© Piotr Piecuch

# OPERATORS IN SECOND QUANTIZATION:

In 1st quantization,

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

k-body component

$$\hat{O}_k = \sum_{1=i_1<\ldots<i_k}^{N} \hat{o}_k(x_{i_1}, \ldots, x_{i_k})$$

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

## Lemma 1:

$$|\Phi_{p_1 \cdots p_N}\rangle \equiv |\{p_1 \cdots p_N\}\rangle = X^\dagger_{p_1} \cdots X^\dagger_{p_N} |0\rangle,$$

$$p_1 < \cdots < p_N$$

(ordered sets of indices)

## Lemma 2:

$$|\Phi_{q_1 \cdots q_N}\rangle \equiv |\{q_1 \cdots q_N\}\rangle = X^\dagger_{q_1} \cdots X^\dagger_{q_N} |0\rangle$$

(ordered or not)

Isomorphism between

$|\Phi_{p_1 \cdots p_N}\rangle$ and $X^\dagger_{p_1} \cdots X^\dagger_{p_N} |0\rangle$

## Lemma 3:

$$X_q X^\dagger_{p_1} \cdots X^\dagger_{p_N} |0\rangle$$

$$= \sum_{i=1}^{N} (-1)^{i-1} \delta_{qp_i}$$

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

$$X_q \prod X^\dagger |0\rangle$$

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

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

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

$X^\dagger_{p_i}$ removed

## Lemma 4:

$$X_r X_s \prod X^\dagger|0\rangle = \sum_{1=i<j}^{N} (-1)^{i+j}\,\delta_{rp_i}\delta_{sp_j} \prod^{p_ip_j} X^\dagger|0\rangle + \sum_{i>j=1}^{N} (-1)^{i+j-1}\,\delta_{rp_i}\delta_{sp_j} \prod^{p_ip_j} X^\dagger|0\rangle$$

$$\Pi^{P_i P_j} X^\dagger|0\rangle = X^\dagger_{p_1}\cdots \cancel{X^\dagger_{p_i}}\cdots \cancel{X^\dagger_{p_j}}\cdots X^\dagger_{p_N}|0\rangle,$$

$$i<j$$

$$\Pi^{P_i P_j} X^\dagger|0\rangle = X^\dagger_{p_1}\cdots \cancel{X^\dagger_{p_j}}\cdots \cancel{X^\dagger_{p_i}}\cdots X^\dagger_{p_N}|0\rangle,$$

$$i>j$$

Main part:

$$\hat{O}_1 = \sum_{i=1}^{N} \hat{o}_1(x_i) \qquad \text{1-body}$$

$$\Downarrow$$

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

$$\langle p|\hat{o}_1|q\rangle = \int \chi_p^*(x)\,\hat{o}_1(x)\,\chi_q(x)\,dx$$

$$\hat{O}_2 = \sum_{1=i<j}^{N} \hat{o}_2(x_i, x_j)$$ 2-body

$$\Downarrow$$

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

$$\langle pq | \hat{o}_2 | rs \rangle = \int \psi_p^*(x_1) \psi_q^*(x_2) \times \hat{o}_2(x_1, x_2) \psi_r(x_1) \psi_s(x_2) \, dx_1 dx_2$$

In general, for a k-body operator,

$$\hat{O}_k = \sum_{1=i_1<\dots<i_k}^{N} \hat{o}_k(x_{i_1}, \dots, x_{i_k})$$

$$\Downarrow$$

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

$$\times X^{+}_{p_1} \cdots X^{+}_{p_k} X_{q_k} \cdots X_{q_1}$$

$$\langle p_1 \cdots p_k | \hat{o}_k | q_1 \cdots q_k \rangle$$

$$= \int \psi^{*}_{p_1}(x_1) \cdots \psi^{*}_{p_k}(x_k)$$

$$\times \hat{o}_k(x_1, \ldots, x_k) \, \psi_{q_1}(x_1) \cdots \psi_{q_k}(x_k) \, dx_1 \ldots dx_k$$

| $p$ | $q$ | $\langle p \mid \hat{o}_1 \mid q \rangle$ |
|---|---|---|
| 1 | 1 | $\langle 1 \mid \hat{o}_1 \mid 1 \rangle$ |
| 1 | 2 | $\langle 1 \mid \hat{o}_1 \mid 2 \rangle$ |
| 1 | 3 | $\langle 1 \mid \hat{o}_1 \mid 3 \rangle$ |

...

# Alternative forms using antisymmetrized matrix elements

2-body:

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

$$= \frac{1}{4} \sum_{pqrs} \langle pq | \hat{o}_2 | rs \rangle_A \times X_p^\dagger X_q^\dagger X_s X_r$$

antisymmetrized matrix element

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

In general,

$$\hat{O}_k = \left(\frac{1}{k!}\right)^2$$

antisymmetrized matrix element

$$\times \sum_{\substack{p_1 \dots p_k \\ q_1 \dots q_k}} \langle p_1 \dots p_k | \hat{o}_k | q_1 \dots q_k \rangle_A$$

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

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

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

sign of permutation R

$$R = \begin{pmatrix} 1 \dots k \\ R_1 \dots R_k \end{pmatrix}$$

Goldstone diagrams $\leftarrow$ nonsymmetric matrix elements

Hugenholtz diagrams $\leftarrow$ antisymmetrized matrix elements

# SPIN-INDEPENDENT OPERATORS

$$\hat{H} = \sum_{i=1}^{N} \hat{z}(x_i) + \sum_{1=i<j}^{N} \hat{v}(x_i, x_j)$$

$$\hat{z}(x_i) = -\frac{1}{2}\Delta_i + \sum_{A=1}^{M} \frac{Z_A}{r_{iA}}$$

$(m_e = 1, \hbar = 1, e = 1)$

atomic units

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

$$\hat{\mu}_z = -\sum_{i=1}^{N} z_i \quad , \text{etc.}$$

orbital

$$\psi_p(x, y, z, s) = \varphi_p(x, y, z)\, \sigma(s)$$

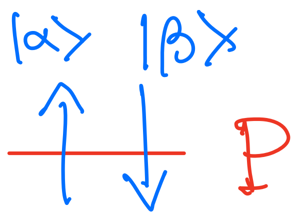
spin-orbital

spin function

$$|\sigma\rangle = \begin{cases} |\frac{1}{2}, \frac{1}{2}\rangle = |\alpha\rangle \text{ or} \\ |\frac{1}{2}, -\frac{1}{2}\rangle = |\beta\rangle \end{cases}$$

$$|P\alpha\rangle = |P\rangle \otimes |\alpha\rangle$$

$$|P\beta\rangle = |P\rangle \otimes |\beta\rangle$$




$$\{X_p, X_q^\dagger\} = \delta_{pq}$$

$$\Downarrow$$

$$\{X_{P\sigma_P}, X^\dagger_{Q\sigma_Q}\} = \delta_{PQ}\,\delta_{\sigma_P \sigma_Q}$$

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

$$= \dots = \sum_{PQ} \langle P|\hat{o}_1|Q\rangle E_{PQ}$$

$$E_{PQ} = \sum_{\sigma=-\frac{1}{2}}^{\frac{1}{2}} X^{\dagger}_{P\sigma} X_{Q\sigma}$$ ✓

$$= X^{\dagger}_{P\alpha} X_{Q\alpha} + X^{\dagger}_{P\beta} X_{Q\beta}$$

$$\hat{O}_2 = \frac{1}{2} \sum_{P,Q,R,S} \langle PQ|\hat{o}_2|RS\rangle$$

$$\times \underbrace{\sum_{\rho\sigma=-\frac{1}{2}}^{\frac{1}{2}} X^{\dagger}_{P\rho} X^{\dagger}_{Q\sigma} X_{S\sigma} X_{R\rho}}_{E_{PR}E_{QS} - \delta_{QR}E_{PS}}$$

$$[E_{PQ}, E_{RS}] = \delta_{QR} E_{PS} - \delta_{PS} E_{RQ}$$ ✓

$E_{PQ}$ s are generators of

$U(n)$ $\;(\subset GL(n))$

number of orbitals

$$\underset{\sim}{A} = \begin{bmatrix} a_{11} & \cdots & a_{1n} \\ & \cdots & \\ a_{n1} & \cdots & a_{nn} \end{bmatrix}$$

$$\underset{\sim}{E}_{ij} = \begin{array}{cl} \begin{bmatrix} 0 & \cdots & 0 \\ \vdots & 1 & \vdots \\ 0 & \cdots & 0 \end{bmatrix} & \leftarrow i\text{th row} \\ \quad\;\; \uparrow & \\ \quad j\text{th column} & \end{array}$$

$$(\underset{\sim}{E}_{ij})_{kl} = \delta_{ik}\delta_{jl}$$

$i,j = 1, \ldots, n$

$$\underset{\sim}{A} = \sum_{i,j=1}^{n} a_{ij}\,\underset{\sim}{E}_{ij}$$

1974, Josef Paldus, UGA

(GUGA)

↑ Isaiah Shavitt

# WICK's THEOREM

Motivation:

$$\langle \Psi | \hat{O}_k | \Psi' \rangle \quad \checkmark$$

$$\downarrow \qquad \downarrow$$

$$\langle \Phi_{p_1 \dots p_N} | \hat{O}_k | \Phi_{q_1 \dots q_N} \rangle \quad \checkmark$$

$$\downarrow$$

$$\frac{1}{k!}\sum_{\substack{r_1\ldots r_k\\ s_1\ldots s_k}} \langle r_1\ldots r_k|\hat{O}_k|s_1\ldots s_k\rangle$$

$$\times \overbrace{\langle 0|X_{p_N}\cdots X_{p_1}}^{\langle\Phi_{p_1\ldots p_N}|} X^\dagger_{r_1}\cdots X^\dagger_{r_k}$$

$$\times X_{s_k}\cdots X_{s_1} \underbrace{X^\dagger_{q_1}\cdots X^\dagger_{q_N}|0\rangle}_{|\Phi_{q_1\ldots q_N}\rangle}$$

$$\langle 0|M_1\ldots M_m|0\rangle \qquad \checkmark$$

$$M_i = X_{p_i} \text{ or } X^\dagger_{p_i}$$

Another typical situation:

$$\hat{O}_k|\Phi\rangle$$

$$\downarrow$$

$$\hat{O}_k \, | \Phi_{p_1 \ldots p_k} \rangle$$

$$\downarrow$$

$$M_1 \ldots M_m |0\rangle,$$

$$M_i = X_{p_i} \text{ or } X_{p_i}^\dagger$$

Wick's theorem requires

- normal product ✓
- contractions ✓
- normal products with contractions ✓

M is $X$ or $X^\dagger$

# Normal products:

$$n[M_1 \dots M_m] = (-1)^R$$
$$\times X^\dagger_{R_1} \dots X^\dagger_{R_j} X_{R_{j+1}} \dots X_{R_m}$$

$$R = \begin{pmatrix} 1 & 2 & \dots & j & j+1 & \dots & m \\ R_1 & R_2 & \dots & R_j & R_{j+1} & \dots & R_m \end{pmatrix}$$

$$n[\emptyset] = \mathbb{1}$$ ← unit operator

1. $n[M] = M$
2. $n[n[M_1 \dots M_m]] = n[M_1 \dots M_m]$ (idempotent)

In particular,

$$n[X^\dagger_{p_1}\dots X^\dagger_{p_j} X_{p_{j+1}}\dots X_{p_m}]$$
$$= X^\dagger_{p_1}\dots X^\dagger_{p_j} X_{p_{j+1}}\dots X_{p_m}],$$

$$n[X^\dagger_{p_1}\dots X^\dagger_{p_m}] = X^\dagger_{p_1}\dots X^\dagger_{p_m},$$

$$n[X_{p_1}\dots X_{p_m}] = X_{p_1}\dots X_{p_m}$$

3. $n[M_{R_1}\dots M_{R_m}] = (-1)^R n[M_1\dots M_m$

sign of R

$$R = \begin{pmatrix} 1 & \dots & m \\ R_1 & \dots & R_m \end{pmatrix}$$

$n[M_2M_1] = -n[M_1M_2]$

# Contractions:

$$\underbracket{M_1 M_2} = M_1 M_2 - n[M_1 M_2],$$

$$M_i = X_{p_i} \text{ or } X^\dagger_{p_i}$$

$$\underbracket{X_p X_q^\dagger} = X_p X_q^\dagger - n[X_p X_q^\dagger]$$

$$= X_p X_q^\dagger + X_q^\dagger X_p = \delta_{pq}$$

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

$$\underbracket{X_p^\dagger X_q} = 0$$

$$\underbracket{X_p^\dagger X_q^\dagger} = 0$$

# Normal products with contractions:

$$n[M_1 \dots M_{i_1} \dots M_{i_\lambda} \dots M_{j_1} \dots M_{j_\lambda} \dots M_m]$$

$$= (-1)^R M_{i_1} M_{j_1} \dots M_{i_\lambda} M_{j_\lambda}$$

$$\times \; n[M_{k_1} \dots M_{k_\mu}]$$

$$2\lambda + \mu = m$$

$\lambda$ contractions in $n[\dots]$, $\lambda \geq 1$

$$R = \begin{pmatrix} 1 & 2 & \dots & (2\lambda-1) & (2\lambda) & (2\lambda+1) & \dots & m \\ i_1 & j_1 & \dots & i_\lambda & j_\lambda & k_1 & \dots & k_\mu \end{pmatrix}$$

Observations:

$$n[\ldots \underbracket{M_i M}_{i+1} \ldots] = + \underbracket{M_i M_{i+1}}\, n[\ldots]$$

In the case of fully contracted expressions, the sign is

$$(-1)^{\nu},$$

where $\nu$ is the number of intersections of contraction lines.

$$n[X_p X_q X_r^\dagger X_s X_t^\dagger X_u^\dagger]$$

$$= + X_p X_r^\dagger \; X_q X_t^\dagger \; X_s X_u^\dagger$$

$$\times\, n[\emptyset]$$

$$= + \delta_{pr}\,\delta_{qt}\,\delta_{su}$$

$$R = \begin{pmatrix} p & q & r & s & t & u \\ p & r & q & t & s & u \end{pmatrix}$$

$$= (p)(qr)(st)(u)$$

$$\quad + \qquad - \qquad - \qquad +$$

$$(-1)^R = +1$$

$\nu = 2$, sign is $(-1)^2 = +1$

The same rule applies to a situation where contracted operators are grouped together.

---

Wick's theorem will be:

no contractions

$$M_1 \dots M_m = n[M_1 \dots M_m]$$

single contractions

$$+ \sum_{1 \le i < j \le m} n[M_1 \dots M_i \dots M_j \dots M_m]$$

double contractions

$$+ \sum_{\substack{i_1 < j_1 \\ i_2 < j_2, \\ i_1 < i_2,\, j_1 \neq j_2}} n[M_1 \dots M_{i_1} \dots M_{i_2} \dots M_{j_1} \dots M_{j_2} \dots M_m]$$

$$+ \dots$$

We already know that we need ~~to~~ learn how to calculate

$$\langle 0 | M_1 \ldots M_m | 0 \rangle$$

and

$$M_1 \ldots M_m | 0 \rangle .$$

Rules 1–4 (4')

Rule 1:

$$n[M_1 \ldots M_m] | 0 \rangle = 0$$

unless all operators M are creators.

Rule 2:

$$\langle 0 | n[M_1 \ldots M_m] | 0 \rangle = 0$$

as long as $m \geq 1$.

Rule 3:

$$n[M_1 \ldots M_i \ldots M_j \ldots M_m]|0\rangle = 0$$

if at least one uncontracted operator among $M$s is an annihilator.

Rule 4:

$$\langle 0| n[M_1 \ldots M_i \ldots M_j \ldots M_m]|0\rangle = 0$$

unless all operators are fully contracted.

Rule 4':

$$\langle 0| n[M_1 \ldots M_i \ldots M_j \ldots M_{2m+1}]|0\rangle = 0.$$

## Intro to Wick's theorem:

Calculate $\langle 0 | M_1 M_2 | 0 \rangle$, $M_i = X_{p_i}$ or $X^\dagger_{p_i}$

Conventional method:

$$\langle 0 | X_p X_q | 0 \rangle = 0$$

$$\langle 0 | X_p X_q^\dagger | 0 \rangle = \langle p | q \rangle = \delta_{pq}$$

$$\langle 0 | X_p^\dagger X_q | 0 \rangle = 0$$

$$\langle 0 | X_p^\dagger X_q^\dagger | 0 \rangle = 0$$

$\langle 0 | M_1 M_2 | 0 \rangle = 0$ unless $M_1 = X_p$ and $M_2 = X_p^\dagger$, in which case we obtain 1.

Alternatively $M_1 M_2 = n[M_1 M_2] + \underbracket{M_1 M_2}$

$$\langle 0 | M_1 M_2 | 0 \rangle$$

$$= \overbrace{\langle 0 | n[M_1 M_2] | 0 \rangle}^{0 \text{ (rule 2)}}$$

$$+ \langle 0 | \underbracket{M_1 M_2} | 0 \rangle$$

$$= \underbracket{M_1 M_2} \langle 0 | 0 \rangle = \underbracket{M_1 M_2}$$

The only nonzero $\underbracket{M_1 M_2}$

is $\underbracket{\cancel{X_p} X_p^\dagger} = 1$.

$$M_1 M_2 = n[M_1 M_2] + n[\underbrace{M_1 M_2}]$$

$$= n[M_1 M_2] + \underbrace{M_1 M_2}\, n[\emptyset]$$

$$= n[M_1 M_2] + \underbrace{M_1 M_2}$$

this is Wick's theorem for $m=2$

Example (out of many):

$$X_p X_q^\dagger X_r^\dagger = n[X_p X_q^\dagger X_r^\dagger]$$

$$+\, n[\underbrace{X_p X_q^\dagger} X_r^\dagger]$$

$$+\, n[\underbrace{X_p X_q^\dagger X_r^\dagger}]$$

(we can skip $n[X_p \underbrace{X_q^\dagger X_r^\dagger}]$ since $\underbrace{X_q^\dagger X_r^\dagger} = 0$)

$$= X_q^\dagger X_r^\dagger X_p + \underbrace{X_p X_q^\dagger}\, n[X_r^\dagger]$$

$$- x_p x_r^\dagger n[x_q^\dagger]$$

$$= x_q^\dagger x_r^\dagger x_p + \delta_{pq} x_r^\dagger - \delta_{pr} x_q^\dagger$$

---

Proof of Wick's theorem requires two lemmas.

**Lemma 1:**

$$n[M_1 \dots M_m] M_{m+1}$$

$$= n[M_1 \dots M_m M_{m+1}] + \sum_{i=1}^{m} n[M_1 \dots M_i \dots M_m M_{m+1}]$$

Proof (sketch):

$$M_{m+1} = X_r^{+} \text{ or } X_r$$

case A (easy) — $X_r$

case B (difficult) — $X_r^{+}$

$$n[M_1 \cdots M_m] X_r^{+}$$

$$= n[M_1 \cdots M_m X_r^{+}]$$

$$+ \sum_{i=1}^{m} n[M_1 \cdots \underbrace{M_{\bar{i}} \cdots M_m}\, X_r^{+}]$$

B1: all $M_1, \ldots, M_m$ are annihilators

$\Downarrow$ hard

B2: there are some creators among $M_1, \ldots, M_m$

easier

$$\Downarrow$$

$$n[X_{p_1}\cdots X_{p_m}]\,X_r^{+}$$

MUST PROVE

$$= n[X_{p_1}\cdots X_{p_m}X_r^{+}] + \sum_{i=1}^{m} n[X_{p_1}\cdots \underbrace{X_{p_i}\cdots X_{p_m}X_r^{+}}]$$

proof by induction (videos 6,7)

B2 (proof by reduction to B1, video 7)

$$(-1)^R \left(X^+_{p_{R_1}} \cdots X^+_{p_{R_k}} X_{p_{R_{k+1}}} \cdots X_{p_{R_m}}\right) X^+_r$$

$$= (-1)^R n\left[X^+_{p_{R_1}} \cdots X^+_{p_{R_k}} X_{p_{R_{k+1}}} \cdots X_{p_{R_m}} X^+_r\right]$$

$$\cancel{+ (-1)^R \sum_{i=1}^{k} n\left[X^+_{p_{R_1}} \cdots X^+_{p_{R_i}} \cdots X^+_{p_{R_k}} X_{p_{R_{k+1}}} \cdots X_{p_{R_m}} X_r\right]} \quad 0$$

$$+ (-1)^R \sum_{i=k+1}^{m} n\left[X^+_{p_{R_1}} \cdots X^+_{p_{R_k}} X_{p_{R_{k+1}}} \cdots X_{p_{R_i}} \cdots X_{p_{R_m}} X^+_r\right]$$

$$(X^\dagger_{PR_1}\cdots X^\dagger_{PR_k})\, n\, [X_{PR_{k+1}}\cdots X_{PR_m}]\, X^\dagger_r$$

$$= (X^\dagger_{PR_1}\cdots X^\dagger_{PR_k})\, n\, [X_{PR_{k+1}}\cdots X_{PR_m}\, X^\dagger_r]$$

$$+ (X^\dagger_{PR_1}\cdots X^\dagger_{PR_k}) \sum_{i=k+1}^{m} n\, [X_{PR_{k+1}}\cdots X_{PR_i}\cdots X_{PR_m}\, X^\dagger_r]$$

→ case B1

$\therefore$