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

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June 7, 2023

Relativistic Fock-space coupled-cluster method

Post–Hartree–Fock method including

✓ Special relativity and electron correlation

✓ Multireference

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

✓ 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

✓ 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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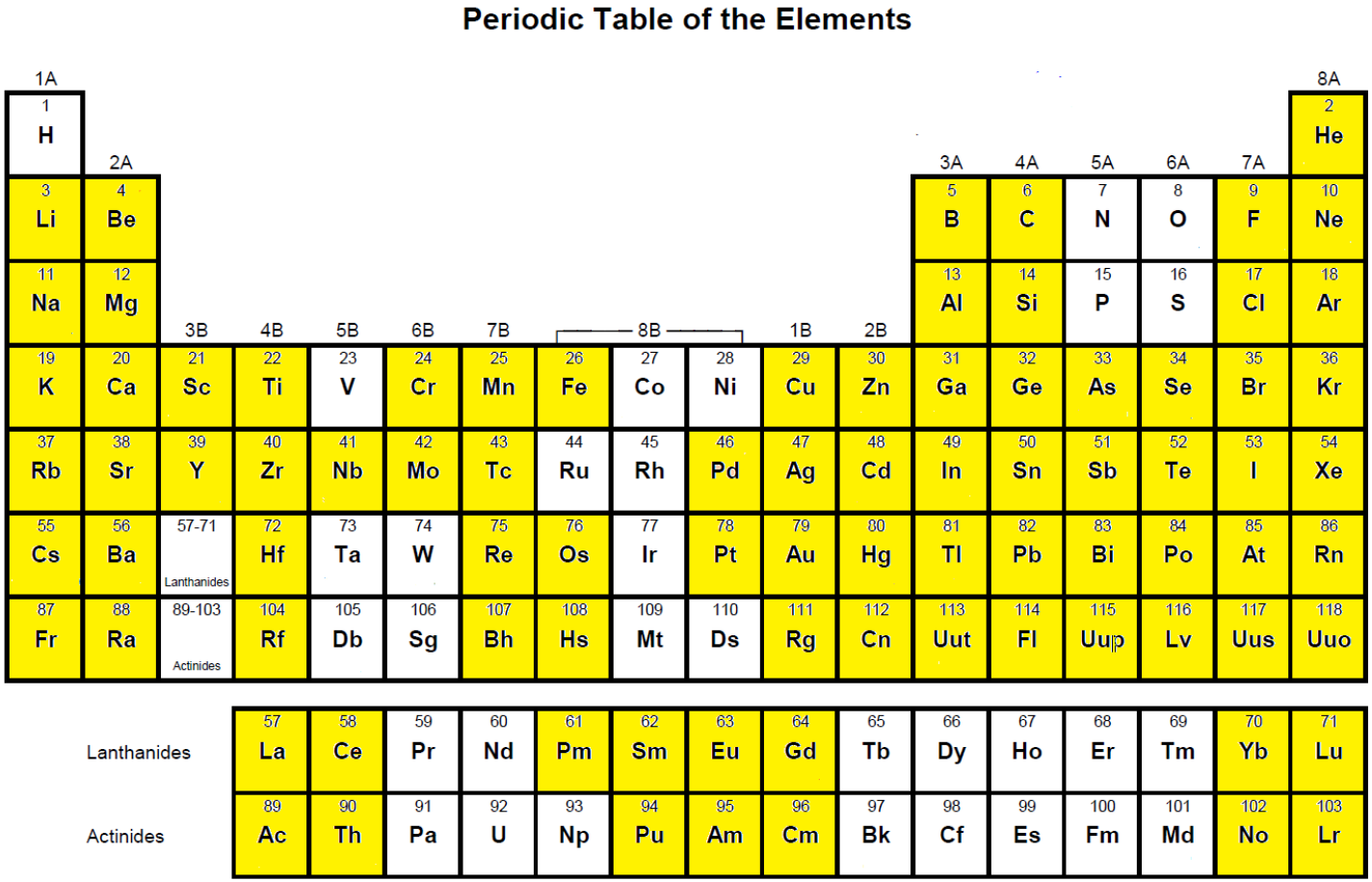
Restricted to 2 holes/particles[1]



[1] Figure from A. Borschevsky.

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

Periodic Table of the Elements

1A												3A	4A	5A	6A	7A	8A
1 H	2A																2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	3B	4B	5B	6B	7B	8B			1B	2B	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71 Lanthanides	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103 Actinides	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

[1] Figure from A. Borschevsky.

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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)

✓ known
✓ 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)

$L_P \rightarrow$ all functions associated with one or several configurations

Example: Be:

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

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

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.

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

Find the wave operator$\rightarrow$

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Derivation of the generalized Bloch equation

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

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

operating on the left with P

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

and operating now with Ω

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

and rearranging,

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

Therefore,

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

Coupled-cluster equation

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

Expanding the wave operator in n-body parts,

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

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

Exponential ansatz[2]

$$\Omega = \{e^T\} = 1 + T + \frac{1}{2}\{T^2\} + ... = \sum_n^\infty \frac{1}{n!}\{T^n\} \tag{17}$$

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

✓ 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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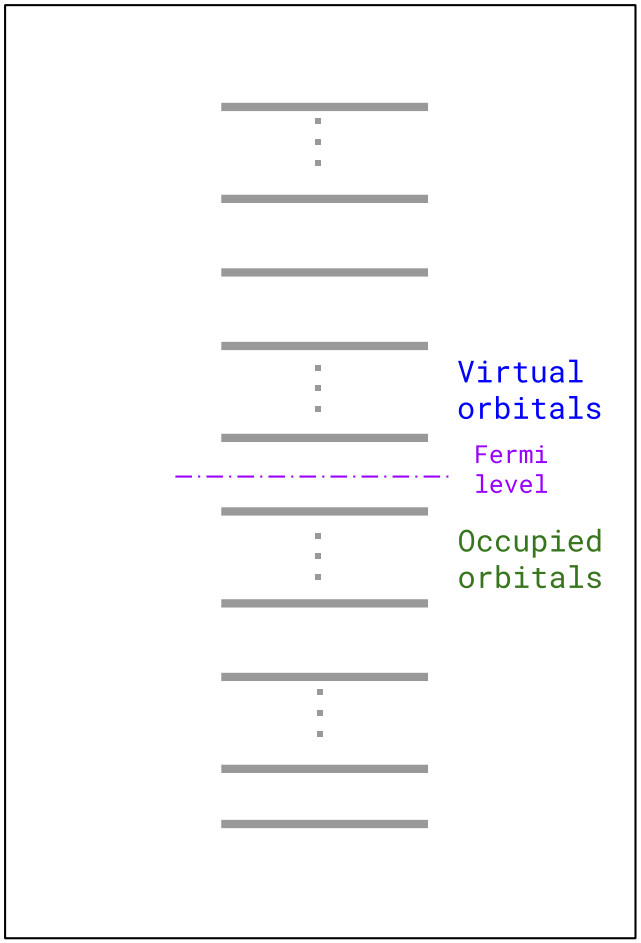
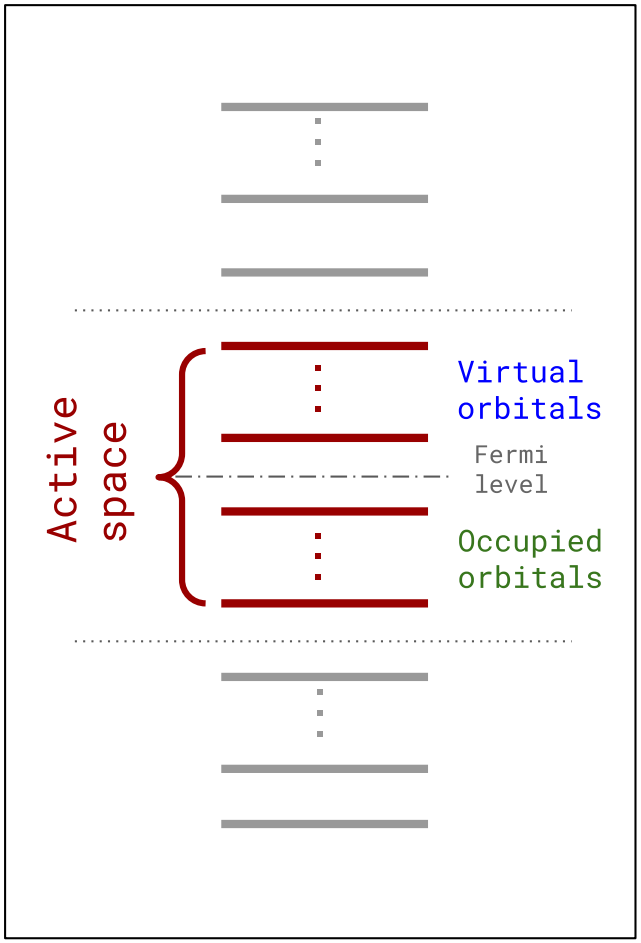


Including **all** determinants obtained by distributing h holes over the active hole states and p particles over active particle states in all possible ways $\rightarrow$ Complete model space

$\rightarrow$**Fock-space sector** (h,p)

Model space



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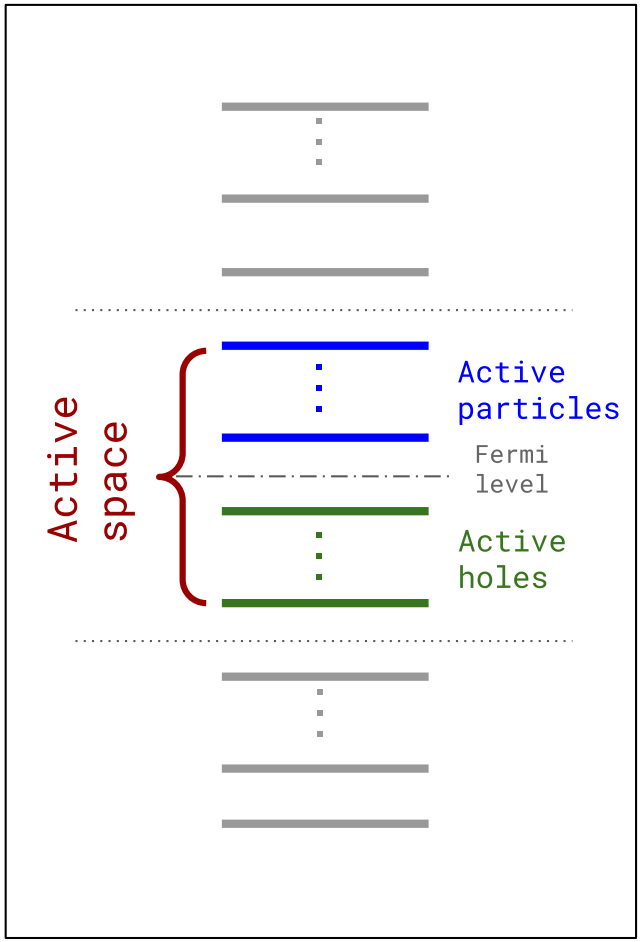

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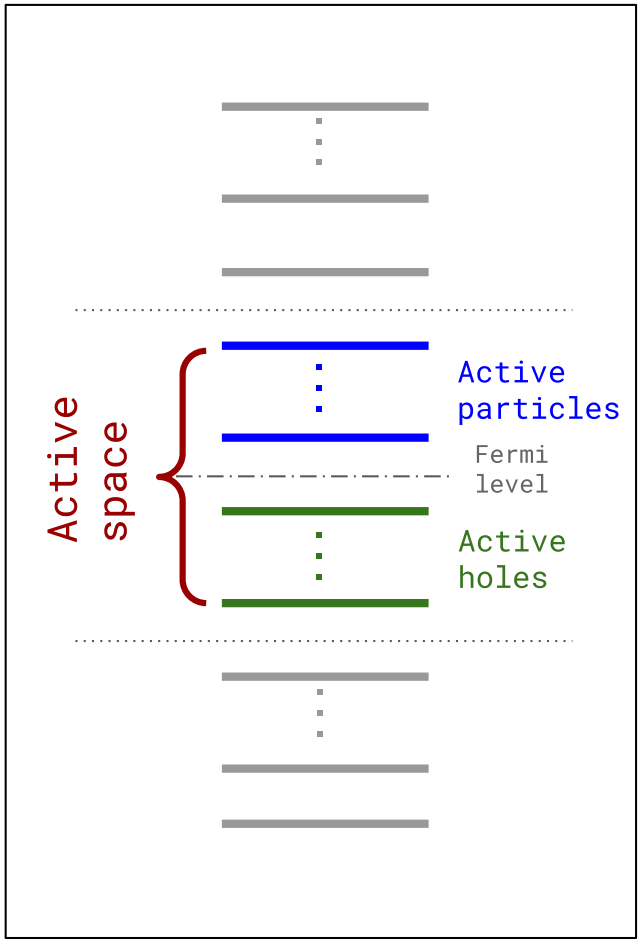

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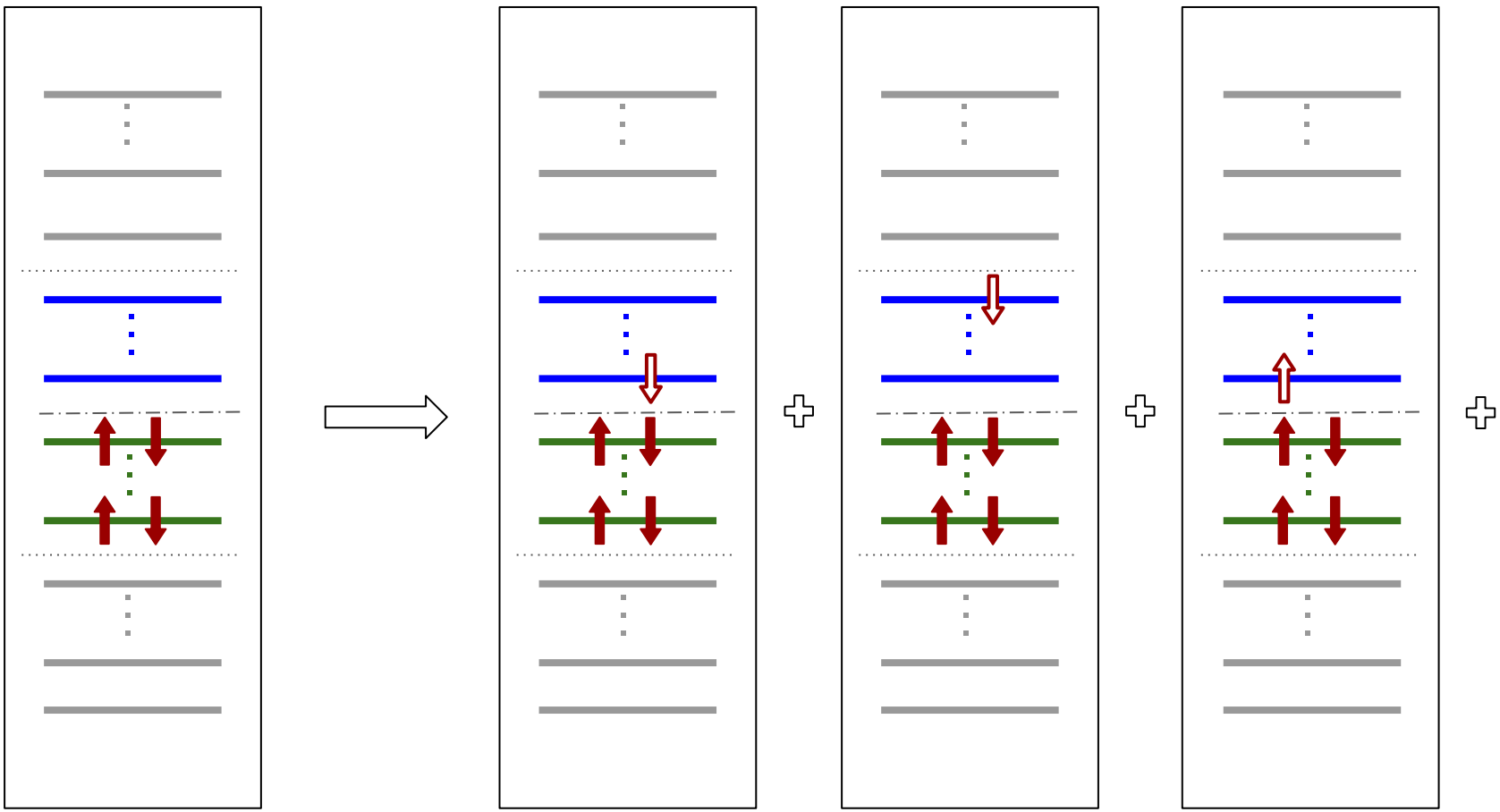
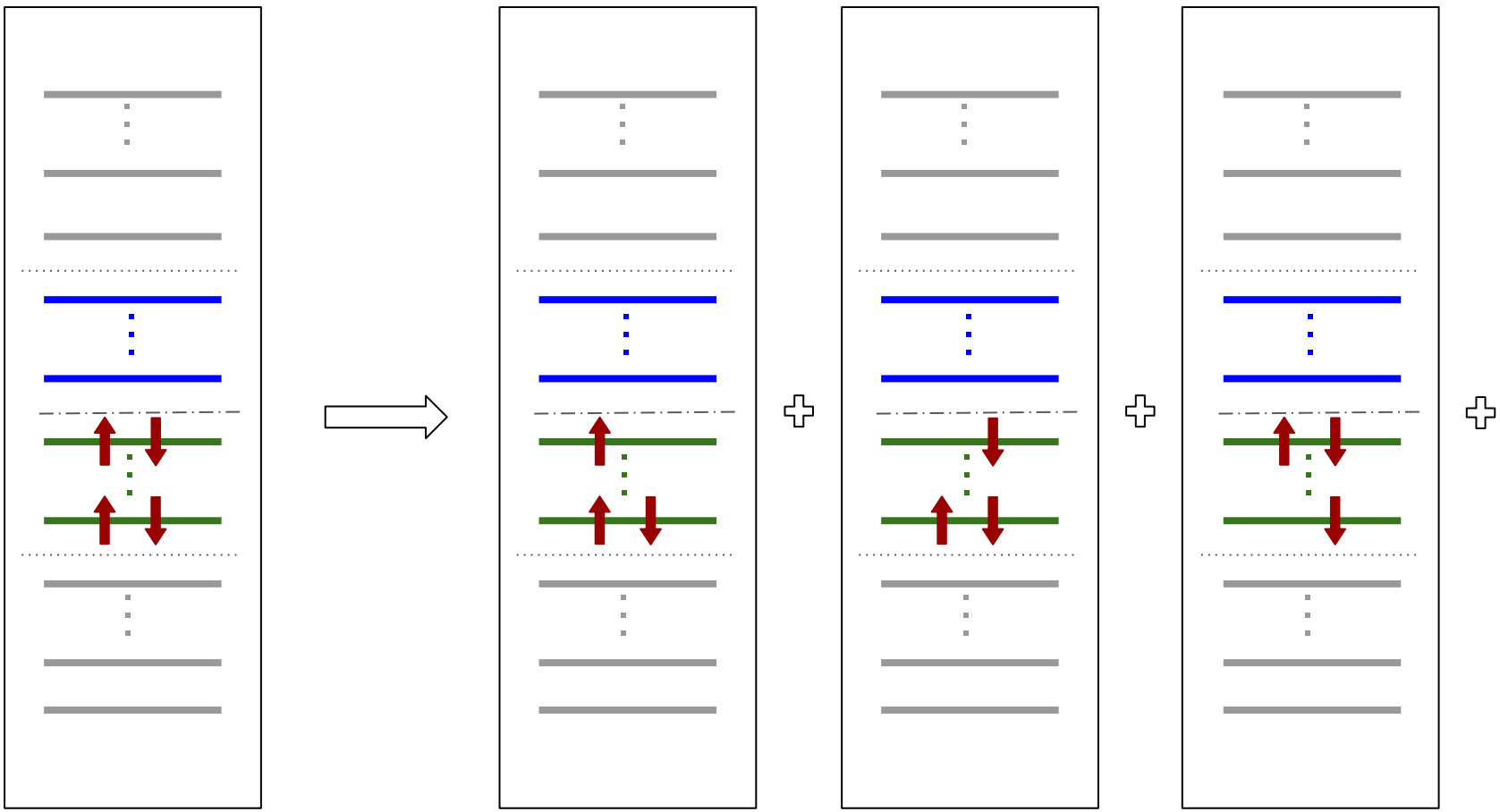
Fock-space coupled-cluster sectors

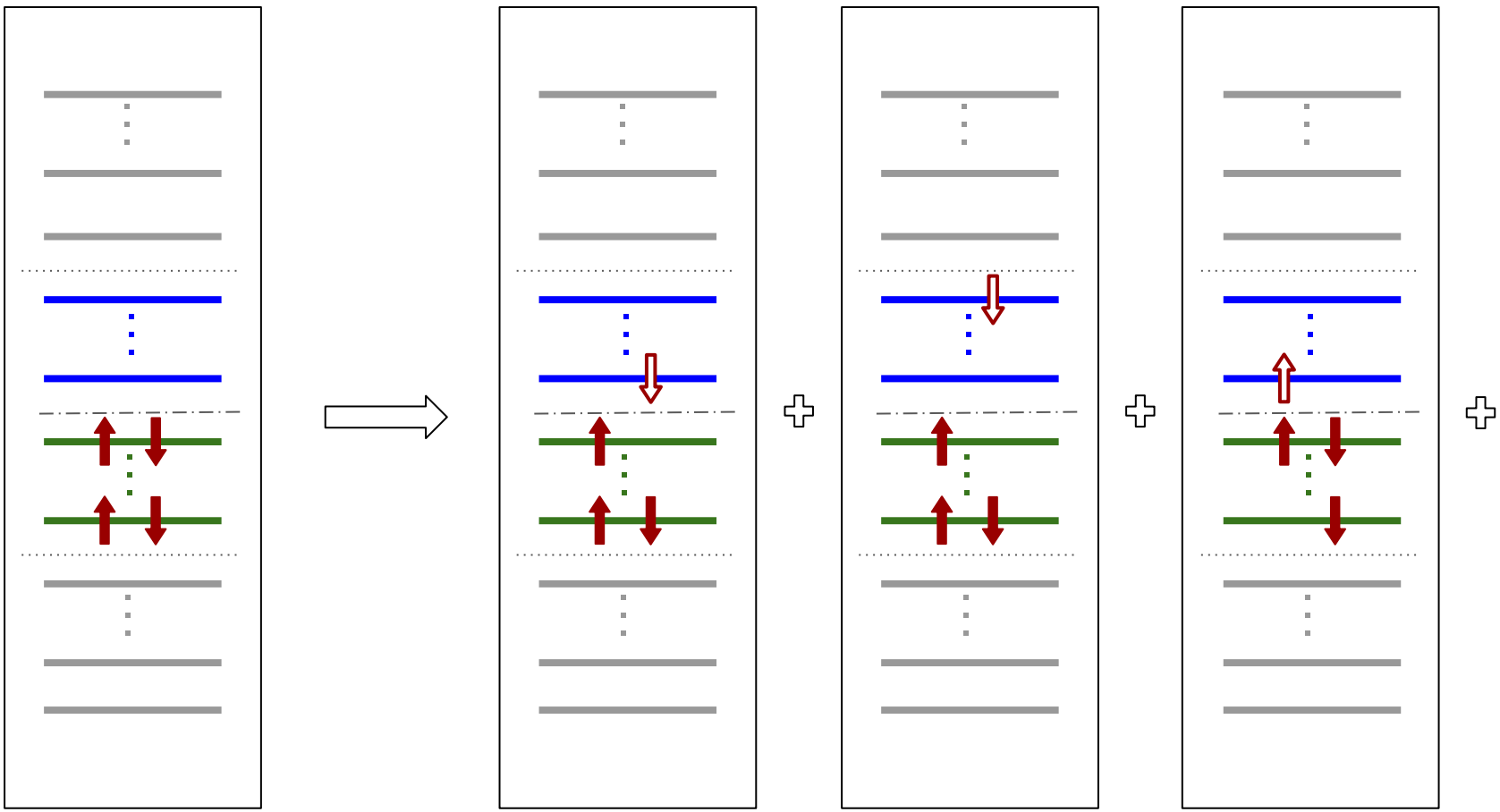


Sector (0,1)

Fock-space coupled-cluster sectors



Fock-space coupled-cluster sectors



Sector (1,1)

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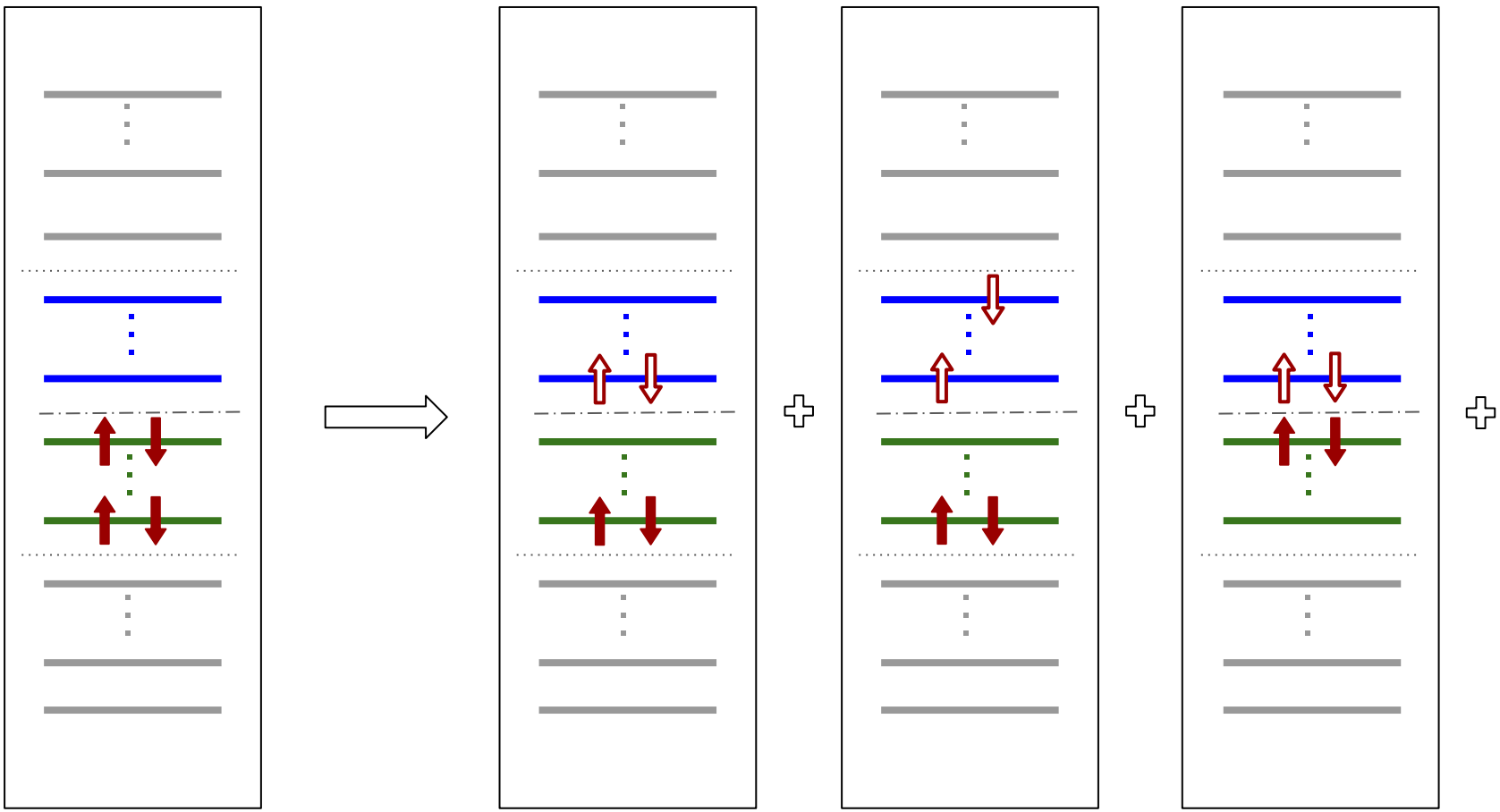

Sector (2,2)

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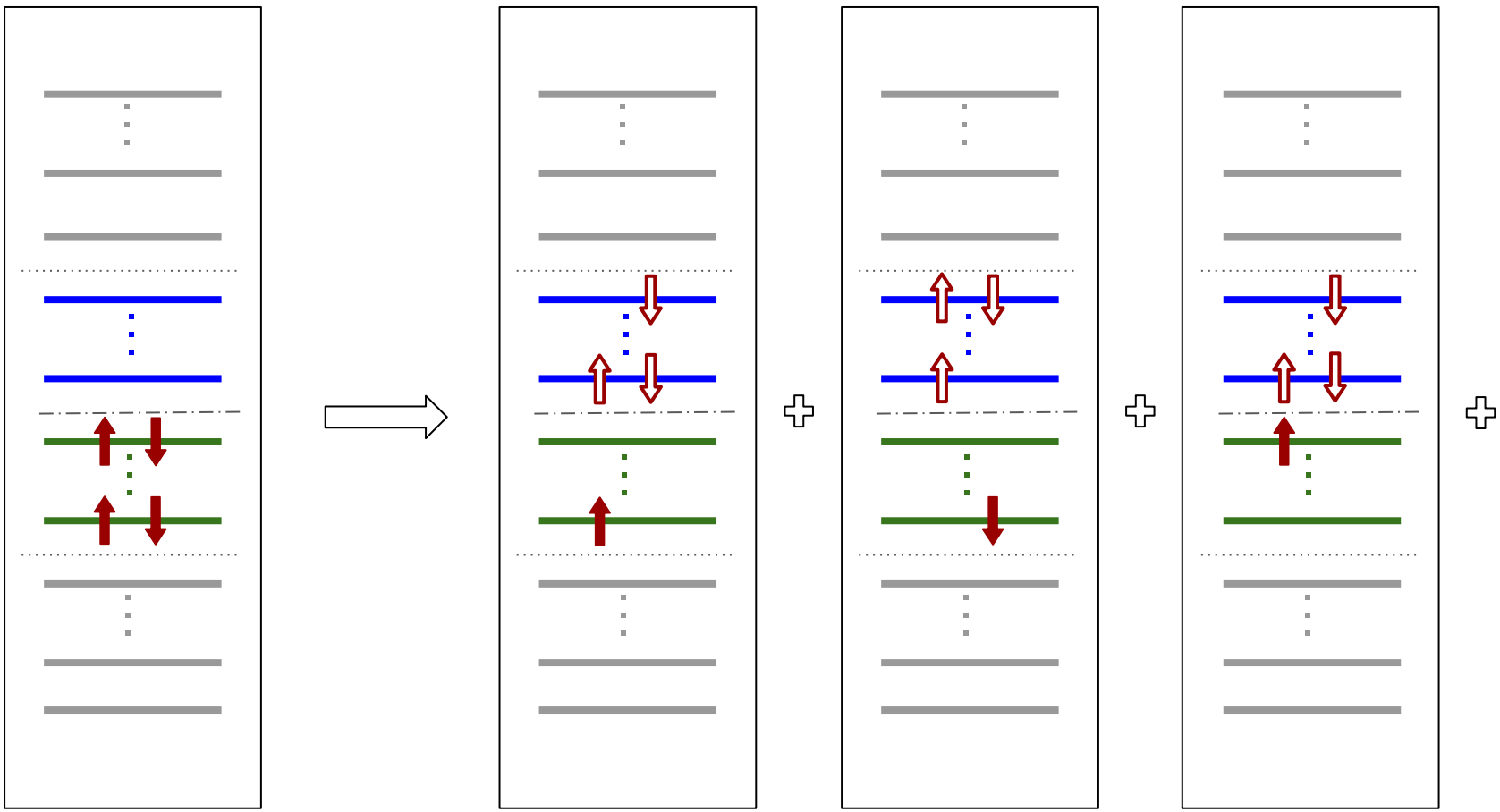

Sector (3,3)

Fock-space coupled-cluster sectors

- Model space

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

- Projector operator

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

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

- 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

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

✓ Partial decoupling according to the subsystem embedding condition[3]

✓ Linked diagram theorem $\rightarrow$ size consistent (for energy and wave function)[4]

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Second quantized operators

- Electronic Hamiltonian

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

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

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

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

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Diagrammatic notation[5]

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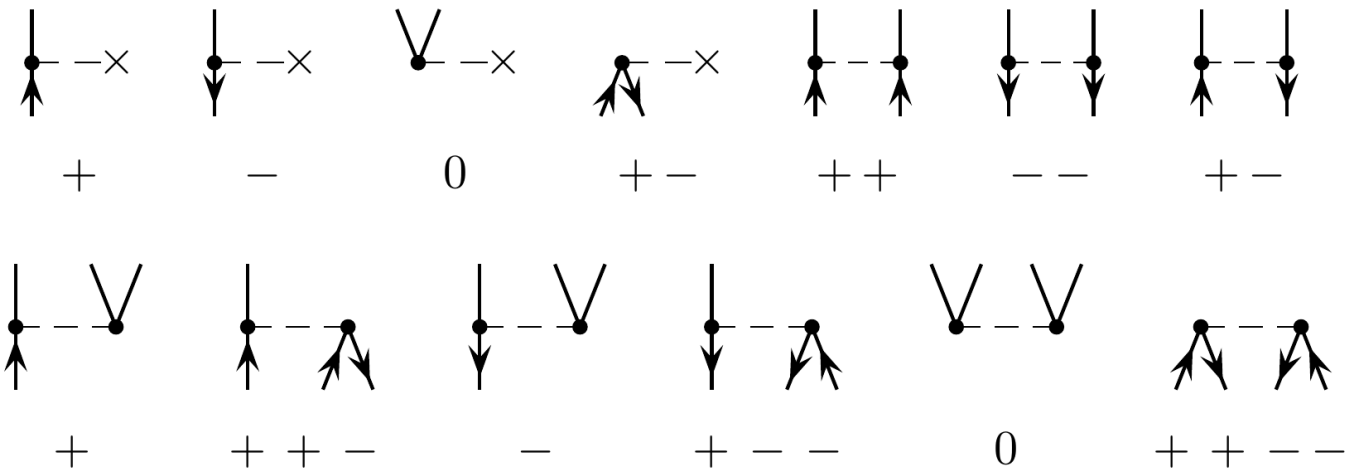

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[5] Figure from Shavitt, I., & Bartlett, R. J. (2009). Cambridge university press.

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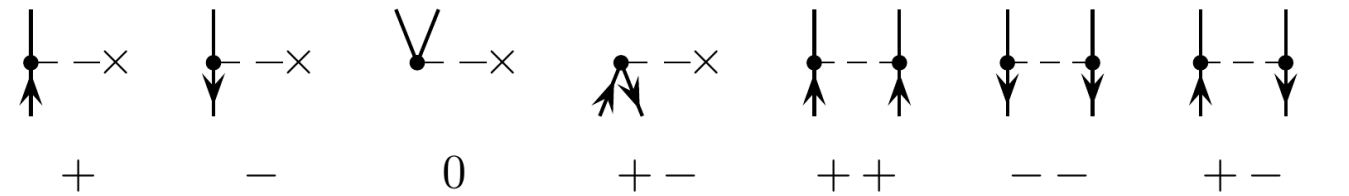

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Amplitude equations

$$[T_n, H^0] = (V\Omega - \Omega P V \Omega)_{\mathrm{n,conn}} \tag{34}$$

- l.h.s.

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

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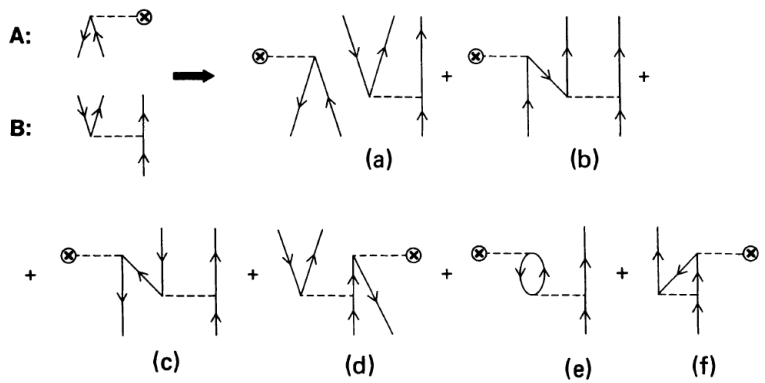

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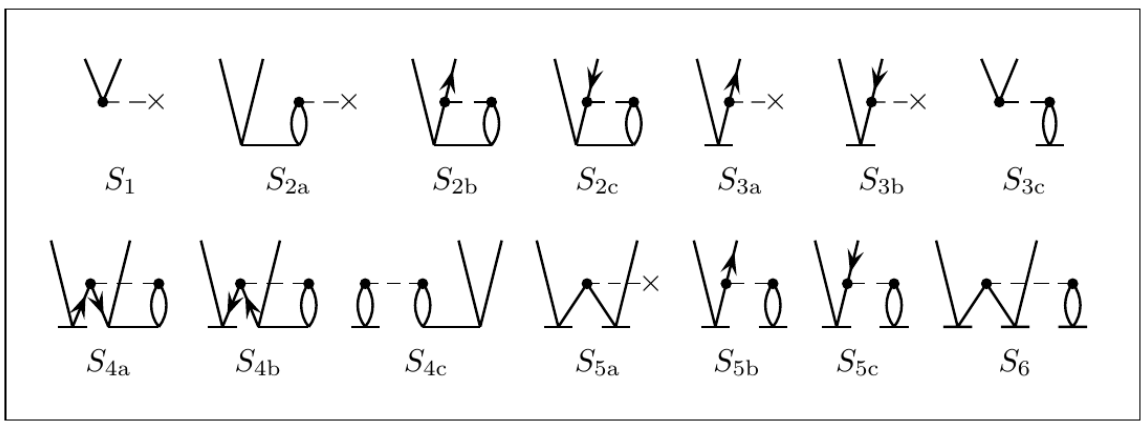

[6] Single particle (in CCSD). Figure from Shavitt, I., & Bartlett, R. J. (2009). Cambridge university press.

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

→ **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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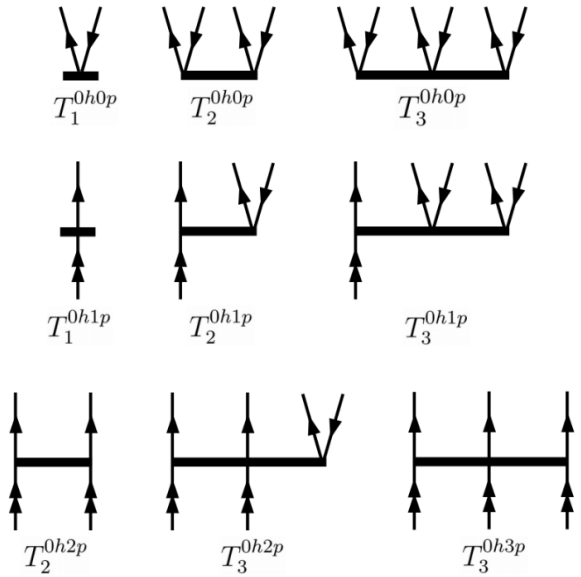
- Higher sectors[7]



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

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

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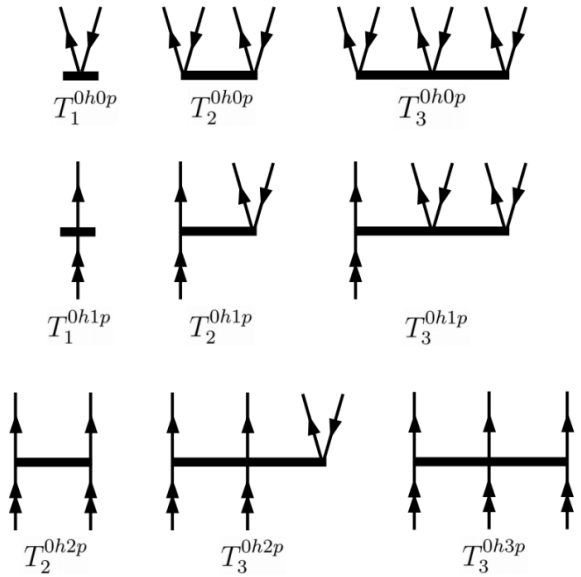

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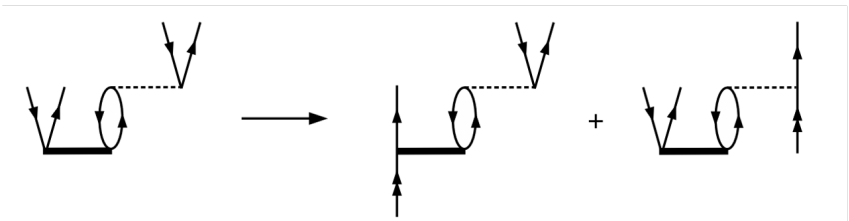

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Coulomb matrix elements

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

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

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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Angular reduction for tensors products

$$\langle ab||cd\rangle t_{klij} =$$

$$\sum_{JJ'MM'} \begin{pmatrix} j_a & j_b & J \\ m_a & m_b & -M \end{pmatrix} \begin{pmatrix} j_c & j_d & J \\ m_c & m_d & -M \end{pmatrix} \begin{pmatrix} j_k & j_l & J' \\ m_k & m_l & -M' \end{pmatrix} \begin{pmatrix} j_i & j_j & J' \\ m_i & m_j & -M' \end{pmatrix} \bar{X}^{J}_{\tilde{a}\tilde{b}\tilde{c}\tilde{d}} \bar{t}^{J'}_{\tilde{k}\tilde{l}\tilde{i}\tilde{j}} \quad (41)$$

$\rightarrow$ 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

$$\begin{aligned}(\varepsilon_a - \varepsilon_i) t_i^a &= \langle a|v|i\rangle + \sum_{kc} \langle k|v|c\rangle t_{ik}^{ac} + \ldots + \sum_{klcd} \langle kl||ic\rangle t_{kl}^{ac} + \ldots \\ &\sim \ldots + \sum_{klcd} [\text{Angularfactor}] \bar{X}_{\tilde{k}\tilde{l}\tilde{i}\tilde{c}} \bar{t}_{\tilde{k}\tilde{l}}^{\tilde{a}\tilde{c}} + \ldots\end{aligned} \tag{42}$$

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
- 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
- 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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Acknowledgements

Internal team

Martijn Reitsma

Aleksandra Kiuberies

Anastasia Borschevsky

Ephraim Eliav

External collaborators

Alexander Tichai

Thomas Duguet

Alexander Oleinichenko

Thank you for your attention!