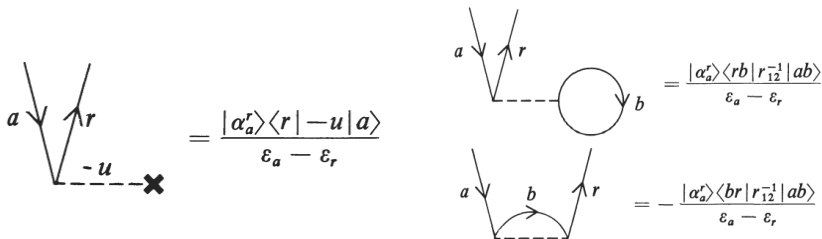


WHAT WE HAVE DONE

- Simple perturbation approach for 2 particles (formal version in Chapter 9)
- Hartree-Fock starting point $V = 1/r_{12} - u_{hf} \rightarrow$ no single excitation corrections in lowest order
- double excitations remain and will dominate

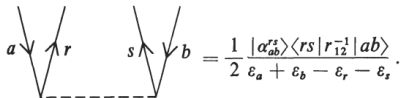


The diagram on the left shows a single excitation process where an incoming line 'a' and an outgoing line 'r' are connected by a dashed line labeled '-u'. This diagram is crossed out with a large 'X'. To its right is the corresponding mathematical expression:
$$= \frac{|\alpha_a^r\rangle \langle r | -u | a \rangle}{\epsilon_a - \epsilon_r}$$

The diagram on the right shows a double excitation process where an incoming line 'a' and an outgoing line 'r' are connected by a dashed line that forms a loop with an internal line 'b'. This diagram is equated to the expression:
$$= \frac{|\alpha_a^r\rangle \langle rb | r_{12}^{-1} | ab \rangle}{\epsilon_a - \epsilon_r}$$

Below this, another double excitation diagram is shown where the incoming line 'a' and outgoing line 'r' are connected by a dashed line that forms a loop with an internal line 'b', but the internal line 'b' has a different orientation. This diagram is equated to the expression:
$$= - \frac{|\alpha_a^r\rangle \langle br | r_{12}^{-1} | ab \rangle}{\epsilon_a - \epsilon_r}$$

- Goldstone diagrams



The diagram shows two separate vertices. The left vertex has incoming line 'a' and outgoing line 'r'. The right vertex has incoming line 's' and outgoing line 'b'. These two vertices are connected by a dashed line. This diagram is equated to the expression:
$$= \frac{1}{2} \frac{|\alpha_{ab}^{rs}\rangle \langle rs | r_{12}^{-1} | ab \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

SECOND QUANTIZATION

- creation operator

$$|\phi_i\rangle \equiv a_i^\dagger |0\rangle, \quad \phi_i : n_i, \ell_i m_\ell^i, m_s^i$$

- hermitian adjoint operation gives

$$\langle 0 | a_i \equiv \langle \phi_i |,$$

- Create a Slater determinant:

$$|\{\phi_i \phi_j \phi_k \dots\}\rangle = a_i^\dagger a_j^\dagger a_k^\dagger \dots |0\rangle, \quad \langle 0 | a_k a_j a_i = \langle \{\phi_i \phi_j \phi_k \dots\} |,$$

- exchange two particles gives minus sign:

$$a_i^\dagger a_j^\dagger = -a_j^\dagger a_i^\dagger$$

PROPERTIES OF CREATION AND ABSORPTION OPERATORS

- The creation and absorption operators *anticommute*

$$\{a_i^\dagger, a_j^\dagger\} = a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0$$

$$\{a_i, a_j\} = 0$$

- Use the orthogonality:

$$\langle \{\phi_i \phi_j\} \rangle | \{\phi_k \phi_l\} \rangle = \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}$$

$$\langle \{\phi_i \phi_j\} \rangle | \{\phi_k \phi_l\} \rangle = \langle 0 | a_j a_i a_k^\dagger a_l^\dagger | 0 \rangle$$

- requires $\{a_m, a_n^\dagger\} = \delta_{mn}$

PROPERTIES OF CREATION AND ABSORPTION OPERATORS

- $\{a_m, a_n\} = 0, \{a_m^\dagger, a_n^\dagger\} = 0, a_n |0\rangle = 0$
- Show that we need $\{a_m, a_n^\dagger\} = \delta_{mn}$

$$\begin{aligned}a_j a_i a_k^\dagger a_l^\dagger &= a_j \left(\delta_{ik} - a_k^\dagger a_i \right) a_l^\dagger = \delta_{ik} \left(\delta_{jl} - a_l^\dagger a_j \right) - \delta_{jk} a_i a_l^\dagger + a_k^\dagger a_j a_i a_l^\dagger \\a_j a_i a_k^\dagger a_l^\dagger &= \delta_{ik} \delta_{jl} - \delta_{jk} \delta_{il} + \delta_{jk} a_l^\dagger a_i + \delta_{il} a_k^\dagger a_j - a_k^\dagger a_j a_i a_l^\dagger \\a_j a_i a_k^\dagger a_l^\dagger &= \delta_{ik} \delta_{jl} - \delta_{jk} \delta_{il} - \delta_{jl} a_k^\dagger a_i + a_k^\dagger a_l^\dagger a_j a_i \\a_j a_i a_k^\dagger a_l^\dagger &= \delta_{ik} \delta_{jl} - \delta_{jk} \delta_{il}\end{aligned}$$

$$a_i | \phi_i \rangle = a_i \left(a_i^\dagger | 0 \rangle \right) = \left(1 - a_i^\dagger a_i \right) | 0 \rangle = | 0 \rangle$$

- a_i is an absorption operator

WHAT IS THE VACUUM LEVEL?

- Particle physics - common to use the real vacuum level
- For atoms/molecules etc better to use the reference state.

For example a closed shell Hartree-Fock Slater determinant

$$| \{abcd \dots\} \rangle = | \alpha \rangle$$

Then

$$a_{core}^\dagger | \alpha \rangle = a_{virt} | \alpha \rangle = 0$$

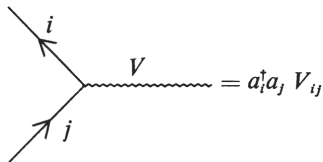
Define excitations

$$| \alpha_a^r \rangle = a_r^\dagger a_a | \alpha \rangle, \quad | \alpha_{ab}^{rs} \rangle = a_r^\dagger a_s^\dagger a_b a_a | \alpha \rangle$$

Creation operators to the **left** of the absorption operators. Note also:

$$| \alpha \rangle = | \{ab\} \rangle \rightarrow | \alpha \rangle = a_a^\dagger a_b^\dagger | 0 \rangle \text{ and } a_b a_a a_a^\dagger a_b^\dagger | 0 \rangle = | 0 \rangle$$

NEW REPRESENTATION OF INTERACTIONS

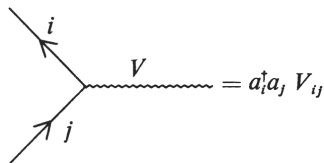


- The sum over $ijkl$ is over all states occupied and unoccupied

$$F = \sum_n^N f_n = \sum_{ij} a_i^\dagger a_j \langle i | f | j \rangle$$

$$G = \sum_{n < m}^N g_{nm} = \sum_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \langle ij | g | kl \rangle$$

NEW REPRESENTATION OF INTERACTIONS



$$F = \sum_n^N f_n = \sum_{ij} a_i^\dagger a_j \langle i | f | j \rangle$$

$$G = \sum_{n < m}^N g_{nm} = \sum_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \langle ij | g | kl \rangle$$

- The sum over $ijkl$ is over all states occupied and unoccupied

$$H_0 = \sum_n^N h_0(n) = \sum_i a_i^\dagger a_i \epsilon_i \quad (\text{Number operator})$$

$$V = - \sum_{ij} a_i^\dagger a_j \langle i | u | j \rangle + \frac{1}{2} \sum_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \langle ij | \frac{1}{r_{12}} | kl \rangle$$

OPERATORS IN NORMAL FORM

- When working on α we cannot create any already occupied orbital or absorb any virtual (excited) orbital.

$$F = \sum_{ij} a_i^\dagger a_j \langle i | f | j \rangle = \sum_{ab} a_a^\dagger a_b \langle a | f | b \rangle + \sum_{ar} a_a^\dagger a_r \langle a | f | r \rangle \\ + \sum_{sb} a_s^\dagger a_b \langle s | f | b \rangle + \sum_{rs} a_r^\dagger a_s \langle r | f | s \rangle$$

- Normal Form: $a_{core}^\dagger, a_{virt}$ to the **right** of $a_{virt}^\dagger, a_{core}$
- Let $\{a_i a_j \dots\}$ mean $a_i a_j$ in Normal Form

$$a_a^\dagger a_r = -a_r a_a^\dagger \text{ already Normal Form}$$

$$a_a^\dagger a_b = \delta_{ab} - a_b a_a^\dagger$$

$$a_s^\dagger a_b = -a_b a_s^\dagger \text{ already Normal Form}$$

$$a_a^\dagger a_b = \delta_{ab} + \{a_a^\dagger a_b\}$$

$$a_r^\dagger a_s \text{ already Normal Form}$$

$$\sum_{ij} a_i^\dagger a_j \langle i | f | j \rangle = \sum_a \langle a | f | a \rangle + \sum_{ij} \{a_i^\dagger a_j\} \langle i | f | j \rangle$$

OPERATORS IN NORMAL FORM

$$H_0 = \sum_i a_i^\dagger a_i \epsilon_i = \sum_a^{\text{occ}} \epsilon_a + \sum_{ij} \{a_i^\dagger a_j\} \epsilon_i$$

$$\begin{aligned} \frac{1}{2} \sum_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \langle ij | \frac{1}{r_{12}} | kl \rangle &= \frac{1}{2} \sum_{rskl} a_r^\dagger a_s^\dagger a_l a_k \langle rs | \frac{1}{r_{12}} | kl \rangle + \\ \frac{1}{2} \sum_{askl} a_a^\dagger a_s^\dagger a_l a_k \langle as | \frac{1}{r_{12}} | kl \rangle &+ \frac{1}{2} \sum_{rbkl} a_r^\dagger a_b^\dagger a_l a_k \langle rb | \frac{1}{r_{12}} | kl \rangle + \\ &\frac{1}{2} \sum_{abkl} a_a^\dagger a_b^\dagger a_l a_k \langle ab | \frac{1}{r_{12}} | kl \rangle \end{aligned}$$

Note: k, l still run over both core and virtual. First term on right-hand side already in normal form.

OPERATORS IN NORMAL FORM

As an example (part of Problem 11.2) term 2-3 (previous page):

$$a_a^\dagger a_s^\dagger a_l a_k = -\delta_{al} a_s^\dagger a_k + a_s^\dagger a_l a_a^\dagger a_k = -\delta_{al} a_s^\dagger a_k + \delta_{ak} a_s^\dagger a_l - a_s^\dagger a_l a_k a_a^\dagger$$

$$a_r^\dagger a_b^\dagger a_l a_k = \delta_{bl} a_r^\dagger a_k - a_r^\dagger a_l a_b^\dagger a_k = \delta_{bl} a_r^\dagger a_k - \delta_{bk} a_r^\dagger a_l + a_r^\dagger a_l a_k a_b^\dagger$$

All terms are now in *Normal Form* and the

$$\delta\text{-terms give } \sum_{ij} \{a_i^\dagger a_j\} \sum_a \langle ai | \frac{1}{r_{12}} | aj \rangle - \langle ai | \frac{1}{r_{12}} | ja \rangle$$

and the last terms on both lines give $\{a_a a_r^\dagger\} = -\{a_r^\dagger a_a\}$

$$\frac{1}{2} \sum_{askl} -a_s^\dagger a_l a_k a_a^\dagger \langle as | \frac{1}{r_{12}} | kl \rangle + \frac{1}{2} \sum_{rbkl} a_r^\dagger a_l a_k a_b^\dagger \langle rb | \frac{1}{r_{12}} | kl \rangle$$

$$= \sum_{rbij} \{a_r^\dagger a_b^\dagger a_i a_j\} \langle rb | \frac{1}{r_{12}} | ij \rangle$$

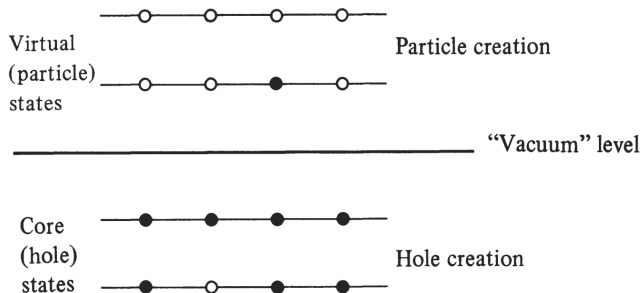
$$V = V_0 + V_1 + V_2$$

$$V_0 = \sum_a \langle a | -u | a \rangle + \frac{1}{2} \sum_{ab} \langle ab | \frac{1}{r_{12}} | ab \rangle - \langle ba | \frac{1}{r_{12}} | ab \rangle$$

$$V_1 = \sum_{ij} \left\{ a_i^\dagger a_j \right\} \left(\langle i | -u | j \rangle + \sum_a \langle ai | \frac{1}{r_{12}} | aj \rangle - \langle ai | \frac{1}{r_{12}} | ja \rangle \right)$$

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

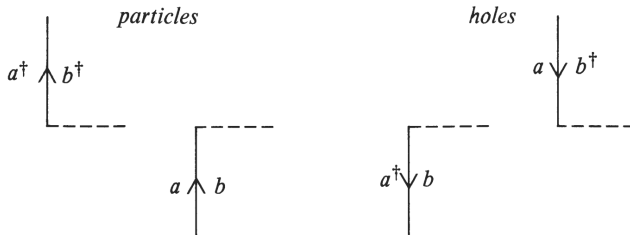
HOLE-PARTICLE FORMALISM



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

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

GRAPHICAL REPRESENTATION



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.

GRAPHICAL REPRESENTATION

$$V_0 = \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3}$$

$$V_0 = \sum_a \langle a | -u | a \rangle + \frac{1}{2} \sum_{ab} \langle ab | \frac{1}{r_{12}} | ab \rangle - \langle ba | \frac{1}{r_{12}} | ab \rangle$$

GRAPHICAL REPRESENTATION

$$V_1 = \begin{array}{c} \uparrow \\ | \\ \uparrow \end{array} \text{---} \otimes + \begin{array}{c} \swarrow \searrow \\ | \\ \swarrow \searrow \end{array} \text{---} \otimes + \begin{array}{c} \swarrow \searrow \\ | \\ \swarrow \searrow \end{array} \text{---} \otimes + \begin{array}{c} \downarrow \\ | \\ \downarrow \end{array} \text{---} \otimes$$

$$V_1 = \sum_{ij} \left\{ a_i^\dagger a_j \right\} \left(\langle i | -u | j \rangle + \sum_a \langle ai | \frac{1}{r_{12}} | aj \rangle - \langle ai | \frac{1}{r_{12}} | ja \rangle \right)$$

- 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.

GRAPHICAL REPRESENTATION

$$\begin{aligned}
 V_2 = & \begin{array}{c} \uparrow \quad \uparrow \\ | \quad | \\ \hline | \quad | \\ \uparrow \quad \uparrow \end{array} + \begin{array}{c} \swarrow \quad \searrow \\ | \quad | \\ \hline | \quad | \\ \uparrow \quad \uparrow \end{array} + \begin{array}{c} \uparrow \quad \uparrow \\ | \quad | \\ \hline \swarrow \quad \searrow \\ \uparrow \quad \uparrow \end{array} + \begin{array}{c} \swarrow \quad \searrow \\ | \quad | \\ \hline \swarrow \quad \searrow \\ \uparrow \quad \uparrow \end{array} \\
 & + \begin{array}{c} \uparrow \quad \uparrow \\ | \quad | \\ \hline \swarrow \quad \searrow \\ \swarrow \quad \searrow \end{array} + \begin{array}{c} \downarrow \quad \downarrow \\ | \quad | \\ \hline | \quad | \\ \downarrow \quad \downarrow \end{array} + \begin{array}{c} \swarrow \quad \searrow \\ | \quad | \\ \hline \swarrow \quad \searrow \\ \swarrow \quad \searrow \end{array} + \begin{array}{c} \downarrow \quad \downarrow \\ | \quad | \\ \hline \swarrow \quad \searrow \\ \downarrow \quad \downarrow \end{array} \\
 & + \begin{array}{c} \uparrow \quad \uparrow \\ | \quad | \\ \hline \swarrow \quad \searrow \\ \swarrow \quad \searrow \end{array} + \begin{array}{c} \uparrow \quad \uparrow \\ | \quad | \\ \hline | \quad | \\ \downarrow \quad \downarrow \end{array} + \begin{array}{c} \swarrow \quad \searrow \\ | \quad | \\ \hline \swarrow \quad \searrow \\ \swarrow \quad \searrow \end{array} + \begin{array}{c} \swarrow \quad \searrow \\ | \quad | \\ \hline \swarrow \quad \searrow \\ \downarrow \quad \downarrow \end{array} \\
 & + \begin{array}{c} \swarrow \quad \searrow \\ | \quad | \\ \hline \swarrow \quad \searrow \\ \swarrow \quad \searrow \end{array} + \begin{array}{c} \downarrow \quad \downarrow \\ | \quad | \\ \hline \swarrow \quad \searrow \\ \swarrow \quad \searrow \end{array} + \begin{array}{c} \downarrow \quad \downarrow \\ | \quad | \\ \hline \swarrow \quad \searrow \\ \downarrow \quad \downarrow \end{array} + \begin{array}{c} \downarrow \quad \downarrow \\ | \quad | \\ \hline \downarrow \quad \downarrow \\ \downarrow \quad \downarrow \end{array}
 \end{aligned}$$

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

WHY ANNIHILATION AND CREATION OPERATORS?

- Keep track of antisymmetrization
- Hole-particle formalism. Easier to handle “vacuum” (closed shell configuration) + few *generalized particles* (particles and holes) than full N -body system
- Convenient with the systematic construction of higher-order effects (to come).

PHASES IN EXERCISE 4.10

4.10

$$= (-1)^{2s} (-1)^{s+e+j} (-1)^{e+e'+k}$$

$\underbrace{\hspace{1cm}}_{-1} \quad \underbrace{\hspace{1cm}}_{\text{even}}$

$$= -(-1)^{s+e+j} \left\{ \begin{matrix} j & j' & k \\ e' & e & s \end{matrix} \right\}$$

$\underbrace{\hspace{1cm}}_{=1}$

$\Rightarrow \{ \} \text{---}^+$

4.10

PHASES IN EXERCISE 4.10

4.10

$$\underbrace{(-1)^{2s} (-1)^{l+s+j}}_{-1} \{ \begin{matrix} j & j' & k \\ l' & l & s \end{matrix} \}$$

$$\underbrace{(-1)^{2j} (-1)^{j+j'+j}}_{(-1)^{j+j'-j}} \{ \begin{matrix} j & j' & k \\ j & j' & j \end{matrix} \}$$

$$\underbrace{\begin{matrix} \chi \\ - \text{---} \text{---} + \\ j' \\ j \end{matrix}}_{=1}$$