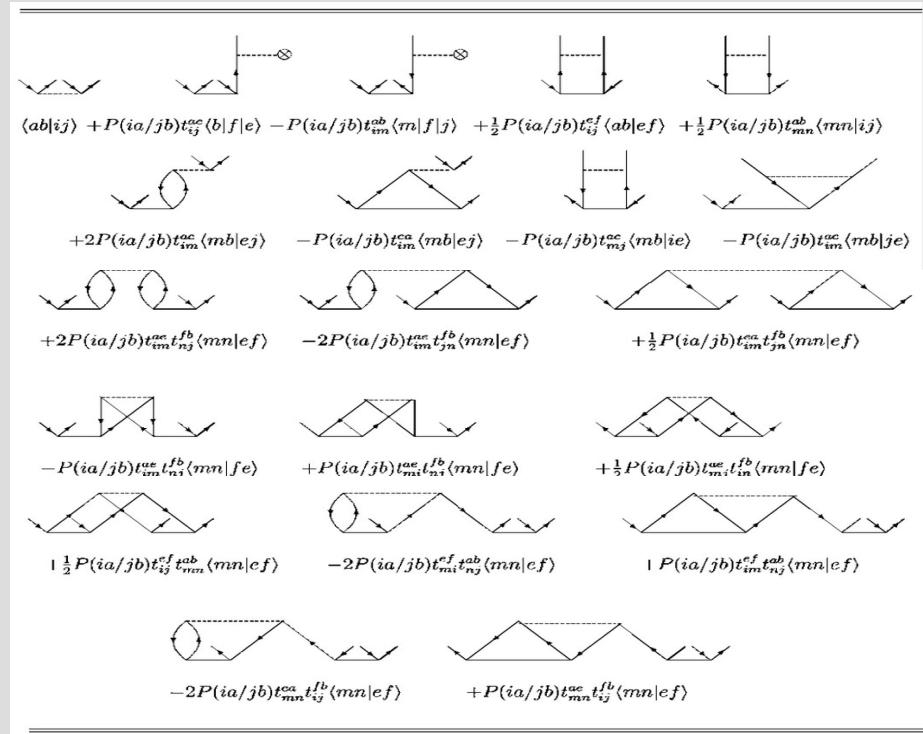


# Perturbation Theory, Linked-Diagrams, Coupled-Cluster, Size-Extensivity and Size-Consistency

$$|\Psi_{CC}\rangle = \exp(\hat{T})|\Phi_0\rangle$$

$$= (1 + \hat{T} + \hat{T}^2/2 + \hat{T}^3/3! + \dots)|\Phi_0\rangle$$

Arik Landau



## Size extensivity

Size-extensivity and size-intensivity refer to properties that scale linearly or become independent of the size of the system in the thermodynamic limit:

## Size extensivity

Size-extensivity and size-intensivity refer to properties that scale linearly or become independent of the size of the system in the thermodynamic limit:



$$\lim_{n \rightarrow \infty} (E_{n+1} - E_n) = C$$

Nooijen, Shamasundar and Mukerjee *Molec. Phys.* **103**, 2277 (2005)

Size consistency [1] deals with two non-interacting systems  $A$  and  $B$  and states that the energy of the compound system should be the sum of the energies of the individual systems

$$E_{AB} = E_A + E_B.$$

Michael Hanrath *Chem. Phys.* **356**, 31 (2009)

# Graphical Representation of Normal-Ordered Operators

$$V = V_0 + V_1 + V_2$$

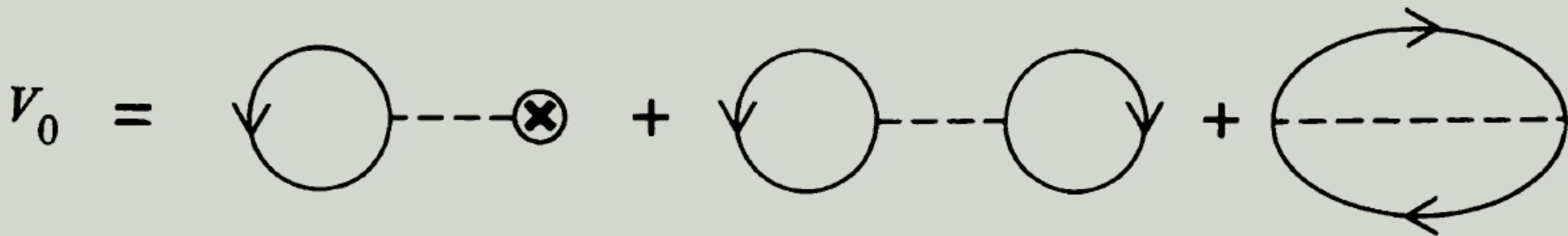
# Graphical Representation of Normal-Ordered Operators

$$V = V_0 + V_1 + V_2$$

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

$$V_1 = \sum_{ij} \{a_i^\dagger a_j\} \langle i | v | j \rangle$$

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



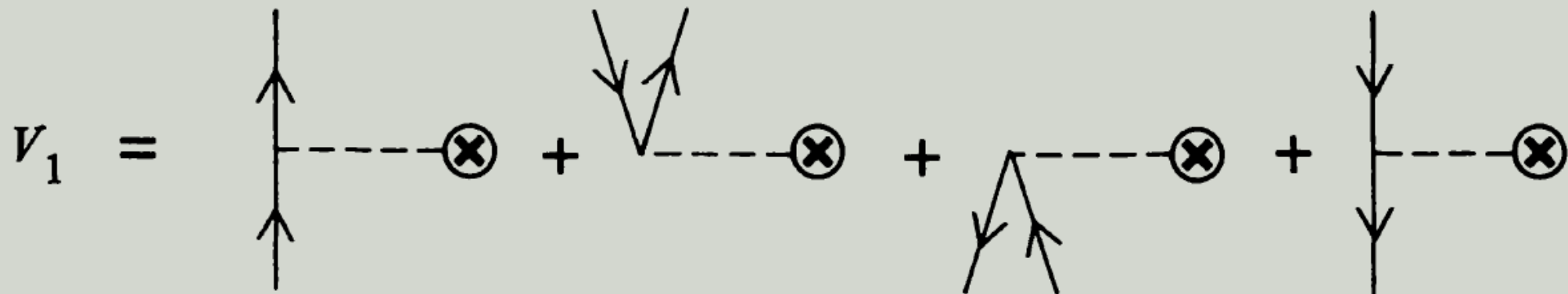
# Graphical Representation of Normal-Ordered Operators

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



# Graphical Representation of Normal-Ordered Operators

$$V_2 = \begin{array}{c} \uparrow \\ | \\ \uparrow \\ | \\ \uparrow \end{array} - \begin{array}{c} \uparrow \\ | \\ \uparrow \\ | \\ \uparrow \end{array} + \begin{array}{c} \swarrow \uparrow \\ | \\ \uparrow \\ | \\ \uparrow \end{array} + \begin{array}{c} \uparrow \\ | \\ \uparrow \\ | \\ \swarrow \uparrow \end{array} + \boxed{\begin{array}{c} \swarrow \uparrow \quad \swarrow \uparrow \\ | \\ \uparrow \\ | \\ \uparrow \end{array}}$$

Topological  
equivalent

$$+ \begin{array}{c} \swarrow \uparrow \quad \uparrow \\ | \\ \uparrow \\ | \\ \uparrow \end{array} + \begin{array}{c} \downarrow \\ | \\ \downarrow \\ | \\ \uparrow \end{array} + \begin{array}{c} \swarrow \uparrow \quad \swarrow \uparrow \\ | \\ \downarrow \\ | \\ \uparrow \end{array} + \begin{array}{c} \downarrow \\ | \\ \downarrow \\ | \\ \swarrow \uparrow \end{array}$$

$$+ \begin{array}{c} \uparrow \\ | \\ \uparrow \\ | \\ \swarrow \uparrow \end{array} + \begin{array}{c} \uparrow \\ | \\ \uparrow \\ | \\ \downarrow \end{array} + \begin{array}{c} \swarrow \uparrow \\ | \\ \swarrow \uparrow \\ | \\ \downarrow \end{array} + \begin{array}{c} \swarrow \uparrow \\ | \\ \downarrow \\ | \\ \downarrow \end{array}$$

$$+ \boxed{\begin{array}{c} \swarrow \uparrow \quad \swarrow \uparrow \\ | \\ \downarrow \\ | \\ \downarrow \end{array}} + \begin{array}{c} \downarrow \\ | \\ \downarrow \\ | \\ \swarrow \uparrow \end{array} + \begin{array}{c} \swarrow \uparrow \\ | \\ \downarrow \\ | \\ \downarrow \end{array} + \begin{array}{c} \downarrow \\ | \\ \downarrow \\ | \\ \downarrow \end{array}$$

# The Wave Operator

$$H_0|\alpha\rangle = E_0|\alpha\rangle$$

$$E_0 = \sum_{i=1}^N \varepsilon_i$$

$$\Psi_0 = |\alpha\rangle$$

$$|\alpha\rangle = |\{\varphi_i\varphi_j\varphi_k \dots\}\rangle$$

$$\Psi_0 = P\Psi$$

$$H\Psi = E\Psi$$

$$P = |\alpha\rangle\langle\alpha|$$

$$Q = \sum_{\beta \neq \alpha} |\beta\rangle\langle\beta| = \mathbf{1} - P$$

$$\Psi = \Omega\Psi_0$$

$$(\Omega - 1)\Psi_0 = \Psi - P\Psi = Q\Psi$$



# The Wave Operator

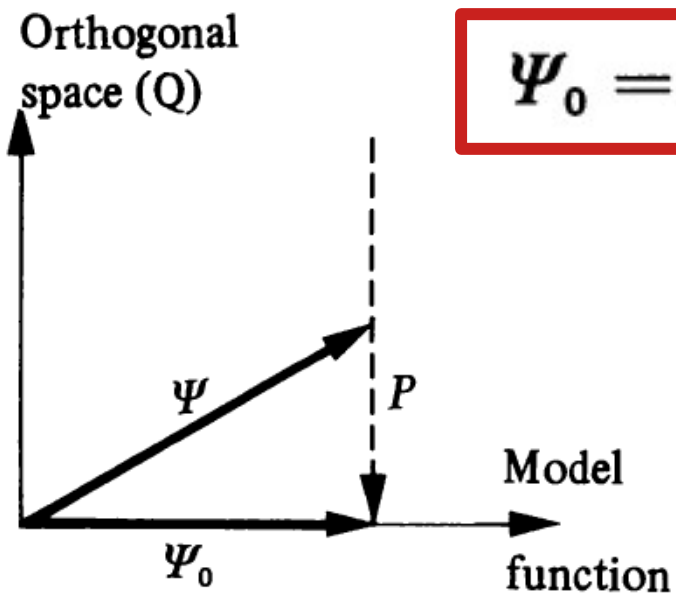
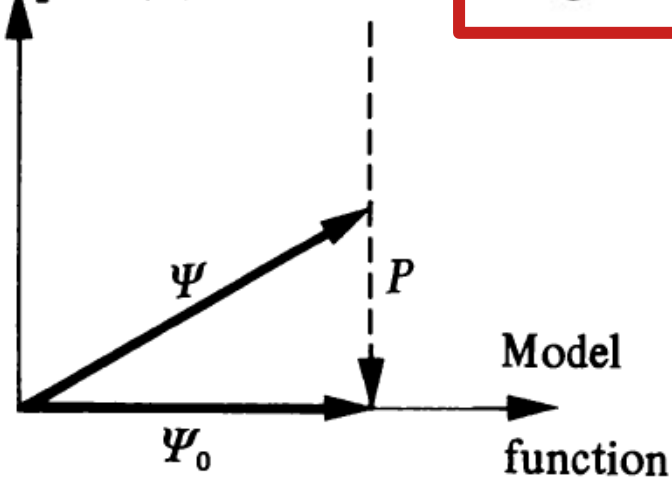


Fig. 9.1. Simple illustration of the wave operator (S projects out of any function the component along the generates the exact wave function by operating on S

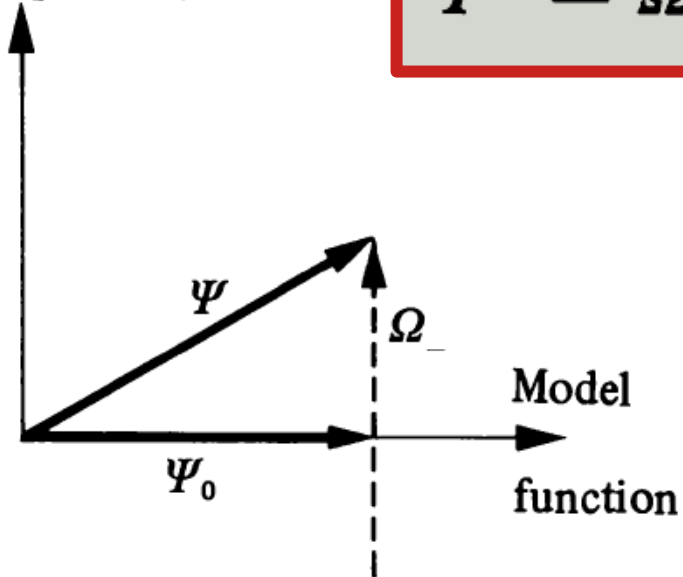
# The Wave Operator

Orthogonal  
space (Q)



$$\Psi_0 = P\Psi$$

Orthogonal  
space (Q)



$$\Psi = \Omega\Psi_0$$

**Fig. 9.1.** Simple illustration of the wave operator ( $\Omega_E$ ) and the projection operator ( $P$ ).  $P$  projects out of any function the component along the model function  $\Psi_0$ , and the wave operator generates the exact wave function by operating on  $\Psi_0$

## The Generalized Bloch Equation

$$H\Psi^a = E^a\Psi^a,$$

$$(E^a - H_0)\Psi_0^a = PV\Psi^a$$

which we rewrite as

$$(E^a - H_0)\Psi^a = V\Psi^a,$$

$a$  = Ground Electronic State

We operate on this equation from the left first with  $P = |\alpha\rangle\langle\alpha|$

## The Generalized Bloch Equation

$$H\Psi^a = E^a\Psi^a,$$

$$(E^a - H_0)\Psi_0^a = PV\Psi^a$$

which we rewrite as

and then with  $\Omega$ ,

$$(E^a - H_0)\Psi^a = V\Psi^a,$$

$$E^a\Psi^a - \Omega H_0\Psi_0^a = \Omega PV\Omega\Psi_0^a,$$

$a$  = Ground Electronic State

$$\Psi^a = \Omega\Psi_0^a$$

$$(\Omega H_0 - H_0\Omega)\Psi_0^a = (V\Omega - \Omega PV\Omega)\Psi_0^a.$$

$$[\Omega, H_0] P = V\Omega P - \Omega PV\Omega P.$$

## The Generalized Bloch Equation

Perturbative  
Expansion

$$[\Omega, H_0] P = V\Omega P - \Omega P V \Omega P .$$

$$\Omega = 1 + \Omega^{(1)} + \Omega^{(2)} + \dots$$

$$[\Omega^{(1)}, H_0] P = QVP$$

$$[\Omega^{(2)}, H_0] P = QV\Omega^{(1)} P - \Omega^{(1)} PVP$$

$$[\Omega^{(3)}, H_0] P = QV\Omega^{(2)} P - \Omega^{(2)} PVP - \Omega^{(1)} PV\Omega^{(1)} P$$

## The Generalized Bloch Equation

Perturbative  
Expansion

$$[\Omega, H_0] P = V\Omega P - \Omega P V \Omega P .$$

$$[\Omega^{(n)}, H_0] P = QV\Omega^{(n-1)} P - \sum_{m=1}^{n-1} \Omega^{(n-m)} P V \Omega^{(m-1)} P .$$

$$[\Omega^{(1)}, H_0] P = QVP$$

$$[\Omega^{(2)}, H_0] P = QV\Omega^{(1)} P - \Omega^{(1)} P V P$$

$$[\Omega^{(3)}, H_0] P = QV\Omega^{(2)} P - \Omega^{(2)} P V P - \Omega^{(1)} P V \Omega^{(1)} P$$

## The Generalized Bloch Equation

Perturbative  
Expansion

$$[\Omega, H_0] P = V\Omega P - \Omega P V \Omega P .$$

$$[\Omega^{(n)}, H_0] P = Q V \Omega^{(n-1)} P - \sum_{m=1}^{n-1} \Omega^{(n-m)} P V \Omega^{(m-1)} P .$$

When the wave operator is known in a certain order, the energy can be obtained in the next higher order by means of (12.37)

$$E^{(n+1)} = \langle \alpha | (V_1 + V_2) \Omega^{(n)} | \alpha \rangle . \quad (12.53)$$

## The Second-Order Energy

The first-order wave function

$$\Psi^{(1)} = \Omega^{(1)} |\alpha\rangle ,$$

$$[\Omega^{(1)}, H_0] P = QVP .$$

the first-order wave operator satisfies the equation



## The Second-Order Energy

The first-order wave function

$$\Psi^{(1)} = \Omega^{(1)} |\alpha\rangle,$$

$$[\Omega^{(1)}, H_0] P = QVP.$$

$$QVP = a \begin{array}{c} \swarrow \searrow \\ \vee \wedge \\ \text{---} \otimes \end{array} + a \begin{array}{c} \swarrow \searrow \\ \vee \wedge \\ \text{---} \end{array} \begin{array}{c} \swarrow \searrow \\ \vee \wedge \\ \text{---} \end{array} b$$

$$P = |\alpha\rangle\langle\alpha|$$

$$\Omega^{(1)} = \begin{array}{c} \swarrow \searrow \\ \vee \wedge \\ \text{---} \otimes \end{array} + \begin{array}{c} \swarrow \searrow \\ \vee \wedge \\ \text{---} \end{array} \begin{array}{c} \swarrow \searrow \\ \vee \wedge \\ \text{---} \end{array}$$

# The Second-Order Energy

$$E^{(2)} = \langle \alpha | (V_1 + V_2) \Omega^{(1)} | \alpha \rangle .$$

$$E^{(2)} = \text{(a)} + \text{(b)} + \text{(c)}$$

**Fig. 12.4 a-c.** Graphical representation of the second-order energy for closed-shell systems. Diagram (a) vanishes if Hartree-Fock orbitals are used

$$\langle \alpha'_a | H | \alpha \rangle = 0 .$$

$$\Omega^{(1)} = \text{(a)} + \text{(b)}$$

## 12.5 The Linked-Diagram Expansion

The procedure we have developed here can easily be extended to higher orders. In this section we shall consider the wave operator in third order, where so-called *unlinked diagrams* appear for the first time.<sup>1</sup> It will be shown that all such diagrams disappear in that order, and this result will be used to formulate the general linked-diagram theorem for closed-shell systems.

## Cancellation of Unlinked Diagrams in Third Order

the generalized Bloch equation.

$$[\Omega^{(n)}, H_0] P = QV\Omega^{(n-1)} P - \sum_{m=1}^{n-1} \Omega^{(n-m)} P V \Omega^{(m-1)} P$$

$$[\Omega^{(3)}, H_0] P = QV\Omega^{(2)} P - \Omega^{(2)} P V P - \Omega^{(1)} P V \Omega^{(1)} P$$

$$-E^{(2)} \hat{\Omega}^{(1)}$$

$$P = |\alpha\rangle\langle\alpha|$$

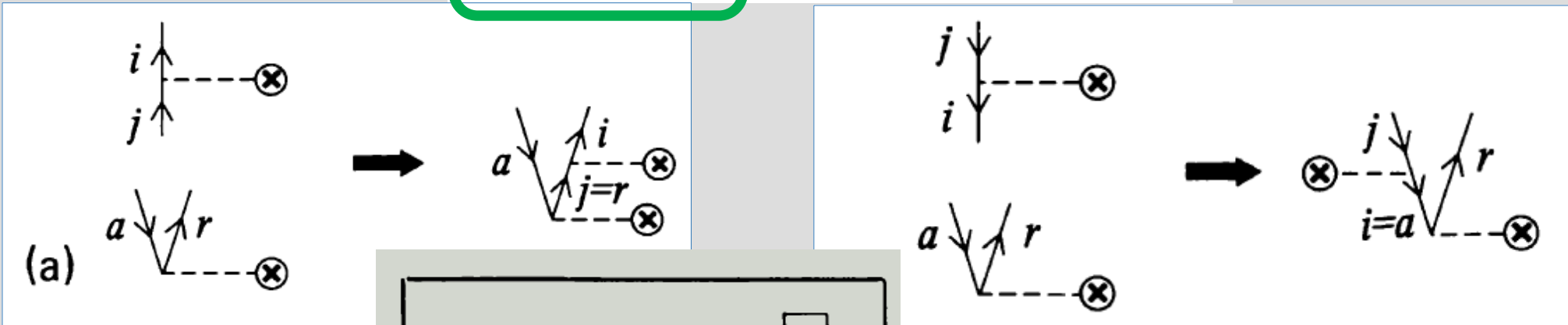
the last term becomes

the second term on the right-hand side cancels the  $V_0$  part of the first term.

$$[\Omega^{(3)}, H_0] = Q(V_1 + V_2)\Omega^{(2)} - E^{(2)}\Omega^{(1)}$$

# Cancellation of Unlinked Diagrams in Third Order

$$[\Omega^{(2)}, H_0] = Q(V_1 + V_2)\Omega^{(1)}$$



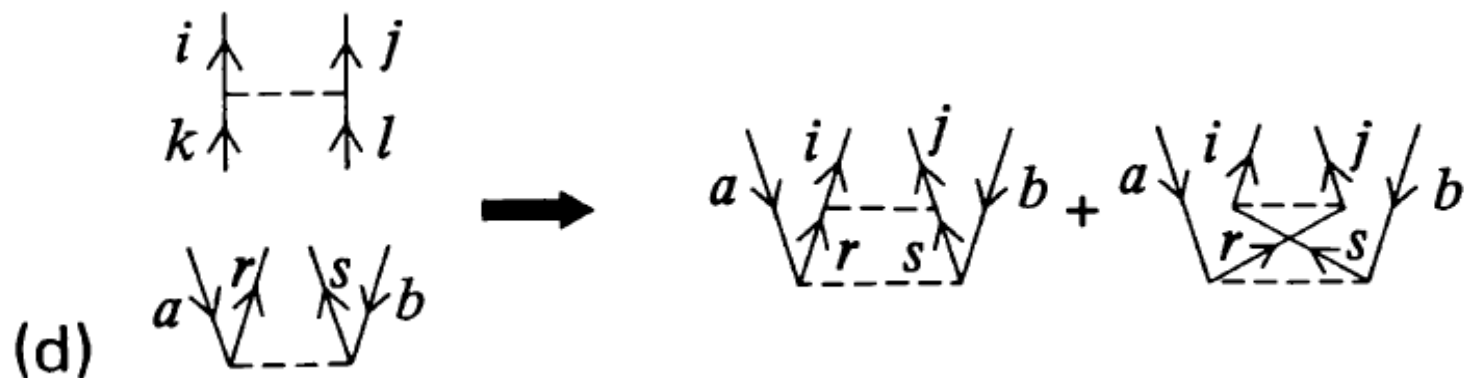
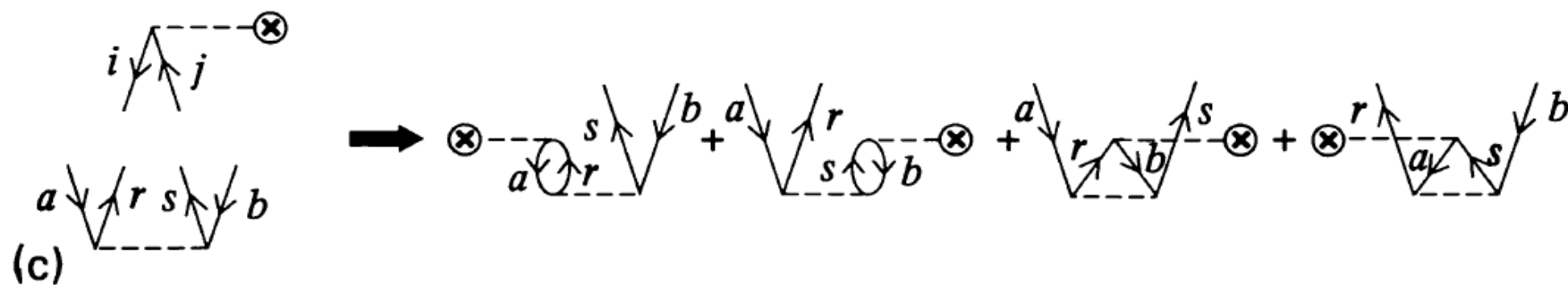
$$AB = \{AB\} + \overline{\{AB\}}$$

Illustration of the commutator equation for the second-order wave-operator diagrams.

$$\Omega^{(1)} = \text{[Diagram 1]} + \text{[Diagram 2]}$$

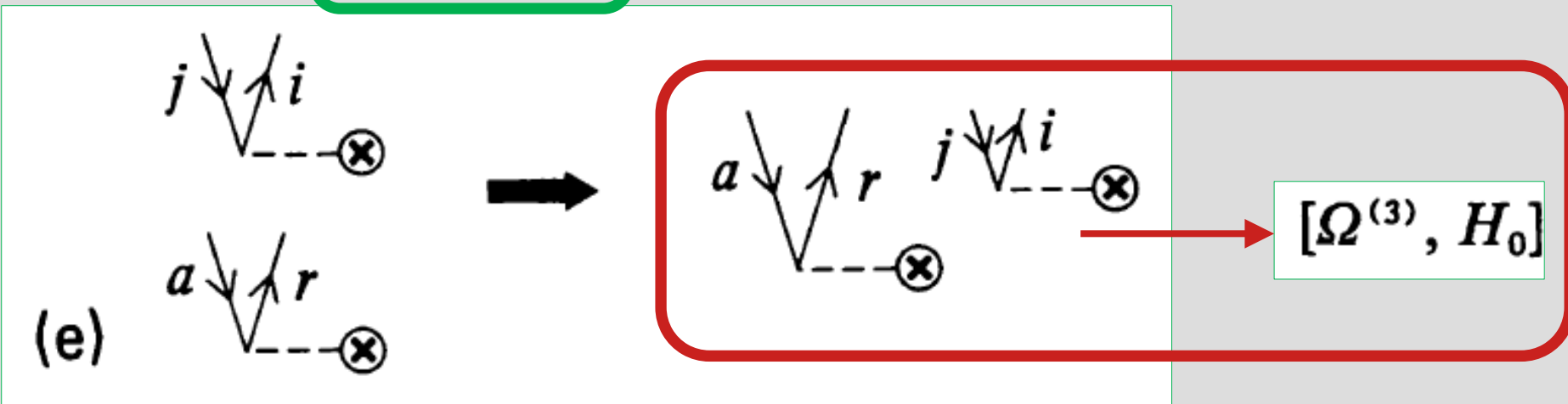
# Cancellation of Unlinked Diagrams in Third Order

$$[\Omega^{(2)}, H_0] = Q(V_1 + V_2)\Omega^{(1)}$$



# Cancellation of Unlinked Diagrams in Third Order

$$[\Omega^{(2)}, H_0] = Q(V_1 + V_2)\Omega^{(1)}$$

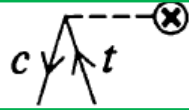


some of the  $\Omega^{(2)}$  diagrams are *disconnected*.

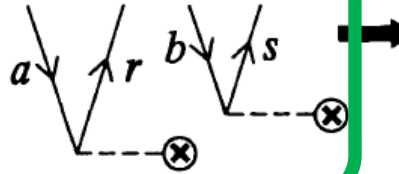
$$AB = \{AB\} + \{\overline{AB}\}$$

# Cancellation of Unlinked Diagrams in Third Order

$$[\Omega^{(3)}, H_0] = Q(V_1 + V_2)\Omega^{(2)} - E^{(2)}\Omega^{(1)}$$



Disconnected  
 $\Omega^{(2)}$  Diagram





# Cancellation of Unlinked Diagrams in Third Order

$$[\Omega^{(3)}, H_0] = Q(V_1 + V_2)\Omega^{(2)} - E^{(2)}\Omega^{(1)}$$

Disconnected  $\Omega^{(2)}$  Diagram

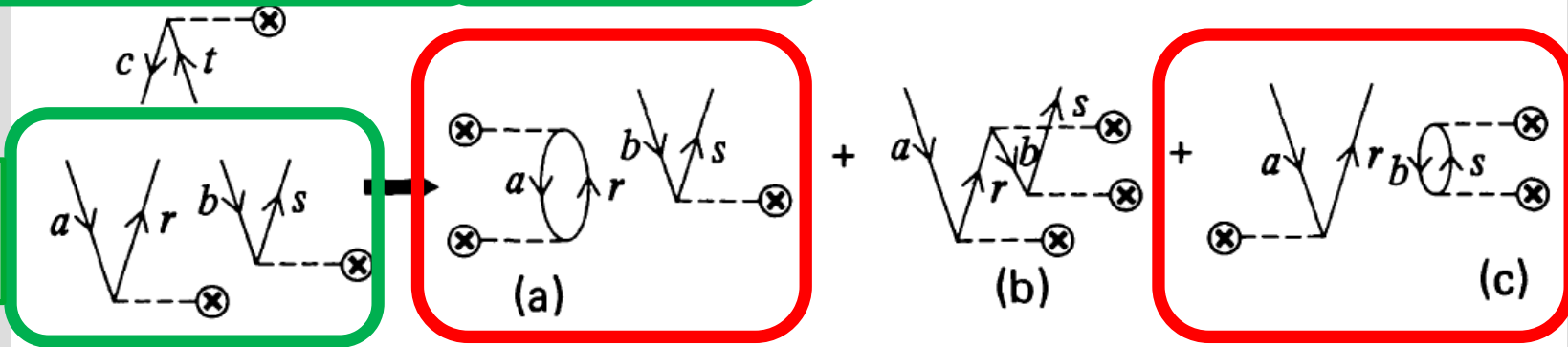


Fig. 12.6 Unlinked diagrams (a, c) can be formed when  $V$  operates on a disconnected wave-

$$E_1^{(2)}\Omega_1^{(1)} = \sum_{ar} \left[ \text{Diagram (a)} \right] \times \sum_{bs} \left[ \text{Diagram (c)} \right] \quad (12.49)$$

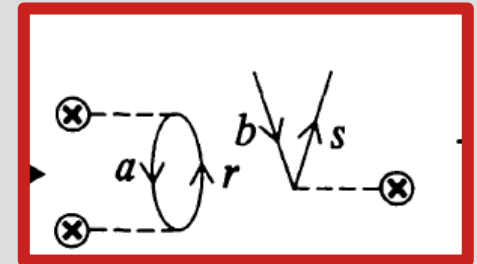
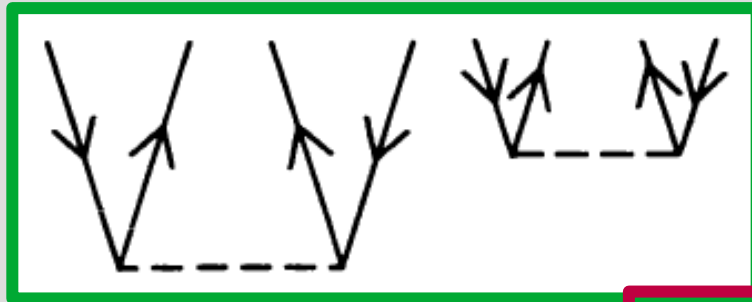
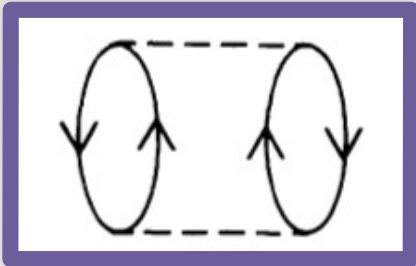
The unlinked diagrams (a) and (c) are used to cancel (12.49).

# The Linked-Diagram Expansion

a diagram is **closed** if it has no free orbital lines

and that

a diagram is **unlinked** if it has a **disconnected, closed part**.

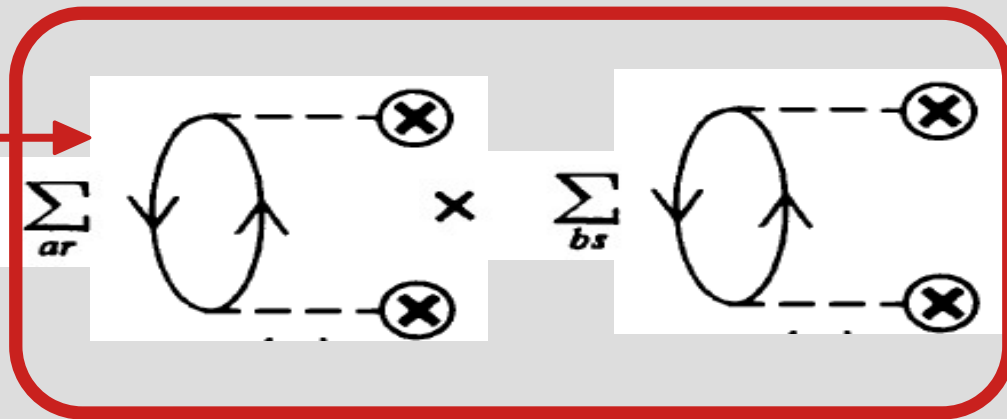
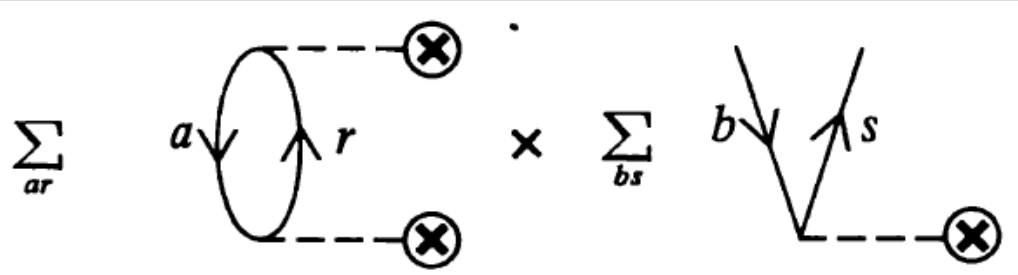
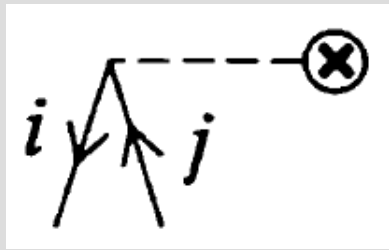


What if we take *unlinked* terms into account ?

# What if we take *unlinked* terms into account ?

$$E^{(n+1)} = \langle \alpha | (V_1 + V_2) \Omega^{(n)} | \alpha \rangle$$

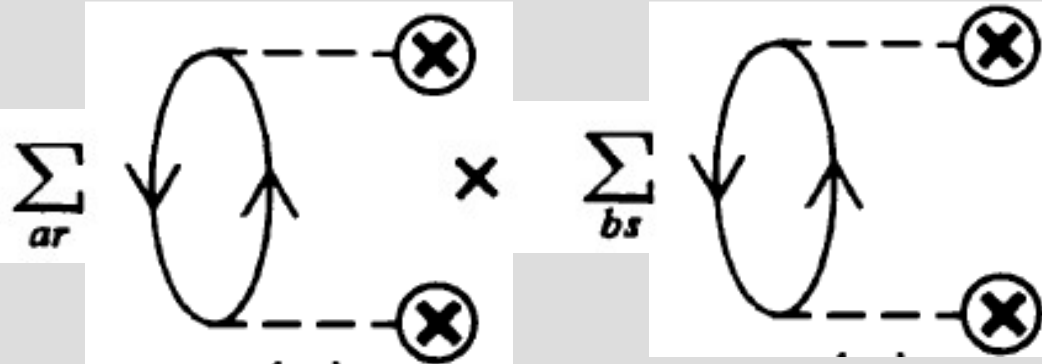
$n=3$



# Unlinked Diagrams in Third Order

## Size extensivity

unlinked diagrams are “unphysical” in the sense that their energy contribution increases nonlinearly with the size of the system. An unlinked energy diagram for a closed-shell system can be separated into two or more diagram parts, each of which is an allowed (linked) energy diagram. In each such part there is an independent summation over *all* electrons of the system.



# Unlinked Diagrams in Third Order

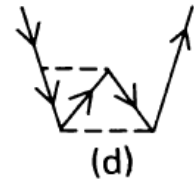
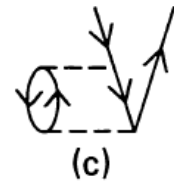
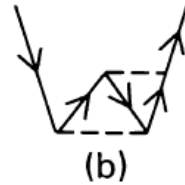
## Size consistency

In each such part there is an independent summation over *all* electrons of the system. For a system of noninteracting atoms this would lead to “cross-terms”, where different parts of the diagram refer to different atoms. Obviously, such nonlinear terms have no physical relevance: and, in particular, they can cause a considerable error in calculations of quantities like dissociation energies. Such nonlinear effects are retained in truncated CI, while they are eliminated in LDE.

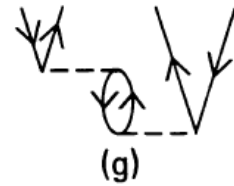
Lets see an other example...

# Unlinked Diagrams in Third Order

$$[\Omega^{(2)}, H_0] = Q(V_1 + V_2)\Omega^{(1)}$$

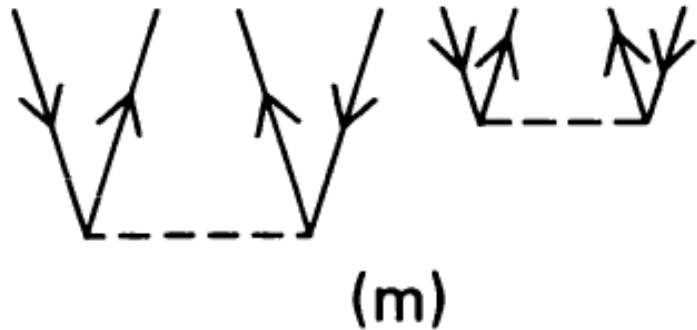


second-order wave-operator diagrams



some of the  $\Omega^{(2)}$  diagrams are *disconnected*.

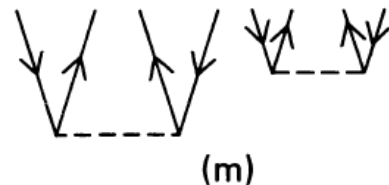
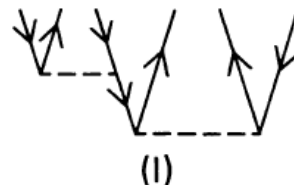
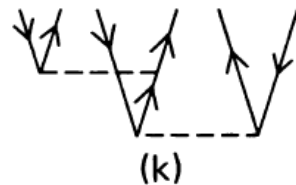
$$[\Omega^{(3)}, H_0] = Q(V_1 + V_2)\Omega^{(2)} - E^{(2)}\Omega^{(1)}$$



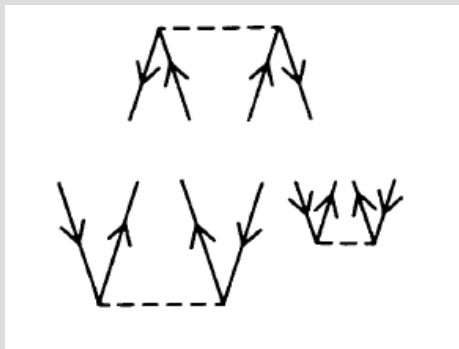
(h)

(i)

(j)



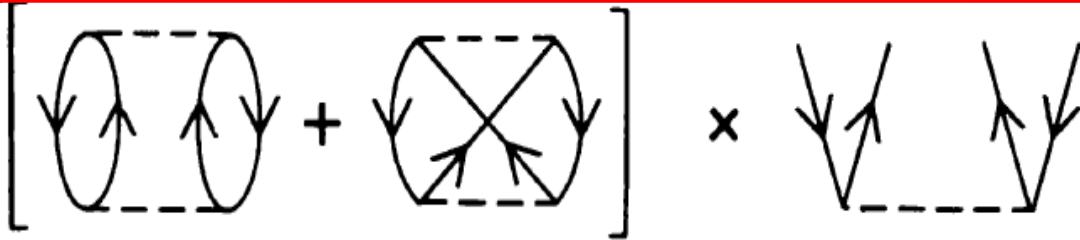
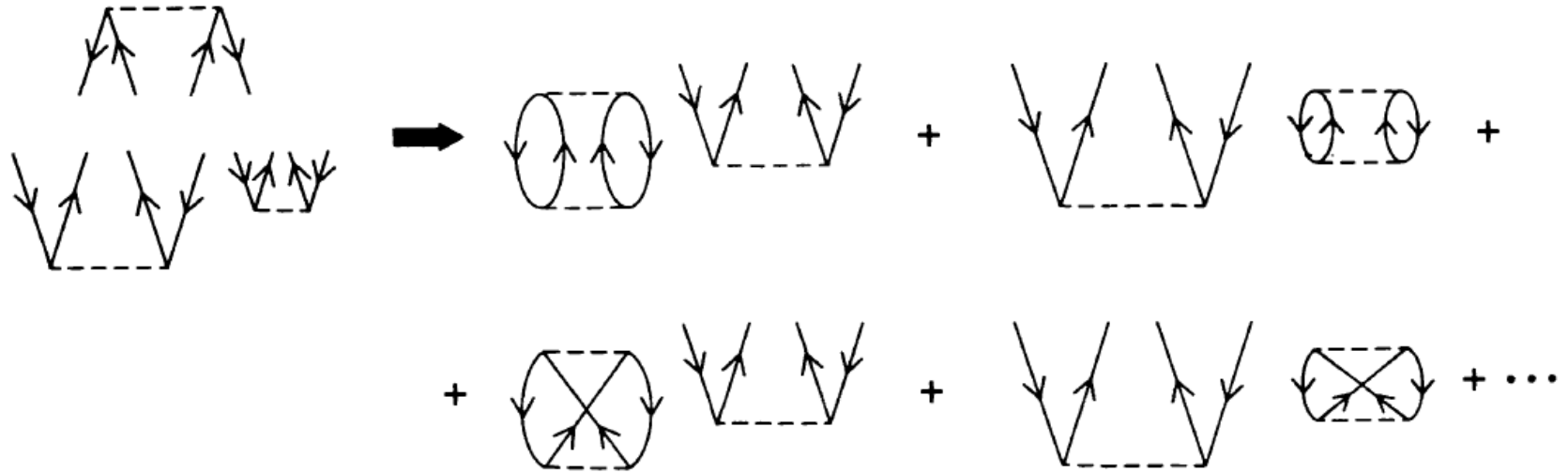
# Unlinked Diagrams



$$[\Omega^{(3)}, H_0] = Q(V_1 + V_2)\Omega^{(2)} - E^{(2)}\Omega^{(1)}$$

# Unlinked Diagrams

$$[\Omega^{(3)}, H_0] = Q(V_1 + V_2)\Omega^{(2)} - E^{(2)}\Omega^{(1)}$$

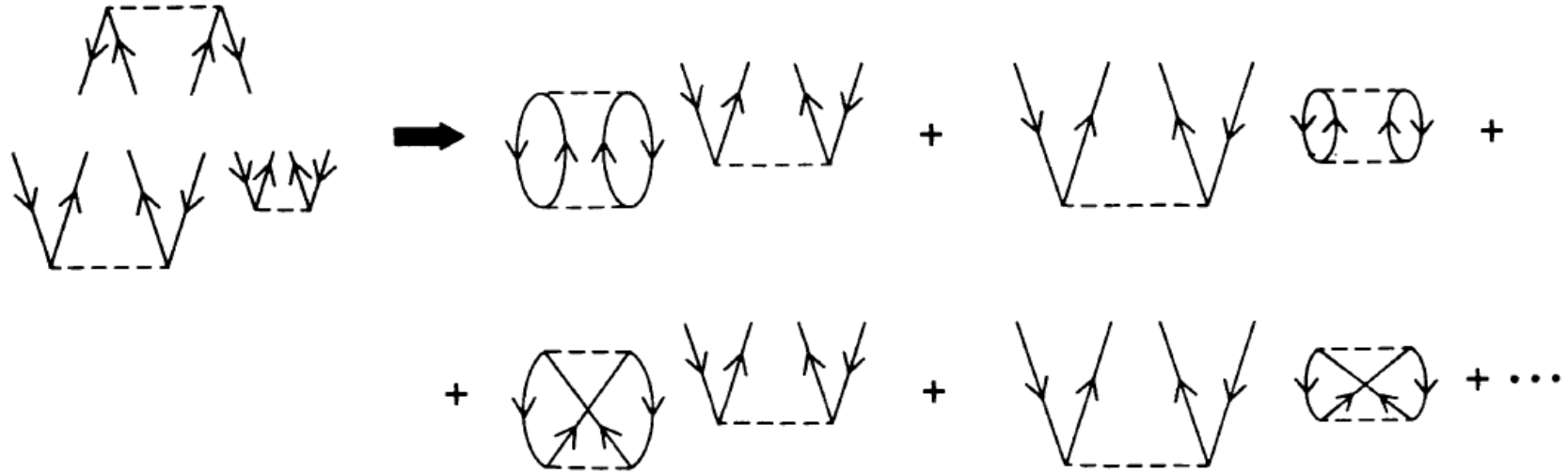


“unphysical” situation



# Unlinked Diagrams

$$[\Omega^{(3)}, H_0] = Q(V_1 + V_2)\Omega^{(2)} - E^{(2)}\Omega^{(1)}$$



$$\left[ \text{diagram with two loops} + \text{diagram with two loops and a cross} \right] \times \text{tree diagram} = E_2^{(2)} \text{tree diagram}$$

cancel the corresponding part of  $-E^{(2)}\Omega^{(1)}$

## Unlinked Diagrams

It can be shown in a similar way that the unlinked diagrams cancel in higher orders. Recalling that  $\Omega^{(0)} \equiv 1$ , this leads to

$$[\Omega^{(n)}, H_0] = (QV\Omega^{(n-1)})_{\text{linked}} \quad (12.52)$$

Thus, we replace the generalized Bloch Eq. For the  $n$ -order  $\Omega^{(n)}$

$$[\Omega^{(n)}, H_0] P = QV\Omega^{(n-1)} P - \sum_{m=1}^{n-1} \Omega^{(n-m)} PV\Omega^{(m-1)} P .$$

with the LDE

# The Linked-Diagram Expansion

$$[\Omega^{(n)}, H_0] = (QV\Omega^{(n-1)})_{\text{linked}}$$

Unlinked, nonlinear terms have no physical relevance, they are retained in truncated CI, while they are eliminated in LDE.

- So why not use LDE?
- why do we need Coupled Cluster?

## The Generalized Bloch Equation

So far we have used the  
Perturbative Expansion

$$[\Omega, H_0] P = V\Omega P - \Omega P V \Omega P .$$

$$\Omega = 1 + \Omega^{(1)} + \Omega^{(2)} + \dots$$

$$[\Omega^{(1)}, H_0] P = QVP$$

$$[\Omega^{(2)}, H_0] P = QV\Omega^{(1)} P - \Omega^{(1)} PVP$$

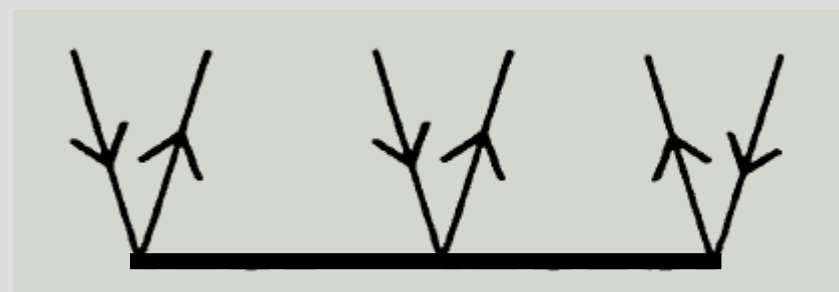
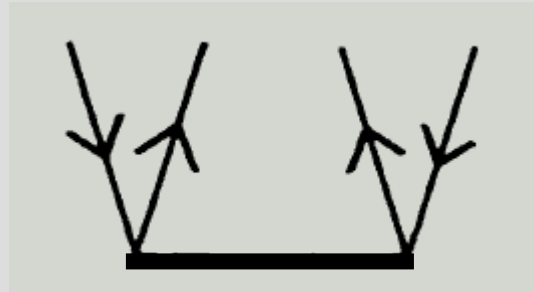
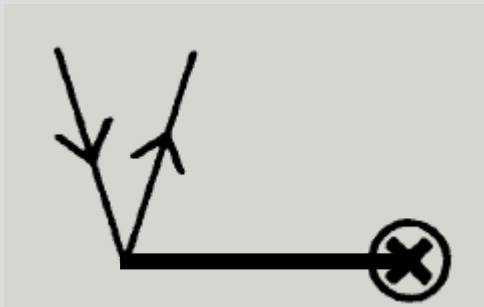
$$[\Omega^{(3)}, H_0] P = QV\Omega^{(2)} P - \Omega^{(2)} PVP - \Omega^{(1)} PV\Omega^{(1)} P$$

## 15.2 Hierarchy of $n$ -Particle Equations

### 15.2.1 General

Instead of expanding the wave operator order by order as in the previous chapters, we shall now separate this operator into one-, two-, ... body parts

$$\Omega = 1 + \chi = 1 + \Omega_1 + \Omega_2 + \Omega_3 + \dots \quad (15.3)$$



## Hierarchy of $n$ -Particle Equations

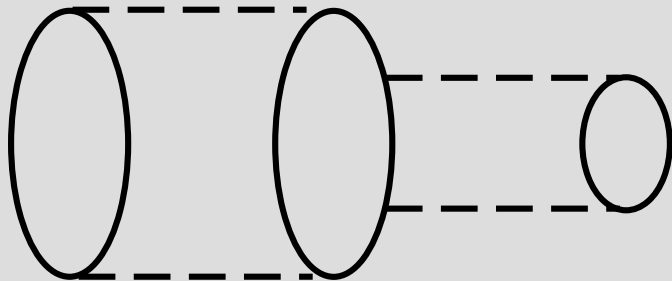
- We have seen how the electron correlation can be treated order by order.
- It is quite obvious, however, that this approach rapidly gets very cumbersome, and it is hardly feasible to go beyond the third-order energy in this way.
- As an alternative to the order-by-order expansion, the equations above can be separated into a *hierarchy of coupled one-, two-, ... particle equations*, which can be solved by means of an iterative procedure.
- This leads to a set of *coupled* equations, and solving them self-consistently is *equivalent to evaluating certain terms of the perturbation expansion to all orders*.

# Hierarchy of $n$ -Particle Equations

**Be atom** for which very accurate configuration-interaction (CI) calculations have been performed by Bunge [1968, 1976a,b].

Single excitations	0.35%
Double excitations	95.2%
Triple excitations	1.1%
Quadruple excitations	3.4%

- Qualitatively, we can understand these results by considering the order-by-order expansion of the energy. Remember the Brillouin condition:  $\langle \alpha'_a | H | \alpha \rangle = 0$ .



- e.g., the first contribution from triples:  
A 4<sup>th</sup> order energy diagram resulting from a 2<sup>nd</sup> order triple excitation  $\Omega^{(2)}$  operator

# Hierarchy of $n$ -Particle Equations

why do we need Coupled Cluster?



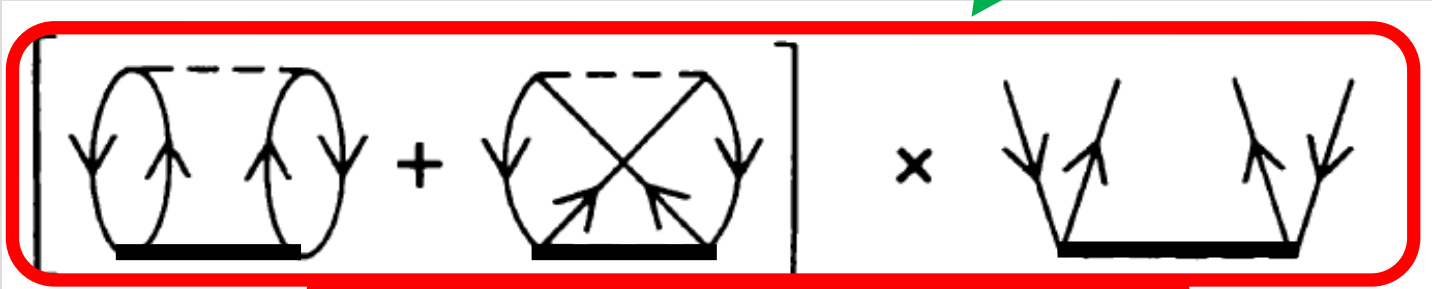
# Hierarchy of $n$ -Particle Equations

why do we need Coupled Cluster?

$$[\Omega, H_0] P = V\Omega P - \Omega P V \Omega P .$$

$V$  times a 4-body  $\Omega$

$V$  times *two* 2-body  $\Omega$



“unphysical” situation

# Hierarchy of $n$ -Particle Equations

$$[\Omega, H_0] P = V\Omega P - \Omega P V \Omega P$$

- In LDE unlinked diagrams of  $\Omega P V \Omega$  are cancelled by unlinked diagrams of  $Q V \Omega$ .
- However, quadruply excited terms of  $\Omega$  in  $Q V \Omega$  are required in order to cancel unlinked diagrams of  $\Omega P V \Omega$  with double excitations in the 2  $\Omega$  operators.
- Therefore, if the Bloch equation – or the Schrodinger equation - is truncated after double excitations, all unlinked diagrams with double excitations will not be cancelled.
- Hence, CI with singles and doubles is not size-extensive.
- By a slight modification of LDE it is possible to include such effects, which leads to the **exp(S) formalism or the coupled-cluster** approach. **I will show...**
- Such a procedure will then be more accurate than ordinary LDE-truncated at the same point-and it would have the important property that the wave function-as well as the energy-separates correctly when a system dissociates into smaller fragments.

# Hierarchy of $n$ -Particle Equations

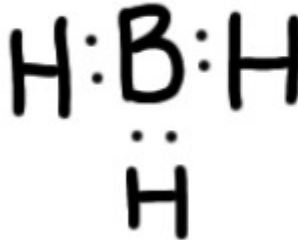
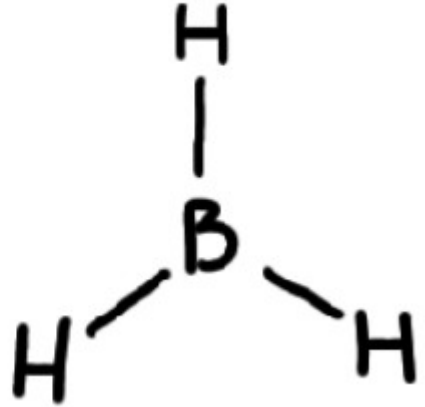
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# Hierarchy of $n$ -Particle Equations

Why more accurate procedure ?

**Table 15.2.** Relative contributions to the correlation energy of the  $\text{BH}_3$  molecule from connected and disconnected  $n$ -body diagrams (from [Paldus et al. 1972])

	$\text{B} - 1s^2 2s^2 2p^1$	Disconnected
One-body	 	—
Two-body		$\lesssim 0.1$
Three-body		$\lesssim 0.01$
Four-body		1.9

# Hierarchy of $n$ -Particle Equations

Why more accurate procedure ?

**Table 15.2.** Relative contributions to the correlation energy of the  $\text{BH}_3$  molecule from connected and disconnected  $n$ -body diagrams (from [Paldus et al. 1972])

	Total	Connected	Disconnected
One-body	0.1%	0.1%	—
Two-body	97.2	97.2	$\lesssim 0.1$
Three-body	0.8	0.8	$< 0.01$
Four-body	1.9	$\lesssim 0.01$	1.9

It has been found that "independent" pair excitations represented by the disconnected diagram corresponds to the most important quadruple excitations.

## The Exponential Ansatz

# The Coupled-Cluster Equations

$$\left\{ \begin{array}{l}
 \Omega_1 = S_1 \\
 \Omega_2 = S_2 + \frac{1}{2} \{S_1^2\} \\
 \Omega_3 = S_3 + \{S_2 S_1\} + \frac{1}{3!} \{S_1^3\} \\
 \Omega_4 = S_4 + \{S_3 S_1\} + \frac{1}{2} \{S_2^2\} + \frac{1}{2} \{S_2 S_1^2\} + \dots \\
 \dots \dots \dots
 \end{array} \right. \quad \begin{array}{l}
 S = S_1 + S_2 + S_3 + \dots \\
 S_n = (\Omega_n)_{\text{conn}}
 \end{array}$$

$S_n$  - is the Cluster Operator of  $n$  excitations, accounting for simultaneous interaction of  $n$  electrons.

$$\{\exp(S)\} = 1 + S + \frac{1}{2} \{S^2\} + \frac{1}{3!} \{S^3\} + \dots = \sum_{n=0}^{\infty} \frac{1}{n!} \{S^n\}, \quad (15.44)$$

# The Exponential Ansatz

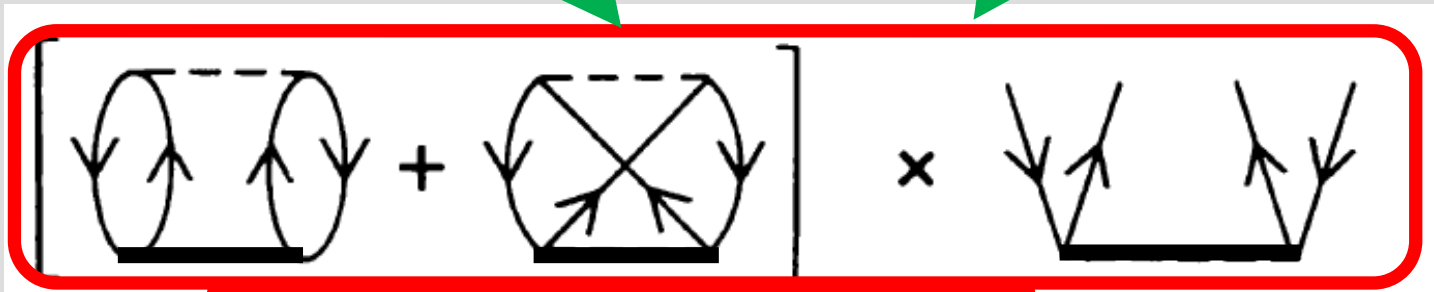
why do we need Coupled Cluster?

$$\Omega = \{\exp(S)\}$$

$$[\Omega, H_0] P = V\Omega P - \Omega P V \Omega P .$$

$V$  time  $\frac{1}{2}\{S^2\}$   
each 2-body

$V$  times two 2-body  $S$



“unphysical” situation

# The Exponential Ansatz

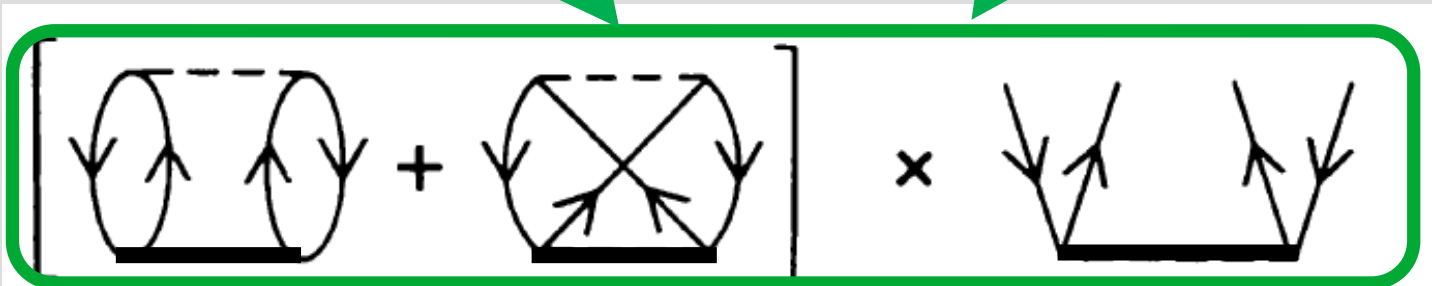
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each 2-body

$V$  times two 2-body  $S$



Thus

“unphysical” situation

does not happen in CC!



# The Coupled-Cluster Equations

equation for the cluster operator  $S$  is obtained from the linked-diagram formula by considering the *connected* parts of both sides

$$[\Omega, H_0] = (QV\Omega)_{\text{linked}}$$

FOR CLOSED SHELL SYSTEMS

$$[S, H_0] = (QV\Omega)_{\text{conn}}$$

separated into one-, two-, ... body equations

$$[S_n, H_0] = (QV\Omega)_{n,\text{conn}}$$

$$\Omega = \{\exp(S)\}$$

## Size extensivity

Size-extensivity is guaranteed by the evaluation of terms that the many-body development identifies as linked diagrams, hence the Brueckner-Goldstone (2–4) linked-diagram theorem of MBPT/CCM serves as the cornerstone of the theory.

Bartlett Ann. Rev. Phys. Chem. 32, 359 (1981)

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If a method is extensive in the general sense it means that if the energy is expressed as a perturbation series with respect to a single determinantal vacuum, the energy will necessarily consist of connected diagrams only.

Nooijen, Shamasundar and Mukerjee *Molec. Phys.* **103**, 2277 (2005)

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The energy of a method is size extensive iff the diagrammatic expansion of the energy contains connected diagrams only [4].

Michael Hanrath *Chem. Phys.* **356**, 31 (2009)

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## Size extensivity

Size-extensivity is an important component of the 'Systematic Treatment of Electron Correlation'

and then methods that satisfy the definition of size-extensivity can also be expected to yield consistent accuracy for systems of increasing size.

Size-extensivity is very important for the accuracy of a method. The accuracy of CISD methods significantly deteriorates with the size of the atom under consideration, while CCSD methods are generally unaffected.

Size consistency

Size extensivity

the exact wavefunction can be shown to have certain qualitative properties.

These are “size consistency” [1] and “size extensivity” [2–4]. Meeting those criteria usually guarantees a fast convergence of the many-body wavefunction.

Michael Hanrath *Chem. Phys.* **356**, 31 (2009)

# The Coupled-Cluster Equations

REVIEWS OF MODERN PHYSICS, VOLUME 79, JANUARY–MARCH 2007

## Coupled-cluster theory in quantum chemistry

Rodney J. Bartlett and Monika Musiał\*

# The Coupled-Cluster Equations

$$|\Psi_0\rangle = e^T |\Phi\rangle$$

$$T^{(\text{CCSD})} = T_1 + T_2$$

$$E_{CC} = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle$$

$$\langle \Phi_{i_1}^{a_1} | \bar{H}^{(\text{CCSD})} | \Phi \rangle = 0,$$

$$\langle \Phi_{i_1 i_2}^{a_1 a_2} | \bar{H}^{(\text{CCSD})} | \Phi \rangle = 0, \quad i_1 < i_2, \quad a_1 < a_2,$$

where

$$\bar{H}^{(\text{CCSD})} = e^{-(T_1+T_2)} H e^{T_1+T_2} = (H e^{T_1+T_2})_C$$

$$\bar{H} = e^{-T} H e^T = (H e^T)_C$$



# The Coupled-Cluster Equations

Hausdorff expansion

$$\bar{H} = e^{-T} H e^T = (H e^T)_C$$

$$\begin{aligned} \bar{H} = H + [H, T] + \frac{1}{2} [[H, T] T] + \frac{1}{3!} [[[[H, T] T] T] \\ + \frac{1}{4!} [[[[[H, T] T] T] T], \end{aligned}$$

$$T_1 = \sum_{i,a} t_i^a \{a^\dagger i\} = \begin{array}{c} i \quad a \\ \searrow \quad \nearrow \\ \text{---} \end{array}$$

$$AB = \{AB\} + \{\overline{AB}\}$$

$$T_2 = \sum_{i>j, a>b} t_{ij}^{ab} \{a^\dagger i b^\dagger j\} = \begin{array}{c} i \quad a \quad j \quad b \\ \searrow \quad \nearrow \quad \searrow \quad \nearrow \\ \text{---} \end{array}$$

# CC vs. CI

$$|\Psi_{FCI}\rangle = \sum_I^{all} C_I |\Phi_0\rangle$$

$\equiv$   
 $\equiv$

$$|\Psi_{CC}\rangle = \exp(\hat{T}) |\Phi_0\rangle$$

S:

$$\hat{C}_1 = \hat{T}_1$$

D:

$$\hat{C}_2 = \hat{T}_2 + \frac{1}{2} \hat{T}_1^2$$

T:

$$\hat{C}_3 = \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \frac{1}{3!} \hat{T}_1^3$$

Q:

$$\hat{C}_4 = \hat{T}_4 + \frac{1}{2} \hat{T}_2^2 + \hat{T}_1 \hat{T}_3 + \frac{1}{2} \hat{T}_1^2 \hat{T}_2 + \frac{1}{4!} \hat{T}_1^4$$

## Similarity of the coupled-cluster (CC) equations

$$\langle \Phi_I | H e^T | \Phi_0 \rangle_C = 0$$

$$H = H_0 + V$$

$$\langle \Phi_I | H_0 T | \Phi_0 \rangle_C + \langle \Phi_I | V e^T | \Phi_0 \rangle_C = 0$$

$$T_I D_I + \langle \Phi_I | V (1 + T + \frac{1}{2} T^2 \dots) | \Phi_0 \rangle_C = 0$$

$$D_I = \Delta \epsilon_{HF}$$

canonical HF case  $f_{pq} = \epsilon_p \delta_{pq}$

$$[S_n, H_0] = (QV\Omega)_{n, \text{conn}}$$

## CCD - Coupled Cluster with Doubles

$$T_I D_I + \langle \Phi_I | V (1 + T + \frac{1}{2} T^2 \dots) | \Phi_0 \rangle_C = 0$$

$$T_2 D_2 + \langle \Phi_2 | V (1 + T_2 + \frac{1}{2} T_2^2 \dots) | \Phi_0 \rangle_C = 0$$

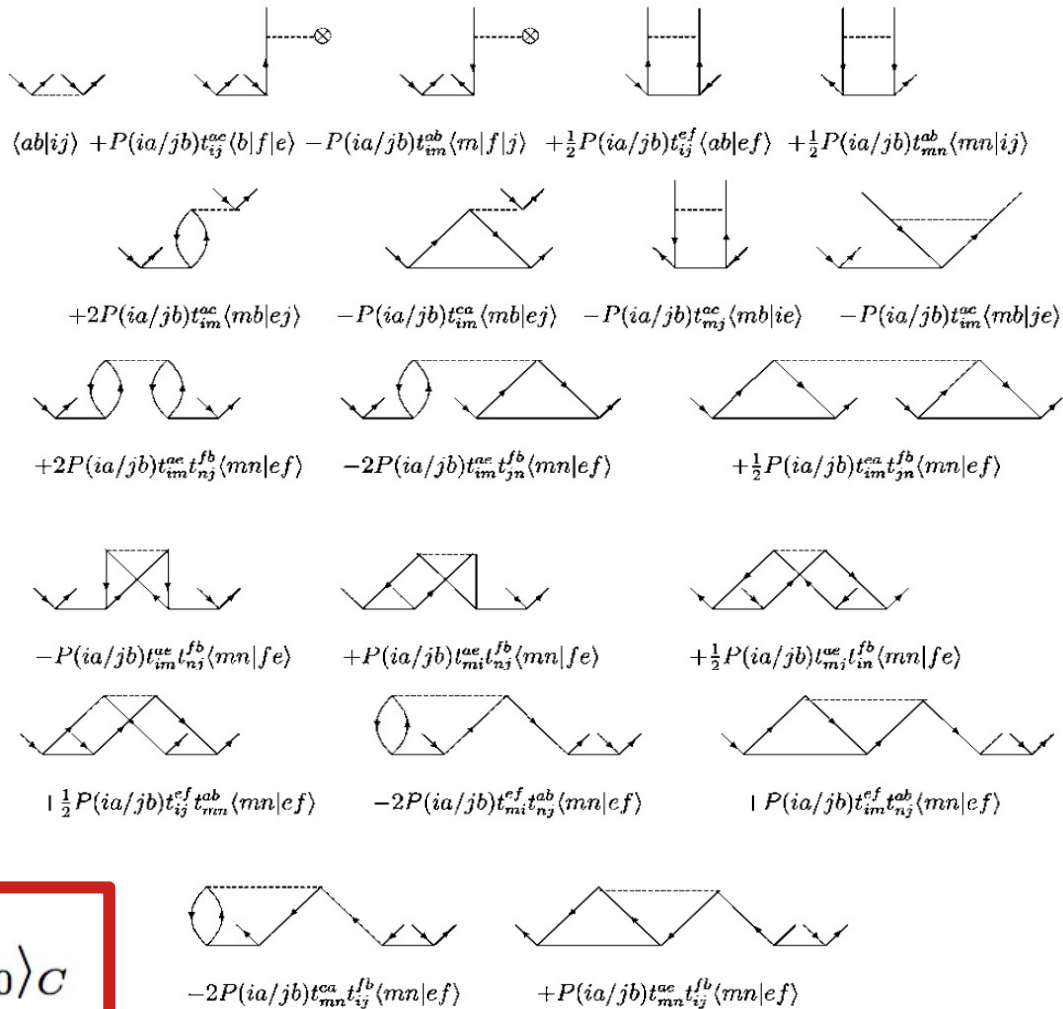
$$- T_{ij}^{ab} D_{ij}^{ab} = \langle \Phi_{ij}^{ab} | V (1 + T_2 + \frac{1}{2} T_2^2 \dots) | \Phi_0 \rangle_C$$

$$- D_{ij}^{ab} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$$

**T - is the Cluster Operator of two excitations**

$$\Psi_{\text{CCD}} = \exp(T_2)\Phi_0$$

CCD equation



$$T_2 = \sum_{i>j, a>b} t_{ij}^{ab} \{a^\dagger i b^\dagger j\} = \text{diagram}$$

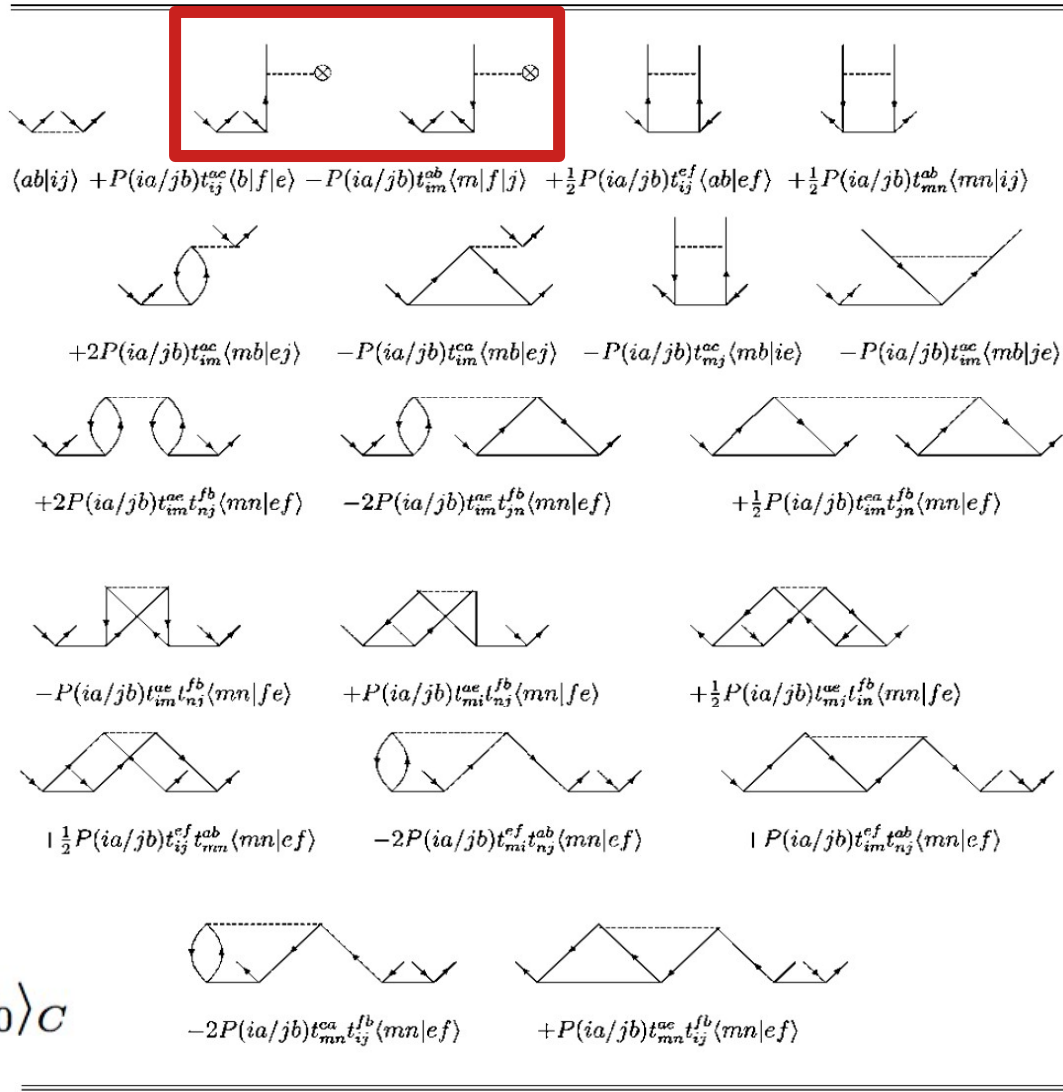
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CCD equation

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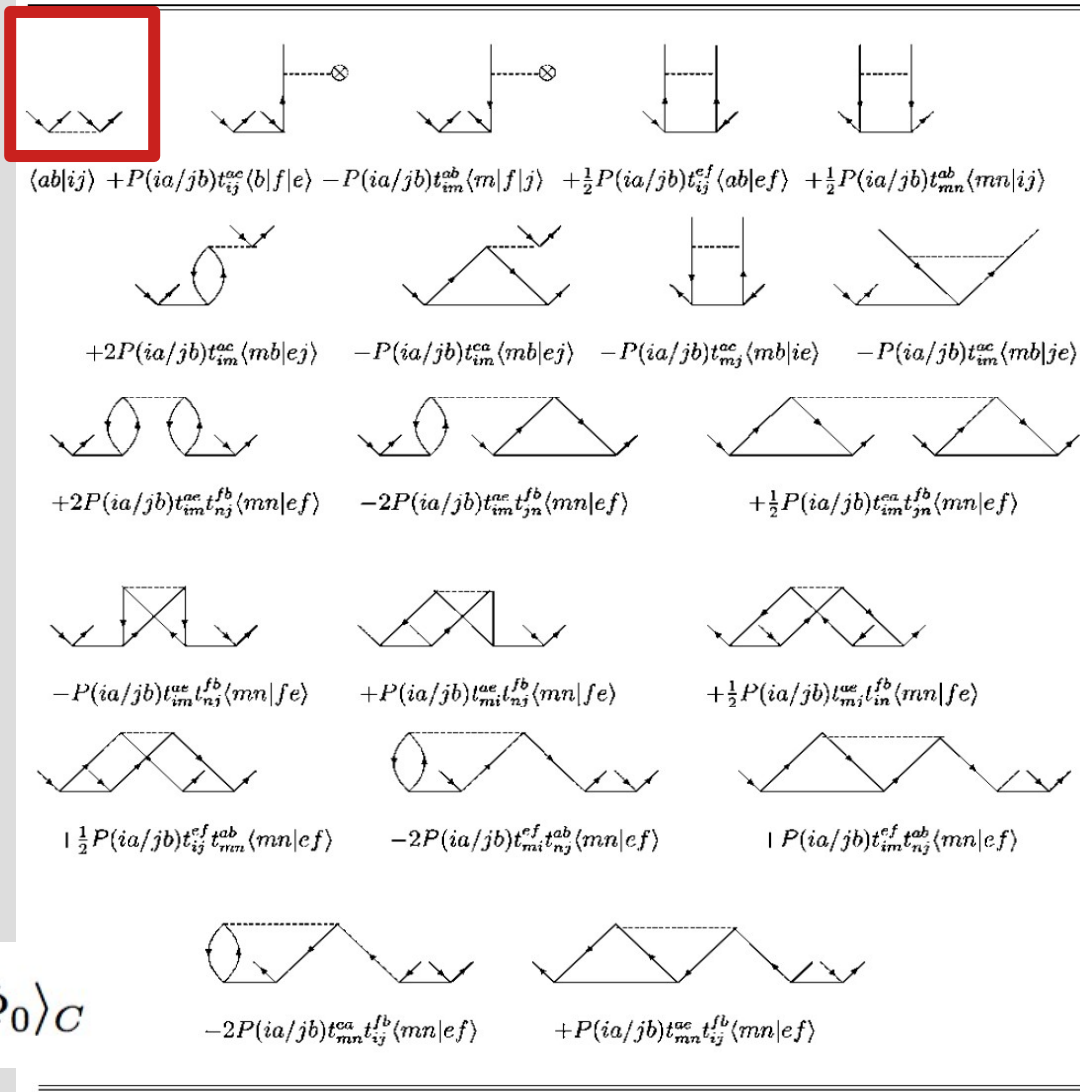
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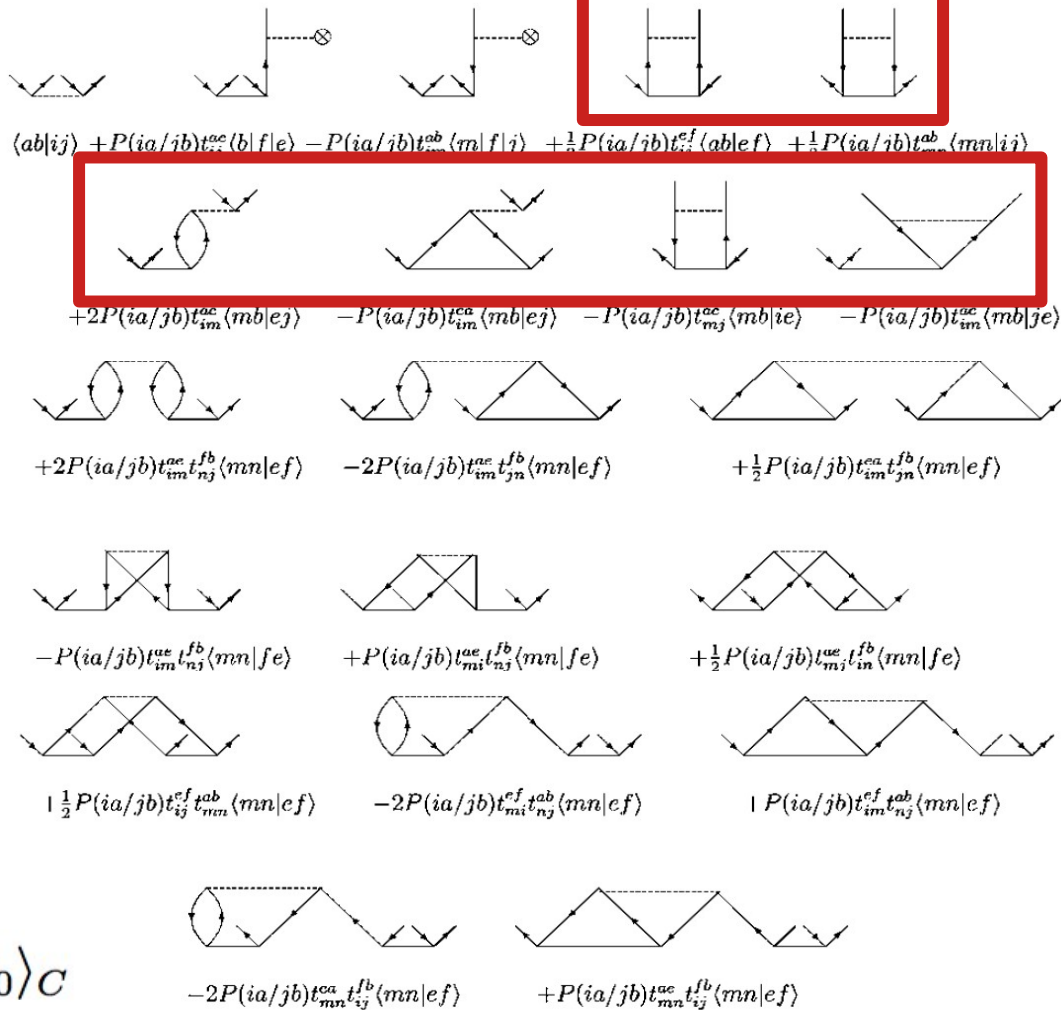
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CCD equation

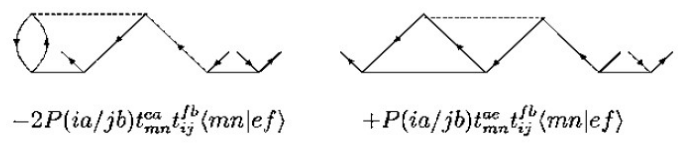
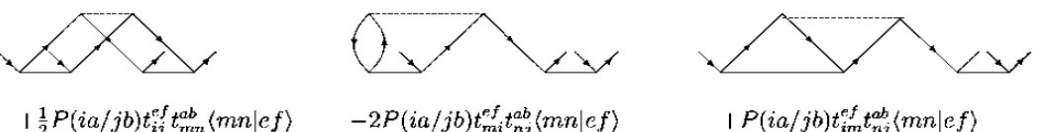
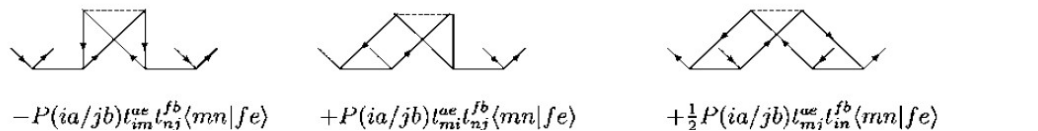
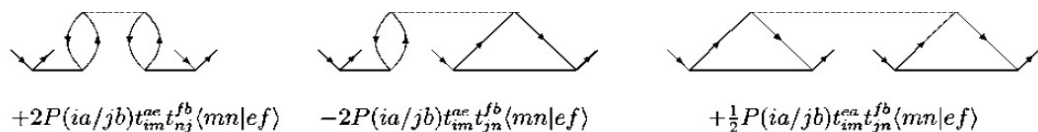
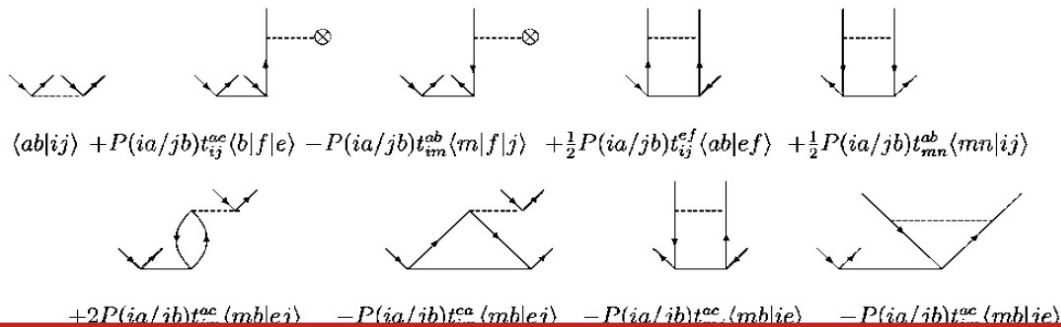


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# CCD equation



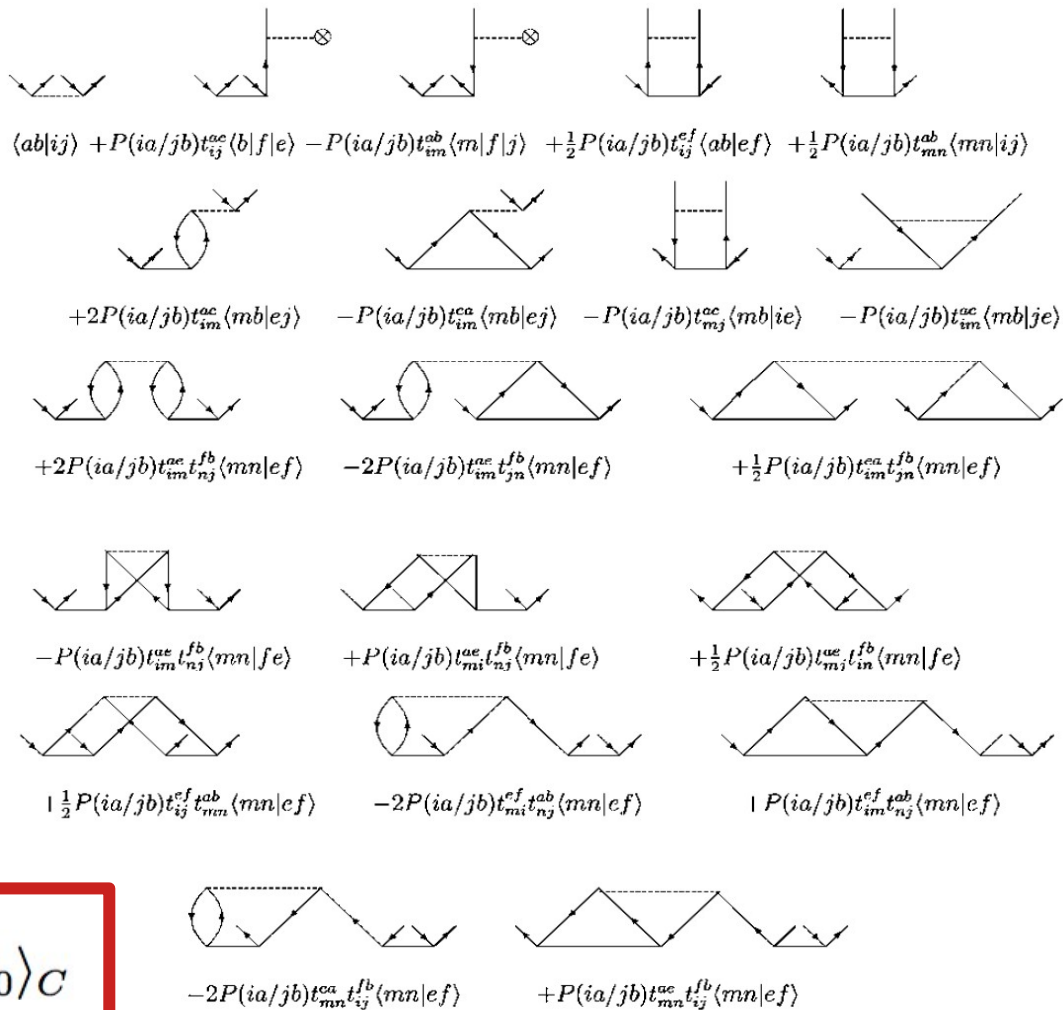
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$$\Psi_{\text{CCD}} = \exp(T_2)\Phi_0$$

## CCD equation

- Initial guess:  $T_2 = V_2$
- After one iteration  $E_{\text{CC}} = E_{\text{MP2}}$   
Solve self-consistently
- Evaluate all diagrams
- Update  $T_2$  at each iteration
- Until convergence of the energy and amplitudes

$$-T_{ij}^{ab} D_{ij}^{ab} = \langle \Phi_{ij}^{ab} | V (1 + T_2 + \frac{1}{2} T_2^2 \dots) | \Phi_0 \rangle_C$$



# CCSD - Coupled Cluster with Singles and Doubles

$$T_I D_I + \langle \Phi_I | V (1 + T + \frac{1}{2} T^2 \dots) | \Phi_0 \rangle_C = 0$$

$$-T_1 D_1 = \langle \Phi_1 | V (1 + T_I + \frac{1}{2} T_I^2 \dots) | \Phi_0 \rangle_C \quad ; \quad I = 1, 2$$

$$-T_2 D_2 = \langle \Phi_2 | V (1 + T_I + \frac{1}{2} T_I^2 \dots) | \Phi_0 \rangle_C \quad ; \quad I = 1, 2$$

The equations for  $I=1$  and  $I=2$  are coupled