate it as $|\Phi_0\rangle$.

Let us reorder the single-particle states such that the first N of them are occupied in $|\Phi_0\rangle$, so that

$$|\Phi_0\rangle = X_1^\dagger \cdots X_N^\dagger |0\rangle = \prod_{i=1}^{N} X_i^\dagger |0\rangle. \quad (1)$$

We will use the notation in which $i, j, \ldots$ are single-particle states occupied in $|\Phi_0\rangle$ (we will call them hole states), $a, b, \ldots$ are single-particle states unoccupied in $|\Phi_0\rangle$ (we will call them particle states) and $p, q, \ldots$ are generic labels used if the particle-hole nature of a given single-particle state is not specified.

The concept of the Fermi vacuum is very useful in representing many-fermion states, especially when one of the Slater determinants dominates the CI expansion,

$$|\Psi\rangle = \sum_{p_1<\cdots<p_N} c_{p_1\cdots p_N} |\Phi_{p_1\cdots p_N}\rangle$$

$$= \sum_{p_1<\cdots<p_N} c_{p_1\cdots p_N} |\{p_1 \cdots p_N\}\rangle . \qquad (2)$$

Choosing this determinant as the Fermi vacuum state ($|\Phi_0\rangle$), we can write

$$|\{1\cdots(i-1)\,a\,(i+1)\cdots N\}\rangle = X_a^\dagger X_i |\{1\cdots(i-1)\,i\,(i+1)\cdots N\}\rangle$$

(i replaced by a)

$$= X_a^\dagger X_i |\{1\cdots N\}\rangle$$

$$= X_a^\dagger X_i |\Phi_0\rangle , \qquad (3)$$

where $|\Phi_0\rangle$ consists of single-particle states 1 through N, for all SINGLY EXCITED (1p-1h) determinants, designated as $|\Phi_i^a\rangle$. Similarly,

i replaced by a $\quad$ j replaced by b

$$|\{1 \cdots (i-1)\, a\, (i+1) \cdots (j-1)\, b\, (j+1) \cdots N\}\rangle$$

$$= X_a^\dagger X_i X_b^\dagger X_j |\{1 \cdots (i-1)\, i\, (i+1) \cdots (j-1)\, j\, (j+1) \cdots N\}\rangle$$

$$= X_a^\dagger X_i X_b^\dagger X_j |\{1 \cdots N\}\rangle$$

$$= X_a^\dagger X_i X_b^\dagger X_j |\Phi_0\rangle \qquad (4)$$

for all DOUBLY EXCITED $(2p\text{-}2h)$ determinants, designated as $|\Phi_{ij}^{ab}\rangle$.

In general,

$$|\Phi_{i_1 \cdots i_n}^{a_1 \cdots a_n}\rangle = X_{a_1}^\dagger X_{i_1} \cdots X_{a_n}^\dagger X_{i_n} |\Phi_0\rangle$$

$$= \prod_{q=1}^{n} X_{a_q}^\dagger X_{i_q} |\Phi_0\rangle \qquad (5)$$

for n-tuply excited $(np\text{-}nh)$ determinants.

Note that we can also write

$$|\Phi_{i_1 \cdots i_n}^{a_1 \cdots a_n}\rangle = X_{a_1}^\dagger \cdots X_{a_n}^\dagger X_{i_n} \cdots X_{i_1} |\Phi_0\rangle \qquad (6)$$

It is also useful to introduce the elementary excitation operators,

$$E_{i_1 \cdots i_n}^{a_1 \cdots a_n} = \prod_{q=1}^{n} X_{a_q}^\dagger X_{i_q} = \prod_{q=1}^{n} E_{i_q}^{a_q} \qquad (7)$$

Where

$$E_i^a = X_a^\dagger X_i \,, \tag{8}$$

so that

$$E_{i_1 \cdots i_n}^{a_1 \cdots a_n} |\Phi_0\rangle = |\Phi_{i_1 \cdots i_n}^{a_1 \cdots a_n}\rangle \,. \tag{9}$$

We can now rewrite Eq. (2) as follows:

$$|\Psi\rangle = c_0 |\Phi_0\rangle + \sum_{a,i} c_a^i |\Phi_i^a\rangle + \sum_{a<b,\, i<j} c_{ab}^{ij} |\Phi_{ij}^{ab}\rangle + \cdots$$

$$= c_0 |\Phi_0\rangle + \sum_{n=1}^{N} \sum_{\substack{a_1<\cdots<a_n \\ i_1<\cdots<i_n}} c_{a_1 \cdots a_n}^{i_1 \cdots i_n} |\Phi_{i_1 \cdots i_n}^{a_1 \cdots a_n}\rangle \tag{10}$$

where

$$c_{a_1 \cdots a_n}^{i_1 \cdots i_n} = \langle \Phi_{i_1 \cdots i_n}^{a_1 \cdots a_n} | \Psi \rangle \tag{11}$$

are the corresponding CI coefficients.

Note that, for example,

$$|\Phi_{ij}^{ab}\rangle = -|\Phi_{ji}^{ab}\rangle = -|\Phi_{ij}^{ba}\rangle = |\Phi_{ji}^{ba}\rangle \,,$$

i.e.,

the $|\Phi^{a_1 \cdots a_n}_{i_1 \cdots i_n}\rangle$ determinants and the corresponding CI coefficient $C^{i_1 \cdots i_n}_{a_1 \cdots a_n}$ are antisymmetric with respect to permutations of $i_1, \ldots, i_n$ and $a_1, \ldots, a_n$.

Thus, we can also write

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{n=1}^{N} C_n|\Phi_0\rangle = (c_0 + \hat{C})|\Phi_0\rangle, \quad (12)$$

where

$$\hat{C} = \sum_{n=1}^{N} C_n, \quad (13)$$

with

$$\hat{C}_n|\Phi_0\rangle = \sum_{\substack{a_1 < \cdots < a_n \\ i_1 < \cdots < i_n}} C^{i_1 \cdots i_n}_{a_1 \cdots a_n} |\Phi^{a_1 \cdots a_n}_{i_1 \cdots i_n}\rangle = \left(\frac{1}{n!}\right)^2 \sum_{\substack{i_1, \ldots, i_n \\ a_1, \ldots, a_n}} C^{i_1 \cdots i_n}_{a_1 \cdots a_n} |\Phi^{a_1 \cdots a_n}_{i_1 \cdots i_n}\rangle. \quad (14)$$

For C_n itself, we can write,

$$C_n = \left(\frac{1}{n!}\right)^2 \sum_{\substack{i_1, \ldots, i_n \\ a_1, \ldots, a_n}} C^{i_1 \cdots i_n}_{a_1 \cdots a_n} \Sigma^{a_1 \cdots a_n}_{i_1 \cdots i_n}. \quad (15)$$

This allows to give a many-fermion state $|\Psi\rangle$ a compact form, which helps one formulate single-reference CI, MBPT, and CC (coupled-cluster) methods,

$$|\Psi\rangle = \Omega |\Phi_0\rangle, \tag{16}$$

where

$$\Omega = C_0 + C, \tag{17}$$

with C given the many-body form consistent with the particle-hole formalism,

CI excitation operator →

$$C = \sum_{n=1}^{N} C_n, \tag{18}$$

np-nh or n-body component of C →

$$C_n = \left(\frac{1}{n!}\right)^2 \sum_{\substack{i_1,\ldots,i_n \\ a_1,\ldots,a_n}} C_{a_1,\ldots,a_n}^{i_1,\ldots,i_n} \Sigma_{i_1,\ldots,i_n}^{a_1,\ldots,a_n}, \tag{19}$$

elementary excitation operators →

$$\Sigma_{i_1,\ldots,i_n}^{a_1,\ldots,a_n} = X_{a_1}^{\dagger} \cdots X_{a_n}^{\dagger} X_{i_n} \cdots X_{i_1} = \prod_{q=1}^{n} X_{a_q}^{\dagger} X_{i_q}, \tag{20}$$

In the FCI case, n runs from 1 to N, in truncated CI

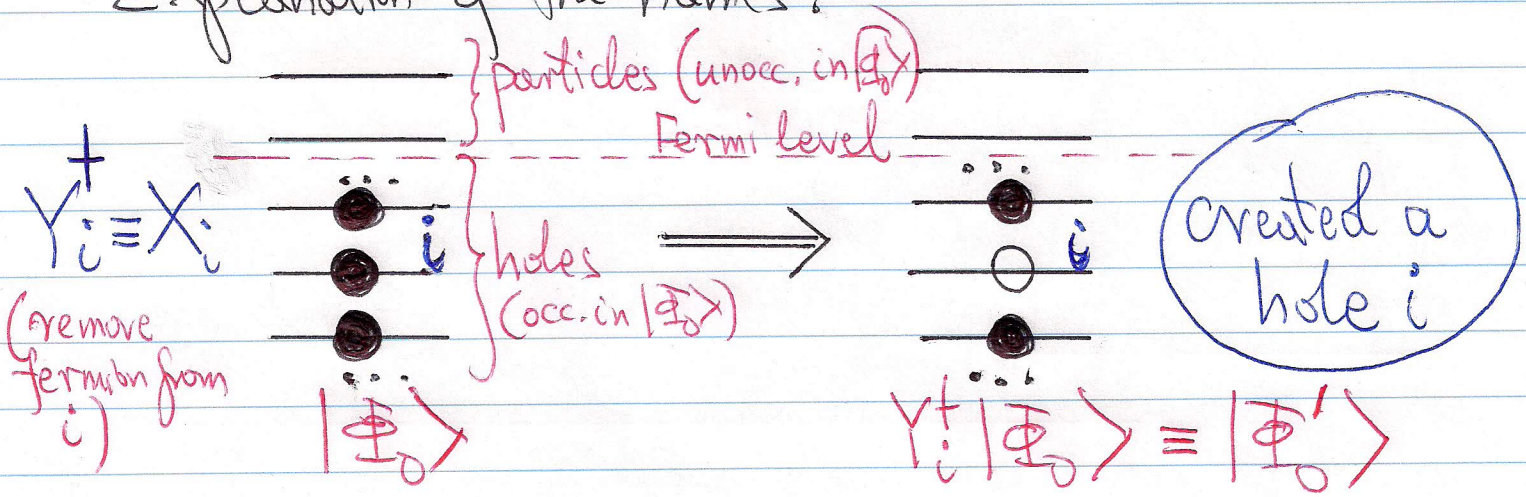
methods, we sum over n from 1 to M < N (typically). With this notation in mind we define particle--hole creation and annihilation operators,

$$Y_i = X_i^\dagger \,, \quad Y_i^\dagger = X_i \quad \text{(hole operators)},$$
$$Y_a = X_a \,, \quad Y_a^\dagger = X_a^\dagger \quad \text{(particle operators)}. \tag{21}$$

Alternatively,

$$Y_p = \begin{cases} X_p^\dagger & \text{for } p = i \\ X_p & \text{for } p = a \end{cases}; \quad Y_p^\dagger = \begin{cases} X_p & \text{for } p = i \\ X_p^\dagger & \text{for } p = a \end{cases}. \tag{22}$$

Explanation of the names:



Clearly, $Y_i |\Phi_0'\rangle = X_i^\dagger |\Phi_0'\rangle = |\Phi_0\rangle$

(annihilated a hole).

↑ putting back fermion in i.

Y and $Y^\dagger$ operators have properties analogous to X and $X^\dagger$ if we replace the free vacuum state $|0\rangle$ by the Fermi vacuum state $|\Phi_0\rangle$. In particular,

(1) $Y_\rho |\Phi_0\rangle = 0$ (just like $X_\rho |0\rangle = 0$).

Indeed, if $\rho = i$ $(i = 1, \dots, N)$,

$$Y_i |\Phi_0\rangle = X_i^\dagger |\Phi_0\rangle = X_i^\dagger |\{1 \dots N\}\rangle = 0.$$

If $\rho = a$ $(a = N+1, \dots)$,

$$Y_a |\Phi_0\rangle = X_a |\Phi_0\rangle = X_a |\{1 \dots N\}\rangle = 0.$$

(2) $\{Y_\rho, Y_q\} = 0$, $\{Y_\rho^\dagger, Y_q^\dagger\} = 0$,

$\{Y_\rho, Y_q^\dagger\} = \delta_{\rho q}$ (cf. the analogous anticommutation rules for X and $X^\dagger$).

We now introduce normal products (relative to the Fermi vacuum $|\Phi_0\rangle$). Let Y_ρ be Y_ρ or $Y_\rho^\dagger$. We define

↓ normal product of $M_1, \dots, M_m$

$$N[M_1 \cdots M_m] = (-1)^R Y^\dagger_{p_{R_1}} \cdots Y^\dagger_{p_{R_\lambda}} Y_{p_{R_{\lambda+1}}} \cdots Y_{p_{R_m}} \quad (23)$$

where

$$R = \begin{pmatrix} 1 & 2 & \cdots & m \\ R_1 & R_2 & \cdots & R_m \end{pmatrix}$$

is the permutation that places operators $Y^\dagger$ before operators Y. For $m=0$, we define

$$N[\emptyset] = 1 \quad \text{(unit operator)} \quad (24)$$

Example:

$$N[X^\dagger_i X_j X^\dagger_a] = N[Y_i Y^\dagger_j Y^\dagger_a] = Y^\dagger_j Y^\dagger_a Y_i$$

$$= X_j X^\dagger_a X^\dagger_i = -X^\dagger_a X_j X^\dagger_i .$$

(0 → j is never a)

Properties of $N[\dots]$:

- $N[M] = M$
- $N[N[M_1 \cdots M_m]] = N[M_1 \cdots M_m]$ (idempotent)

In particular,

$$N[Y^\dagger_{p_1} \cdots Y^\dagger_{p_\lambda} Y_{p_{\lambda+1}} \cdots Y_{p_m}] = Y^\dagger_{p_1} \cdots Y^\dagger_{p_\lambda} Y_{p_{\lambda+1}} \cdots Y_{p_m} . \quad (25)$$

- $$N[M_{R_1} \cdots M_{R_m}] = (\mathcal{A})^R N[M_1 \cdots M_m],$$

where $R = \begin{pmatrix} 1 & \cdots & m \\ R_1 & \cdots & R_m \end{pmatrix}$.

In particular, $N[M_2 M_1] = -N[M_1 M_2]$.

Contractions:

$$\overbrace{M_1 M_2} = M_1 M_2 - N[M_1 M_2]. \quad (26)$$

It is easy to see that the only contraction type that has a chance to be nonzero is

$$\overbrace{Y_p Y_q^\dagger} = \delta_{pq}. \quad (27)$$

All other types are zero. In the case of X and $X^\dagger$ operators, the only contraction types that can be nonzero are

$$\overbrace{X_i^\dagger X_j} = \overbrace{Y_i^\dagger Y_j} = \delta_{ij}, \quad \overbrace{X_a X_b^\dagger} = \overbrace{Y_a Y_b^\dagger} = \delta_{ab}. \quad (28)$$

Normal products with contractions:

$$N[M_1 \cdots \overbrace{M_{p_1} \cdots M_{q_1}} \cdots \overbrace{M_{p_\lambda} \cdots M_{q_\lambda}} \cdots M_m] \qquad (29)$$

$$= (-1)^R \overbrace{M_{p_1} M_{q_1}} \cdots \overbrace{M_{p_\lambda} M_{q_\lambda}} N[M_{r_1} \cdots M_{r_\rho}],$$

where

$$R = \begin{pmatrix} 1\,2 \cdots (2\lambda-1)(2\lambda)\,(2\lambda+1) \cdots m \\ p_1 q_1 \cdots p_\lambda\, q_\lambda\, r_1 \cdots r_\rho \end{pmatrix},$$

with $2\lambda + \rho = m$. Since $\overbrace{M_1 M_2}$ is generally not the same as $\overbrace{M_2 M_1}$, the order in which contracted pairs $\overbrace{M_p M_q}$ appear in Eq. (29) cannot be altered.

Example:

$$N[\overbrace{X_p X_q X_r^\dagger X_s^\dagger} X_t X_u^\dagger]$$

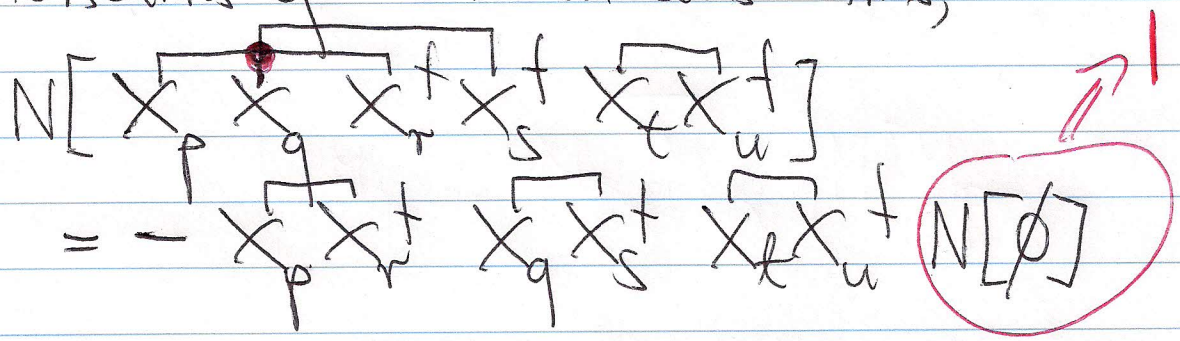
$$= - \overbrace{X_p X_r^\dagger}\; X_q X_s^\dagger\, N[X_t X_u^\dagger]$$

$$(R = \begin{pmatrix} p & q & r & s & t & u \\ p & r & q & s & t & u \end{pmatrix} = (p)(\underbrace{qr}_{\text{solid}})(s)(t)(u)).$$

To determine the above expression further, one needs to know if p, q, r, s, t, u are holes or particles.

Observation: for a group of fully contracted operators, the sign is determined by counting

intersections of contraction lines. Thus,



3. Wick's theorem.

We can prove that

$$M_1 \cdots M_m = N[M_1 \cdots M_m] + \sum_{1 \le p < q \le m} N[M_1 \cdots \overbrace{M_p \cdots M_q} \cdots M_m] \quad \text{(single contractions)}$$

$$+ \sum_{\substack{p_1 < q_1,\ p_2 < q_2 \\ p_1 < p_2,\ q_1 \neq q_2}} N[M_1 \cdots \overbrace{M_{p_1} \cdots M_{q_1} \cdots \overbrace{M_{p_2} \cdots M_{q_2}}} \cdots M_m] \quad \text{(double contractions)} \tag{30}$$

$+ \cdots$. [WICK'S THEOREM]

If some operators in $M_1 \cdots M_m$ are already in normal-product form (inside $N[\cdots]$), contractions of such operators can be skipped (generalized Wick's theorem). This is because

$$\overbrace{V_p V_q} = \overbrace{V_p^\dagger V_q} = \overbrace{V_p V_q^\dagger} = 0 .$$

Useful consequences of Wick's theorem.

- $$\langle \Phi_0 | M_1 \cdots M_{2m} | \Phi_0 \rangle$$
$$= \sum_{\substack{\text{fully contracted} \\ \text{terms (f.c.)}}} \langle \Phi_0 | N[M_1 \cdots M_{2m}] | \Phi_0 \rangle \qquad (31)$$
$$= \sum_{(\text{f.c.})} (-1)^R M_{p_1} M_{q_1} \cdots M_{p_m} M_{q_m},$$

where $$R = \begin{pmatrix} 1 & 2 & \cdots & (2m-1) & (2m) \\ p_1 & q_1 & \cdots & p_m & q_m \end{pmatrix}.$$

Proof. From Wick's theorem, $M_1 \cdots M_{2m}$ is a sum of $N[M_1 \cdots M_{2m}]$ and various N-products with contractions. If some operators are left uncontracted, we end up with expressions of the type

$$\langle \Phi_0 | N[M_{p_{r_1}} \cdots M_{p_{r_s}}] | \Phi_0 \rangle,$$

which are zero, since if one of the $M_{p_{r_1}}, \cdots, M_{p_{r_s}}$ operators is of the Y type, we obtain

$$N[\cdots \overbrace{Y \cdots}] | \Phi_0 \rangle = \cdots Y | \Phi_0 \rangle = 0,$$

and if all operators $M_{p_{r_1}}, \ldots, M_{p_{r_s}}$ are of the $Y^\dagger$ type, we have

$$\langle \Phi_0 | N[Y^\dagger_{p_{r_1}} \cdots Y^\dagger_{p_{r_s}}] | \Phi_0 \rangle$$
$$= \langle \Phi_0 | Y^\dagger_{p_{r_1}} \cdots Y^\dagger_{p_{r_s}} | \Phi_0 \rangle = 0$$

$$\left(\langle \Phi_0 | Y^\dagger = 0 \right).$$

(turn-over rule)

By the same analysis, we can easily show that

- $\langle \Phi_0 | M_1 \cdots M_{2m+1} | \Phi_0 \rangle = 0$ (one cannot fully contract an odd number of operators)

- $$M_1 \cdots M_m | \Phi_0 \rangle = \sum_{\substack{\text{annihilators} \\ \text{fully contracted}}} (-1)^R \prod_{p_\mu q_\mu \in C} \overbrace{M_{p_\mu} M_{q_\mu}}^{(32)}$$

$$\times \prod_{r \notin C} Y^\dagger_r | \Phi_0 \rangle \,, \qquad (33)$$

where C stands for indices of fully contracted operators.

Proof:

Again, this is obvious, since for terms emerging from Wick's theorem that have some operators left uncontracted, we have

$$N[M_{p_{r_1}} \cdots M_{p_{r_s}}]\,|\Phi_0\rangle = 0,$$

if one or more M operators above are of the Y type.

4. Standard vs normal-product (or normal-ordered) forms of one- and two-body operators.

Some operators used in many-body theory are in the normal-product form without additional manipulations. For example,

$$E^a_i = X^\dagger_a X_i = N[X^\dagger_a X_i], \text{ since}$$

$X^\dagger_a = Y^\dagger_a$ and $X_i = Y^\dagger_i$ (see Eq. (23) above).

In general,

$$E^{a_1 \cdots a_n}_{i_1 \cdots i_n} = X^\dagger_{a_1} X_{i_1} \cdots X^\dagger_{a_n} X_{i_n}$$

$$= N[X^\dagger_{a_1} X_{i_1} \cdots X^\dagger_{a_n} X_{i_n}]. \quad (34)$$

They are in the normal-product form. But one cannot say the same about operators, such as

$$Z = \sum_{pq} \langle p|\hat{z}|q\rangle \chi_p^\dagger \chi_q$$

or

$$V = \frac{1}{2} \sum_{pq,rs} \langle pq|\hat{v}|rs\rangle \chi_p^\dagger \chi_q^\dagger \chi_s \chi_r$$

$$= \frac{1}{4} \sum_{pq,rs} \langle pq|\hat{v}|rs\rangle_A \chi_p^\dagger \chi_q^\dagger \chi_s \chi_r .$$

However, we can always relate generic one-, two-, and other many-body operators with their N-product forms, such as

$$Z_N = \sum_{pq} \langle p|\hat{z}|q\rangle N[\chi_p^\dagger \chi_q], \quad (35)$$

for Z, or

$$V_N = \frac{1}{2} \sum_{pq,rs} \langle pq|\hat{v}|rs\rangle N[\chi_p^\dagger \chi_q^\dagger \chi_s \chi_r]$$

$$= \frac{1}{4} \sum_{pq,rs} \langle pq|\hat{v}|rs\rangle_A N[\chi_p^\dagger \chi_q^\dagger \chi_s \chi_r] \quad (36)$$

for V.

Indeed, using Wick's theorem,

$$Z = \sum_{pq} \langle p|\hat{z}|q\rangle \left(N[X_p^\dagger X_q] + N[\overbrace{X_p^\dagger X_q}] \right)$$

$$= Z_N + \sum_{pq} \langle p|\hat{z}|q\rangle \, N[\overbrace{X_p^\dagger X_q}] .$$

We know that the only case where the nonzero contraction is possible is when $X_p^\dagger$ is Y_p and X_q is $Y_q^\dagger$ (see Eq. (27) above). This means that p must be occupied (e.g., $p = i$) and q must be occupied as well (e.g., $q = j$). We obtain

$$Z = Z_N + \sum_{i,j=1}^{N} \langle i|\hat{z}|j\rangle \, \overbrace{X_i^\dagger X_j}$$

sum over $i,j = 1,\ldots,N$; $\overbrace{X_i^\dagger X_j} = \delta_{ij}$ (see Eq. (28))

$$= Z_N + \sum_{i=1}^{N} \langle i|\hat{z}|i\rangle , \qquad (37)$$

where Z_N is defined by Eq. (35). It is well known that

$$\sum_{i=1}^{N} \langle i|\hat{z}|i\rangle = \langle \Phi_0|Z|\Phi_0\rangle .$$

Thus, $\hat{Z}$ in N-product form; expectation value of $\hat{Z}$ in $|\Phi_0\rangle$.

$$\hat{Z} = Z_N + \langle \Phi_0 | \hat{Z} | \Phi_0 \rangle . \quad (38)$$

Similarly we can show (again, using Wick's Theorem)[11] that

$$\hat{V} = V_N + G_N + \langle \Phi_0 | \hat{V} | \Phi_0 \rangle , \quad (39)$$

where V_N is given by Eq. (36), which we can also rewrite as

$$V_N = \frac{1}{2} \sum_{pq,rs} \langle pq | \hat{v} | rs \rangle \, N[X_p^\dagger X_r^\dagger X_s X_q]$$

$\hat{V}$ in N-product form

$$= \frac{1}{4} \sum_{pq,rs} \langle pq | \hat{v} | rs \rangle_A \, N[X_p^\dagger X_r^\dagger X_s X_q] , \quad (40)$$

one-body operator in N-product form emerging from $\hat{V}$; mean-field one-body potential created by $|\Phi_0\rangle$

$$G_N = \sum_{pq} \langle p | \hat{g} | q \rangle \, N[X_p^\dagger X_q] , \quad (41)$$

with

$$\langle p | \hat{g} | q \rangle = \sum_{i=1}^{N} \langle pi | \hat{v} | qi \rangle_A , \quad (42)$$

and

$$\langle \Phi_0 | \hat{V} | \Phi_0 \rangle = \frac{1}{2} \sum_{ij=1}^{N} \langle ij | \hat{v} | ij \rangle_A$$

expectation value of $\hat{V}$ in $|\Phi_0\rangle$

$$= \sum_{i<j}^{N} \langle ij | \hat{v} | ij \rangle_A . \quad (43)$$

Similar formulas can be developed for other many-body operators.

It is interesting to examine the Hamiltonian in this context,

$$H = Z + V = Z_N + \langle \Phi_0 | Z | \Phi_0 \rangle + V_N + G_N + \langle \Phi_0 | V | \Phi_0 \rangle = (Z_N + G_N) + V_N + \langle \Phi_0 | H | \Phi_0 \rangle . \quad (44)$$

($Z_N + G_N$: one-body; V_N: two-body)

As we can see, the Hamiltonian in the N-product form

$$H_N \equiv F_N + V_N , \quad (45)$$

where

$$F_N = Z_N + G_N \quad (46)$$

is its one-body part and V_N is its two-body component, is related to the standard form of H as follows:

$$H_N = H - \langle \Phi_0 | H | \Phi_0 \rangle . \quad (47)$$

This means that the Hamiltonian in the normal-product form describes that part of energy which is not captured by $|\Phi_0\rangle$. If we, for example, examine the ground-state problem,

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle, \quad (48)$$

then H_N corresponds to

$$\Delta E_0 = E_0 - \langle\Phi_0|H|\Phi_0\rangle, \quad (49)$$

which defines the correlation energy not captured by $|\Phi_0\rangle$ (the significance of determinants other than $|\Phi_0\rangle$ in $|\Psi\rangle$). It should be noted that the one-body part of H_N equals

$$F_N = \sum_{pq} \langle p|\hat{f}|q\rangle N[X_p^\dagger X_q], \quad (50)$$

where

$$\hat{f} = \hat{z} + \hat{g}, \quad (51)$$

or

$$\langle p|\hat{f}|q\rangle = \langle p|\hat{z}|q\rangle + \sum_i \langle pi|\hat{v}|qi\rangle_A$$
$$= \langle p|\hat{z}|q\rangle + \sum_i \left(\langle pi|\hat{v}|qi\rangle - \langle pi|\hat{v}|iq\rangle\right). \quad (52)$$

[redacted]

The latter two terms are matrix elements of the Coulomb and exchange operators $\hat{J}$ and $\hat{K}$ seen in the Hartree-Fock theory (assuming that $\hat{v}(i,j) = \frac{e^2}{r_{ij}}$). $\hat{f}$ is the Fock operator, which we often use to determine optimum single-particle states (spin-orbitals) by solving the SCF equations,

$$\hat{f}[\chi_1, \ldots, \chi_N]\, \chi_i(x) = \varepsilon_i \chi_i(x),$$

for the occupied states, and then (assuming that we use a basis set larger than the minimum one),

$$\hat{f}[\chi_1, \ldots, \chi_N]\, \chi_a(x) = \varepsilon_a \chi_a(x)$$

for the unoccupied ones.

THIS ENDS THE PRELIMINARIES.

THE MBPT IS NEXT.