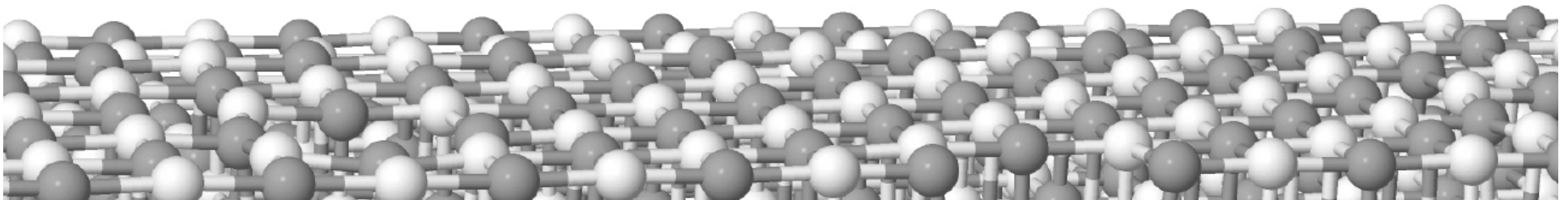


Advanced Materials Modeling:

Wavefunction Methods

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Skolkovo Institute of Science and Technology
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DFT versus wavefunction methods

Density functional theory

Density functional theory: Hohenberg-Kohn theorem

$$n(\mathbf{r}) \begin{cases} \rightarrow \hat{H} & \text{-- many-body Hamiltonian} \\ \rightarrow \Psi(\mathbf{r}_1\sigma_1, K, \mathbf{r}_N\sigma_N) & \text{-- many-body wave function} \\ \rightarrow E_{\text{tot}} & \text{-- total energy} \end{cases}$$

$$E_{\text{tot}} = T[n] - \sum_{I=1}^M Z_I \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_I|} d^3r + \frac{1}{2} \sum_{I=1}^M \sum_{J=1}^M \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{\text{xc}}[n]$$

Approximations to $E_{\text{xc}}[n]$: Local density approximation (LDA), generalized gradient approximation (GGA), meta-GGA

No systematic way to improve accuracy!

Ground-state electronic structure problem

$$\left[-\frac{1}{2} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} - \sum_i \sum_J \frac{Z_J}{|\mathbf{r}_i - \mathbf{R}_J|} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + V^{\text{ext}}(\{\mathbf{r}_i\}) \right] \Psi(\{\mathbf{r}_i\}, \{\sigma_i\}) = E \Psi(\{\mathbf{r}_i\}, \{\sigma_i\})$$

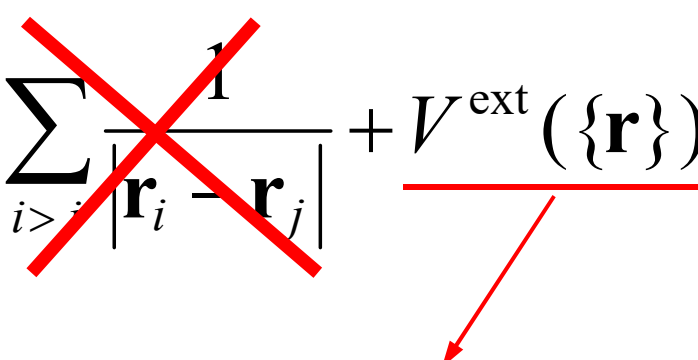
$\Psi(\{\mathbf{r}_i\}, \{\sigma_i\})$ – many-body wave function, depends on spatial (\mathbf{r}_i) and spin (σ_i) coordinates of particles (also on nuclear coordinates (\mathbf{R}_J) and $V^{\text{ext}}(\{\mathbf{r}_i\})$)

- already includes approximations (Born-Oppenheimer, non-relativistic, no magnetic field)
- wave function depends on $4N$ variables (spatial + spin)
- electrons interact via Coulomb forces

Ground-state electronic structure problem

$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} - \sum_i \sum_J \frac{Z_J}{|\mathbf{r}_i - \mathbf{R}_J|} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + V^{\text{ext}}(\{\mathbf{r}\})$$

Ground-state electronic structure problem

$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} - \sum_i \sum_J \frac{Z_J}{|\mathbf{r}_i - \mathbf{R}_J|} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{V^{\text{ext}}(\{\mathbf{r}\})}{}$$


$$V^{\text{ext}}(\{\mathbf{r}\}) = \sum_i v(\mathbf{r}_i)$$



$$\hat{H}_1 = \sum_i \hat{h}_i, \hat{h}_i \psi_i = \varepsilon_i \psi_i$$

$$\Psi(\{\mathbf{r}\}) = \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N) = \prod_i \psi_i(\mathbf{r}_i)$$

$$\hat{H}_1 \Psi(\{\mathbf{r}\}) = \left(\sum_i \varepsilon_i \right) \Psi(\{\mathbf{r}\})$$

Ground-state electronic structure problem

$$\hat{H}_1 = \sum_i \hat{h}_i, \hat{h}_i \psi_i = \varepsilon_i \psi_i$$

$$\hat{H}_1 \Psi(\{\mathbf{r}\}) = \left(\sum_i \varepsilon_i \right) \Psi(\{\mathbf{r}\})$$

$$\Psi(\{\mathbf{r}\}) = \prod_i \psi_i(\mathbf{r}_i) \text{ – eigenfunction of } \hat{H}_1$$

Ground-state electronic structure problem

$$\hat{H}_1 = \sum_i \hat{h}_i, \hat{h}_i \psi_i = \varepsilon_i \psi_i$$

$$\hat{H}_1 \Psi(\{\mathbf{r}\}) = \left(\sum_i \varepsilon_i \right) \Psi(\{\mathbf{r}\})$$

$$\Psi(\{\mathbf{r}\}) = \prod_i \psi_i(\mathbf{r}_i) \text{ – eigenfunction of } \hat{H}_1$$

However,

$$\tilde{\Psi}(\{\mathbf{r}\}) = \psi_1(\mathbf{r}_1) K \psi_n(\mathbf{r}_{n+1}) \psi_{n+1}(\mathbf{r}_n) \dots \psi_N(\mathbf{r}_N)$$

is also a solution of $\hat{H}_1 \Psi(\{\mathbf{r}\}) = E \Psi(\{\mathbf{r}\})$ with exactly the same energy

Ground-state electronic structure problem

$$\hat{H}_1 = \sum_i \hat{h}_i, \hat{h}_i \psi_i = \varepsilon_i \psi_i$$

$$\Psi(\{\mathbf{r}\}, \{\sigma\}) = \sum_{\mathbf{q}} C_{\mathbf{q}} \hat{P}_{\mathbf{q}} \left[\prod_i \psi_i(\mathbf{r}_{q_i}) s_i(\sigma_{q_i}) \right]$$

index-permutation operator

$$\hat{H}_1 \Psi(\{\mathbf{r}\}, \{\sigma\}) = \left(\sum_i \varepsilon_i \right) \Psi(\{\mathbf{r}\}, \{\sigma\})$$

In general, the coefficients $C_{\mathbf{q}}$ are almost arbitrary (apart from normalization) ... **but not for electrons!**

Fermions versus bosons

Indistinguishable particles



Permutation of two particles cannot change any observable



Wavefunction can change only by a phase factor



$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \rightarrow e^{i\phi} \Psi(\mathbf{r}_2, \mathbf{r}_1)$$

Permuting again should change the wavefunction back

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \rightarrow e^{i\phi} \Psi(\mathbf{r}_2, \mathbf{r}_1) \rightarrow e^{2i\phi} \Psi(\mathbf{r}_1, \mathbf{r}_2) \Rightarrow e^{2i\phi} = 1$$

Fermions versus bosons

Indistinguishable particles



Permutation of two particles cannot change any observable





Wavefunction can change only by a phase factor



$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \rightarrow e^{i\phi} \Psi(\mathbf{r}_2, \mathbf{r}_1)$$

Permuting again should change the wavefunction back


$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$$


$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1)$$

Fermions versus bosons

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$$

fermions:

cannot occupy the same
quantum state

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1)$$

bosons:

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Fermions versus bosons

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bosons:

can occupy the same
quantum state

Spin-statistics theorem: spin-1/2 particles are all fermions, integer-spin – bosons (from relativity)



electrons are fermions

Many-electron wave function

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1)$$

fermions:

cannot occupy the same
quantum state

bosons:

can occupy the same
quantum state

electrons are fermions

$$\Psi(\{\mathbf{r}\}, \{\sigma\}) = \sum_{\mathbf{q}} C_{\mathbf{q}} \hat{P}_{\mathbf{q}} \left[\prod_i \psi_i(\mathbf{r}_{q_i}) s_i(\sigma_{q_i}) \right]$$

$$C_{\mathbf{q}} = \frac{(-1)^{n(\mathbf{q})}}{\sqrt{N!}}$$

smallest number of permutations to
revert back to original order

normalization factor

Many-electron wave function

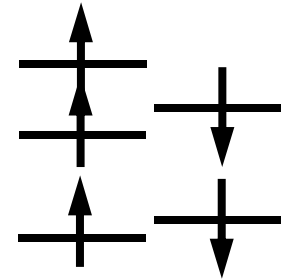
$$\Psi(\{\mathbf{r}\}, \{\sigma\}) = \frac{1}{\sqrt{N!}} \sum_{\mathbf{q}} (-1)^{n(\mathbf{q})} \hat{P}_{\mathbf{q}} \left[\prod_i \psi_i(\mathbf{r}_{q_i}) s_i(\sigma_{q_i}) \right]$$



$$\Psi = \frac{1}{\sqrt{N!}} \det \begin{bmatrix} \psi_1(r_1) s_1(\sigma_1) & \psi_2(r_1) s_2(\sigma_1) & \dots & \psi_N(r_1) s_N(\sigma_1) \\ \psi_1(r_2) s_1(\sigma_2) & \psi_2(r_2) s_2(\sigma_2) & \dots & \psi_N(r_2) s_N(\sigma_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_N) s_1(\sigma_N) & \psi_2(r_N) s_2(\sigma_N) & \dots & \psi_N(r_N) s_N(\sigma_N) \end{bmatrix}$$

Slater determinant

$$\left(\sum_i \hat{h}_i \right) \Psi = E \Psi, \quad \hat{h}_i \psi_i = \varepsilon_i \psi_i$$



Non-interacting fermions – periodic system

$$\left(-\frac{1}{2} \frac{\partial^2}{\partial \mathbf{r}^2} - \sum_J \sum_{\mathbf{R}} \frac{Z_J}{|\mathbf{r} - \mathbf{R}_J - \mathbf{R}|} + v(\mathbf{r}) \right) \psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r})$$

n – band index,
 \mathbf{k} – k-point

$$\Psi = \begin{array}{c} \begin{array}{c} \uparrow \\ \hline \hline \hline \hline \hline \end{array} \quad n = 3, \mathbf{k} = \mathbf{k}_1, \dots, \mathbf{k}_4 \\ \begin{array}{c} \uparrow \\ \hline \hline \hline \hline \hline \end{array} \quad n = 2, \mathbf{k} = \mathbf{k}_1, \dots, \mathbf{k}_4 \\ \begin{array}{c} \uparrow \\ \hline \hline \hline \hline \hline \end{array} \quad n = 1, \mathbf{k} = \mathbf{k}_1, \dots, \mathbf{k}_4 \end{array}$$

Born-von Karman periodic boundary conditions $\psi_{n\mathbf{k}}(\mathbf{r}) = \psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R})$
→ finite number of k-points, infinite (macroscopic) system as physical limit

Interacting fermions (electrons)

$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} - \sum_i \sum_J \frac{Z_J}{|\mathbf{r}_i - \mathbf{R}_J|} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi \approx \Phi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \det|\psi_1(\mathbf{r}_1)s(\sigma_1) \dots \psi_1(\mathbf{r}_N)s(\sigma_N)|$$



variational principle

$$\min_{\psi_i^*} \langle \Phi | \hat{H} | \Phi \rangle \rightarrow \frac{\delta \langle \Phi | \hat{H} | \Phi \rangle}{\delta \psi_i^*} = 0$$

The Hartree-Fock (HF) approximation

$$\Psi \approx \Phi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \det|\psi_1(\mathbf{r}_1)s(\sigma_1) \dots \psi_1(\mathbf{r}_N)s(\sigma_N)|$$

$$\min_{\psi_i^*} \langle \Phi | \hat{H} | \Phi \rangle \rightarrow \frac{\delta \langle \Phi | \hat{H} | \Phi \rangle}{\delta \psi_i^*} = 0$$



Fock operator

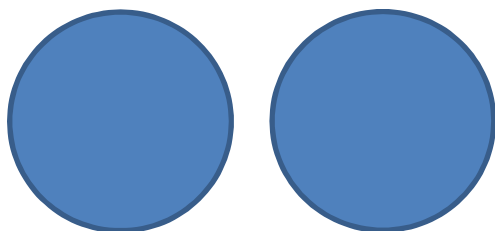
$$\hat{f}\psi_i = \left(\hat{h} + \sum_j (\hat{U}_j - \hat{J}_j) \right) \psi_i = \varepsilon_i \psi_i$$

$$\hat{h}\psi_i = \left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}\right)\psi_i \quad \hat{U}_j\psi_i = \sum_{k \neq i} \int d^3r' \frac{|\psi_k(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r})$$

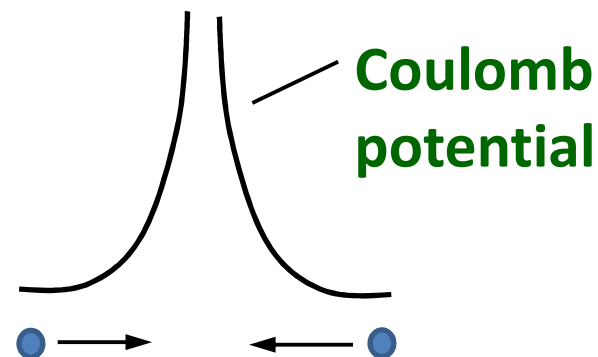
$$\hat{J}_j\psi_i = \sum_{k \neq i} \delta_{s_k, s_i} \int d^3r' \frac{\psi_k^*(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_k(\mathbf{r})$$

Two types of correlation

Dynamic correlation:

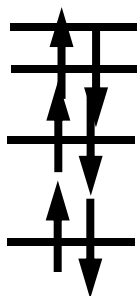


versus

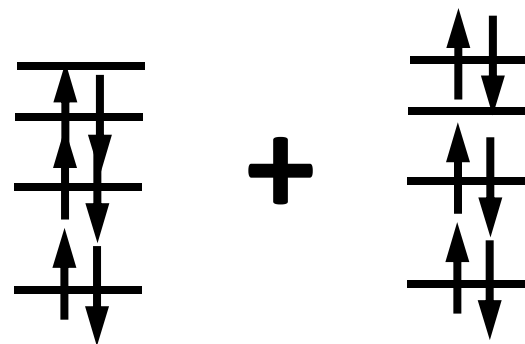


smaller e density, large $\partial\psi / \partial\mathbf{r}$

Non-dynamic (static) correlation:



versus



(quasi)degenerate HOMO-LUMO

HF approximation \rightarrow $\geq 90\%$ of total energy, overestimates ionicity

Beyond mean-field approximation

Finite-order perturbation theory

□ Rayleigh-Schrödinger perturbation theory (RSPT)

$$\hat{H} = \hat{H}_0 + \hat{V}$$

$$\hat{H}_0 \psi_m^{(0)} = E_m^{(0)} \psi_m^{(0)}, \quad \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle = \delta_{mn}$$

$$\hat{H} \psi = E \psi, \quad E, \psi - ?$$

$$\psi = \sum_m c_m \psi_m^{(0)}$$

$$(\hat{H}_0 + \hat{V}) \sum_m c_m \psi_m^{(0)} = \sum_m c_m (E_m^{(0)} + \hat{V}) \psi_m^{(0)} = \sum_m c_m E \psi_m^{(0)}$$

L.D. Landau and E.M. Lifshitz, Course of Theoretical Physics **3**:
Quantum Mechanics (non-relativistic theory)

Finite-order perturbation theory

□ Rayleigh-Schrödinger perturbation theory (RSPT)

$$\psi = \sum_m c_m \psi_m^{(0)}$$

$$\sum_m c_m (E_m^{(0)} + \hat{V}) \psi_m^{(0)} = \sum_m c_m E \psi_m^{(0)}$$

$$c_m = c_m^{(0)} + c_m^{(1)} + c_m^{(2)} + \dots, \quad E = E^{(0)} + E^{(1)} + E^{(2)} + \dots$$

Corrections to ground-state energy:

$$E^{(0)} = E_0^{(0)} \qquad E^{(1)} = \left\langle \psi_0^{(0)} \left| \hat{V} \right| \psi_0^{(0)} \right\rangle$$

$$E^{(2)} = \sum_{m \neq 0} \frac{\langle \psi_0^{(0)} | \hat{V} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \hat{V} | \psi_0^{(0)} \rangle}{E_0^{(0)} - E_m^{(0)}} = \sum_{m \neq 0} \frac{|\langle \psi_0^{(0)} | \hat{V} | \psi_m^{(0)} \rangle|^2}{E_0^{(0)} - E_m^{(0)}}$$

Finite-order perturbation theory

□ Møller-Plesset perturbation theory (MP n)

$$\hat{H} = \hat{H}_0 + \hat{V} = \sum_i \hat{f}(\mathbf{r}_i) + (\hat{H} - \sum_i \hat{f}(\mathbf{r}_i))$$

$$\hat{f} = \hat{h} + \sum_j (\hat{U}_j - \hat{J}_j) \text{ -- Hartree-Fock approximation}$$

$$\psi_0^{(0)} = \Phi \text{ -- Slater determinant with Hartree-Fock orbitals}$$


$$\hat{H}_0 \Phi = (\sum_i \hat{f}(\mathbf{r}_i)) \Phi = (\sum_i \varepsilon_i) \Phi$$

$$E_0^{(0)} = \sum_i \varepsilon_i \quad E_0^{(1)} = \langle \Phi | (\hat{H} - \sum_i \hat{f}(\mathbf{r}_i)) | \Phi \rangle = \langle \Phi | \hat{H} | \Phi \rangle - E_0^{(0)}$$

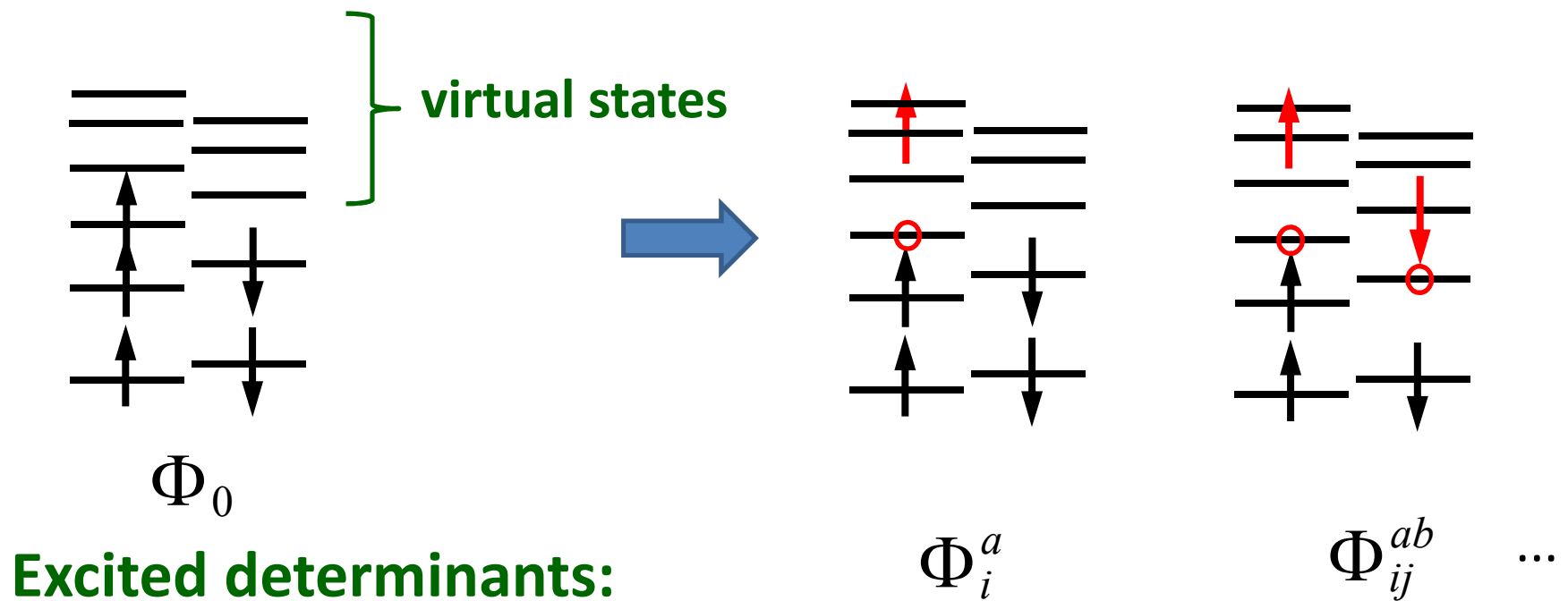
$$\longrightarrow E_0^{(0)} + E_0^{(1)} = \langle \Phi | \hat{H} | \Phi \rangle \text{ -- Hartree-Fock energy}$$

Higher orders: Need to know **excited** states of the unperturbed system!

Virtual (unoccupied) orbitals

$$\hat{f}\psi_i = \left(\hat{h} + \sum_j (\hat{U}_j - \hat{J}_j) \right) \psi_i = \varepsilon_i \psi_i$$


The Fock operator has *infinite* number of eigenstates



Finite-order perturbation theory

□ Møller-Plesset perturbation theory

$$\hat{H} = \hat{H}_0 + \hat{V} = \sum_i \hat{f}(\mathbf{r}_i) + (\hat{H} - \sum_i \hat{f}(\mathbf{r}_i))$$

$$(\sum_j \hat{f}(\mathbf{r}_j))\Phi_i^a = (\sum_{j \neq i} \varepsilon_j + \varepsilon_a)\Phi_i^a, \quad \langle \psi_i | \psi_j \rangle = \delta_{ij} \rightarrow \langle \Phi_p | \Phi_q \rangle = \delta_{pq}$$

$$E^{(2)} = \sum_{m \neq 0} \frac{|\langle \psi_0^{(0)} | \hat{V} | \psi_m^{(0)} \rangle|^2}{E_0^{(0)} - E_m^{(0)}}$$



$$E^{(2)} = \sum_{i,a} \frac{|\langle \Phi | \hat{V} | \Phi_i^a \rangle|^2}{\varepsilon_i - \varepsilon_a} + \frac{1}{4} \sum_{ij,ab} \frac{|\langle \Phi | \hat{V} | \Phi_{ij}^{ab} \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + \dots$$

Finite-order perturbation theory

□ Møller-Plesset perturbation theory

$$\hat{H} = \hat{H}_0 + \hat{V} = \sum_i \hat{f}(\mathbf{r}_i) + (\hat{H} - \sum_i \hat{f}(\mathbf{r}_i))$$

$$E^{(2)} = \sum_{i,a} \frac{|\langle \Phi | \hat{V} | \Phi_i^a \rangle|^2}{\varepsilon_i - \varepsilon_a} + \frac{1}{4} \sum_{ij,ab} \frac{|\langle \Phi | \hat{V} | \Phi_{ij}^{ab} \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + \dots$$

$$\langle \Phi | \hat{V} | \Phi_i^a \rangle = \langle \Phi | \hat{H} - \sum_i \hat{f}(\mathbf{r}_i) | \Phi_i^a \rangle = \langle \Phi | \hat{H} | \Phi_i^a \rangle = 0$$

Brillouin's theorem

Finite-order perturbation theory

□ Møller-Plesset perturbation theory

$$\hat{H} = \hat{H}_0 + \hat{V} = \sum_i \hat{f}(\mathbf{r}_i) + (\hat{H} - \sum_i \hat{f}(\mathbf{r}_i))$$

$$E^{(2)} = \sum_{i,a} \frac{|\langle \Phi | \hat{V} | \Phi_i^a \rangle|^2}{\varepsilon_i - \varepsilon_a} + \frac{1}{4} \sum_{ij,ab} \frac{|\langle \Phi | \hat{V} | \Phi_{ij}^{ab} \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + \dots$$

$$\langle \Phi | \hat{V} | \Phi_i^a \rangle = \langle \Phi | \hat{H} - \sum_i \hat{f}(\mathbf{r}_i) | \Phi_i^a \rangle = \langle \Phi | \hat{H} | \Phi_i^a \rangle = 0$$

Brillouin's theorem

$$\langle \Phi | \hat{V} | \Phi_{ijk}^{abc} \rangle = \langle \Phi | \hat{H} - \sum_i \hat{f}(\mathbf{r}_i) | \Phi_{ijk}^{abc} \rangle = \langle \Phi | \hat{H} | \Phi_{ijk}^{abc} \rangle = 0$$

Finite-order perturbation theory

□ Møller-Plesset perturbation theory

$$\hat{H} = \hat{H}_0 + \hat{V} = \sum_i \hat{f}(\mathbf{r}_i) + (\hat{H} - \sum_i \hat{f}(\mathbf{r}_i))$$

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$$\langle \Phi | \hat{V} | \Phi_i^a \rangle = \langle \Phi | \hat{H} - \sum_i \hat{f}(\mathbf{r}_i) | \Phi_i^a \rangle = \langle \Phi | \hat{H} | \Phi_i^a \rangle = 0$$

Brillouin's theorem

$$\langle \Phi | \hat{V} | \Phi_{ijk}^{abc} \rangle = \langle \Phi | \hat{H} - \sum_i \hat{f}(\mathbf{r}_i) | \Phi_{ijk}^{abc} \rangle = \langle \Phi | \hat{H} | \Phi_{ijk}^{abc} \rangle = 0$$



$$E^{(2)} = \frac{1}{4} \sum_{ij,ab} \frac{|\langle \Phi | \hat{H} | \Phi_{ij}^{ab} \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

MP2 energy correction

Finite-order perturbation theory

□ Møller-Plesset perturbation theory

$$\hat{H} = \hat{H}_0 + \hat{V} = \sum_i \hat{f}(\mathbf{r}_i) + (\hat{H} - \sum_i \hat{f}(\mathbf{r}_i))$$

Wavefunction first-order correction:

$$\Psi \approx \Phi + \frac{1}{4} \sum_{ijab} \frac{\langle \Phi_{ij}^{ab} | \hat{V} | \Phi \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \Phi_{ij}^{ab}$$

- 1) A linear combination of determinants
- 2) Single excitations do not contribute at first order (Brillouin's theorem), but they do contribute at higher orders
- 3) Higher excitations at higher orders

Finite-order perturbation theory

□ Møller-Plesset perturbation theory

$$\hat{H} = \hat{H}_0 + \hat{V} = \sum_i \hat{f}(\mathbf{r}_i) + (\hat{H} - \sum_i \hat{f}(\mathbf{r}_i))$$

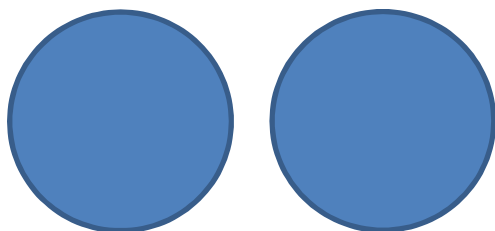
Wavefunction first-order correction:

$$\Psi \approx \Phi + \frac{1}{4} \sum_{ijab} \frac{\langle \Phi_{ij}^{ab} | \hat{V} | \Phi \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \Phi_{ij}^{ab}$$

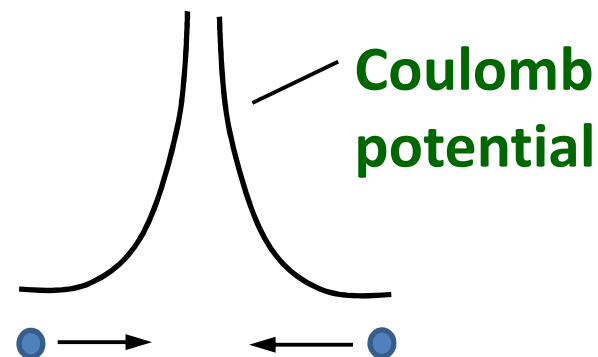
- 1) A linear combination of determinants
- 2) Single excitations do not contribute at first order (Brillouin's theorem), but they do contribute at higher orders
- 3) Higher excitations at higher orders
- 4) Fails when HOMO and LUMO are close -- higher-order terms are needed, wavefunction is not a single determinant

Two types of correlation

Dynamic correlation:

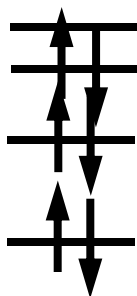


versus

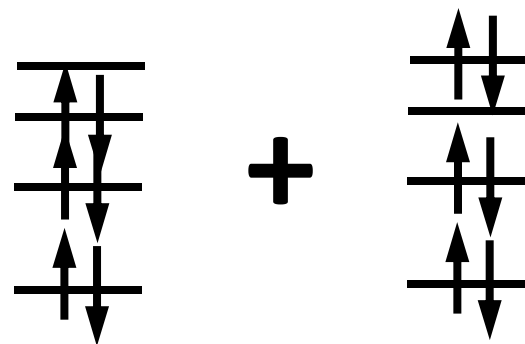


smaller e density, large $\partial\psi / \partial\mathbf{r}$

Non-dynamic (static) correlation:



versus



(quasi)degenerate HOMO-LUMO

Finite-order perturbation theory

□ RSPT for degenerate states

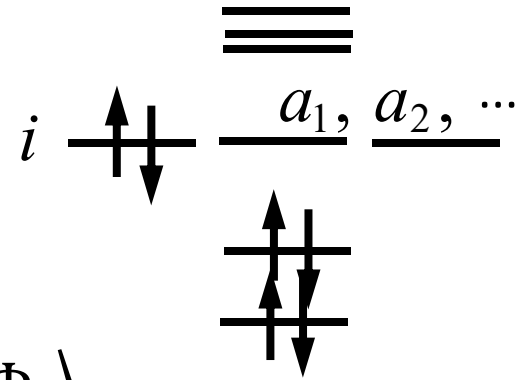
For degenerate states $\psi_1^{(0)}, \psi_2^{(0)}, \text{etc.}$:

$$\sum_{n'} \left(\langle \psi_n^{(0)} | \hat{V} | \psi_{n'}^{(0)} \rangle - \delta_{nn'} E^{(1)} \right) c_{n'}^{(0)} = 0$$

-- an eigenvalue problem

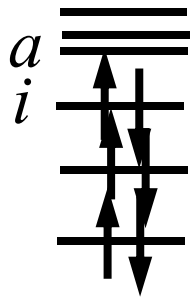


In our case: Diagonalize matrix $\langle \Phi_i | \hat{H} | \Phi_j \rangle$



$$\Psi = \sum_i C_i \Phi_i = \Phi + \sum_{ia} C_i^a \Phi_i^a + \sum_{ijab} C_{ij}^{ab} \Phi_{ij}^{ab} + \dots$$

Configuration interaction



$$\sum_{n'} \left(\langle \Phi_n | \hat{H} - \sum_i \hat{f}_i | \Phi_{n'} \rangle - \delta_{nn'} E^{(1)} \right) C_{n'} = 0$$

$$|\Psi_0\rangle \approx |\Phi_0\rangle + \frac{1}{4} \sum_{ij,ab} \frac{\langle ab || ij \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} |\Phi_{ij}^{ab}\rangle$$

Both dynamic and static correlation can be accounted for by mixing excitations → configuration interaction method:

$$|\Psi\rangle = C_0 |\Phi_0\rangle + \sum_{i,a} C_i^a |\Phi_i^a\rangle + \sum_{ij,ab} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots$$

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \rightarrow \min \Rightarrow \frac{\partial E}{\partial \{C\}} = 0$$



$$\mathbf{HC} = EC$$

The concept of mixing excitations

$$\hat{H}_0 \Phi_i = E_i^0 \Phi_i - \text{non-interacting effective particles (HF, DFT, etc.)}$$

$$|\Phi_0\rangle = \text{diagram}, |\Phi_1\rangle = \text{diagram} + \text{diagram}, |\Phi_2\rangle = \text{diagram} + \text{diagram}, \dots$$

The diagrams represent orbital occupation for N-electron wavefunctions. For example, $|\Phi_0\rangle$ shows four orbitals with two electrons each (up and down arrows). $|\Phi_1\rangle$ is a sum of two configurations where one electron has been promoted to a higher orbital. $|\Phi_2\rangle$ is a sum of two configurations where two electrons have been promoted.

$\{\Phi_i\}$ – a basis set for N -electron wavefunctions



$$\Psi_i = \sum_j c_{ij} \Phi_j, [\hat{H}_0 + (\hat{H} - \hat{H}_0)] \sum_j c_{ij} \Phi_j = E_i \sum_j c_{ij} \Phi_j$$

Project onto $\langle \Phi_k | \rightarrow$ equations for c_{ij} :

$$\sum_j c_{ij} \langle \Phi_k | \Delta \hat{H} | \Phi_j \rangle = (E_i - E_k^0) c_{ik}$$

configuration interaction

Configuration interaction – matrix diagonalization

$$|\Phi_0\rangle, |S\rangle \equiv \{|\Phi_i^a\rangle\}, |D\rangle \equiv \{|\Phi_{ij}^{ab}\rangle\}, \dots \quad \frac{M!}{(M-n)!n!} \quad \begin{array}{l} M \text{ orbitals} \\ n\text{-tuple} \\ \text{excitations} \end{array}$$

Configuration interaction – matrix diagonalization

$$|\Phi_0\rangle, |S\rangle \equiv \{|\Phi_i^a\rangle\}, |D\rangle \equiv \{|\Phi_{ij}^{ab}\rangle\}, \dots \quad \frac{M!}{(M-n)!n!} \quad \begin{array}{l} M \text{ orbitals} \\ n\text{-tuple} \\ \text{excitations} \end{array}$$

$$\begin{array}{c} |\Phi_0\rangle \quad |S\rangle \quad |D\rangle \quad |T\rangle \quad |Q\rangle \quad \dots \\ \langle \Phi_0| \left(\begin{array}{cccccc} \langle \Phi_0|\hat{H}|\Phi_0\rangle & \langle \Phi_0|\hat{H}|S\rangle & \langle \Phi_0|\hat{H}|D\rangle & 0 & 0 & \dots \\ \langle S|\hat{H}|\Phi_0\rangle & \langle S|\hat{H}|S\rangle & \langle S|\hat{H}|D\rangle & \langle S|\hat{H}|T\rangle & 0 & \dots \\ \langle D|\hat{H}|\Phi_0\rangle & \langle D|\hat{H}|S\rangle & \langle D|\hat{H}|D\rangle & \langle D|\hat{H}|T\rangle & \langle D|\hat{H}|Q\rangle & \dots \\ \langle T|\hat{H}|\Phi_0\rangle & \langle T|\hat{H}|S\rangle & \langle T|\hat{H}|D\rangle & \langle T|\hat{H}|T\rangle & \langle T|\hat{H}|Q\rangle & \dots \\ \langle Q|\hat{H}|\Phi_0\rangle & \langle Q|\hat{H}|S\rangle & \langle Q|\hat{H}|D\rangle & \langle Q|\hat{H}|T\rangle & \langle Q|\hat{H}|Q\rangle & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{array} \right) \end{array}$$

E.g., $\langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{klmn}^{cdef} \rangle \neq 0$ **only when** $i, j \in \{klmn\}$ **and** $a, b \in \{cdef\}$

Configuration interaction in periodic systems

n – band index,
 \mathbf{k} – k-point

$$\Phi_0 = \begin{array}{c} \begin{array}{|c|} \hline \uparrow \\ \hline \uparrow \\ \hline \uparrow \\ \hline \end{array} \\ \begin{array}{|c|} \hline \uparrow \\ \hline \uparrow \\ \hline \downarrow \\ \hline \end{array} \\ \begin{array}{|c|} \hline \uparrow \\ \hline \downarrow \\ \hline \downarrow \\ \hline \end{array} \end{array} \quad \begin{array}{l} n = 3, \mathbf{k} = \mathbf{k}_1, \dots, \mathbf{k}_4 \\ n = 2, \mathbf{k} = \mathbf{k}_1, \dots, \mathbf{k}_4 \\ n = 1, \mathbf{k} = \mathbf{k}_1, \dots, \mathbf{k}_4 \end{array}$$

excitations can change not only n but also k -point

$$\Psi = \Phi_0 + \sum_{\substack{ik, aq \\ \mathbf{k}=\mathbf{q}}} c_{ik}^{aq} \Phi_{ik}^{aq} + \sum_{\substack{ik, aq \\ jp, br \\ \mathbf{k}+\mathbf{p}=\mathbf{q}+\mathbf{r}}} c_{ik, jp}^{aq, br} \Phi_{ik, jp}^{aq, br} + \dots$$

$$\langle \Phi_{ik}^{aq} | \hat{H} | \Phi_{ik, jp}^{aq, br} \rangle$$

momentum conservation

Full configuration interaction (FCI)

$$\Psi_i = \sum_j c_{ij} \Phi_j \quad \text{– include ALL excitations of } N \text{ electrons on } M \text{ orbitals (} M \text{ is determined by the basis set size)}$$

+ FCI is exact within given basis set

+ The result does not depend on the choice of orbitals in Φ_0

+ Gives ground and excited states

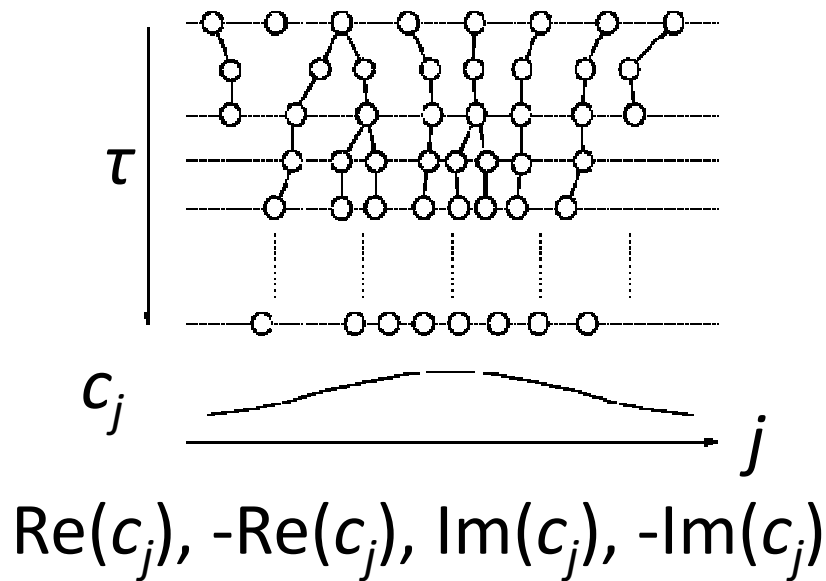
- The scaling with system size is combinatorial: $\frac{M!}{(M-N)!N!}$

50 electrons on 100 orbitals $\rightarrow 10^{29} \times 10^{29}$ matrix diagonalization

Sparsity: $\langle \Phi^{(n)} | \hat{H} | \Phi^{(n \pm 2)} \rangle \neq 0$

FCI quantum Monte Carlo (FCIQMC) method

Walkers – determinants



**converges to ground-state
eigenvector (similar to DMC)**

$$\Psi_0 = \sum_j c_j \Phi_j$$

From Schrödinger equation:

$$-\frac{dN_i}{d\tau} = (\langle \Phi_i | \hat{H} | \Phi_i \rangle - E_T) N_i + \sum_{j \neq i} \langle \Phi_i | \hat{H} | \Phi_j \rangle N_j$$

↓

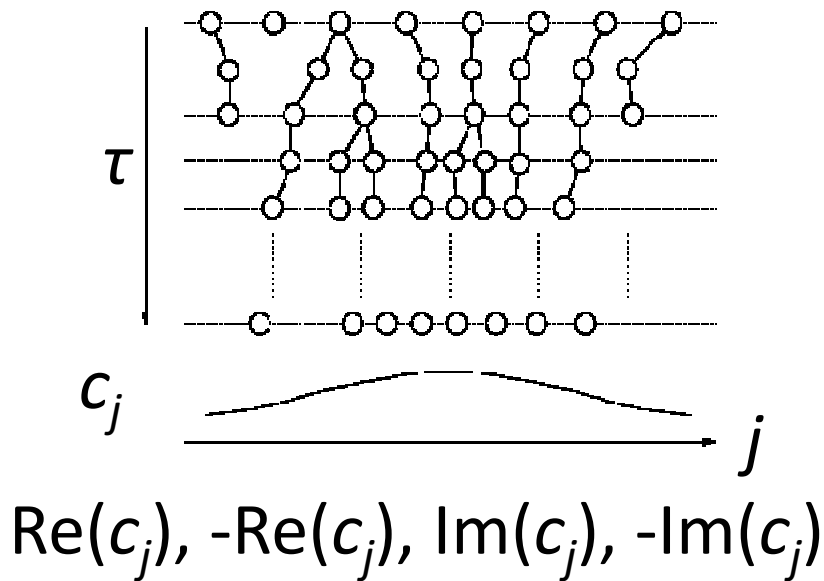
$$E, \quad c_i = (-1)^{x_i} \sqrt{\frac{\langle N_i \rangle}{\langle N \rangle}}$$

Each determinant is represented by a number of instances (walkers) that can multiply, die, or spawn another determinant stochastically with probability $\sim H_{ij}$

Booth, Grüneis, Kresse, and Alavi, Nature **493**, 365 (2013)

FCI quantum Monte Carlo (FCIQMC) method

Walkers – determinants



No sign problem (positive and negative coefficients can be evolved independently)

$$\Psi_0 = \sum_j c_j \Phi_j$$

From Schrödinger equation:

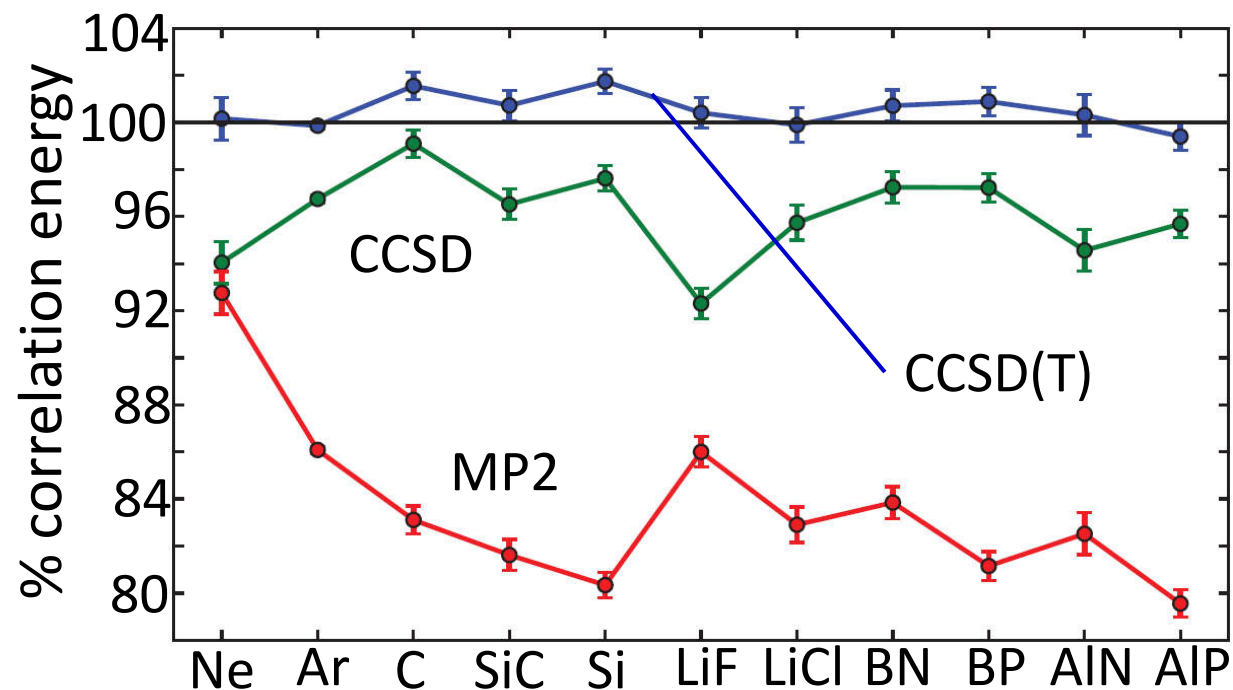
$$-\frac{dN_i}{d\tau} = (\langle \Phi_i | \hat{H} | \Phi_i \rangle - E_T) N_i + \sum_{j \neq i} \langle \Phi_i | \hat{H} | \Phi_j \rangle N_j$$

$$E, \quad c_i = (-1)^{x_i} \sqrt{\frac{\langle N_i \rangle}{\langle N \rangle}}$$

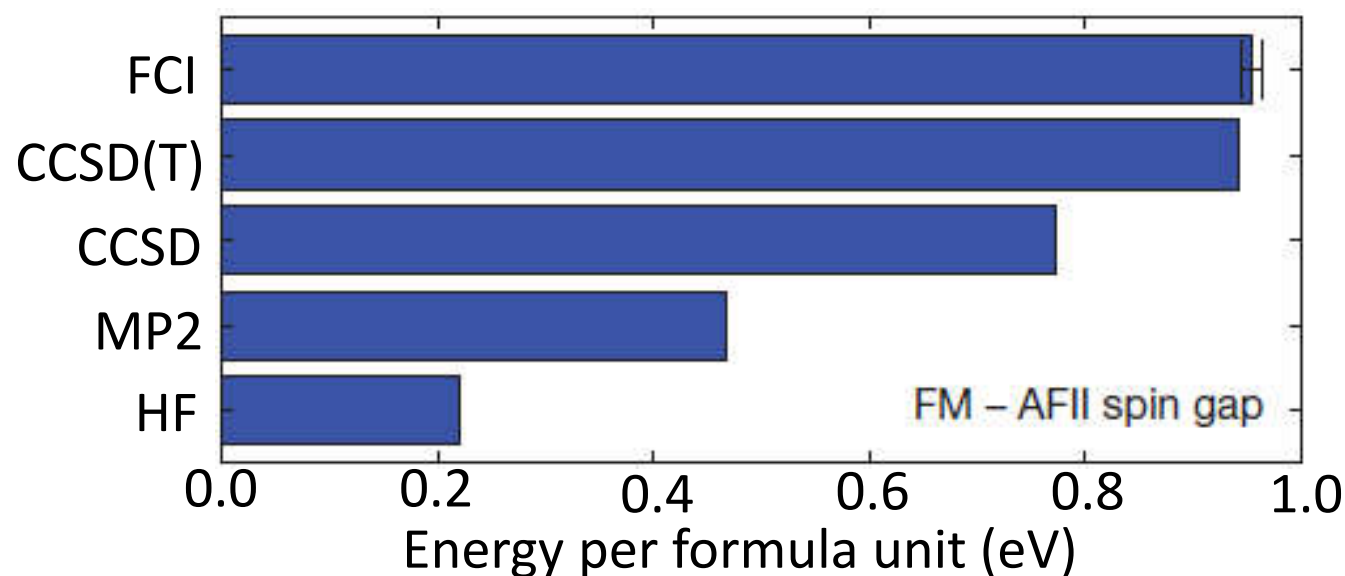
Timing example: diamond, 4x4x4 k-points – 25,000 CPU hours, ± 20 meV per atom remaining error in correlation energy

Booth, Grüneis, Kresse, and Alavi, Nature **493**, 365 (2013)

FCI quantum Monte Carlo (FCIQMC) method



Percent of correlation energy captured by different methods relative to FCI (VASP, PAW)



Ferromagnetic-antiferromagnetic spin gap in NiO (VASP, PAW)

Booth, Grüneis, Kresse, and Alavi, Nature **493**, 365 (2013)

Truncated CI

$$|\Psi_0\rangle = C_0|\Phi_0\rangle + \sum_{i,a} C_i^a |\Phi_i^a\rangle + \sum_{ij,ab} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots$$

$$|\Psi_0\rangle \approx |\Phi_0\rangle + \frac{1}{4} \sum_{ij,ab} \frac{\langle ab || ij \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} |\Phi_{ij}^{ab}\rangle$$



For the first-order correction, can truncate CI expansion at double excitations (in case they are enough to account for the static correlation), 2nd-order – at quadruple excitations

Truncated CI

$$|\Psi_0\rangle = C_0|\Phi_0\rangle + \sum_{i,a} C_i^a |\Phi_i^a\rangle + \sum_{ij,ab} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots$$

$$|\Psi_0\rangle \approx |\Phi_0\rangle + \frac{1}{4} \sum_{ij,ab} \frac{\langle ab || ij \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} |\Phi_{ij}^{ab}\rangle$$



For the first-order correction, can truncate CI expansion at double excitations (in case they are enough to account for the static correlation), 2nd-order – at quadruple excitations

$$|\Psi_0\rangle \approx C_0|\Phi_0\rangle + \sum_{i,a} C_i^a |\Phi_i^a\rangle + \sum_{ij,ab} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle$$

(CISD method)

Truncated CI: Properties

$$|\Psi\rangle = C_0|\Phi_0\rangle + \sum_{i,a} C_i^a |\Phi_i^a\rangle + \sum_{ij,ab} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots$$

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \rightarrow \min \Rightarrow \frac{\partial E}{\partial\{C\}} = 0$$

Truncated CI is *variational* $\rightarrow E \geq E_{\text{exact}}$

MPn is not variational

Size-extensivity

An electronic-structure method is *size-extensive* if

for N equivalent parts (e. g., He atoms at large distance):

$$E_{NA} = NE_A$$

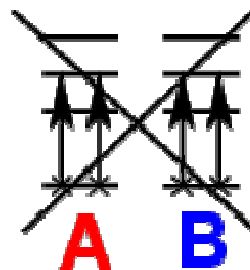
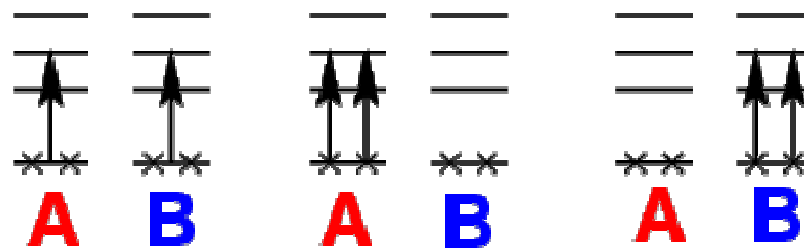
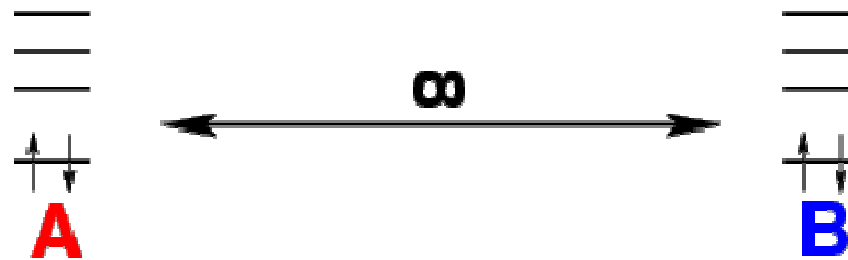
This insures that the error per unit does not increase with system size

Hartree-Fock is size extensive

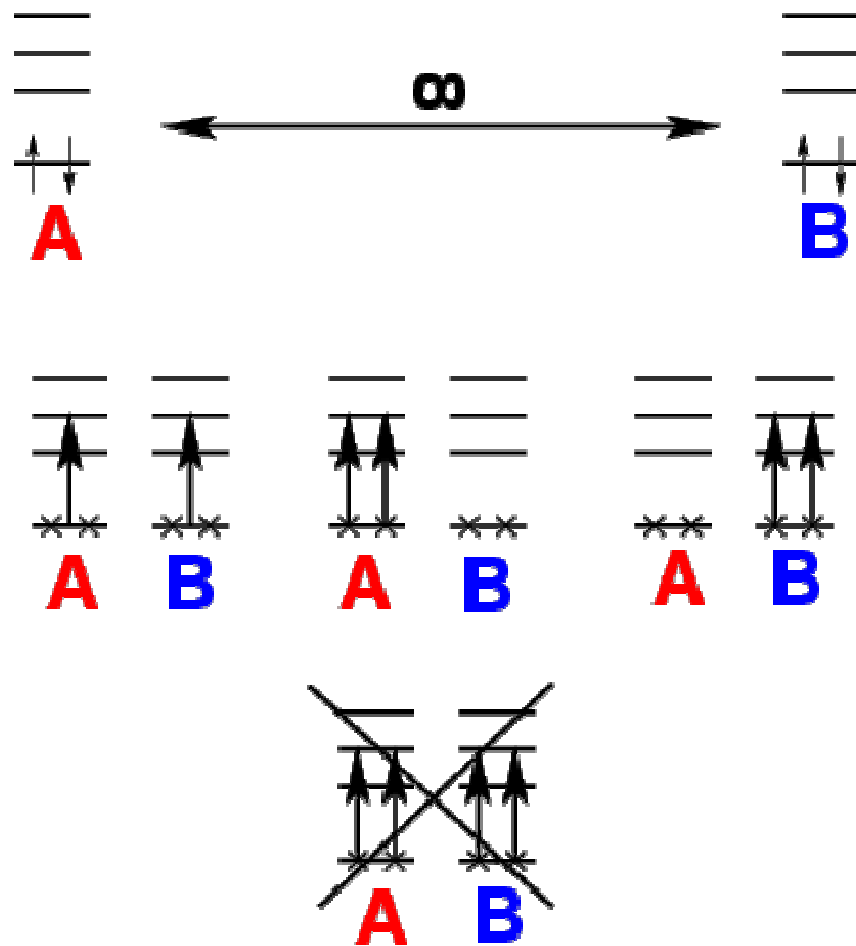
Approximate DFT is size extensive

MP n is size-extensive for any n (Goldstone's linked-diagram theorem)

Truncated CI is not size-extensive



Truncated CI is not size-extensive

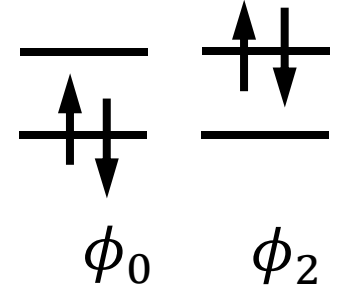


But full CI is size-extensive

FCI: The role of higher excitations

The FCI wave function for N isolated He atoms (single excitations can be eliminated – Brueckner orbitals):

$$\psi^A = \phi_0^A + c \phi_2^A$$



$$\Psi = A[(\phi_0^1 + c \phi_2^1)(\phi_0^2 + c \phi_2^2) \dots (\phi_0^N + c \phi_2^N)]$$

$$\Phi_i = A[\phi_0^1 \dots \phi_0^{i-1} \phi_2^i \phi_0^{i+1} \dots \phi_0^N]$$

$$\Psi = \Phi_0 + c \sum_i \Phi_i + \frac{1}{2!} c^2 \sum_{i,j} \Phi_{ij} + \frac{1}{3!} c^3 \sum_{i,j,k} \Phi_{ijk} + \dots$$

doubles: $\sim N c^2$, **quadruples:** $\sim \frac{N^2 c^4}{2!}$, **sextuples:** $\sim \frac{N^3 c^6}{3!}$, ...

No matter how small c is, there is N that makes higher excitations important

FCI: The role of higher excitations

$$\Psi = \Phi_0 + c \sum_i \Phi_i + \frac{1}{2!} c^2 \sum_{i,j} \Phi_{ij} + \frac{1}{3!} c^3 \sum_{i,j,k} \Phi_{ijk} + \dots$$

No matter how small c is, there is N that makes higher excitations important

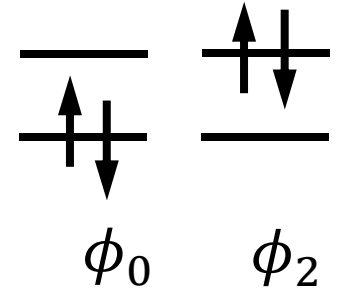
Contributions of higher excitations are expressed as products of the contributions of doubles

Coupled cluster theory

The FCI wave function for N isolated He atoms (single excitations can be eliminated – Brueckner orbitals):

$$\psi^A = \phi_0^A + c \phi_2^A$$

$$\Psi = A[(\phi_0^1 + c \phi_2^1)(\phi_0^2 + c \phi_2^2) \dots (\phi_0^N + c \phi_2^N)]$$



$$\Phi_i = A[\phi_0^1 K \phi_0^{i-1} \phi_2^i \phi_0^{i+1} \dots \phi_0^N]$$

$$\Psi = \Phi_0 + c \sum_i \Phi_i + \frac{1}{2!} c^2 \sum_{i,j} \Phi_{ij} + \frac{1}{3!} c^3 \sum_{i,j,k} \Phi_{ijk} + \dots$$



$$|\Psi\rangle = (\hat{1} + \hat{T}_2 + \frac{\hat{T}_2^2}{2!} + \dots) |\Phi_0\rangle = e^{\hat{T}_2} |\Phi_0\rangle, \quad \hat{T}_2 = c \sum_{\text{atoms}} \hat{a}^+ \hat{b}^+ \hat{j} \hat{i}$$

Coupled cluster theory

$$|\Psi\rangle = e^{\hat{T}}|\Phi_0\rangle \quad \hat{T} = 1 + \sum_{ia} t_i^a a^+ i + \frac{1}{4} \sum_{ijab} t_{ij}^{ab} b^+ a^+ ij + \dots$$

For two non-interacting subsystems:

$$|\Phi_0(A \dots B)\rangle = |\Phi_0(A)\Phi_0(B)\rangle, \quad \hat{T}(A \dots B) = \hat{T}(A) + \hat{T}(B)$$

$$|\Psi\rangle = e^{\hat{T}(A) + \hat{T}(B)} |\Phi_0(A)\Phi_0(B)\rangle = |\Psi(A)\Psi(B)\rangle$$

$$\hat{H}|\Psi\rangle = (\hat{H}_A + \hat{H}_B)|\Psi(A)\Psi(B)\rangle = [E(A) + E(B)]|\Psi\rangle$$

The coupled-cluster ansatz is size-extensive even for truncated \hat{T}

For RSPT, $|\Psi\rangle \neq |\Psi(A)\Psi(B)\rangle$, but the energy is size-extensive

Coupled cluster theory

$$|\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle$$

$$\hat{T} = 1 + \sum_{ia} t_i^a a^+ i + \frac{1}{4} \sum_{ijab} t_{ij}^{ab} b^+ a^+ ij + \dots$$

\uparrow \hat{T}_1 \nwarrow \hat{T}_2

$$\Psi = (1 + \hat{T}_1 + \hat{T}_2 + \text{connected terms} + \frac{1}{2} \hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 + \text{disconnected terms} + \frac{1}{6} \hat{T}_1^3 + \frac{1}{2} \hat{T}_1^2 \hat{T}_2 + \frac{1}{2} \hat{T}_1 \hat{T}_2^2 + \frac{1}{6} \hat{T}_2^3 + \dots) \Phi_0$$

(note: intermediate normalization above - $\langle \Phi_0 | \Psi \rangle = 1$)

Formally, all excitations from Φ_0 are present

$t_{ij\dots}^{ab\dots}$ are called *amplitudes*

Coupled-cluster equations

$$\hat{H} e^{\hat{T}} |\Phi_0\rangle = E e^{\hat{T}} |\Phi_0\rangle$$

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Phi_0\rangle = \bar{H} |\Phi_0\rangle = E |\Phi_0\rangle$$

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}} \quad \text{-- similarity-transformed hamiltonian}$$

$$E = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle$$

Amplitude equations:

$$\langle \Phi_i^a | \bar{H} | \Phi_0 \rangle = 0, \quad \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle = 0, \dots$$

-- as many equations as unknown amplitudes

\bar{H} is non-Hermitian, energy is non-variational (variational CC is intractable)

Coupled-cluster equations

$$\hat{H} e^{\hat{T}} |\Phi_0\rangle = E e^{\hat{T}} |\Phi_0\rangle$$

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Phi_0\rangle = \bar{H} |\Phi_0\rangle = E |\Phi_0\rangle$$

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}} \quad \text{-- similarity-transformed hamiltonian}$$

$$E = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle$$

$$E = E_0 + \sum_{ia} f_i^a t_i^a + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab} + \frac{1}{2} \sum_{ijab} \langle ij || ab \rangle t_i^a t_j^b$$

Popular flavors: CCD, CCSD, CCSD(T) (perturbative triple excitations)

T. Daniel Crawford and Henry F. Schaefer III, Reviews in Computational Chemistry, Volume 14
Wiley-VCH, New York 2000

Hierarchies of GS wavefunction methods

Truncated CI
(CISD, CISDT,...)

$$|\Psi_0^{\{m\}}\rangle = \sum_{i \leq m} \hat{T}_i |\Phi_0\rangle$$

CI{m}: $\sim n^m N^{m+2}$

Møller-Plesset
perturbation theory
(MP2, MP3, MP4,...)

$$E_0^{(2)} = \sum_{i \neq 0} \frac{|\langle \Phi_0 | \hat{H}' | \Phi_i \rangle|^2}{E_0^{(0)} - E_i^{(0)}}$$

MPm: $\sim n N^{m+2}$

Coupled-cluster
(CCD, CCSD, CCSDT,...)

$$|\Psi_0^{\{m\}}\rangle = e^{\sum_{i \leq m} \hat{T}_i} |\Phi_0\rangle$$

CC{m}: $\sim n^m N^{m+2}$

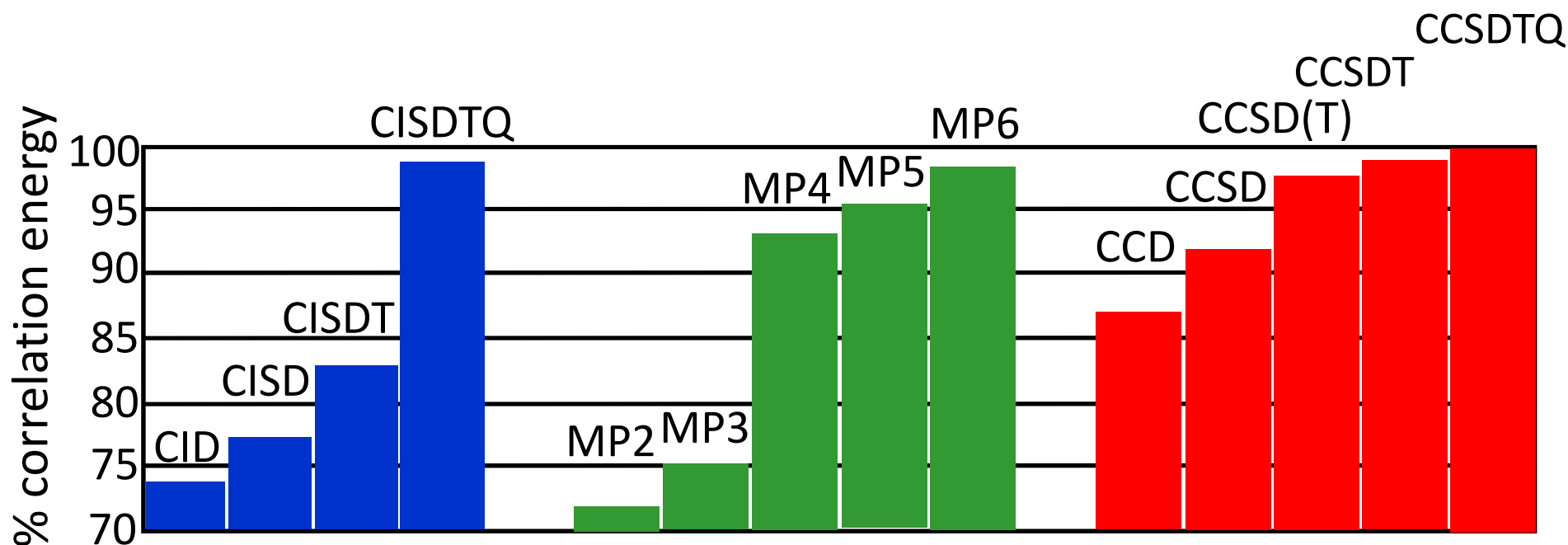
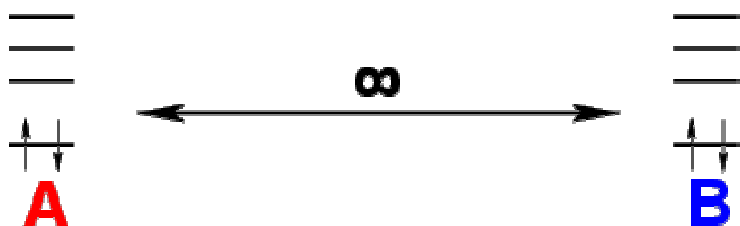


figure courtesy of R.J. Bartlett

Excited states

$$\sum_j C_{ij} \langle \Phi_k | \hat{H} | \Phi_j \rangle = E_i C_{ik}$$

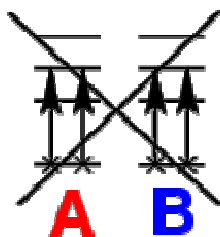
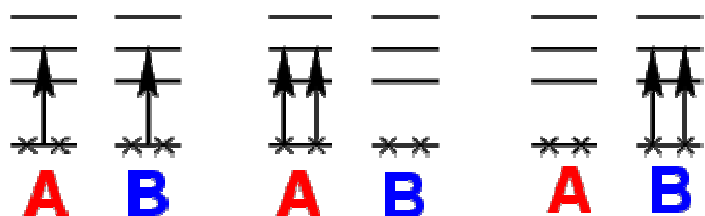
CI gives both ground AND excited states



Ground state is not size-extensive



Accuracy of CI excitation energies on **fragment A**, **fragment B** or both degrade with number of fragments - not size-extensive



Equation-of-motion CC methods

$$|\Psi\rangle \approx (\hat{R}_0 + \hat{R}_1 + \hat{R}_2 + \dots) \exp(\hat{T}_1 + \hat{T}_2 + \dots) |\Phi_0\rangle$$

\hat{R} , \hat{T} -- **excitation operators** (e. g. $\hat{R}_2 = \sum_{ijab} r_{ij}^{ab} a^+ b^+ ji$, $\hat{T}_2 = \sum_{ijab} t_{ij}^{ab} a^+ b^+ ji$)

(\hat{T} is determined from CC equations)

$$\hat{H} \hat{R} \exp(\hat{T}) |\Phi_0\rangle = E \hat{R} \exp(\hat{T}) |\Phi_0\rangle$$



$$[\hat{T}, \hat{R}] = 0$$



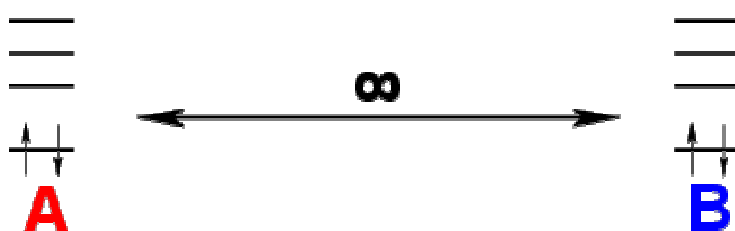
$$\underbrace{\exp(-\hat{T}) \hat{H} \exp(\hat{T})}_{\bar{H}} \hat{R} |\Phi_0\rangle = E \hat{R} |\Phi_0\rangle$$

\bar{H}

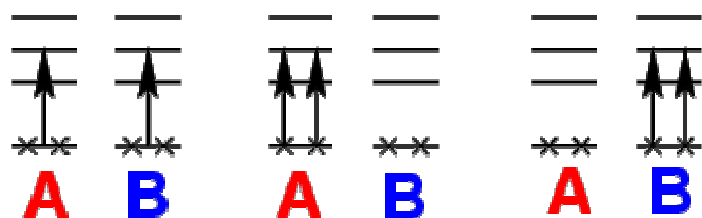
\bar{H} has the same eigenvalues as H for any \hat{T} !

Equation-of-motion CC methods

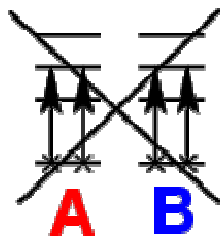
$$\sum_j C_{ij} \langle \Phi_k | \bar{H} | \Phi_j \rangle = E_i C_{ik}$$



Ground-state energy (CC) is size-extensive

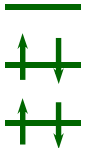
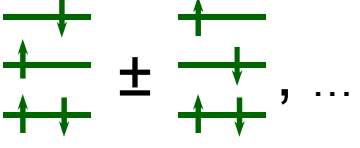
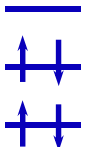
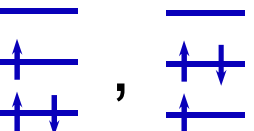


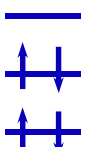
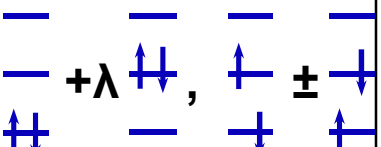

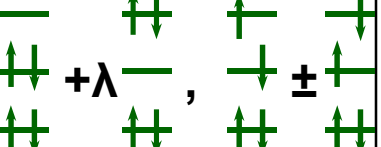

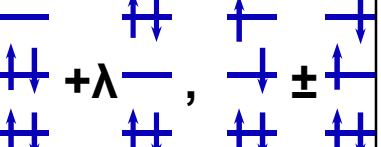


EOM-CC excitation energies on **fragment A** or on **fragment B** are THE SAME as for single fragments -- size-extensive!



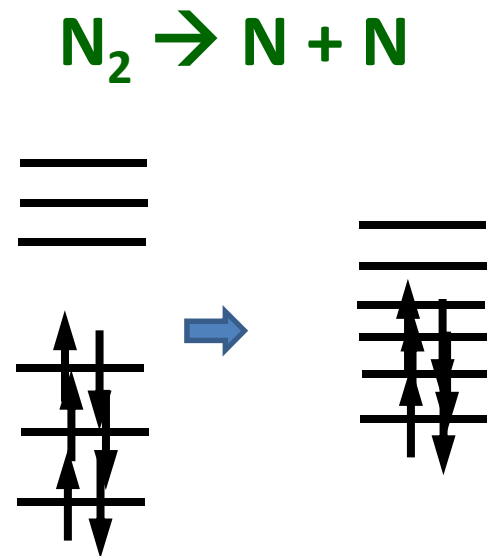
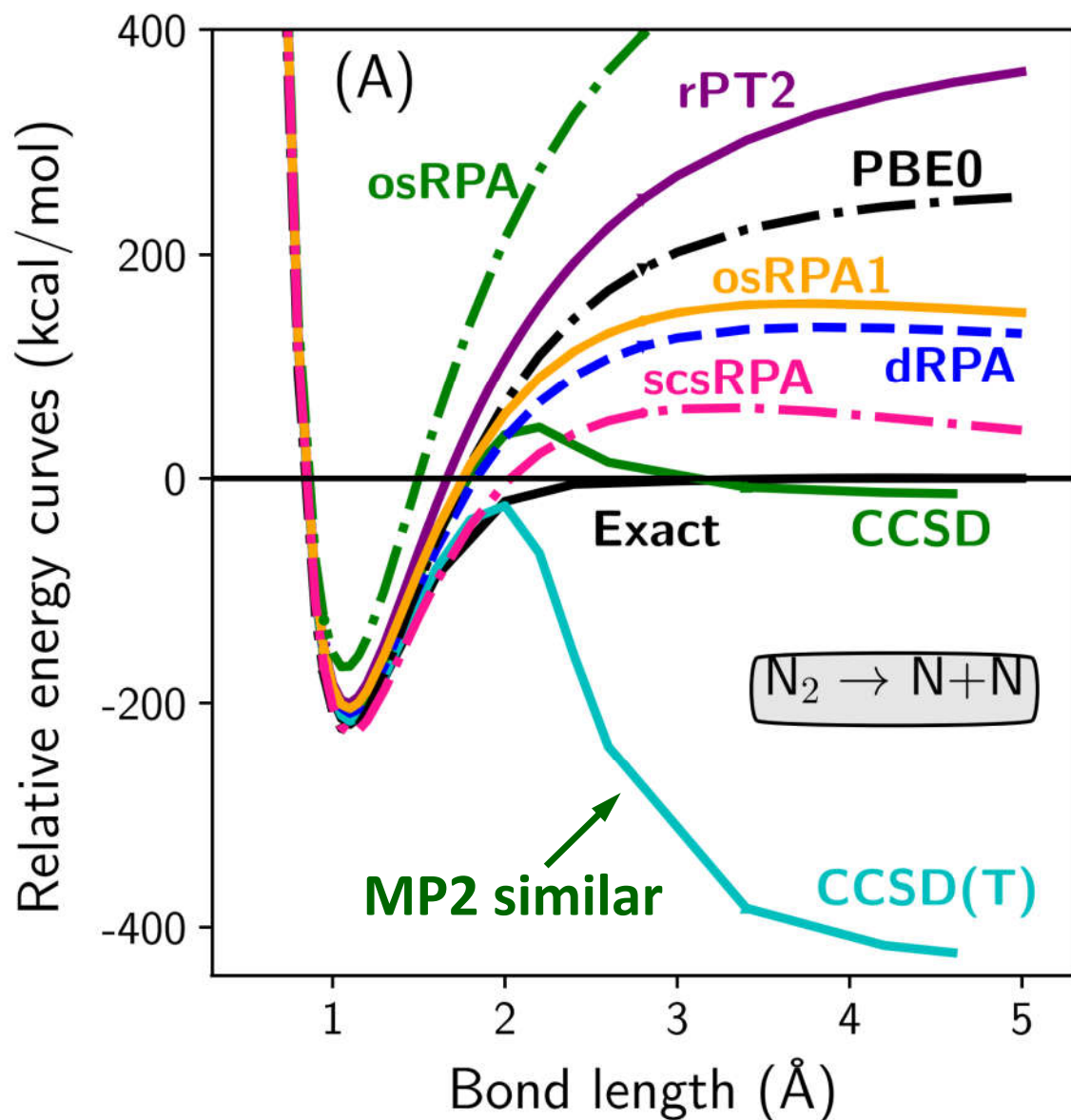
EOM-CC excitation energies on both A and B simultaneously are not size-extensive

Demonstrative summary of EOM-CCSD models.

Model	Reference	Target	ΔM_S	ΔN_{el}
EOM-EE ^(a)		 , ...	0	0
EOM-IP ^(b)			1/2	-1
EOM-EA ^(b)			1/2	+1
EOM-DIP ^(c)			0	-2
EOM-DEA ^(c)			0	+2
EOM-SF <small>SVL&AIK, JCP 120, 175 (2004)</small>			-1	0

^(a)D.Sinha,et al. CPL **129**, 369 (1986), ^(b)J. Stanton,et al. JCP **98**, 7029 (1993), ^(c) M.Wladyslawski,et al. ACSSS **828**, 65 (2002)

The curse of non-dynamic correlation



Non-dynamic correlation: reference determinant Φ is not a good starting point!

Multireference methods

Idea: include all degenerate determinants as a reference

$$\Psi^{(0)} = c_1 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow \downarrow \\ \vdots \\ \uparrow \downarrow \\ \uparrow \downarrow \\ \psi_2 \\ \psi_1 \end{array} + c_2 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow \downarrow \\ \vdots \\ \uparrow \downarrow \\ \uparrow \downarrow \end{array} + c_3 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow \downarrow \\ \vdots \\ \uparrow \downarrow \\ \uparrow \downarrow \end{array} + c_4 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow \downarrow \\ \vdots \\ \uparrow \downarrow \\ \uparrow \downarrow \end{array}$$

$$\min_{\psi_i, c_I} \frac{\langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \rightarrow \psi_i, c_I$$

-- multireference self-consistent field (MR-SCF)

Multireference methods

Idea: include all degenerate determinants as a reference

$$\Psi^{(0)} = c_1 \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \uparrow \downarrow \\ \uparrow \downarrow \\ \vdots \\ \uparrow \downarrow \\ \uparrow \downarrow \end{array} + c_2 \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \uparrow \downarrow \\ \uparrow \downarrow \\ \vdots \\ \uparrow \downarrow \\ \uparrow \downarrow \end{array} + c_3 \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \uparrow \downarrow \\ \uparrow \downarrow \\ \vdots \\ \uparrow \downarrow \\ \uparrow \downarrow \end{array} + c_4 \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \uparrow \downarrow \\ \uparrow \downarrow \\ \vdots \\ \uparrow \downarrow \\ \uparrow \downarrow \end{array}$$

ψ_2
 ψ_1

$$\min_{\psi_i, C_I} \frac{\langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \rightarrow \psi_i, C_I$$

-- multireference self-consistent field (MR-SCF)

Complete **active space** SCF (CASSCF) -- all excitations within "active space"

Multireference methods

Idea: include all degenerate determinants as a reference

$$\Psi^{(0)} = c_1 \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} + c_2 \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} + c_3 \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} + c_4 \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array}$$

The diagram illustrates the wavefunction $\Psi^{(0)}$ as a linear combination of four determinants. Each determinant is represented by a horizontal line with two vertical lines below it, forming a box. The first determinant has two red arrows (one up, one down) on the top line, and two black arrows (one up, one down) on the bottom line. The second determinant has two black arrows on the top line and two red arrows on the bottom line. The third determinant has one red arrow on the top line and one black arrow on the bottom line. The fourth determinant has one black arrow on the top line and one red arrow on the bottom line. The coefficients c_1, c_2, c_3, c_4 are placed to the left of each determinant. Above each determinant is a double horizontal line. To the right of the first determinant, there are two vertical lines labeled ψ_2 and ψ_1 .

Complete **active space** SCF (CASSCF): All excitations within “active space”

Multireference CI (MRCI): CI with single, double, etc., excitations on every determinant in CASSCF

CASPT n : RSPT up to n -th order for CASSCF wavefunction

MR-CC and MR-EOM-CC: under development, complex formalism, not a trivial extension of single-reference CC

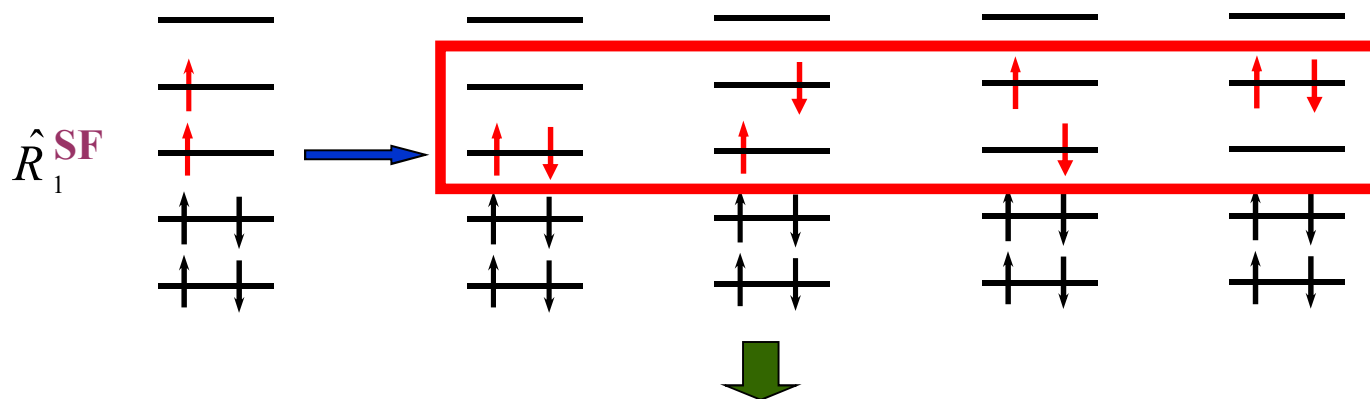
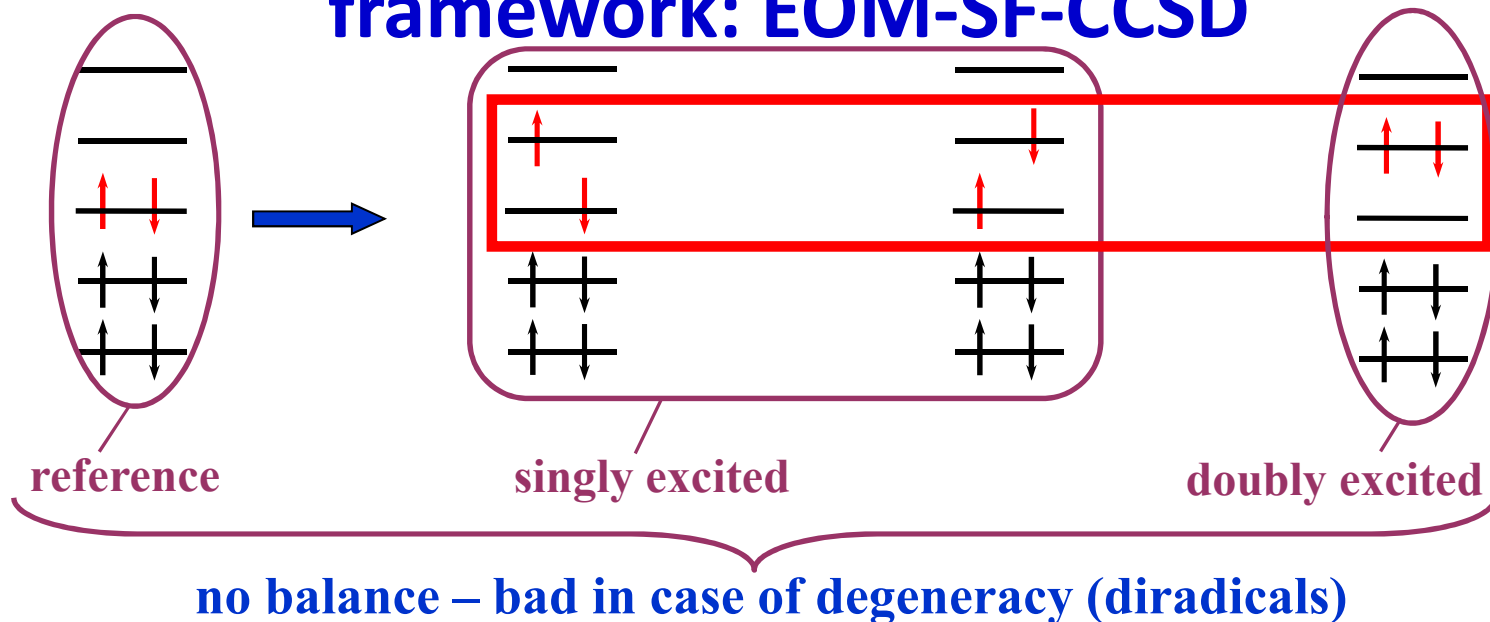
Multireference methods: Problems

Choice of active space is not trivial (state-specific, Rydberg versus valence states)

Choice of active space can have a strong effect on the results

Truncated MRCI is not size-extensive

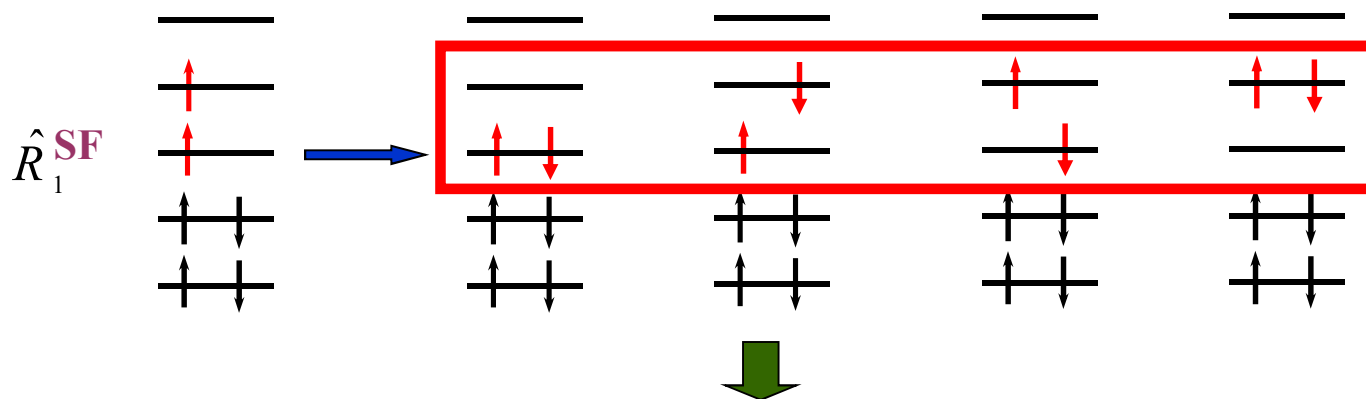
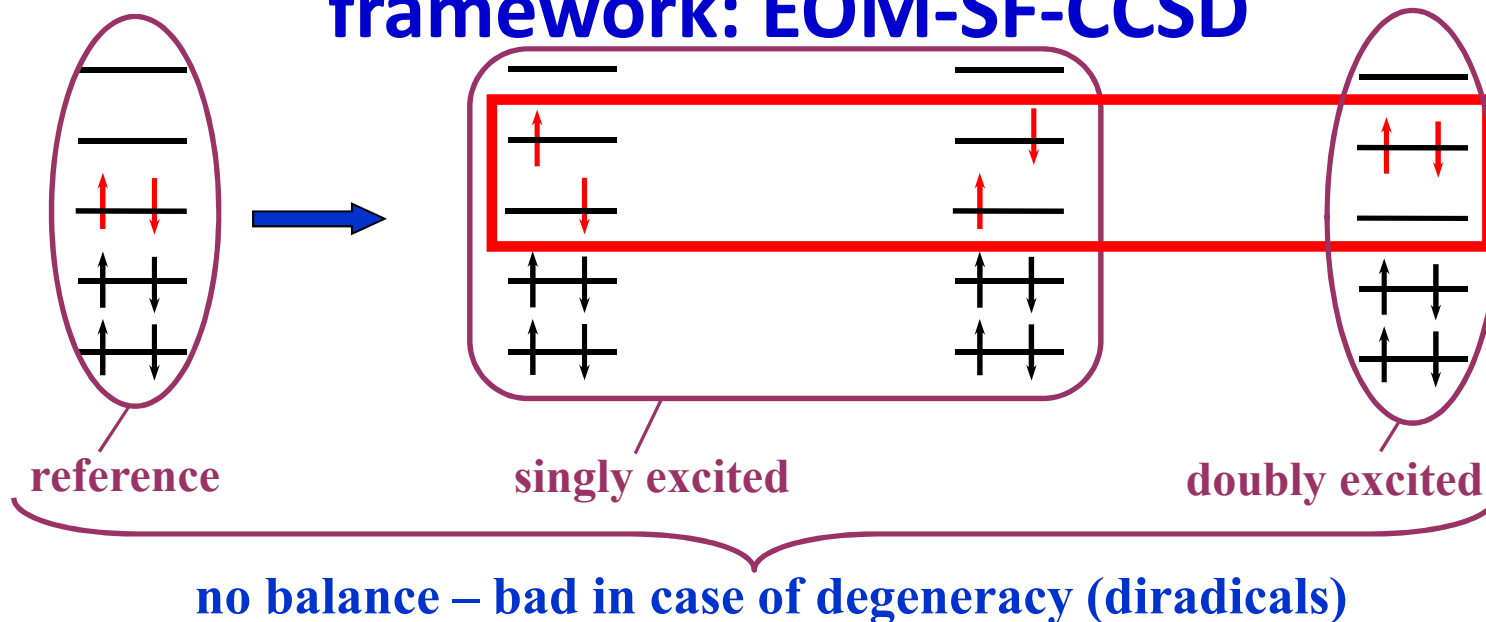
Non-dynamic correlation in single-reference framework: EOM-SF-CCSD



Balanced description -- all quasidegenerate $M_S=0$ determinants are treated on equal footing

Levchenko and Krylov, J. Chem. Phys. **120**, 175 (2004)

Non-dynamic correlation in single-reference framework: EOM-SF-CCSD



Dynamic correlation in high-spin reference is smaller (Pauli repulsion)

Levchenko and Krylov, J. Chem. Phys. **120**, 175 (2004)

Implementations

Many implementations for molecules, e.g.:

Commercial: Gaussian, Q-Chem, TURBOMOLE, Molpro (includes FCIQMC)

Free: GAMESS, NWChem (parallel), ORCA, ACES III (parallel)

Handful of implementations for solids:

Commercial:

VASP (MP2; CCSD, CCSD(T), and FCIQMC via external interface)

FHI-aims (MP2, CCSD)

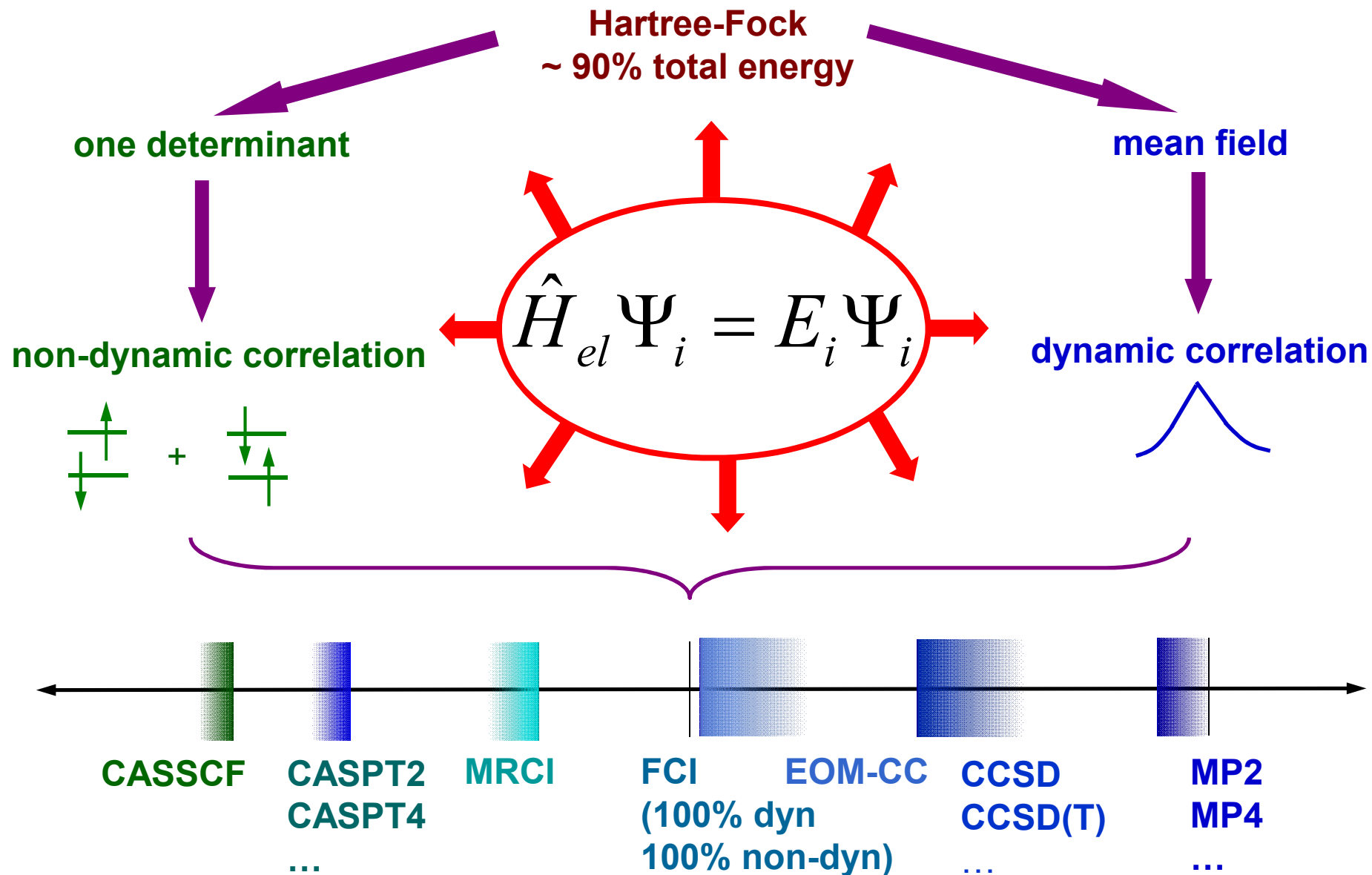
Free:

CP2K (MP2)

EOM-CC methods for solids are also in active development:

<https://doi.org/10.1021/acs.jctc.0c00101>

Wavefunction methods: Summary



Systematically improvable benchmark methods for solids

A potential breakthrough: Wavefunction and other methods on quantum computers

S. McArdle, S. Endo, A. Aspuru-Guzik, S. C. Benjamin, and X. Yuan

“Quantum computational chemistry”

(<https://doi.org/10.1103/RevModPhys.92.015003>)

In particular, developments at IBM, e.g.:

“Quantum algorithms for electronic structure calculations: Particle-hole Hamiltonian and optimized wave-function expansions”,

P. Kl. Barkoutsos, J. F. Gonthier, I. Sokolov, N. Moll, G. Salis, A.

Fuhrer, M. Ganzhorn, D. J. Egger, M. Troyer, A. Mezzacapo, S. Filipp, and I. Tavernelli, Phys. Rev. A 98, 022322 (2018)