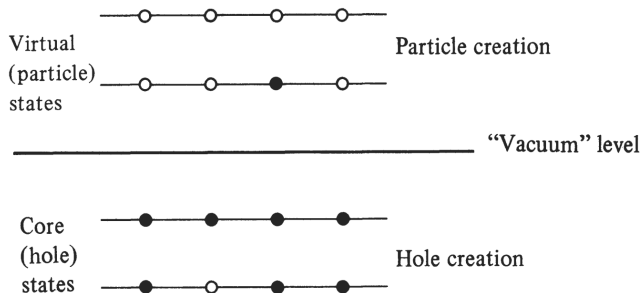


HOLE-PARTICLE FORMALISM

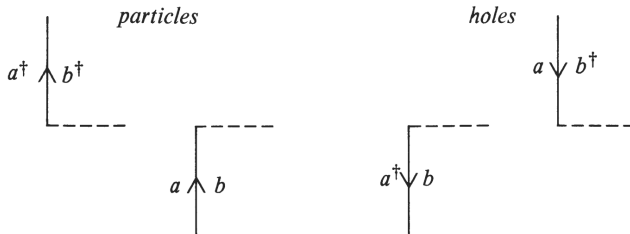


$$b^\dagger = a^\dagger, b = a \text{ virtual orbitals}$$

$$b^\dagger = a, b = a^\dagger \text{ core orbitals}$$

OPERATORS IN NORMAL FORM

- Normal Form: $a_{core}^\dagger, a_{virt}$ to the **right** of $a_{virt}^\dagger, a_{core}$
- Normal Form: b to the **right** of $b^\dagger$



Virtual orbitals (particles) lines directed upwards, and core orbitals (holes) lines directed downwards. Creation operators ($a^\dagger$) lines directed away from the vertex, absorption operators (a) lines directed toward the vertex.

- Normal form: **right** below the vertex (b)
- **left** above the vertex ($b^\dagger$)

PARTICLE-HOLE OPERATORS

- Normal Form: b to the **right** of $b^\dagger$

$$\begin{aligned}\{b_i^\dagger b_j\} &= b_i^\dagger b_j \\ \{b_i b_j^\dagger\} &= -b_j^\dagger b_i \\ \{b_i^\dagger b_j^\dagger\} &= b_i^\dagger b_j^\dagger \\ \{b_i b_j\} &= b_i b_j\end{aligned}$$

Define the *the contraction of creation/annihilation operators*

- **Contraction** $\widehat{xy} = xy - \{xy\}$

$$\begin{aligned}\widehat{b_i^\dagger b_j^\dagger} &= \widehat{b_i b_j} = \widehat{b_i^\dagger b_j} = 0 \\ \widehat{b_i b_j^\dagger} &= b_i b_j^\dagger - \{b_i b_j^\dagger\} = b_i b_j^\dagger + b_j^\dagger b_i = \delta_{ij}\end{aligned}$$

WICK'S THEOREM

If A is a product of creation and annihilation operators then:

$$A = \{A\} + \{\hat{A}\}$$

- the second term is the sum of all normal-ordered terms obtained by making all possible contractions within A

EXAMPLE

$$b_i b_j^\dagger b_k b_l^\dagger = \left\{ b_i b_j^\dagger b_k b_l^\dagger \right\} + \left\{ \widehat{b_i b_j^\dagger} b_k b_l^\dagger \right\} + \left\{ b_i b_j^\dagger \widehat{b_k b_l^\dagger} \right\} + \left\{ b_i b_j^\dagger \widehat{b_k b_l^\dagger} \right\} + \left\{ \widehat{b_i b_j^\dagger} \widehat{b_k b_l^\dagger} \right\}$$

EXAMPLE

$$b_i b_j^\dagger b_k b_l^\dagger = \left\{ b_i b_j^\dagger b_k b_l^\dagger \right\} + \left\{ \widehat{b_i b_j^\dagger} b_k b_l^\dagger \right\} + \left\{ b_i \widehat{b_j^\dagger b_k} b_l^\dagger \right\} + \left\{ b_i b_j^\dagger \widehat{b_k b_l^\dagger} \right\} + \left\{ \widehat{b_i b_j^\dagger} \widehat{b_k b_l^\dagger} \right\}$$

Note $b_i b_j^\dagger + b_j^\dagger b_i = \delta_{ij} \rightarrow b_i b_j^\dagger = \delta_{ij} - b_j^\dagger b_i = \delta_{ij} + \left\{ b_i b_j^\dagger \right\}$
 $\rightarrow \widehat{b_i b_j^\dagger} = b_i b_j^\dagger - \left\{ b_i b_j^\dagger \right\} = \delta_{ij}$

EXAMPLE

$$b_i b_j^\dagger b_k b_l^\dagger = \left\{ b_i b_j^\dagger b_k b_l^\dagger \right\} + \left\{ \widehat{b_i b_j^\dagger} b_k b_l^\dagger \right\} + \left\{ b_i \widehat{b_j^\dagger b_k} b_l^\dagger \right\} + \left\{ b_i b_j^\dagger \widehat{b_k b_l^\dagger} \right\} + \left\{ \widehat{b_i b_j^\dagger} \widehat{b_k b_l^\dagger} \right\}$$

$$\text{Permutate : } b_i b_j^\dagger b_k b_l^\dagger = \delta_{ij} b_k b_l^\dagger - b_j^\dagger b_i b_k b_l^\dagger =$$

$$\delta_{ij} \delta_{kl} - \delta_{ij} b_l^\dagger b_k - \delta_{kl} b_j^\dagger b_i + b_j^\dagger b_i b_l^\dagger b_k =$$

$$\delta_{ij} \delta_{kl} - \delta_{ij} b_l^\dagger \textcolor{red}{b_k} - \delta_{kl} b_j^\dagger \textcolor{red}{b_i} + \delta_{il} b_j^\dagger \textcolor{red}{b_k} - b_j^\dagger b_l^\dagger \textcolor{red}{b_i} \textcolor{red}{b_k} =$$

EXAMPLE

$$b_i b_j^\dagger b_k b_l^\dagger = \left\{ b_i b_j^\dagger b_k b_l^\dagger \right\} + \left\{ \widehat{b_i b_j^\dagger} b_k b_l^\dagger \right\} + \left\{ b_i \widehat{b_j^\dagger b_k} b_l^\dagger \right\} + \left\{ b_i b_j^\dagger \widehat{b_k b_l^\dagger} \right\} + \left\{ \widehat{b_i b_j^\dagger} \widehat{b_k b_l^\dagger} \right\}$$

$$\text{Permutate : } b_i b_j^\dagger b_k b_l^\dagger = \delta_{ij} b_k b_l^\dagger - b_j^\dagger b_i b_k b_l^\dagger =$$

$$\delta_{ij} \delta_{kl} - \delta_{ij} b_l^\dagger b_k - \delta_{kl} b_j^\dagger b_i + b_j^\dagger b_i b_l^\dagger b_k =$$

$$\delta_{ij} \delta_{kl} - \delta_{ij} b_l^\dagger \textcolor{red}{b_k} - \delta_{kl} b_j^\dagger \textcolor{red}{b_i} + \delta_{il} b_j^\dagger \textcolor{red}{b_k} - b_j^\dagger b_l^\dagger \textcolor{red}{b_i} \textcolor{red}{b_k} =$$

$$\delta_{ij} \delta_{kl} + \delta_{ij} \left\{ b_k b_l^\dagger \right\} + \delta_{kl} \left\{ b_i b_j^\dagger \right\} + \delta_{il} \left\{ b_j^\dagger b_k \right\} + \left\{ b_i b_j^\dagger b_k b_l^\dagger \right\} \widehat{\textcolor{red}{b_i} \textcolor{red}{b_j^\dagger}} = \delta_{ij}$$

see also Problem 11.3

WICK'S THEOREM FOR OPERATOR PRODUCTS

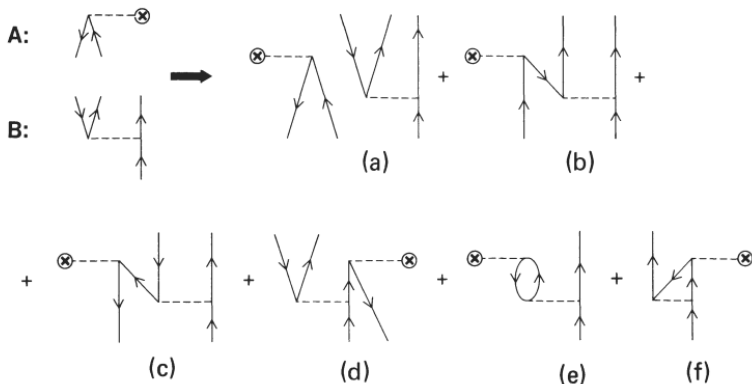
When A and B are products of creation and annihilation operators in normal form then:

$$AB = \{AB\} + \{\widehat{AB}\}$$

IN GRAPHICAL FORM:

If A and B are two operators in normal form represented by Goldstone diagrams, then the graphical representation of the operator product AB is the sum of diagrams obtained by joining zero, one, two, . . . lines at the bottom of the diagram of A with lines at the top of the diagram of B in all possible ways so that the direction of the arrows is continuous.

WICK'S THEOREM FOR OPERATOR PRODUCTS



b,c,d single contractions. e,f double contractions

- Normal form: b below the vertex $b^\dagger$ above the vertex

GOLDSTONE DIAGRAMS

Lecture 7: double excitation
corrections to the wave function
(first order wave operator)


$$= \frac{1}{2} \frac{|\alpha_{ab}^{rs}\rangle \langle rs | r_{12}^{-1} | ab \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}.$$

GOLDSTONE RULES FOR WAVE-OPERATOR DIAGRAMS

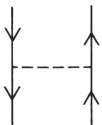
- a creation (absorption) operator for each outgoing (incoming) line. In normal form.
- a matrix element for each interaction line
- an energy denominator for each interaction line
 $\sum (\epsilon_{down} - \epsilon_{up})$
- a factor of 1/2 for each two-particle interaction
- an equivalence factor for each equivalent diagram
- a summation over all internal orbital lines
- a phase factor $(-1)^{h+l}$

2ND ORDER WAVE OPERATOR: V ON 1ST ORDER

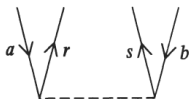
$$V_2 =$$

$$V_2 = \frac{1}{2} \sum_{ijkl} \left\{ a_i^\dagger a_j^\dagger a_l a_k \right\} \langle ij | \frac{1}{r_{12}} | kl \rangle$$

EXAMPLE



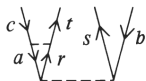
$$\sum_{cd}^{core} \sum_{pt}^{virt} a_t^\dagger a_p a_c a_d^\dagger \langle dt | \frac{1}{r_{12}} | cp \rangle$$



$$= \frac{1}{2} \frac{|\alpha_{ab}^{rs}\rangle \langle rs | r_{12}^{-1} | ab \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}.$$

$$a_r^\dagger a_s^\dagger a_b a_a$$

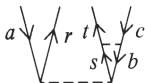
gives (just one example!):



$$= -\frac{1}{2} a_t^\dagger a_s^\dagger a_b a_c \sum_{ar} \frac{\langle at | r_{12}^{-1} | cr \rangle \langle rs | r_{12}^{-1} | ab \rangle}{(\epsilon_c + \epsilon_b - \epsilon_t - \epsilon_s)(\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s)}$$

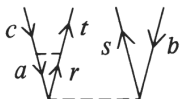
$$-\delta_{ad} \delta_{rp} a_t^\dagger a_s^\dagger a_b a_c$$

$$-\delta_{bd} \delta_{sp} a_r^\dagger a_t^\dagger a_c a_a$$



$$= -\frac{1}{2} a_t^\dagger a_r^\dagger a_c a_a \sum_{bs} \frac{\langle tb | r_{12}^{-1} | sc \rangle \langle rs | r_{12}^{-1} | ab \rangle}{(\epsilon_a + \epsilon_c - \epsilon_r - \epsilon_t)(\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s)}$$

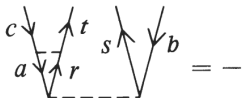
Topologically equivalent



$$= - \sum_{ar} \frac{\langle at | r_{12}^{-1} | cr \rangle \langle rs | r_{12}^{-1} | ab \rangle}{(\epsilon_c + \epsilon_b - \epsilon_t - \epsilon_s)(\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s)}$$

GOLDSTONE RULES FOR WAVE-OPERATOR DIAGRAMS

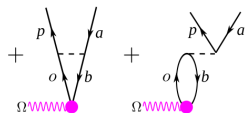
- a creation (absorption) operator for each outgoing (incoming) line. In normal form.
- a matrix element for each interaction line
- an energy denominator for each interaction line
 $\sum (\epsilon_{down} - \epsilon_{up})$
- a factor of 1/2 for each two-particle interaction
- an equivalence factor for each equivalent diagram
- a summation over all internal orbital lines
- a phase factor $(-1)^{h+l}$, see 12.8 for the proof. **Net effect of all the permutations!**



- sum over a, r ?
- energy diagrams?
- other examples:

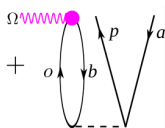
$$a_t^\dagger a_s^\dagger a_b a_c \sum_{ar} \frac{\langle at | r_{12}^{-1} | cr \rangle \langle rs | r_{12}^{-1} | ab \rangle}{(\varepsilon_c + \varepsilon_b - \varepsilon_t - \varepsilon_s)(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)}$$

There is a factor of $1/2$ for each symmetry operation-like reflection in a vertical plane or interchange of the vertices of an interaction line-which transforms the diagram into itself or to any other diagram appearing in the expansion.



$$\begin{aligned}
 & - \sum_{po}^{exc} \sum_{a,b}^{core} \sum_k \frac{|p\rangle \langle bp| \frac{r_{<}^k}{r_{>}^{k+1}} |ao\rangle \langle o|r|b\rangle}{(\epsilon_a + \hbar\Omega - \epsilon_p)(\epsilon_b + \hbar\Omega - \epsilon_o)} \\
 & \times \left\{ \begin{array}{ccc} 1 & \ell_a & \ell_p \\ k & \ell_o & \ell_b \end{array} \right\} XK(k, \ell_b, \ell_o, \ell_a, \ell_o) \langle \ell_o | \mathbf{C}^1 | \ell_b \rangle \\
 & + \sum_{po}^{exc} \sum_{a,b}^{core} \frac{|p\rangle \langle pb| \frac{r_{<}^k}{r_{>}^{k+1}} |ao\rangle \langle o|r|b\rangle}{(\epsilon_a + \hbar\Omega - \epsilon_p)(\epsilon_b + \hbar\Omega - \epsilon_o)} \\
 & \times \frac{2}{3} XK(1, \ell_p, \ell_b, \ell_a, \ell_o) \langle \ell_o | \mathbf{C}^1 | \ell_b \rangle
 \end{aligned}$$

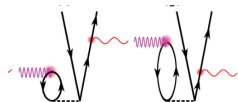
RPAE - GROUND STATE CORRELATION



Goldstone rule first denominator:

$$\frac{1}{\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_o} \rightarrow \frac{1}{\epsilon_b - \epsilon_o - \hbar\Omega}$$

On-shell: $\epsilon_p = \epsilon_a + \hbar\Omega$



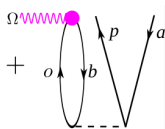
sum the time-orders

$$\begin{aligned} & \times \left(\frac{1}{\epsilon_a + \hbar\Omega - \epsilon_p} + \frac{1}{\epsilon_a + \epsilon_b - \epsilon_o - \epsilon_t + \hbar\omega} \right) = \\ & \frac{1}{\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_o} \\ & \times \left(\frac{1}{\epsilon_a + \hbar\Omega - \epsilon_p} + \frac{1}{\epsilon_b - \epsilon_o - \hbar\Omega} \right) \end{aligned}$$

final on-shell

$$\epsilon_t = \epsilon_a + \hbar\Omega + \hbar\omega$$

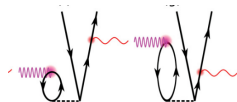
RPAE - GROUND STATE CORRELATION



On-shell: $\epsilon_p = \epsilon_a + \hbar\Omega$

Goldstone rule first denominator:

$$\frac{1}{\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_o} \rightarrow \frac{1}{\epsilon_b - \epsilon_o - \hbar\Omega}$$



sum the time-orders

$$\begin{aligned} & \times \left(\frac{1}{\epsilon_a + \hbar\Omega - \epsilon_p} + \frac{1}{\epsilon_a + \epsilon_b - \epsilon_o - \epsilon_t + \hbar\omega} \right) = \\ & \frac{1}{\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_o} \\ & \times \left(\frac{\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_o}{(\epsilon_a + \hbar\Omega - \epsilon_p)(\epsilon_b - \epsilon_o - \hbar\Omega)} \right) \end{aligned}$$

final on-shell

$$\epsilon_t = \epsilon_a + \hbar\Omega + \hbar\omega$$

REMAINING EXERCISES

- Problem 10.1-10.2
- Problem 11.1- 11.5