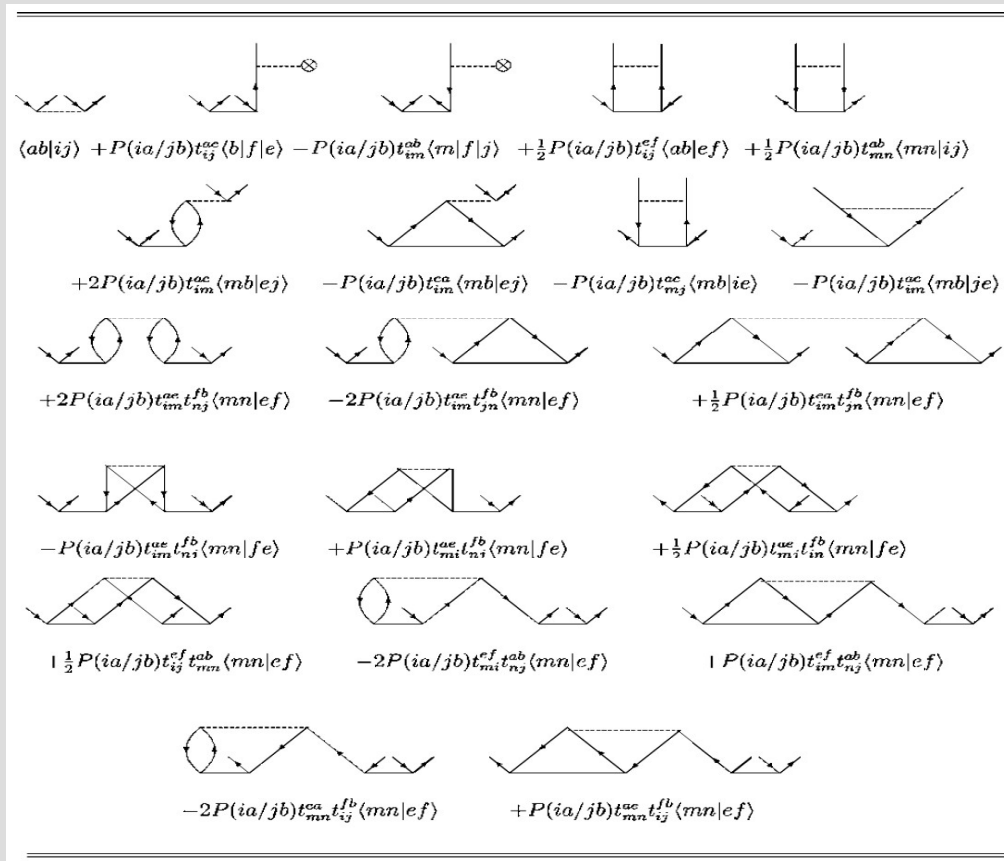# The Coupled-Cluster (CC) Formalism for Atomic and Molecular Electronic Structures

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

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

Arik Landau

Coupled cluster

From Wikipedia, the free encyclopedia

Coupled cluster (**CC**) is a numerical technique

The method was initially developed by Fritz **Coester** and Hermann **Kümmel** in the 1950s for studying nuclear-physics phenomena, but became more frequently used when in 1966 Jiří **Čížek** (and later together with Josef **Paldus**) reformulated the method for electron correlation in atoms and molecules. It is now one of the most prevalent methods in quantum chemistry that includes electronic correlation.

The life and work of Jiří Čížek

Ajit J. Thakkar

Department of Chemistry, University of New Brunswick, Fredericton, NB E3B 5A3, Canada

Jiří Čížek born in **Prague** on 24 August, 1938. Did his doctoral studies in 1961 at the Institute of Physical Chemistry of the Czechoslovak Academy of Sciences (csas), now the J. Heyrovský Institute.

In his doctoral dissertation (1965) **he proposed the use of a coupled-cluster methodology for the study of electron correlation effects in atoms and molecules.** This fundamental work laid the ground work for many further developments in quantum chemistry, and was summarized in his famous 1966 Journal of Chemical Physics paper [1] and elaborated upon in his heavily-cited 1968 Advances in Chemical Physics article [2]. The former paper earned him a csas prize in the chemistry division. After the completion of his CSc, he obtained a position as Junior **Scientist at the Institute of Physical Chemistry in Prague in 1964**.
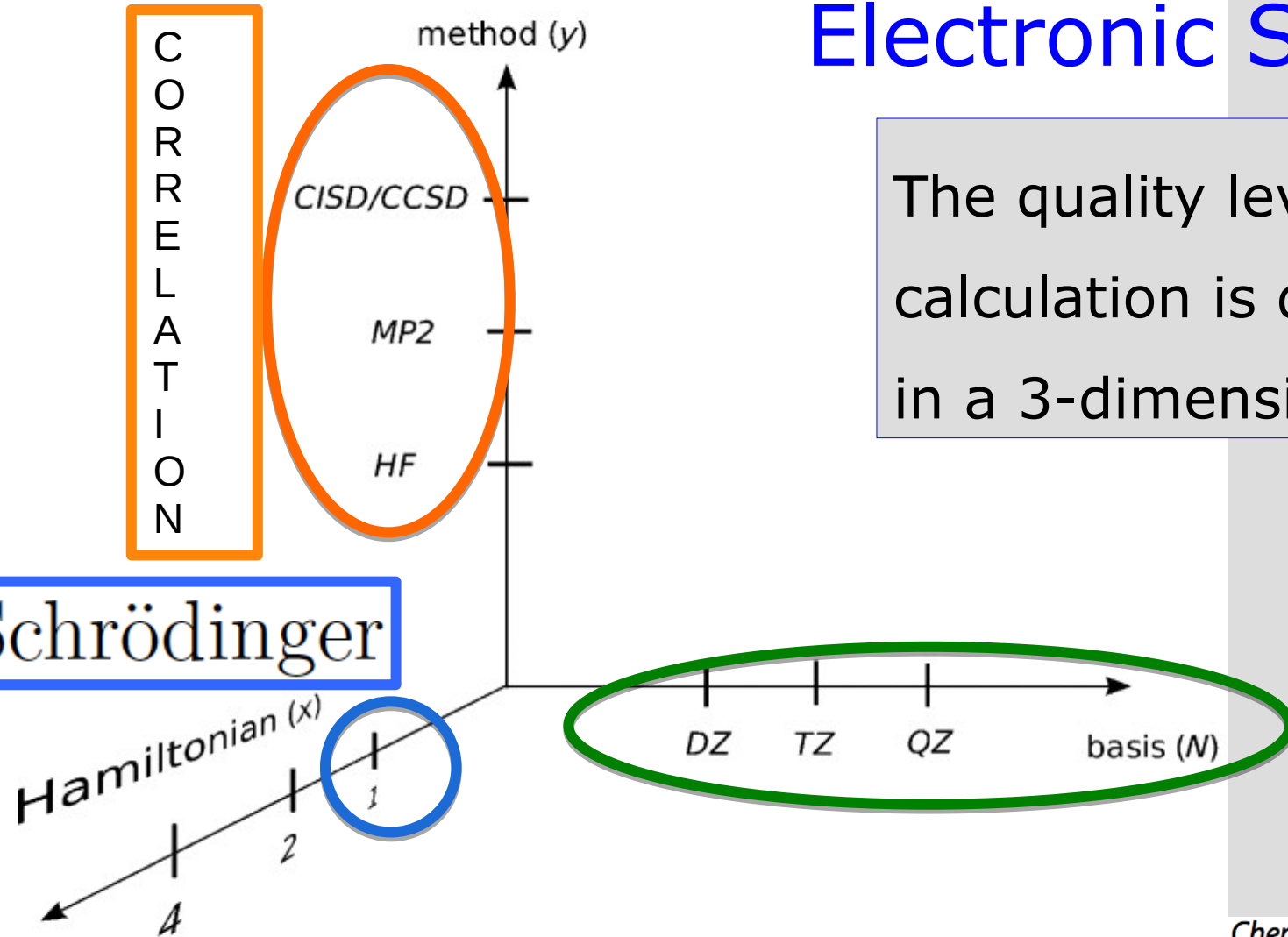
[1] J. Čížek, *J. Chem. Phys.* 45, 4256 (1966).

[2] J. Čížek, *Adv. Chem. Phys.* 14, 35 (1968).

Electronic Structure

CORRELATION

Schrödinger

method (y)

CISD/CCSD

MP2

HF

Hamiltonian (x)

1

2

4

DZ TZ QZ basis (N)

The quality level of a calculation is determined in a 3-dimensional space

Coupled Cluster with Singles Doubles and Perturbative Triples Excitations

Comput Mol Sci 2013, 3: 482–503

With CCSD(T) becoming the *gold standard* for quantum chemical calculations,[126]

126. Paldus J. QCI and related CC approaches: a retrospection. *Mol Phys* 2010, 108:2941–2950.

Machine learning and data science

Data reduction, singular-value decomposition, reduced density matrics, natural orbitals, response functions, correlators...
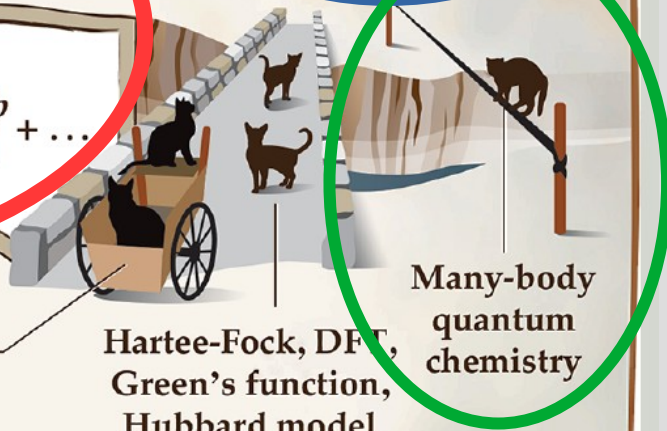
Quantum computing

Finish

Physical properties and observables

The exact many-body wavefunction gorge

$$\psi = \phi_0 + \sum_{ia} C_i^a \phi_i^a + \frac{1}{4} \sum_{ijab} C_{ij}^{ab} \phi_{ij}^{ab} + \dots$$

Start

Electrons and nuclei: the exact Hamiltonian

Semiempirical models, DFTB, CINDO, MNDO, PM6, ...

Hartee-Fock, DFT, Green's function, Hubbard model

Many-body quantum chemistry

Full Configuration Interaction (FCI)

$$|\Psi\rangle = |\Phi_0\rangle + \sum_{ia} c_i^a |\Phi_i^a\rangle + \sum_{ijab} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \cdots$$

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

Operators   **Coefficients**

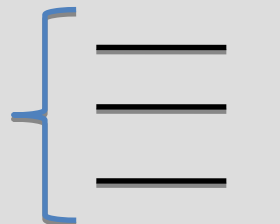**FCI is the exact solution of the Schrödinger equation in a given one-electron basis set**
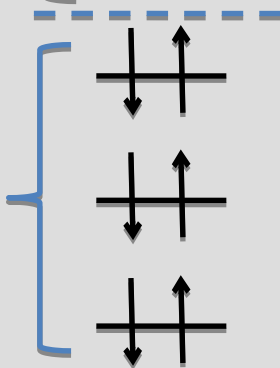
Hilbert space

Hilbert space

HF

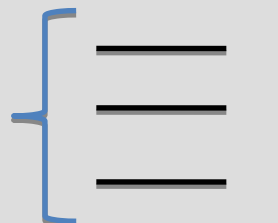Virts..
$a, b, \ldots$

Occ.
$i, j, \ldots$

$|\Phi_0\rangle$

Hilbert space

HF
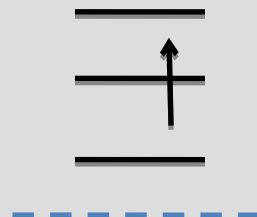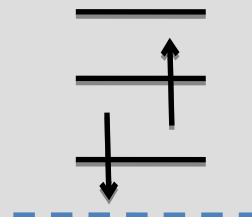
Excited determinants...

Virts..
$a, b, ...$

Occ.
$i, j, ...$

$|\Phi_0\rangle$

$|\Phi_i^a\rangle$

$|\Phi_{ij}^{ab}\rangle$

......

Machine learning and data science

Data reduction, singular-value decomposition, reduced density matrics, natural orbitals, response functions, correlators...

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Many-body quantum chemistry

Cite This: https://doi.org/10.1021/acscentsci.1c00685

The Many-Body Hamiltonian

Many electrons atoms

$$H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \frac{Ze^2}{r_i} + \sum_{i=1}^{n-1} \sum_{j>i}^{n} \frac{e^2}{r_{ij}}$$
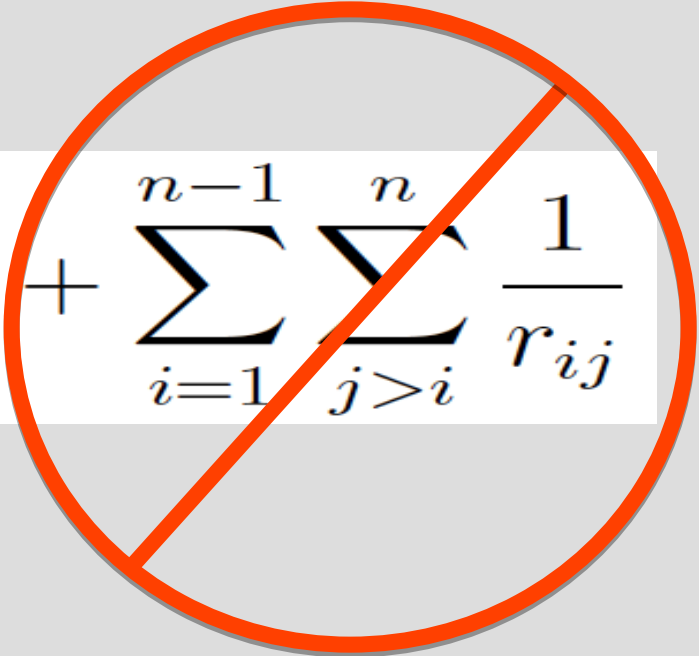
Kinetic

Coulomb attraction

Coulomb repulsion

The Many-Body Hamiltonian

Many electrons atoms

$$e^2 = \hbar = m = 1$$

$$H = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\frac{Z}{r_i} + \sum_{i=1}^{n-1}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

The (three-days course) Outline

1. Hartree Fock, Second Quantization, Normal Form, Goldstone Diagrams and writing the Many-Body Hamiltonian with Diagrams

2. Perturbation Theory, Linked-Diagram Theorem, Coupled Cluster (CC) for Closed-Shell Systems

3. CC in Fock-Space for Open-Shell Systems (IP, EA, EE... states)

4. Electronic Resonance (Aoutoionization) States in Chemistry

I. Lindgren   J. Morrison

Atomic Many-Body Theory

Part II

Perturbation Theory and the Treatment of Atomic Many-Body Effects

9.1 Basic Problem

The basic problem in nonrelativistic atomic theory is to find an approximate solution of the time-independent Schrödinger equation

$$H\Psi = E\Psi \tag{9.1}$$

In the *perturbation* approach the Hamiltonian of the system (H) is split into two parts, a *model Hamiltonian* (H_0) and a *perturbation* (V)

$$H = H_0 + V. \tag{9.2}$$

9.1 Basic Problem

In the *perturbation* approach the Hamiltonian of the system (H) is split into two parts, a *model Hamiltonian* (H_0) and a *perturbation* (V)

$$H = H_0 + V. \tag{9.2}$$

The model Hamiltonian should be a reasonable approximation to the full Hamiltonian and it should be simple enough to manage. For atoms, the natural choice of H_0 is some central-field approximation, such as the Hartree-Fock model, and it is, in fact, the presence of a natural first approximation which makes perturbation theory such a promising method for atoms.

Hartree-Fock

Hartree-Fock equation

$$\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \sum_{j}^{n/2} (2J_j - K_j) \right) \phi_i = \epsilon_i \phi_i$$

Fock operator

$$F\phi_i = \epsilon_i \phi_i$$

Coulomb operator

$$J_j(r_1)\phi_i(r_1) = \phi_i(r_1) \int |\phi_j(r_2)|^2 \frac{1}{r_{12}} dv_2$$

Exchange operator

$$K_j(r_1)\phi_i(r_1) = \phi_j(r_1) \int \phi_j^*(r_2)\phi_i(r_2) \frac{1}{r_{12}} dv_2$$

Restricted Hartree Fock

Closed-shells (equal spins up and down)

$$E_{HF} = \langle D|H|D \rangle =$$

$$= 2 \sum_{i}^{n/2} \epsilon_i - \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij})$$

Coulomb integral

$$J_{ij} = \langle \phi_i(r_1)\phi_j(r_2) \left| \frac{1}{r_{12}} \right| \phi_i(r_1)\phi_j(r_2) \rangle$$

Exchange integral

$$K_{ij} = \langle \phi_i(r_1)\phi_j(r_2) \left| \frac{1}{r_{12}} \right| \phi_j(r_1)\phi_i(r_2) \rangle$$

Hartree-Fock The total wave function of **_n_ identical fermions**

$$|D\rangle = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \cdots & \phi_n(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \cdots & \phi_n(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(r_n) & \phi_2(r_n) & \cdots & \phi_n(r_n) \end{vmatrix}$$

- The total wave function for _n_ identical fermions is **anti-symmetric** with respect to exchange of the particles.
- This is a rigorous statement of the **Pauli exclusion principle**

But we are after the a FCI like approximation

$$|\Psi\rangle = |\Phi_0\rangle + \sum_{ia} c_i^a |\Phi_i^a\rangle + \sum_{ijab} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \cdots$$
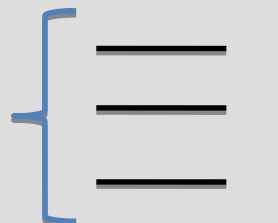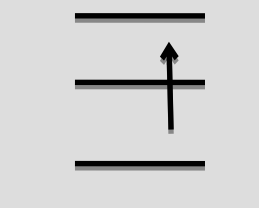
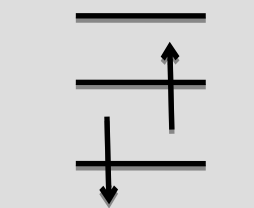Hilbert space

HF

Excited determinants...

Virts..
$r, s, t...$

Occ.
$a, b, c...$

$|\alpha\rangle$ $|\alpha_a^r\rangle$ $|\alpha_{ab}^{rs}\rangle$ ......
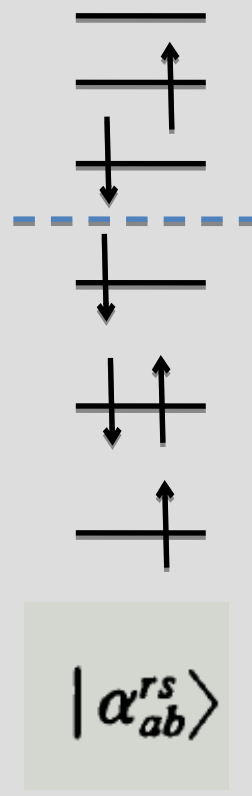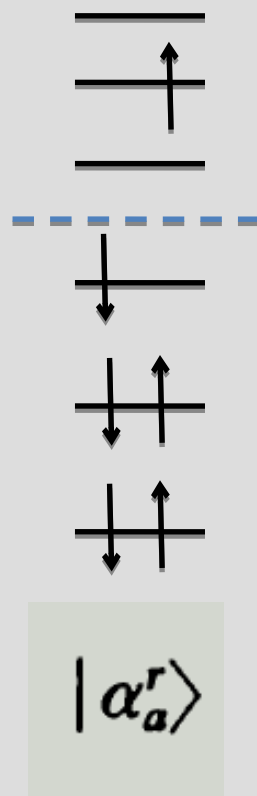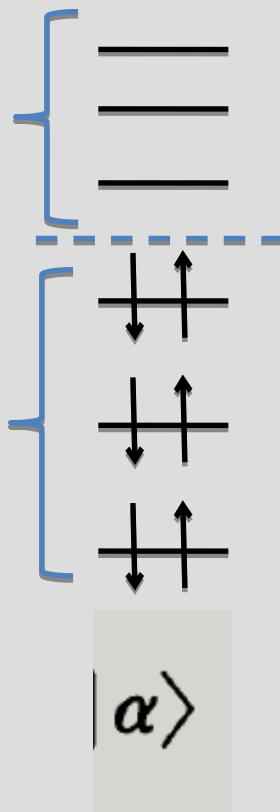
Second Quantization and the Particle-Hole Formalism

Intuitively, we know that the state $|\alpha_a^r\rangle$ is related to the state $|\alpha\rangle$ in a simple way, but it is not possible to express this relation easily with the formalism we have been using.

the idea of second quantization is to express the operators in terms of elementary (single, double, ...) excitations.

Second Quantization

A single-particle state φ_i is represented in the formalism of second quantization as an operator $a_i^\dagger$ acting on the *vacuum state* $|0\rangle$

$$|\varphi_i\rangle \equiv a_i^\dagger |0\rangle .$$

Since the operator $a_i^\dagger$ produces the state $|\varphi_i\rangle$ called a *creation operator.*

Hartree-Fock

$$|\alpha\rangle = |\varphi_i \varphi_j \cdots\rangle = a_i^\dagger a_j^\dagger \cdots |0\rangle$$

Second Quantization

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$$|\varphi_i\rangle \equiv a_i^\dagger|0\rangle \, .$$

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the hermitian adjoint $\qquad \langle 0|a_i \equiv \langle \varphi_i| \, .$

an *absorption, destruction* or *annihilation operator.*

Second Quantization and the Particle-Hole Formalism

anticommutation relations.

Since a determinant changes sign
if two rows or columns are interchanged,

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

$$a_i a_j = -a_j a_i$$

$$\{a_i^\dagger, a_j^\dagger\} = 0$$
$$\{a_i, a_j\} = 0$$
$$\{a_i, a_j^\dagger\} = \delta_{ij}$$

.

The orthonormality of the determinantal product states
imposes further conditions on these operators.

Second Quantization and the Particle-Hole Formalism

In applying the formalism of second quantization to perturbation theory, we shall normally use a Slater determinant (10.7)

$$|\alpha\rangle = |\varphi_i\varphi_j\cdots\rangle = a_i^\dagger a_j^\dagger \cdots|0\rangle \tag{11.14}$$

Second Quantization and the Particle-Hole Formalism

In applying the formalism of second quantization to perturbation theory, we shall normally use a Slater determinant (10.7)

$$|\alpha\rangle = |\varphi_i \varphi_j \cdots\rangle = a_i^\dagger a_j^\dagger \cdots |0\rangle \qquad (11.14)$$

a Hartree-Fock determinant. Orbitals appearing in this determinant are referred to as *core* orbitals and the remaining, unoccupied ones as *virtual* orbitals. When operating on the reference state, it is not possible to create a particle in a core orbital or to absorb a particle from an virtual orbital. This means that

$$a_{\text{core}}^\dagger |\alpha\rangle = a_{\text{virt}} |\alpha\rangle = 0 . \qquad (11.15)$$

Notice that the vacuum is changed from |0⟩ to |α⟩

Second Quantization and the Particle-Hole Formalism

$$a^\dagger_{\text{core}}|\alpha\rangle = a_{\text{virt}}|\alpha\rangle = 0 .$$

(11.15)

Denoting, as before, core orbitals by a, b, ... and virtual orbitals by r, s, ..., the states $|\alpha^r_a\rangle$, $|\alpha^{rs}_{ab}\rangle$, for which one or two electrons are excited, can be expressed
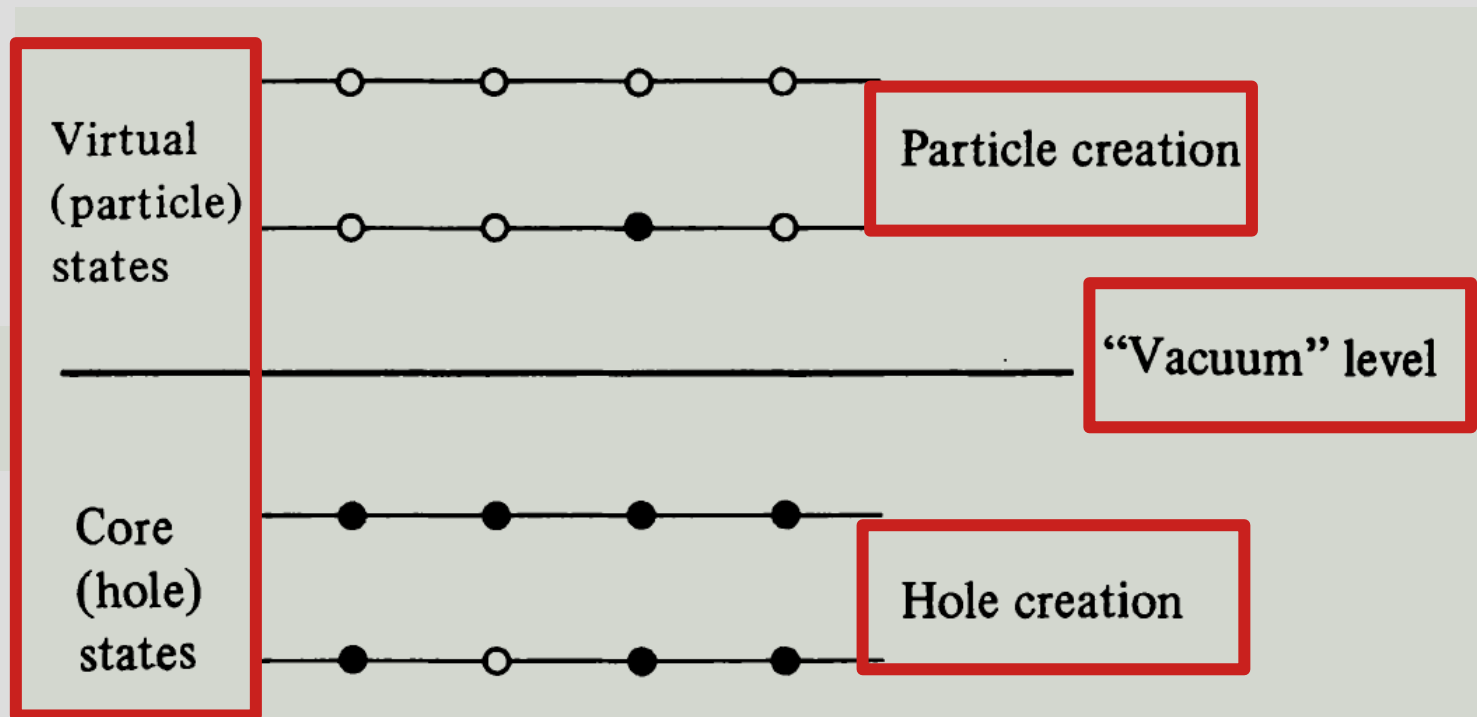
$$|\alpha^r_a\rangle = a^\dagger_r a_a |\alpha\rangle$$

(11.16a)

An intuitive relation between HF and the excited determinants

$$|\alpha^{rs}_{ab}\rangle = a^\dagger_r a^\dagger_s a_b a_a |\alpha\rangle .$$

(11.16b)

Second Quantization and the Particle-Hole Formalism

$$|\alpha_a^r\rangle = a_r^\dagger a_a |\alpha\rangle$$

Virtual (particle) states

Particle creation

"Vacuum" level

Core (hole) states

Hole creation

Many-Body Hamiltonian

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\frac{Z}{r_i} + \sum_{i<j}^{N}\frac{1}{r_{ij}}$$

Many-Body Hamiltonian

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\frac{Z}{r_i} + \sum_{i<j}^{N}\frac{1}{r_{ij}}$$

$$H = H_0 + V$$

Many-Body Hamiltonian

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$$H = H_0 + V$$

$$H_0 = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + u(r_i)\right] = \sum_{i=1}^{N}h_0(i)$$

Many-Body Hamiltonian

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J (Coulomb) and *K* (exchange)

Many-Body Hamiltonian

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J (Coulomb) and *K* (exchange)

The perturbation

$$V = H - H_0$$

Many-Body Hamiltonian

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\frac{Z}{r_i} + \sum_{i<j}^{N}\frac{1}{r_{ij}}$$

$$H = H_0 + V$$

$$H_0 = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \boxed{u(r_i)}\right] = \sum_{i=1}^{N}h_0(i)$$

J and *K*

The perturbation

$$V = H - H_0 = \sum_{i<j}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N}u(r_i)$$

The zeroth-order Hamiltonian H_0,

$$H_0 = \sum_{i=1}^{N} h_0(i) = \sum_i a_i^\dagger a_i \varepsilon_i$$

$$h_0|i\rangle = \varepsilon_i|i\rangle$$

The ideas applied above can easily be extended to two-body operators.

Many-Body Hamiltonian

$$H_0 = \sum_{i=1}^{N} h_0(i) = \sum_i a_i^\dagger a_i \, \varepsilon_i$$

$$V = - \sum_{i=1}^{N} u_i + \sum_{i<j}^{N} r_{ij}^{-1}$$

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

11.2 Operators in Normal Form

As we have mentioned, the idea of second quantization is to express the operators in terms of elementary (single, double, ...) excitations. We can easily see,

11.2 Operators in Normal Form

As we have mentioned, the idea of second quantization is to express the operators in terms of elementary (single, double, ...) excitations. We can easily see, however, that the operators (11.25) do not always have such a simple interpretation.

As an illustration, we consider the one-body operator

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

(11.27)

As before, we choose a particular Slater determinant $|\alpha\rangle$ as the reference and define core and virtual orbitals with respect to this state. If $i(= a)$ in (11.27)

Operators in Normal Form

As an illustration, we consider the one-body operator

$$F = \sum_{ij} a_i^\dagger a_j \langle i | f | j \rangle \, . \qquad \text{if:} \quad i = a, \qquad a_{\text{core}}^\dagger | \alpha \rangle = a_{\text{virt}} | \alpha \rangle = 0 \, .$$

rewrite the operators by means of the anticommutation rules

$$a_a^\dagger a_j = -a_j a_a^\dagger + \delta_{aj}$$

the first term on the right-hand side does not contribute while the last term reproduces $|\alpha\rangle$ for $j = a$.

So in this case $a_i^\dagger a_j$ does not represent any excitation at all.

Operators in Normal Form

In order to see in a more systematic way which terms do correspond to real excitations when operating on $|\alpha\rangle$, we shall rearrange the creation and absorption operators so that

$$a^\dagger_{\text{core}} \quad \text{and} \quad a_{\text{virt}}$$

appear to the right of

$$a_{\text{core}} \quad \text{and} \quad a^\dagger_{\text{virt}}$$

$$\{a^\dagger_i, a^\dagger_j\} = 0$$
$$\{a_i, a_j\} = 0$$
$$\{a_i, a^\dagger_j\} = \delta_{ij}$$

$$a^\dagger_{\text{core}}|\alpha\rangle = a_{\text{virt}}|\alpha\rangle = 0 .$$

Operators in Normal Form

$a_{core}^{\dagger}$ and a_{virt} appear to the right of a_{core} and $a_{virt}^{\dagger}$

The terms which contain the former operators will then give zero when operating on $|\alpha\rangle$, while the remaining ones will produce real excitations. operator written in this way is said to be in *normal order* or in *normal form*.

Many-Body Hamiltonian

$$H_0 = \sum_{i=1}^{N} h_0(i) = \sum_i a_i^\dagger a_i \, \varepsilon_i$$

$$V = - \sum_{i=1}^{N} u_i + \sum_{i<j}^{N} r_{ij}^{-1}$$

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

We consider first the one-body part of the perturbation

$$-U = \sum_{ij} a_i^\dagger a_j \langle i|-u|j \rangle$$

Operators in Normal Form

$$-U = \sum_{ij} a_i^\dagger a_j \langle i | -u | j \rangle$$

Operators in Normal Form

$$-U = \sum_{ij} a_i^\dagger a_j \langle i| -u | j \rangle$$

$$= \sum_a^{core} \langle a| -u | a \rangle + \sum_{ij} \{a_i^\dagger a_j\} \langle i| -u | j \rangle .$$

Wick's theorem can now be formulated as follows:

If A is a product of creation and absorption operators, then

$$\boxed{A = \{A\} + \{\overset{\frown}{A}\}} , \qquad\qquad (11.49)$$

where $\{A\}$ represents the normal form of A and $\{\overset{\frown}{A}\}$ represents the sum of the normal-ordered terms obtained by making all possible single, double, ... contractions within A.

Operators in Normal Form

$$-U = \sum_{ij} a_i^\dagger a_j \langle i| -u|j\rangle$$

$$= \sum_a^{\text{core}} \langle a| -u|a\rangle + \sum_{ij} \{a_i^\dagger a_j\} \langle i| -u|j\rangle .$$

first sum is a number—or a zero-body operator-
-while the second sum repre-
sents a normal-ordered, one-body operator.
each operator in the second summation
either gives zero or produces
a determinantal state of the form $|\alpha_a^r\rangle$

Operators in Normal Form

$$H_0 = \sum_{i=1}^{N} h_0(i) = \sum_i a_i^\dagger a_i \, \varepsilon_i$$

$$V = -\sum_{i=1}^{N} u_i + \sum_{i<j}^{N} r_{ij}^{-1}$$

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

The second term of the perturbation

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

Operators in Normal Form

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

normal order or in *normal form.*

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

$$+ \sum_{ij} \{a_i^\dagger a_j\} \sum_a (\langle ia | r_{12}^{-1} | ja \rangle - \langle ai | r_{12}^{-1} | ja \rangle)$$

$$+ \frac{1}{2} \sum_{ab} (\langle ab | r_{12}^{-1} | ab \rangle - \langle ba | r_{12}^{-1} | ab \rangle).$$

Operators in Normal Form

The perturbation may thus be separated into the following normal-ordered zero-, one- and two-body parts:

$$V = V_0 + V_1 + V_2$$

Operators in Normal Form

The perturbation may thus be separated into the following normal-ordered zero-, one- and two-body parts:

$$V = V_0 + V_1 + V_2$$

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

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

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

Graphical representation of a one-body

The meaning of the formalism of second quantization

can be illustrated by

means of the simple scattering process

$$= a_i^\dagger a_j \, V_{ij}$$
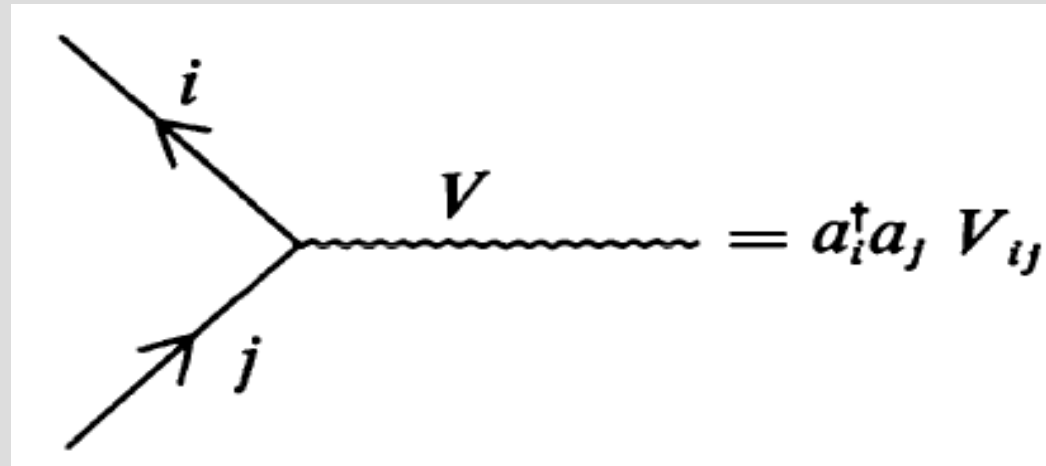
Graphical representation of a two-body interaction

$$a_i^\dagger a_j^\dagger a_l a_k \; W_{ijkl}$$

interaction by means of the scattering process
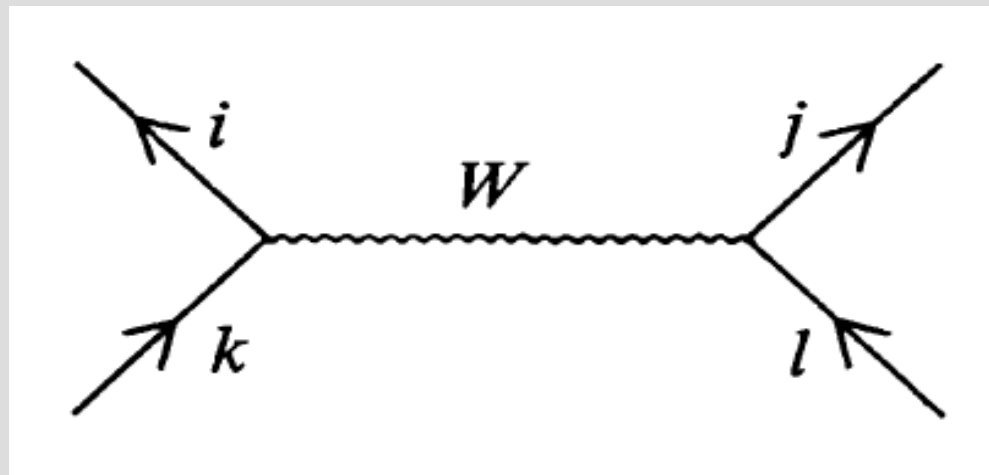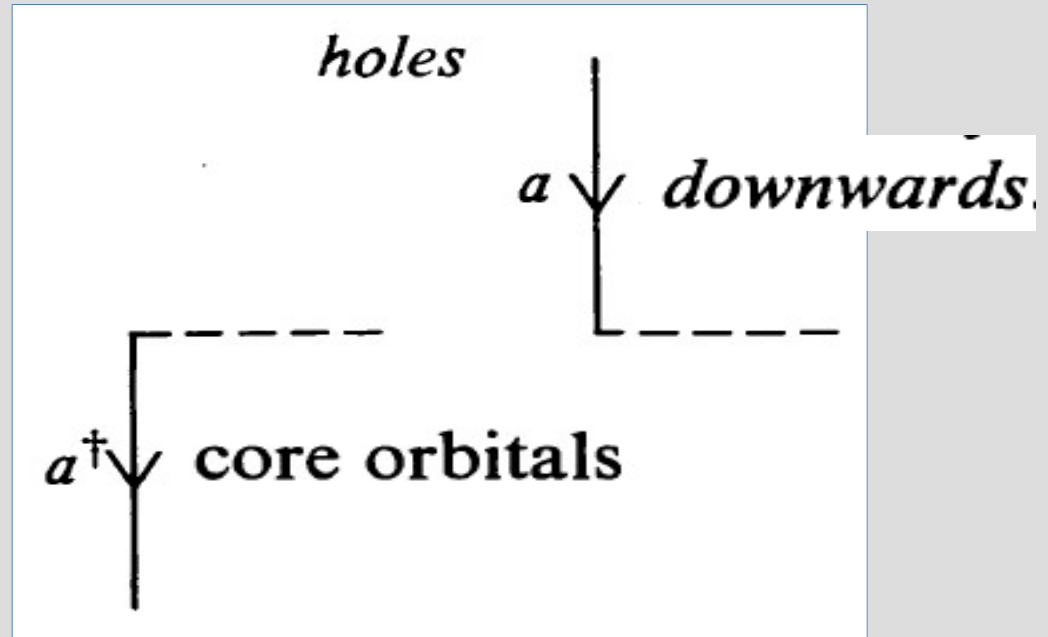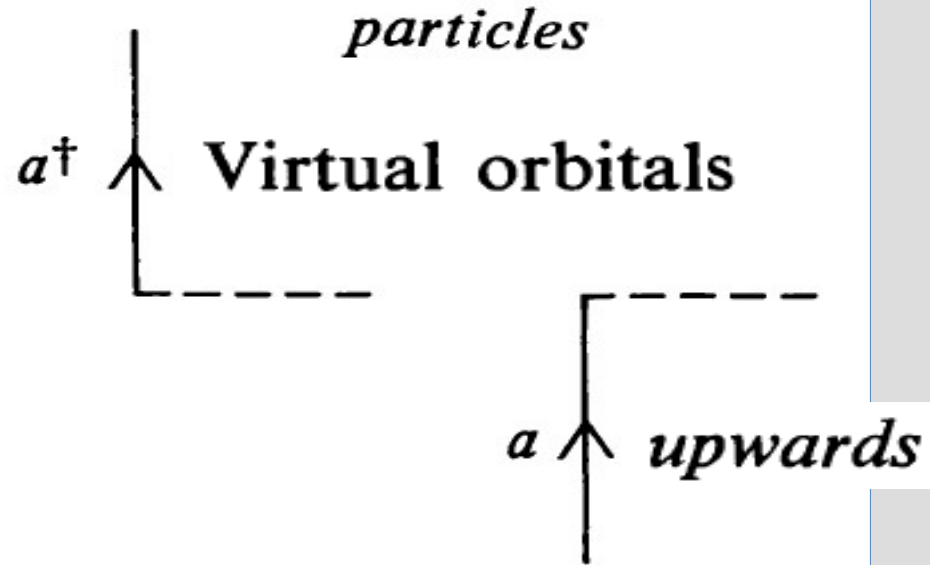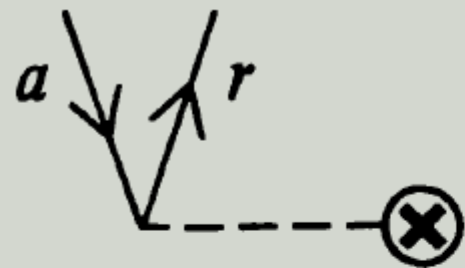
Graphical Representation of Normal-Ordered Operators

$$= \{a_r^\dagger a_a\} \langle r | v | a \rangle = a_r^\dagger a_a \langle r | v | a \rangle$$
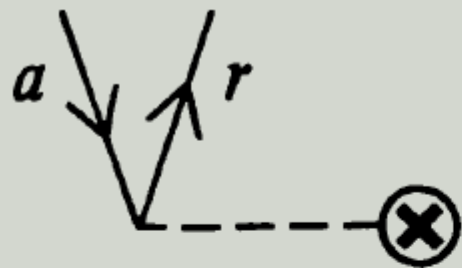
$$= \{a_r^\dagger a_a\} \langle r|v|a \rangle = a_r^\dagger a_a \langle r|v|a \rangle$$

$$= \{a_a^\dagger a_b\} \langle a|v|b \rangle = -a_b a_a^\dagger \langle a|v|b \rangle \;.$$

$$r \uparrow \qquad \uparrow s = \frac{1}{2} \{a_r^\dagger a_s^\dagger a_u a_t\} \langle rs | r_{12}^{-1} | tu \rangle$$

$$t \uparrow \qquad \uparrow u = \frac{1}{2} a_r^\dagger a_s^\dagger a_u a_t \langle rs | r_{12}^{-1} | tu \rangle$$

$$r \uparrow \qquad \uparrow s \quad = \frac{1}{2} \{a_r^\dagger a_s^\dagger a_u a_t\} \langle rs | r_{12}^{-1} | tu \rangle$$

$$t \uparrow \qquad \uparrow u \quad = \frac{1}{2} a_r^\dagger a_s^\dagger a_u a_t \langle rs | r_{12}^{-1} | tu \rangle$$

$$b \downarrow \quad c \downarrow \uparrow r \quad = \frac{1}{2} \{a_a^\dagger a_r^\dagger a_c a_b\} \langle ar | r_{12}^{-1} | bc \rangle$$

$$a \downarrow \qquad\qquad = -\frac{1}{2} a_r^\dagger a_c a_b a_a^\dagger \langle ar | r_{12}^{-1} | bc \rangle$$

Graphical Representation

The Goldstone Evaluation Rules

The Goldstone rules can be formulated as follows:

For each wave-operator diagram there is

a) *a creation (absorption) operator for each free outgoing (incoming) orbital line. These are written in normal form*

$$\{a_i^\dagger a_j^\dagger a_k^\dagger \ldots a_{k'} a_{j'} a_{i'}\} ;$$

where $(a_i^\dagger a_{i'})$, etc., originate from the same vertex or from vertices connected by orbital lines;

b) *a matrix element for each interaction line;*

c) *an energy denominator for each interaction line*

$$D = \sum(\varepsilon_{\text{down}} - \varepsilon_{\text{up}}),$$

single-particle eigenvalue associated with the down- ...ut by a line immediately above the interaction line; ...ternal orbital lines;

$$(-1)^{h+l},$$

where h is the number of internal core (hole) lines and l the number of closed loops of orbital lines;

f) *a factor of 1/2 for each two-particle interaction and an equivalence factor equal to the number of equivalent diagrams represented by the diagram considered.*

The rules above hold also for the energy diagrams, except that rule a) does not apply, and there is

g) *no energy denominator associated with the last interaction.*

Graphical Representation of Normal-Ordered Operators

$$V = V_0 + V_1 + V_2$$

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

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

$$V_2 = \frac{1}{2} \sum_{ijkl} \{a_i^\dagger a_j^\dagger a_l a_k\} \langle ij | r_{12}^{-1} | kl \rangle .$$
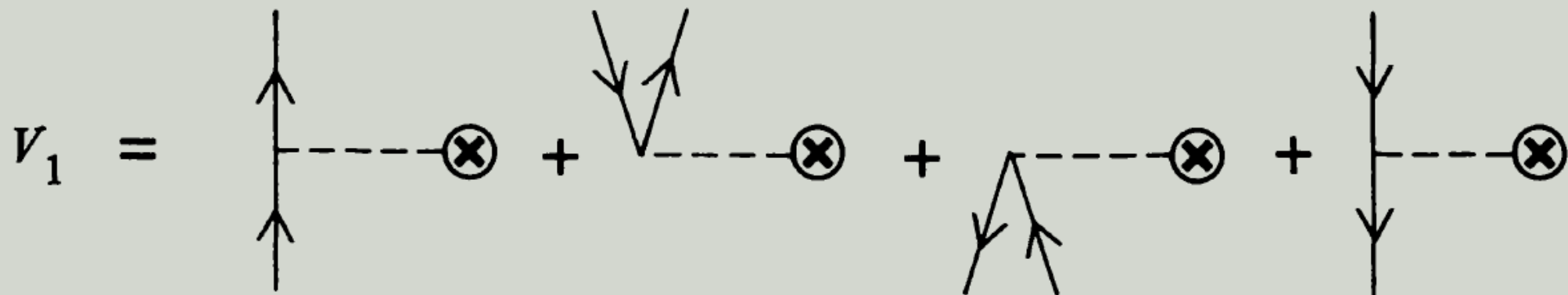
$$V = V_0 + V_1 + V_2$$

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

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

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

Topological equivalent

The Wave Operator

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

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

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

$$|\alpha\rangle = |\{\varphi_i\varphi_j\varphi_k \ldots\}\rangle$$
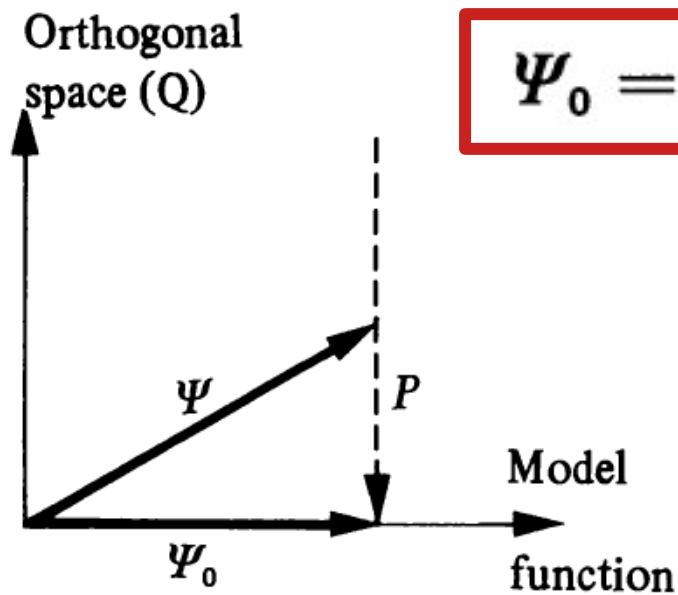
$$\Psi_0 = P\Psi$$

$$H\Psi = E\Psi$$

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

$$\Psi = \Omega\Psi_0$$

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

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

The Wave Operator

Orthogonal space (Q)

$$\Psi_0 = P\Psi$$

Ψ

P

Ψ_0

Model

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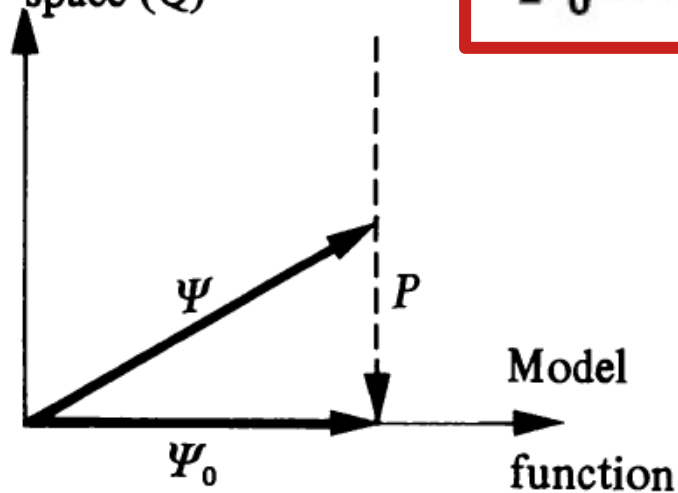
Fig. 9.1. Simple illustration of the wave operator (s
jects out of any function the component along the
generates the exact wave function by operating on

The Wave Operator

$$\Psi_0 = P\Psi$$
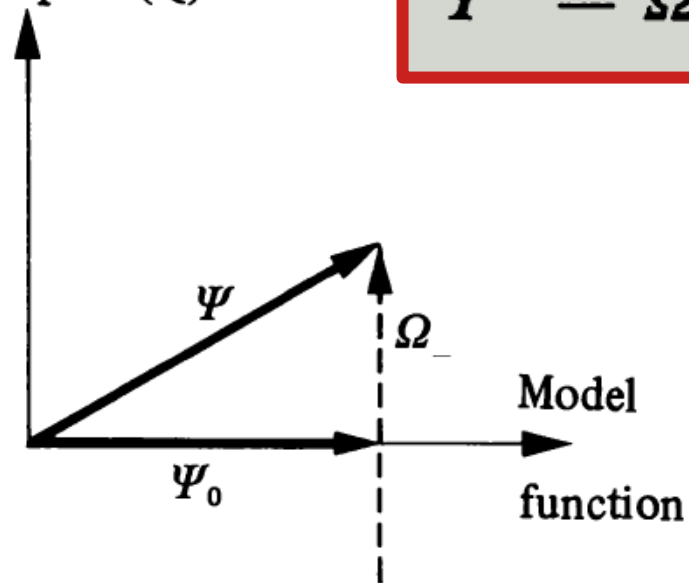
$$\Psi = \Omega\Psi_0$$

Fig. 9.1. Simple illustration of the wave operator (Ω_E) and the projection operator (P). P projects out of any function the component along the model function Ψ_0, and the wave operator generates the exact wave function by operating on Ψ_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

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

which we rewrite as

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

a = Ground Electronic State

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

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

and then with Ω,

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

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

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

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

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

Perturbative Expansion

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

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

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

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

The Generalized Bloch Equation

Perturbative Expansion

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

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

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)

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