Towards High sectors Fock-space coupled-cluster theory for atomic calculations

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Relativistic Fock-space coupled-cluster method

Post–Hartree–Fock method including

X Special relativity and electron correlation

X Multireference

- closed-shell systems (with quasi-degenerate levels)
- open-shell systems (such as transition metal atoms)
- excited states in general

X Single wave operator for all states

- many electronic states obtained in one calculation
- energy differences: ionization potentials, electron affinities, excitation energies

Highly accurate and large applicability

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EXP-T

a relativistic multireference coupled cluster program

v 1.7.0

Atomic relativistic Fock space coupled-cluster method

Atomic systems

X Spherical symmetry

- Separation of angular and radial terms
- Angular momentum reduction

! TRAFS-3C, Tel Aviv atomic computational package
E. Eliav and U. Kaldor

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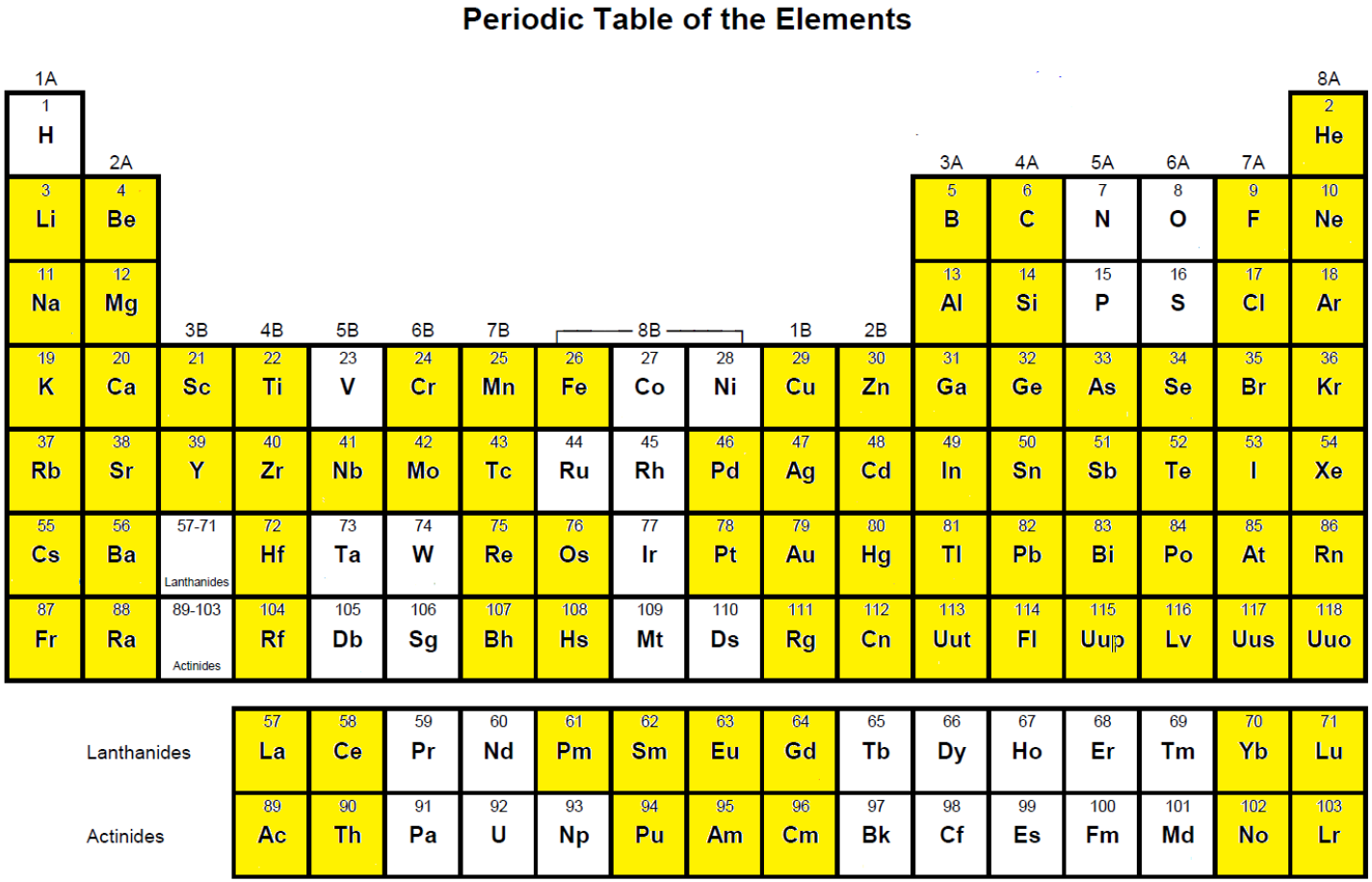
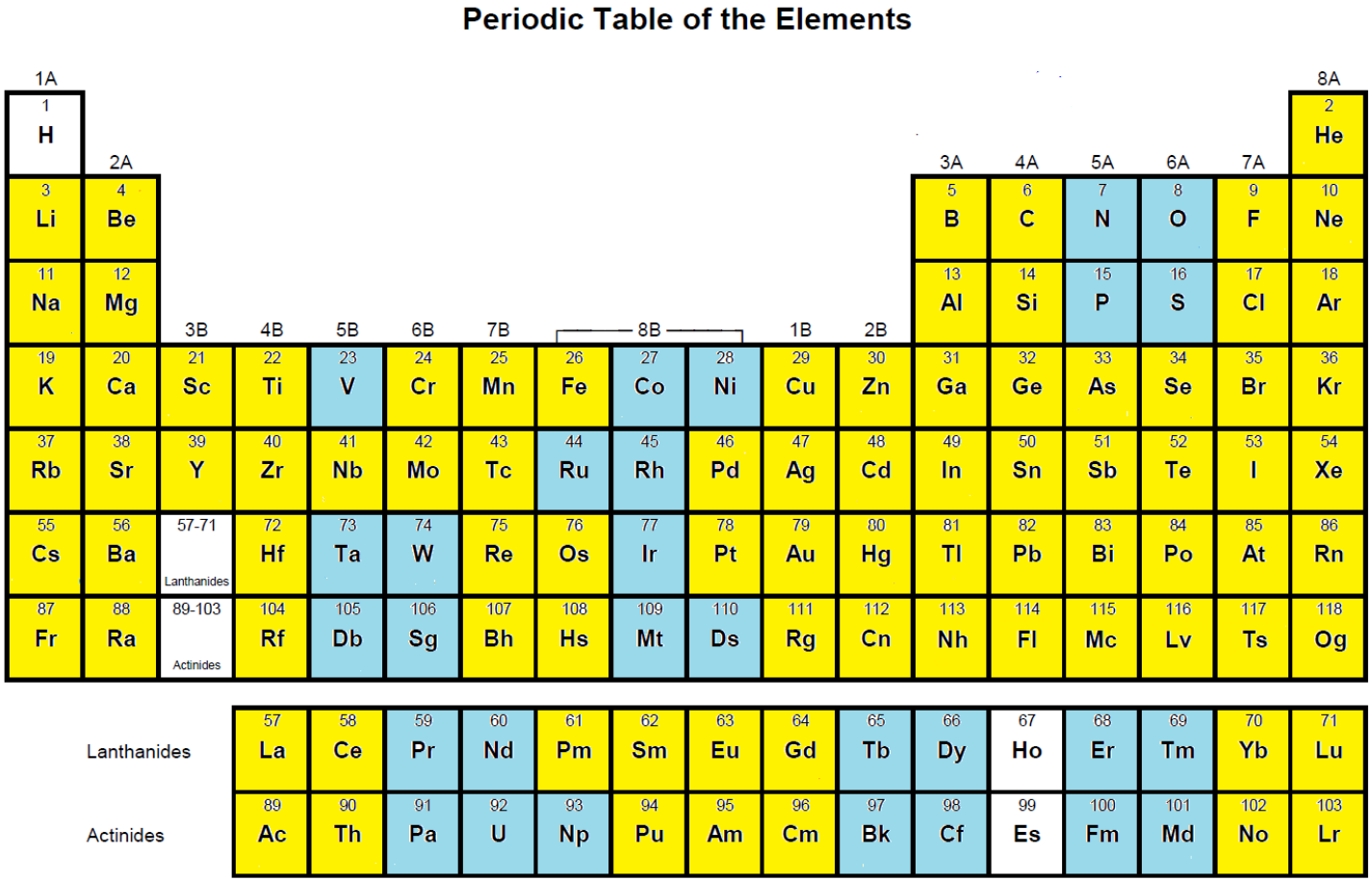
Restricted to 2 holes/particles[1]



[1] Figure from A. Borschevsky.

! Extend scope of applicability to 4 holes/particles[1]



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! Extend the **applicability** and **accuracy** of the atomic relativistic FSCC method

! Triple excitations must be included in computations for HSFSCC

Part I: Derivation of the equations (this talk)

Part II: Implementation (Martijn's talk)

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Part II: Implementation (Martijn's talk)

Outline

Effective operator

Schrödinger (or Dirac) equation

$$H|\Psi_\mu\rangle = E_\mu|\Psi_\mu\rangle \tag{1}$$

H is divided in the zero-order Hamiltonian and a perturbation

$$H = H_0 + V \tag{2}$$

The zero-order Hamiltonian follows the eigenvalue equation

$$H_0|\phi_\mu\rangle = E^0_\mu|\phi_\mu\rangle \tag{3}$$

$|\phi_\mu\rangle$ zero-order solutions (Slater determinants)

- X known
- X good approximation to the exact wave function $|\Psi_\mu\rangle$

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Effective operator

Wave function:

Model space (L_P) and orthogonal space (L_Q)

L_P ! all functions associated with one or several configurations

Example: Be:

$$|\Psi_\mu\rangle = a|1s^2 2s^2\ {}^1S\rangle + b|1s^2 2p^2\ {}^1S\rangle + \ldots$$

L_P: $1s^2 2s^2$, $1s^2 2p^2$ (^{1}S)

$$|\Phi_\mu\rangle = a|1s^2 2s^2\ {}^1S\rangle + b|1s^2 2p^2\ {}^1S\rangle$$

Projection operator:

$$P|\Psi_\mu\rangle = |\Phi_\mu\rangle \tag{4}$$

Wave operator:

$$\Omega|\Phi_\mu\rangle = |\Psi_\mu\rangle \tag{5}$$

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Example: Be:

$$j\Psi_\mu i = aj1s^2 2s^2\ ^1S i + bj1s^2 2p^2\ ^1S i + ...$$

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$$H|\Psi_\mu\rangle = E_\mu|\Psi_\mu\rangle \tag{6}$$

replacing $|\Psi_\mu\rangle = \Omega|\Phi_\mu\rangle$ and operating on the left with P,

$$PH\Omega|\Phi_\mu\rangle = E_\mu|\Phi_\mu\rangle \tag{7}$$

Effective Hamiltonian

$$\tilde{H}|\Phi_\mu\rangle = E_\mu|\Phi_\mu\rangle \tag{8}$$

The effective Hamiltonian acting on the **model wave function** gives the **exact energy** of the μ state.

! By diagonalizing $\tilde{H}$ we obtain the electronic state energies E_μ and the model functions Φ_μ

Find the wave operator *!*

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Derivation of the generalized Bloch equation

$$H|\Psi_\mu\rangle = E_a|\Psi_\mu\rangle \tag{9}$$

$$(E_a \quad H_0)|\Psi_\mu\rangle = V|\Psi_\mu\rangle \tag{10}$$

operating on the left with P

$$(E_a \quad H_0)|\Phi_\mu\rangle = PV|\Psi_\mu\rangle \tag{11}$$

and operating now with Ω

$$E_a|\Psi_\mu\rangle \quad \Omega H_0|\Phi_\mu\rangle = \Omega PV|\Psi_\mu\rangle \tag{12}$$

and rearranging,

$$\begin{aligned} H|\Psi_\mu\rangle \quad & \Omega H_0|\Phi_\mu\rangle = \Omega PV|\Psi_\mu\rangle \\ (H_0 + V)\Omega|\Phi_\mu\rangle \quad & \Omega H_0|\Phi_\mu\rangle = \Omega PV|\Psi_\mu\rangle \\ H_0\Omega|\Phi_\mu\rangle \quad & \Omega H_0|\Phi_\mu\rangle = \quad V\Omega|\Phi_\mu\rangle + \Omega PV\Omega|\Phi_\mu\rangle \end{aligned} \tag{13}$$

Therefore,

$$[\Omega, H_0]P = (V\Omega \quad \Omega PV\Omega)P \tag{14}$$

Coupled-cluster equation

$$[\Omega, H^0]P = (V\Omega \quad \Omega PV\Omega)P \tag{15}$$

Expanding the wave operator in n-body parts,

$$\Omega = 1 + \Omega_1 + \Omega_2 + ... \tag{16}$$

! Solving the non-perturbative equations self-consistently is equivalent to summing the corresponding terms in the perturbation expansion to all orders

Exponential ansatz[2]

$$\Omega = fe^T g = 1 + T + \frac{1}{2} fT^2 g + ... = \sum_n^1 \frac{1}{n!} fT^n g \tag{17}$$

$$T = T_1 + T_2 + ... \tag{18}$$

X Truncating T after the 2-body term, 4-body terms are included in Ω (T^2)

[2] The brackets represent the normal ordered operators: annihilation operators moved to the right of creation operators.

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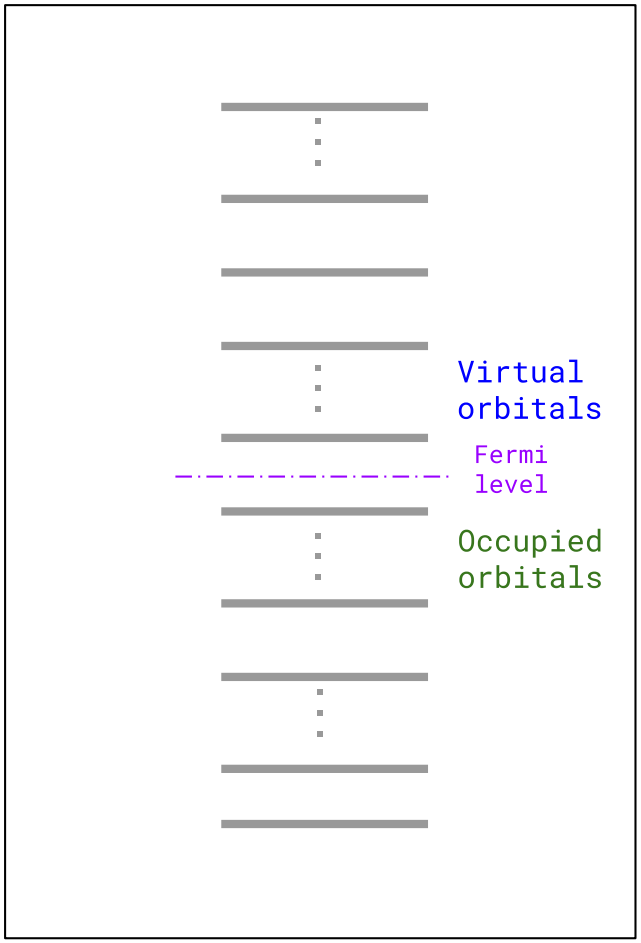
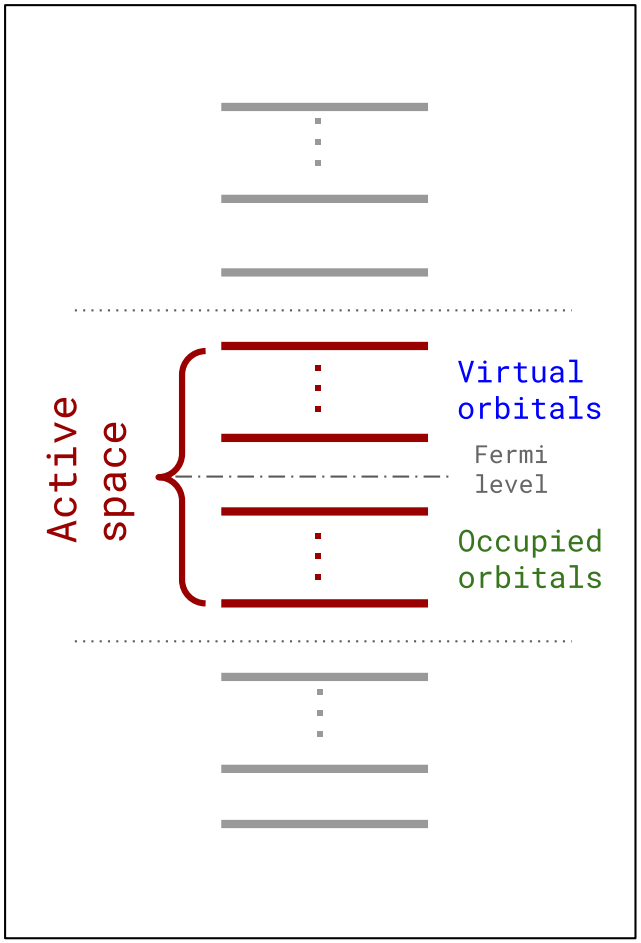


Including **all** determinants obtained by distributing h holes over the active hole states and p particles over active particle states in all possible ways ! Complete model space

! **Fock-space sector (h,p)**

Model space



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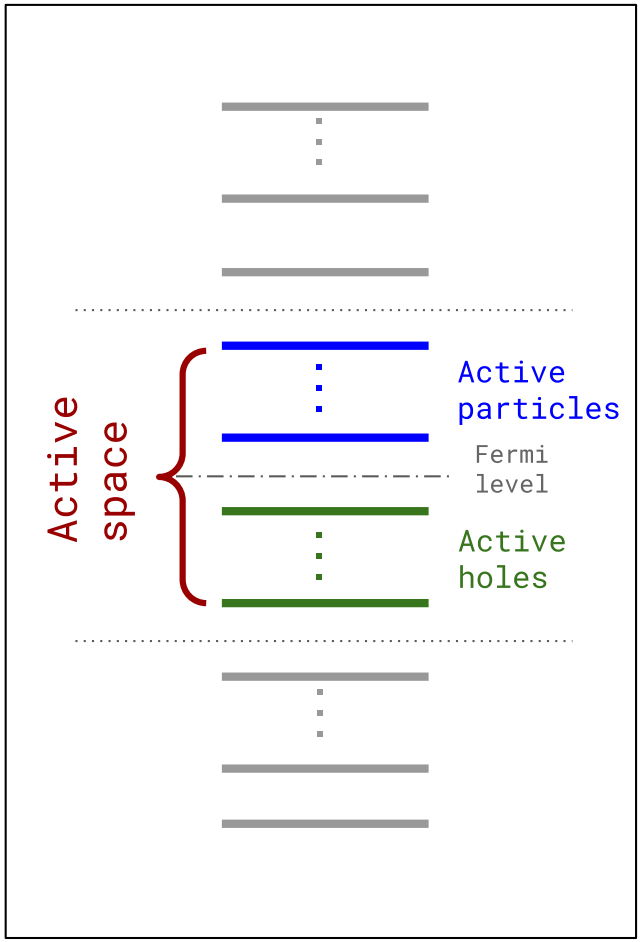

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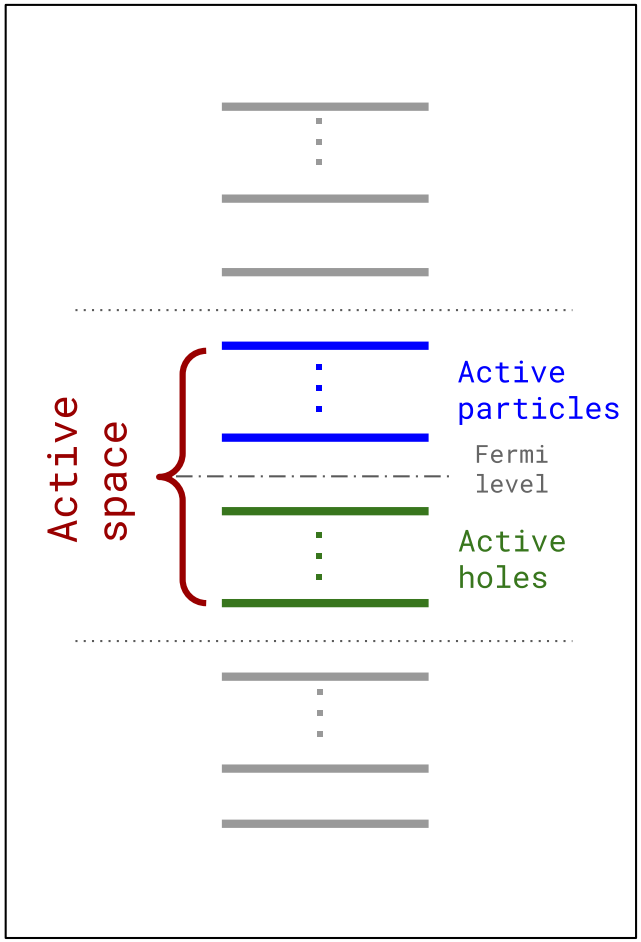

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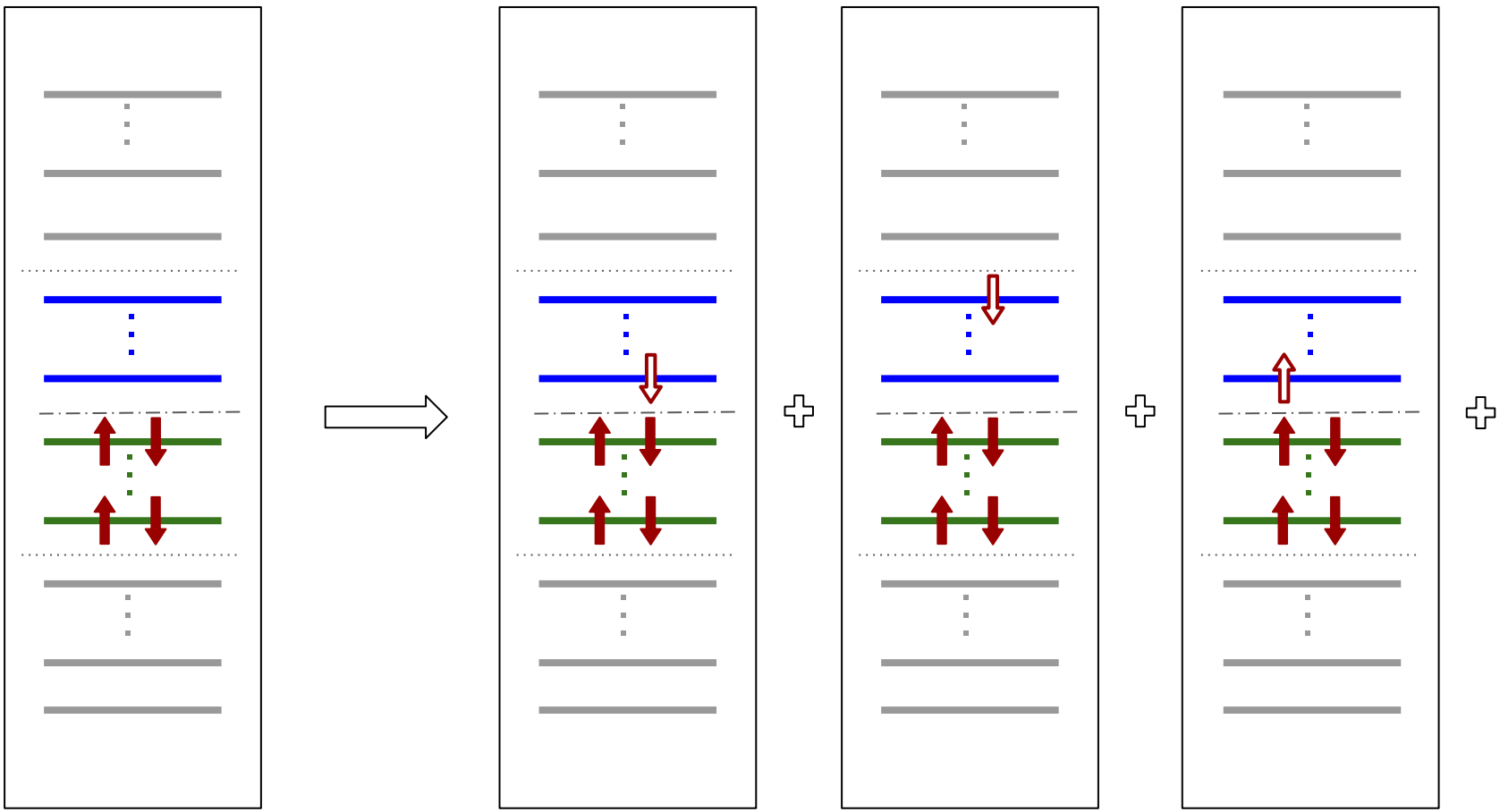
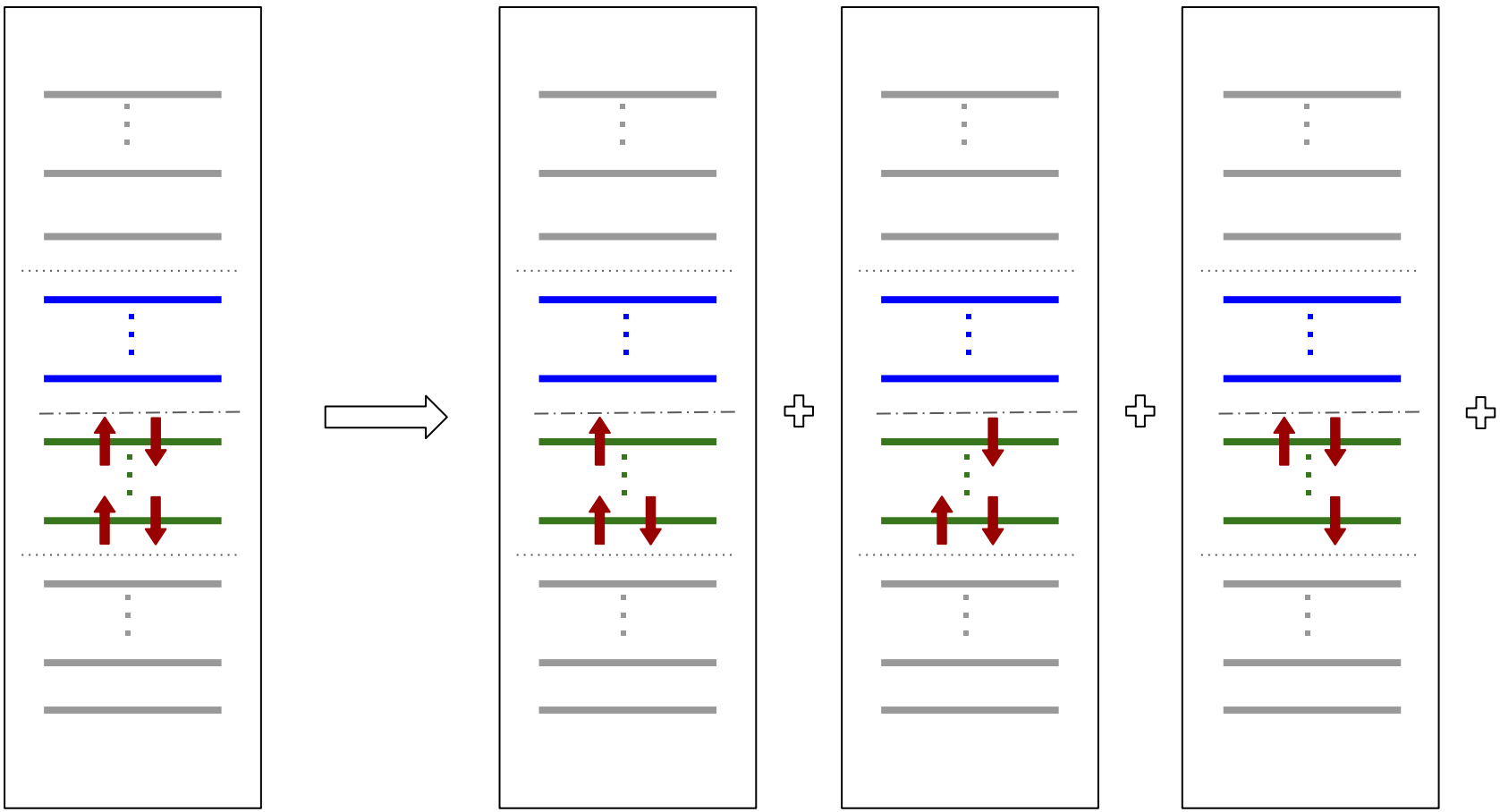
Fock-space coupled-cluster sectors

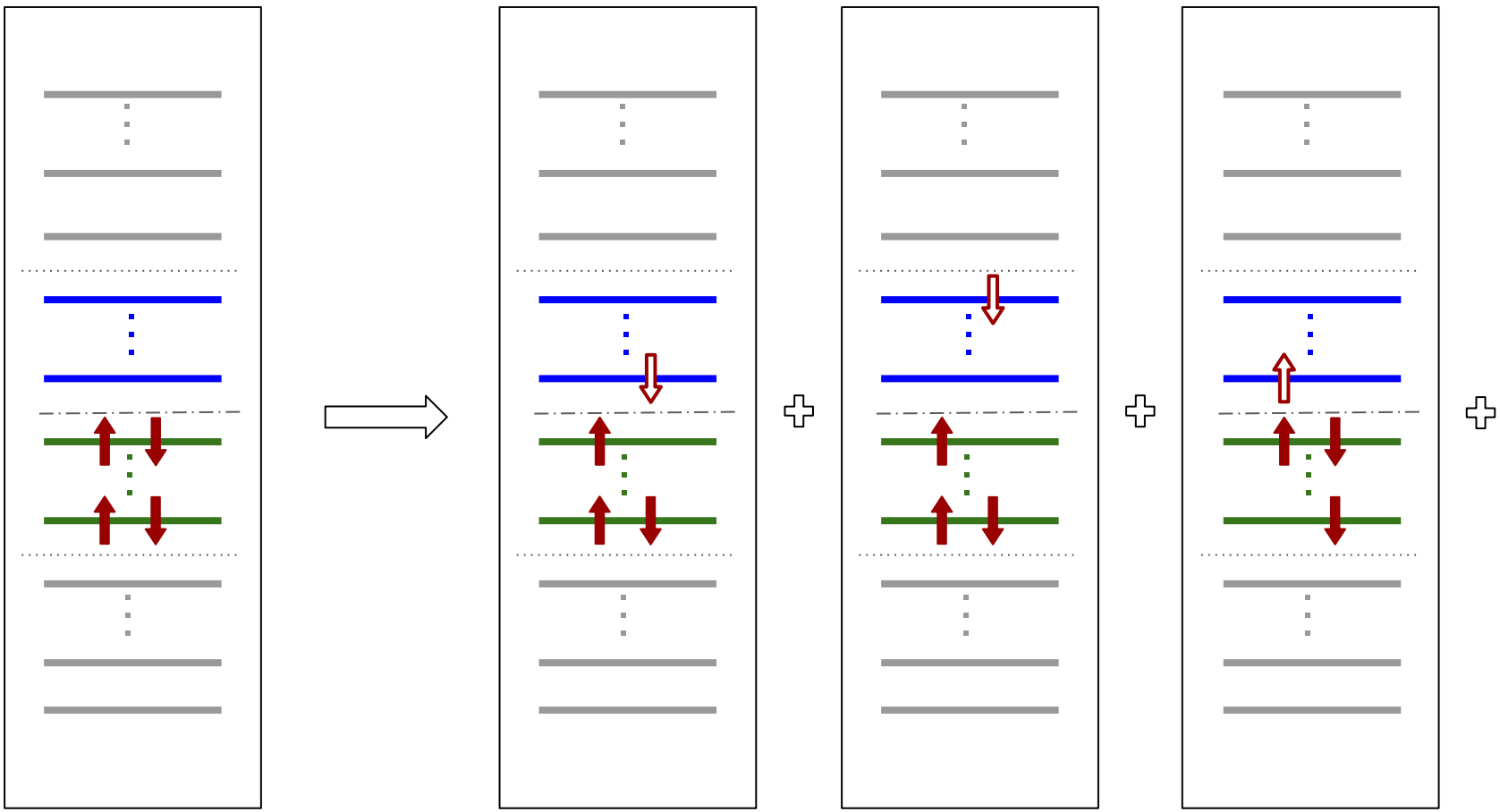


Sector (0,1)

Fock-space coupled-cluster sectors



Fock-space coupled-cluster sectors



Sector (1,1)

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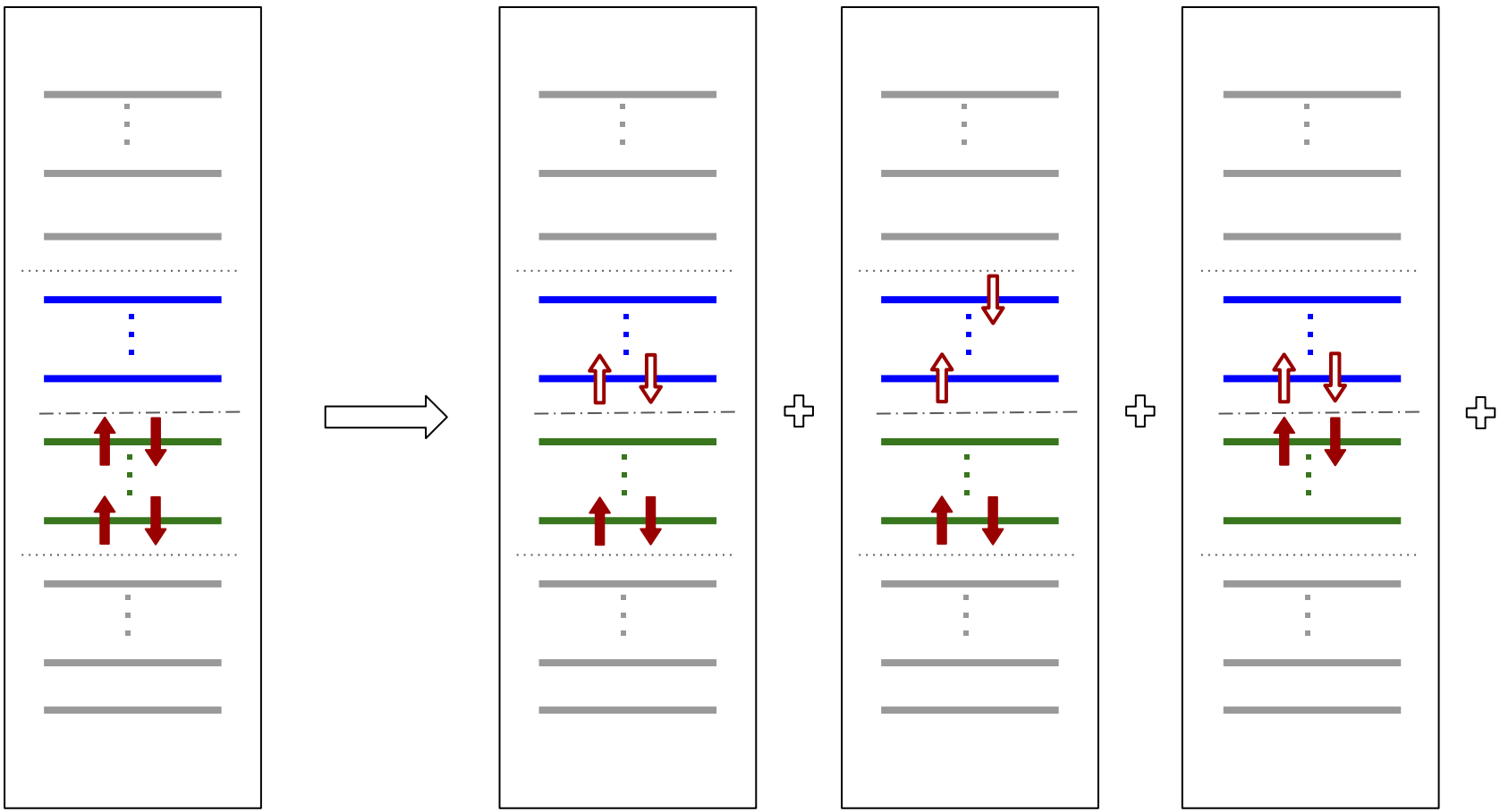

Sector (2,2)

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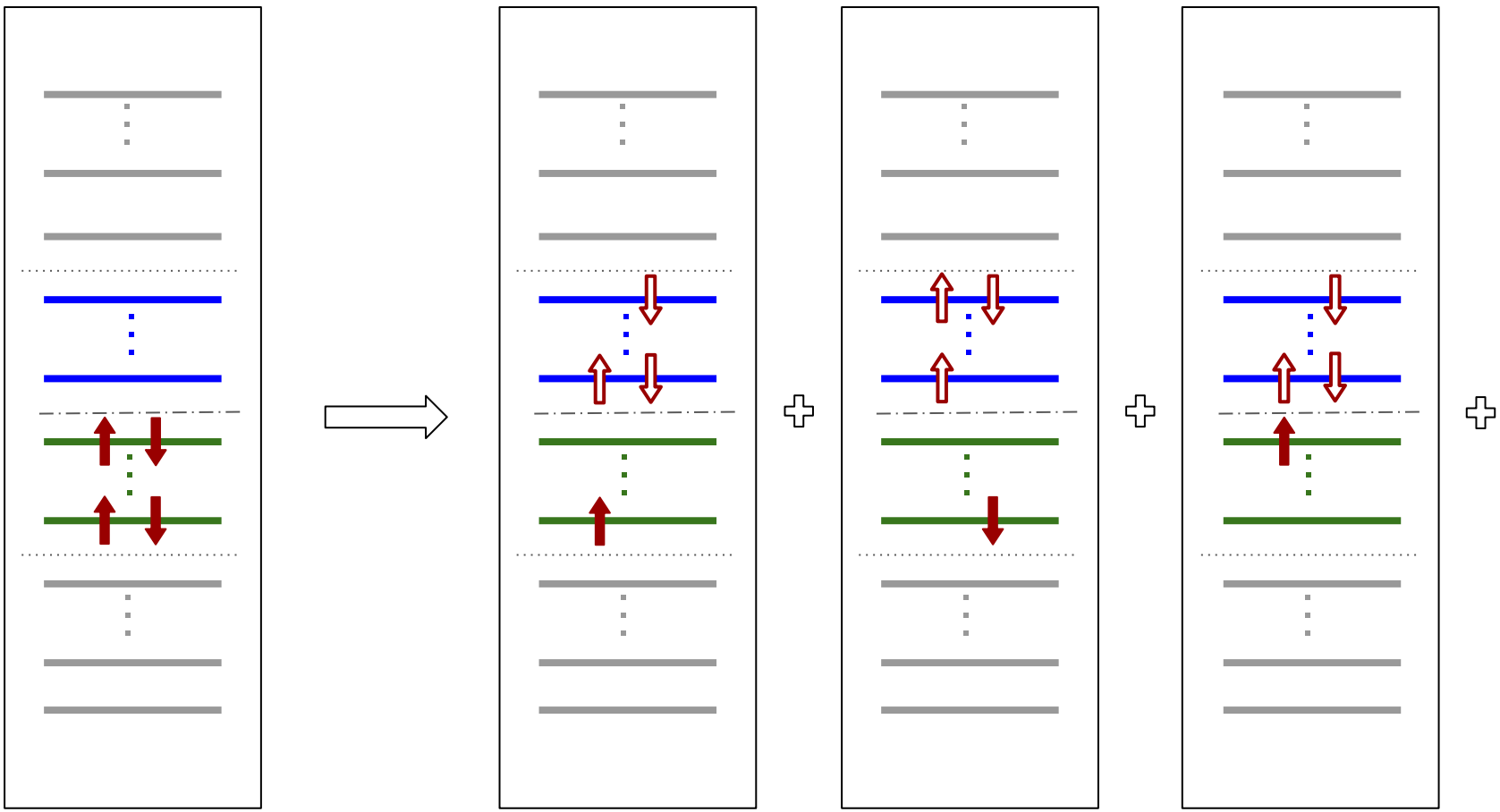

Sector (3,3)

Fock-space coupled-cluster sectors

Model space

$$L_P = L_P^{00} \quad L_P^{10} \quad L_P^{01} \quad L_P^{11} \quad ... \tag{19}$$

Projector operator

$$P = P^{00} + P^{10} + P^{01} + P^{11} + ... \tag{20}$$

$$Q^{hp} = 1 \quad P^{hp} \tag{21}$$

Effective Hamiltonian

$$\tilde{H} = \tilde{H}^{00} + \tilde{H}^{10} + \tilde{H}^{01} + \tilde{H}^{11} + ... \tag{22}$$

diagonalizing the $\tilde{H}^{hp}$ matrices in each (h, p) sector we obtain the corresponding electronic state energies and model functions

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Fock-space coupled-cluster equation

$$[T_n^{hp}, H_0]P^{hp} = (V\Omega \quad \Omega P^{hp} V\Omega)_{\mathrm{n,conn}} P^{hp} \tag{24}$$

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X Linked diagram theorem ! size consistent (for energy and wave function)[4]

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Second quantized operators

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$$H = H_0 + V \tag{26}$$

$$H_0 = \sum_{i=1}^{N}\left(\frac{1}{2} r_i^2 \quad \frac{Z}{r_i} + u(r_i)\right) \qquad V = \sum_{i<j}^{N}\frac{1}{r_{ij}} \quad \sum_{i=1}^{N} u(r_i) \tag{27}$$

Second quantization

$$H_0 = \sum_i a_i^y a_i \varepsilon_i \tag{28}$$

$$V = \sum_{ij} a_i^y a_j \hbar i j u j j i + \frac{1}{2}\sum_{ijkl} a_i^y a_j^y a_l a_k \hbar i j j \frac{1}{r_{12}} j k l i \tag{29}$$

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$$V = \sum_{ij} a_i^y a_j \hbar i j u j j i + \frac{1}{2}\sum_{ijkl} a_i^y a_j^y a_l a_k \hbar i j j \frac{1}{r_{12}} j k l i \tag{29}$$

Second quantized operators

Electronic Hamiltonian

$$H = \frac{1}{2}\sum_{i=1}^{N} r_i^2 \quad \sum_{i=1}^{N}\frac{Z}{r_i} + \sum_{i<j}^{N}\frac{1}{r_{ij}} \tag{25}$$

$$H = H_0 + V \tag{26}$$

$$H_0 = \sum_{i=1}^{N}\left(\frac{1}{2} r_i^2 \quad \frac{Z}{r_i} + u(r_i)\right) \qquad V = \sum_{i<j}^{N}\frac{1}{r_{ij}} \quad \sum_{i=1}^{N} u(r_i) \tag{27}$$

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Normal-ordered operators

Zero-order Hamiltonian

$$H_0 = \sum_a^{\text{occ}} \varepsilon_a + \sum_i f a_i^y a_i g \varepsilon_i \tag{30}$$

Perturbation

$$\begin{aligned} V &= V_0 + V_1 + V_2 \\ V_0 &= \sum_a^{\text{core}} haj \quad uja i + \frac{1}{2} \sum_{ab}^{\text{core}} \left(habj \frac{1}{r_{12}} jab i \quad hbaj \frac{1}{r_{12}} jab i \right) \\ V_1 &= \sum_{ij} f a_i^y a_j g hi j v jj i \\ V_2 &= \sum_{ijkl} f a_i^y a_j^y a_l a_k g hij j \frac{1}{r_{12}} jkl i \end{aligned} \tag{31}$$

Cluster operator

$$T \quad T_1 + T_2 + \ldots \tag{32}$$

$$T_n = \frac{1}{n!} \sum_{a_1 \ldots a_n} \sum_{i_1 \ldots i_n} t_{i_1 \ldots i_n}^{a_1 \ldots a_n} f a_{i_1}^y \ldots a_{i_n}^y a_{a_n} \ldots a_{a_1} g \tag{33}$$

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Diagrammatic notation[5]

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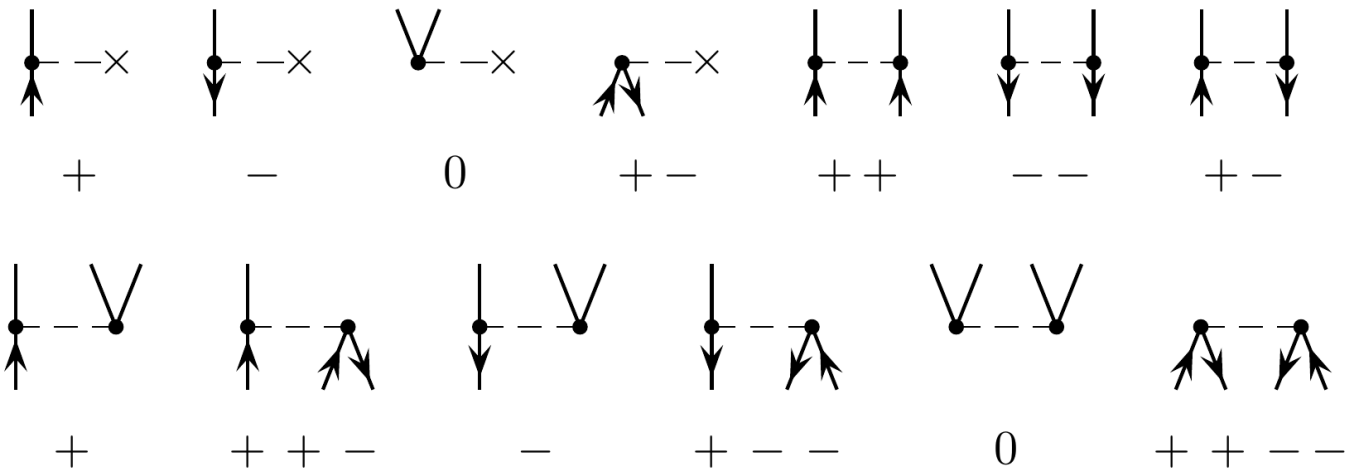

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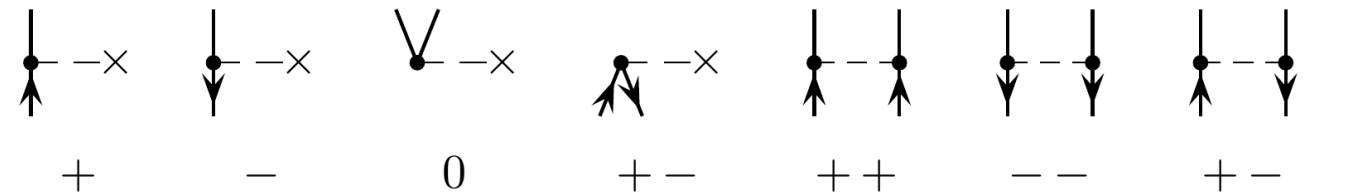

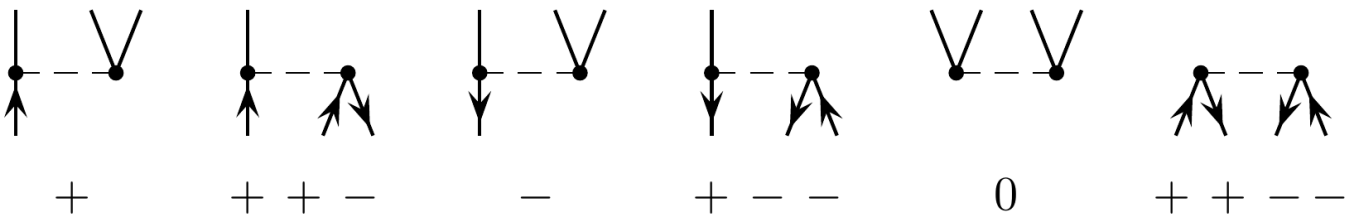

$$T = T_1 + T_2 + T_3 + ...$$

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Amplitude equations

$$[T_n, H^0] = (V\Omega \quad \Omega PV\Omega)_{\text{n,conn}} \tag{34}$$

l.h.s.

$$\sum_{pq} f a_p^y a_q g(\varepsilon_q \quad \varepsilon_p) t_q^p + \frac{1}{2} \sum_{pqsr} f a_p^y a_q^y a_s a_r g(\varepsilon_s + \varepsilon_r \quad \varepsilon_p \quad \varepsilon_q) t_{rs}^{pq} + \ldots \tag{35}$$

r.h.s. ! [6]

[6] Figure from Lindgren, I., & Morrison, J. (2012). Springer Science & Business Media.

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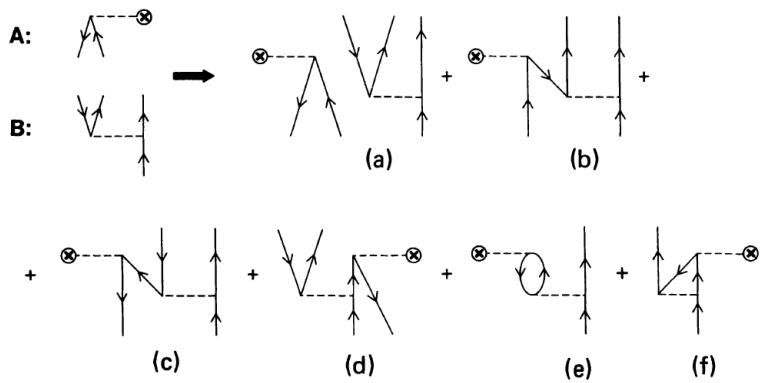
r.h.s. ! [6]Wick's theorem for operator products



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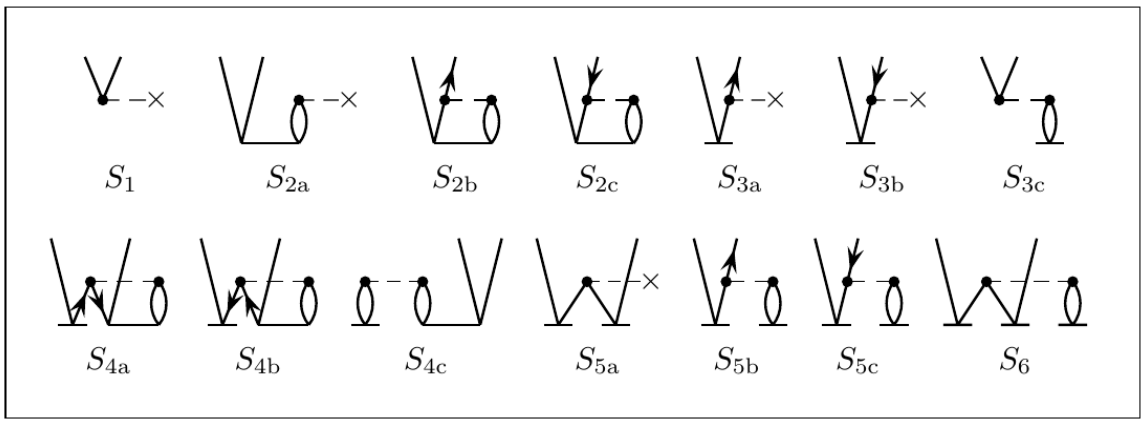

[6] Single particle (in CCSD). Figure from Shavitt, I., & Bartlett, R. J. (2009). Cambridge university press.

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r.h.s. [6] Goldstone diagrams

$$\begin{aligned}
&f_{ai} + \sum_{kc} f_{kc} t_{ik}^{ac} + \tfrac{1}{2} \sum_{kcd} \langle ak \| cd \rangle t_{ik}^{cd} - \tfrac{1}{2} \sum_{klc} \langle kl \| ic \rangle t_{kl}^{ac} + \sum_{c} f_{ac} t_i^c \\
&- \sum_{k} f_{ki} t_k^a + \sum_{kc} \langle ak \| ic \rangle t_k^c - \tfrac{1}{2} \sum_{klcd} \langle kl \| cd \rangle t_i^c t_{kl}^{ad} - \tfrac{1}{2} \sum_{klcd} \langle kl \| cd \rangle t_k^a t_{il}^{cd} \\
&+ \sum_{klcd} \langle kl \| cd \rangle t_k^c t_{li}^{da} - \sum_{kc} f_{kc} t_i^c t_k^a + \sum_{kcd} \langle ak \| cd \rangle t_i^c t_k^d \\
&- \sum_{klc} \langle kl \| ic \rangle t_k^a t_l^c - \sum_{klcd} \langle kl \| cd \rangle t_i^c t_k^a t_l^d = 0 \qquad \text{(for all } i, a\text{)}.
\end{aligned}$$

! **identifying** the n-body terms on the l.h.s. and r.h.s, we can write down a series of coupled equations that can be solved iteratively to find the cluster amplitudes.

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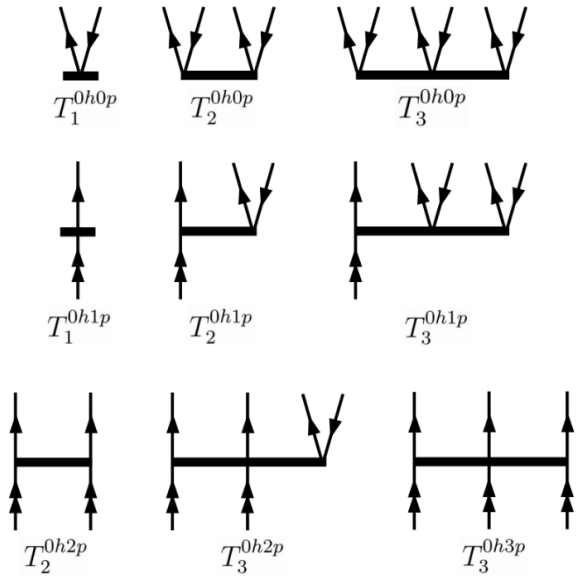
Higher sectors[7]



Fock-space from single-reference coupled-cluster diagrams[8]

[7] Figure taken from A. Oleynichenko PhD thesis.

[8] Example for sector (0,1). Figure taken from A. Oleynichenko PhD thesis.

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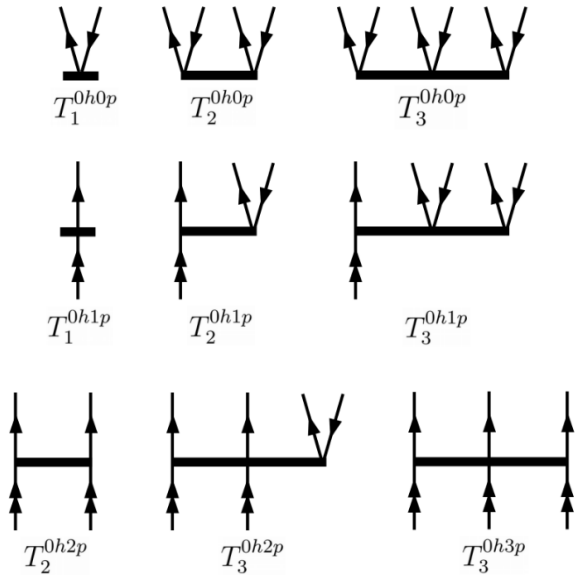

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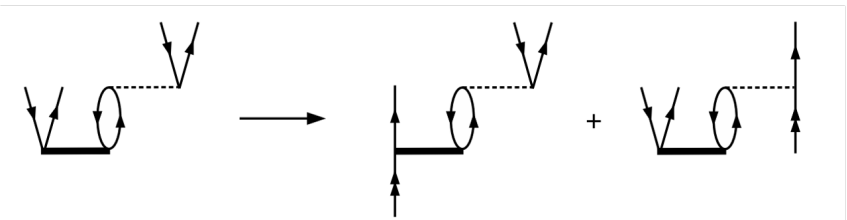

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Coulomb matrix elements

Considering the Coulomb interaction, separating radial[9] and angular variables,

$$\langle ab|\frac{1}{r_{12}}|cd\rangle = \sum_k (-1)^k \hat{k}\, R^k_{\tilde{A}\tilde{B}\tilde{C}\tilde{D}}\, \langle ab||\vec{C}^k(1)\vec{C}^k(2)g^0_0|cd\rangle. \tag{36}$$

Coupling ab and cd,

$$\sum_{J_{ab},J_{cd}} \sum_{M_{ab},M_{cd}} \begin{pmatrix} j_a & j_b & J_{ab} \\ m_a & m_b & M_{ab} \end{pmatrix} \begin{pmatrix} j_c & j_d & J_{cd} \\ m_c & m_d & M_{cd} \end{pmatrix} (-1)^{j_a+j_b-M_{ab}} (-1)^{j_c+j_d-M_{cd}} \hat{J}_{ab}\hat{J}_{cd}$$
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Filling in the known reduced matrix element and rearranging,[10]

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Angular reduction for tensors products

$$\langle ab|jjcd|i\rangle t_{klij} =$$

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! Making use of graph-theory-based angular momentum reduction[11] the 3-j symbols product can be reduced to a factor that can be calculated analytically.

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Reduced amplitude equations

After the angular momentum reduction, the amplitude equations can be simplified

$$(\varepsilon_a \quad \varepsilon_i)t_i^a = hajvjii + \sum_{kc} hkjvjcit_{ik}^{ac} + \ldots + \sum_{klcd} hkljjicit_{kl}^{ac} + \ldots$$
$$\ldots + \sum_{klcd} [\text{Angularfactor}]\bar{X}_{\tilde{k}\tilde{l}\tilde{i}\tilde{c}}\bar{t}_{\tilde{k}\tilde{l}}^{\tilde{a}\tilde{c}} + \ldots \tag{42}$$

Summary

The energies of the states can be obtained by diagonalizing the effective Hamiltonian. The Bloch equation can be solved to find the wave operator

The Fock-space coupled-cluster method can be used to study electronic states with a different number of electrons. Its equations can be obtained from the single-reference coupled-cluster ones

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Outlook

Derive the coupled-cluster amplitude equations in the CCSDT approximation ($T = T_1 + T_2 + T_3$) for FSCC (0,0) and higher sectors

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Implement the reduced coupled-cluster amplitude equations to calculate electronic energies in atoms with a higher precision and a broader applicability

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The energies of the states can be obtained by diagonalizing the effective Hamiltonian. The Bloch equation can be solved to find the wave operator

The Fock-space coupled-cluster method can be used to study electronic states with a different number of electrons. Its equations can be obtained from the single-reference coupled-cluster ones

The use of angular momentum theory and spherical symmetry reduce the coupled-cluster amplitude equations

Outlook

Derive the coupled-cluster amplitude equations in the CCSDT approximation ($T = T_1 + T_2 + T_3$) for FSCC (0,0) and higher sectors

Reduce the coupled-cluster amplitude equations using angular momentum graph theory

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