Advanced Materials Modeling:

Wavefunction Methods

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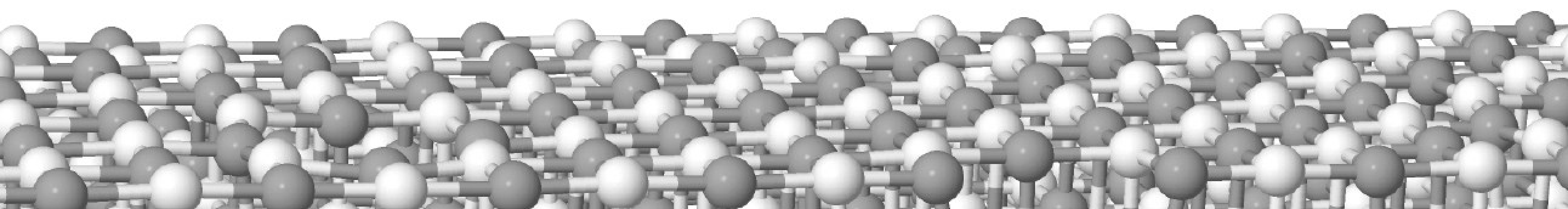

DFT versus wavefunction methods

Density functional theory

Density functional theory: Hohenberg-Kohn theorem

$n(\mathbf{r})$ →

- $\hat{H}$ – many-body Hamiltonian
- $\Psi(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_N\sigma_N)$ – many-body wave function
- E_{tot} – total energy

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

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

No systematic way to improve accuracy!

Ground-state electronic structure problem

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

$\Psi\left(\{\mathbf{r}_i\},\{\sigma_i\}\right)$ – 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 $V^{\mathrm{ext}}(\{\mathbf{r}_i\})$)

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

Ground-state electronic structure problem

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

Ground-state electronic structure problem

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

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

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

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

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

Ground-state electronic structure problem

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

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

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

Ground-state electronic structure problem

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

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

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

However,

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

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

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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

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

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

bosons:
***can* occupy the same quantum state**

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

$$\Downarrow$$

electrons are fermions

Many-electron wave function

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

fermions:
***cannot* occupy the same quantum state**

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

bosons:
***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 (refers to $n(\mathbf{q})$)

normalization factor (refers to $\sqrt{N!}$)

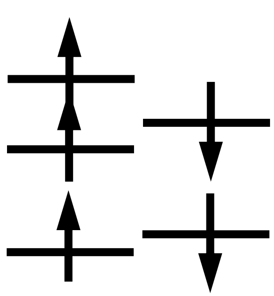
Many-electron wave function

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

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

Slater determinant

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



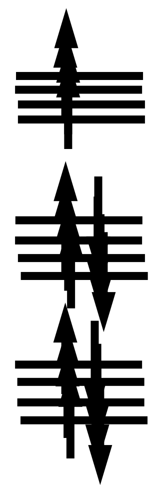
Non-interacting fermions – periodic system

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

n **– band index,**

k – k-point

$$\Psi =$$



$n=3,\ \mathbf{k}=\mathbf{k}_1,\ \ldots,\mathbf{k}_4$

$n=2,\ \mathbf{k}=\mathbf{k}_1,\ \ldots,\mathbf{k}_4$

$n=1,\ \mathbf{k}=\mathbf{k}_1,\ \ldots,\mathbf{k}_4$

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)

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

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

⇩ variational principle

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

The Hartree-Fock (HF) approximation

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

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

Fock operator

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

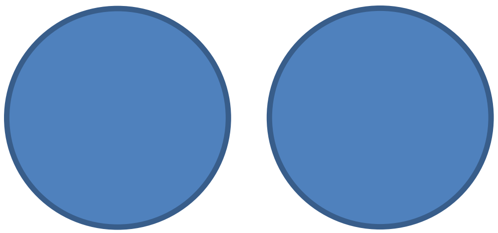
$$\hat{h}\psi_i = (-\tfrac{1}{2}\nabla^2 + V_{\text{ext}})\psi_i \qquad \hat{U}_j\psi_i = \sum_{k \neq i} \int d^3r' \frac{|\psi_k(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \psi_i(\boldsymbol{r})$$

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

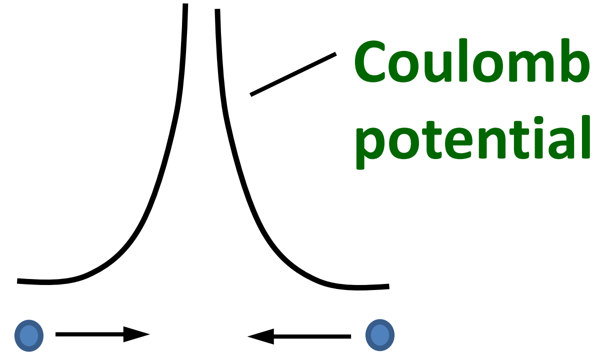
A. Szabo and N.O. Ostlund, Modern Quantum Chemistry

Two types of correlation

Dynamic correlation:

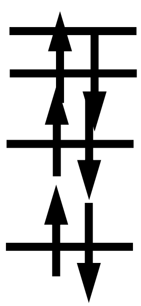


versus



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

Non-dynamic (static) correlation:



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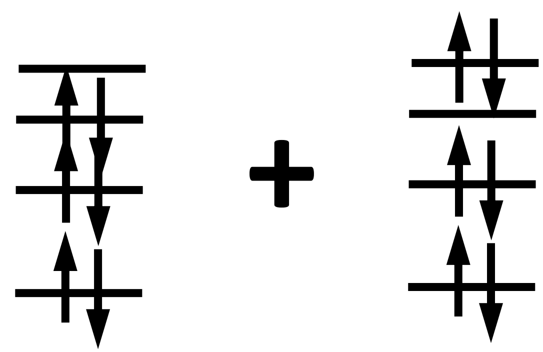


(quasi)degenerate HOMO-LUMO)

HF approximation → ≥90% of total energy, overestimates ionicity

Beyond mean-field approximation

Finite-order perturbation theory

❒ Rayleigh-Schrödinger perturbation theory (RSPT)

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

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

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

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

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

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)

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

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

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

Corrections to ground-state energy:

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

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

Finite-order perturbation theory

❒ Møller-Plesset perturbation theory (MP*n*)

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

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

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

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

$$E_0^{(0)} = \sum_i \varepsilon_i \qquad E_0^{(1)} = \langle \Phi | \left(\hat{H} - \sum_i \hat{f}(\boldsymbol{r}_i)\right) | \Phi \rangle = \langle \Phi | \hat{H} | \Phi \rangle - E_0^{(0)}$$

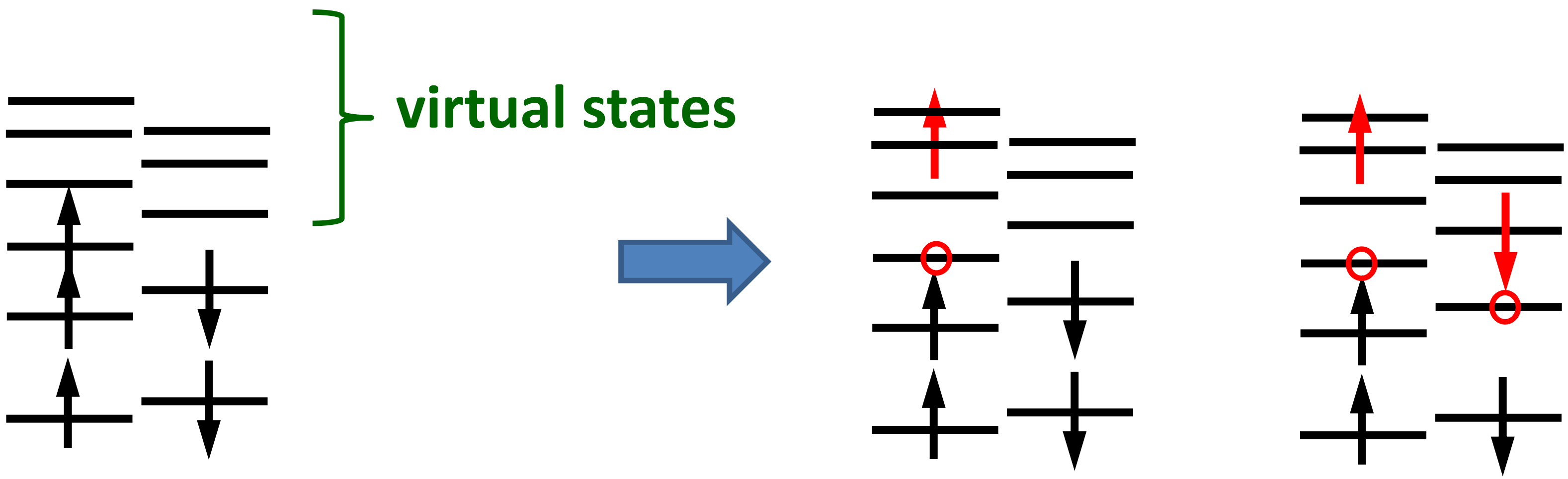
⇒ $$E_0^{(0)} + E_0^{(1)} = \langle \Phi | \hat{H} | \Phi \rangle$$ -- Hartree-Fock energy

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

Virtual (unoccupied) orbitals

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

The Fock operator has *infinite* number of eigenstates



Φ_0

Excited determinants: Φ_i^a Φ_{ij}^{ab} …

Finite-order perturbation theory

❐ Møller-Plesset perturbation theory

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

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

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

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

Finite-order perturbation theory

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

Brillouin's theorem

Finite-order perturbation theory

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

Brillouin's theorem

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

Finite-order perturbation theory

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

Brillouin's theorem

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

⇩

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

MP2 energy correction

Finite-order perturbation theory

❒ Møller-Plesset perturbation theory

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

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

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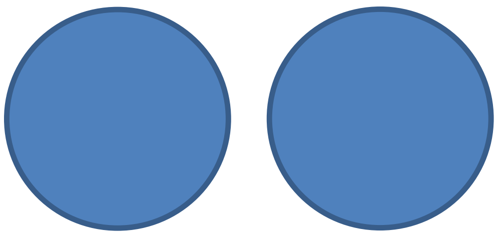
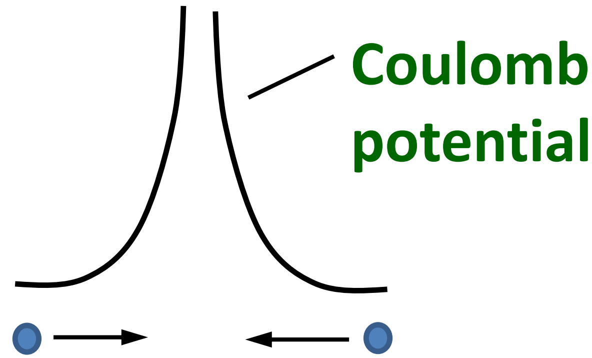
1) A linear combination of determinants
2) Single excitations do not contribute at first order (Brillouin's theorem) , but they do contribute at higher orders
3) Higher excitations at higher orders
4) Fails when HOMO and LUMO are close -- higher-order terms are needed, wavefunction is not a single determinant

Two types of correlation

Dynamic correlation:

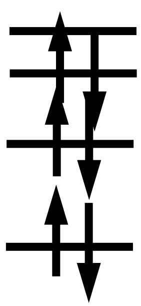


versus



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

Non-dynamic (static) correlation:



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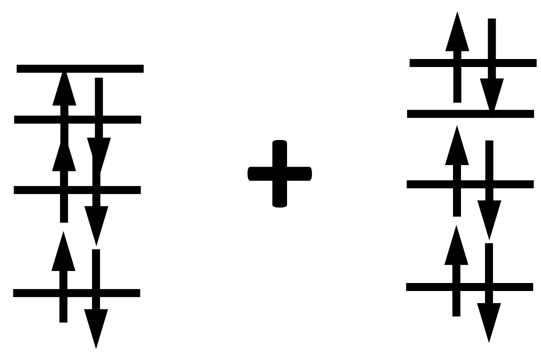


(quasi)degenerate HOMO-LUMO)

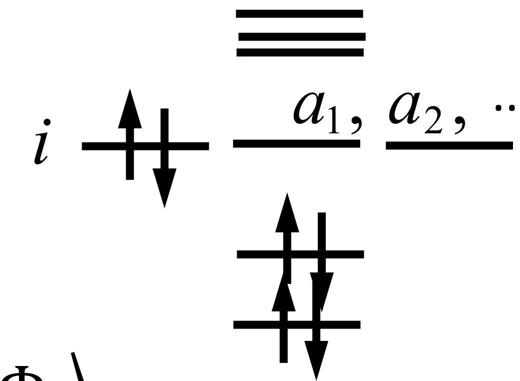
Finite-order perturbation theory

❒ RSPT for degenerate states

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

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

-- an eigenvalue problem



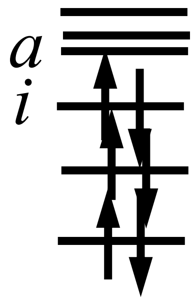
⇩

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

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

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

Configuration interaction



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

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

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

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

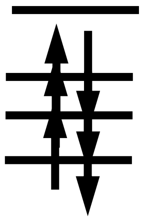
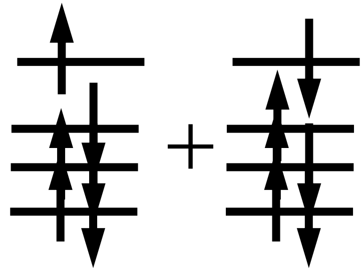
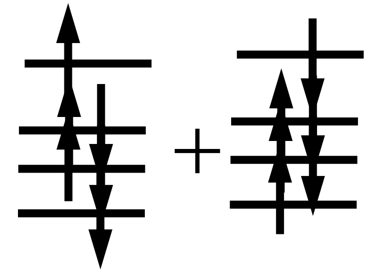
$$E = \frac{\left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle}{\left\langle \Psi \middle| \Psi \right\rangle} \rightarrow \min \Rightarrow \frac{\partial E}{\partial \{C\}} = 0$$

⇩

$$\mathbf{HC} = E\mathbf{C}$$

The concept of mixing excitations

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

$|\Phi_0\rangle =$  , $|\Phi_1\rangle =$  , $|\Phi_2\rangle =$  , $\cdots$

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

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

Project onto $\langle \Phi_k |$ **→ 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

$$\left|\Phi_0\right\rangle, \left|S\right\rangle \equiv \left\{\left|\Phi_i^a\right\rangle\right\}, \left|D\right\rangle \equiv \left\{\left|\Phi_{ij}^{ab}\right\rangle\right\}, \ldots$$

$$\frac{M!}{(M-n)!n!}$$

M **orbitals**

n**-tuple excitations**

Configuration interaction – matrix diagonalization

$$\left|\Phi_0\right\rangle, \left|S\right\rangle \equiv \left\{\left|\Phi_i^a\right\rangle\right\}, \left|D\right\rangle \equiv \left\{\left|\Phi_{ij}^{ab}\right\rangle\right\}, \ldots \qquad \frac{M!}{(M-n)!n!}$$

M **orbitals**
n**-tuple excitations**

$$\begin{array}{c|cccccc}
 & \left|\Phi_0\right\rangle & \left|S\right\rangle & \left|D\right\rangle & \left|T\right\rangle & \left|Q\right\rangle & \cdots \\
\hline
\left\langle\Phi_0\right| & \left\langle\Phi_0\middle|\hat{H}\middle|\Phi_0\right\rangle & \left\langle\Phi_0\middle|\hat{H}\middle|S\right\rangle & \left\langle\Phi_0\middle|\hat{H}\middle|D\right\rangle & 0 & 0 & \cdots \\
\left\langle S\right| & \left\langle S\middle|\hat{H}\middle|\Phi_0\right\rangle & \left\langle S\middle|\hat{H}\middle|S\right\rangle & \left\langle S\middle|\hat{H}\middle|D\right\rangle & \left\langle S\middle|\hat{H}\middle|T\right\rangle & 0 & \cdots \\
\left\langle D\right| & \left\langle D\middle|\hat{H}\middle|\Phi_0\right\rangle & \left\langle D\middle|\hat{H}\middle|S\right\rangle & \left\langle D\middle|\hat{H}\middle|D\right\rangle & \left\langle D\middle|\hat{H}\middle|T\right\rangle & \left\langle D\middle|\hat{H}\middle|Q\right\rangle & \cdots \\
\left\langle T\right| & 0 & \left\langle T\middle|\hat{H}\middle|S\right\rangle & \left\langle T\middle|\hat{H}\middle|D\right\rangle & \left\langle T\middle|\hat{H}\middle|T\right\rangle & \left\langle T\middle|\hat{H}\middle|Q\right\rangle & \cdots \\
\left\langle Q\right| & 0 & 0 & \left\langle Q\middle|\hat{H}\middle|D\right\rangle & \left\langle Q\middle|\hat{H}\middle|T\right\rangle & \left\langle Q\middle|\hat{H}\middle|Q\right\rangle & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots &
\end{array}$$

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

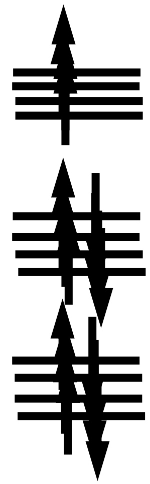
C. David Sherrill, Introduction to configuration interaction theory (1995)

Configuration interaction in periodic systems

n **– band index,**

k – k-point

$$\Phi_0 =$$



$$n = 3,\ \mathbf{k} = \mathbf{k}_1, \dots, \mathbf{k}_4$$

$$n = 2,\ \mathbf{k} = \mathbf{k}_1, \dots, \mathbf{k}_4$$

$$n = 1,\ \mathbf{k} = \mathbf{k}_1, \dots, \mathbf{k}_4$$

excitations can change not only *n* but also *k*-point

$$\Psi = \Phi_0 + \sum_{\substack{i\mathbf{k},a\mathbf{q} \\ \mathbf{k}=\mathbf{q}}} c_{i\mathbf{k}}^{a\mathbf{q}} \Phi_{i\mathbf{k}}^{a\mathbf{q}} + \sum_{\substack{i\mathbf{k},a\mathbf{q} \\ j\mathbf{p},b\mathbf{r} \\ \mathbf{k}+\mathbf{p}=\mathbf{q}+\mathbf{r}}} c_{i\mathbf{k},j\mathbf{p}}^{a\mathbf{q},b\mathbf{r}} \Phi_{i\mathbf{k},j\mathbf{p}}^{a\mathbf{q},b\mathbf{r}} + \cdots$$

$$\left\langle \Phi_{i\mathbf{k}}^{a\mathbf{q}} \middle| \hat{H} \middle| \Phi_{i\mathbf{k},j\mathbf{p}}^{a\mathbf{q},b\mathbf{r}} \right\rangle$$

momentum conservation

Full configuration interaction (FCI)

$$\Psi_i = \sum_j c_{ij} \Phi_j$$ – include ALL excitations of *N* electrons on *M* orbitals (*M* 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

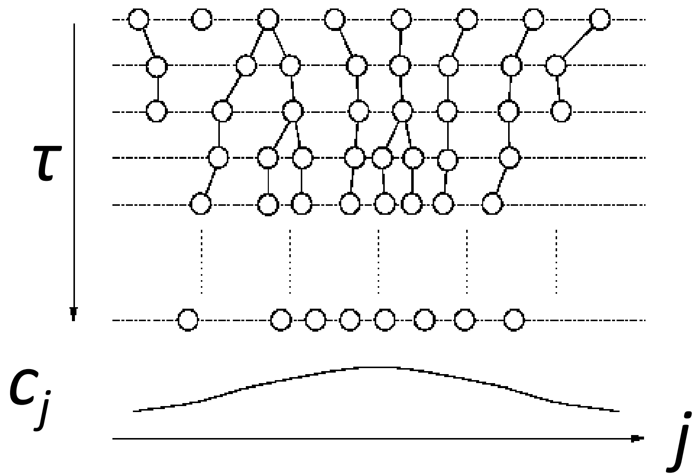
- The scaling with system size is combinatorial: $$\frac{M!}{(M-N)!N!}$$

50 electrons on 100 orbitals → 10^{29}x10^{29} matrix diagonalization

Sparsity: $\left\langle \Phi^{(n)} \middle| \hat{H} \middle| \Phi^{(n\pm2)} \right\rangle \neq 0$

FCI quantum Monte Carlo (FCIQMC) method

Walkers – determinants



Re(c_j), -Re(c_j), Im(c_j), -Im(c_j)

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

From Schrödinger equation:

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

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

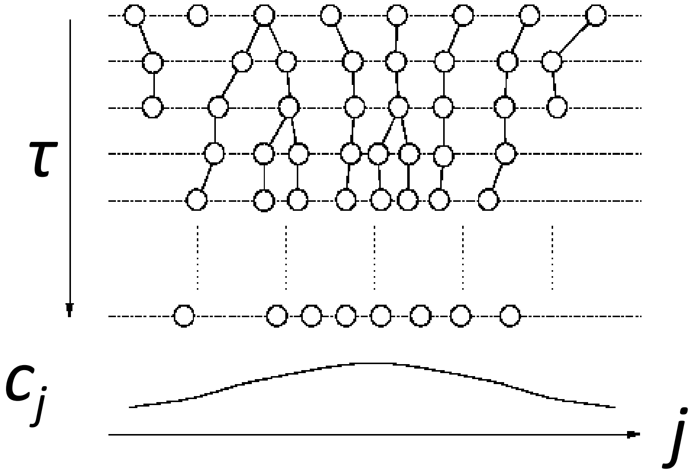
converges to ground-state eigenvector (similar to DMC)

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

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

FCI quantum Monte Carlo (FCIQMC) method

Walkers – determinants



Re(c_j), -Re(c_j), Im(c_j), -Im(c_j)

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

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

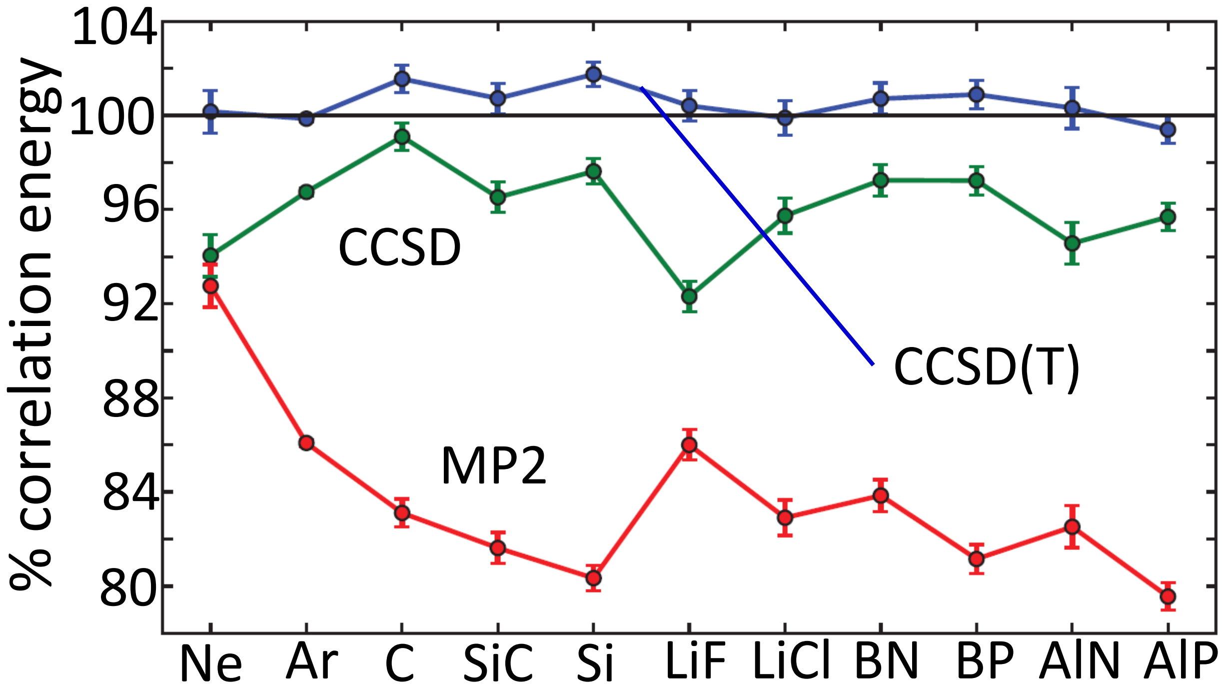
$$E, \;\; c_i = (-1)^{x_i} \sqrt{\frac{\langle N_i \rangle}{\langle N \rangle}}$$

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

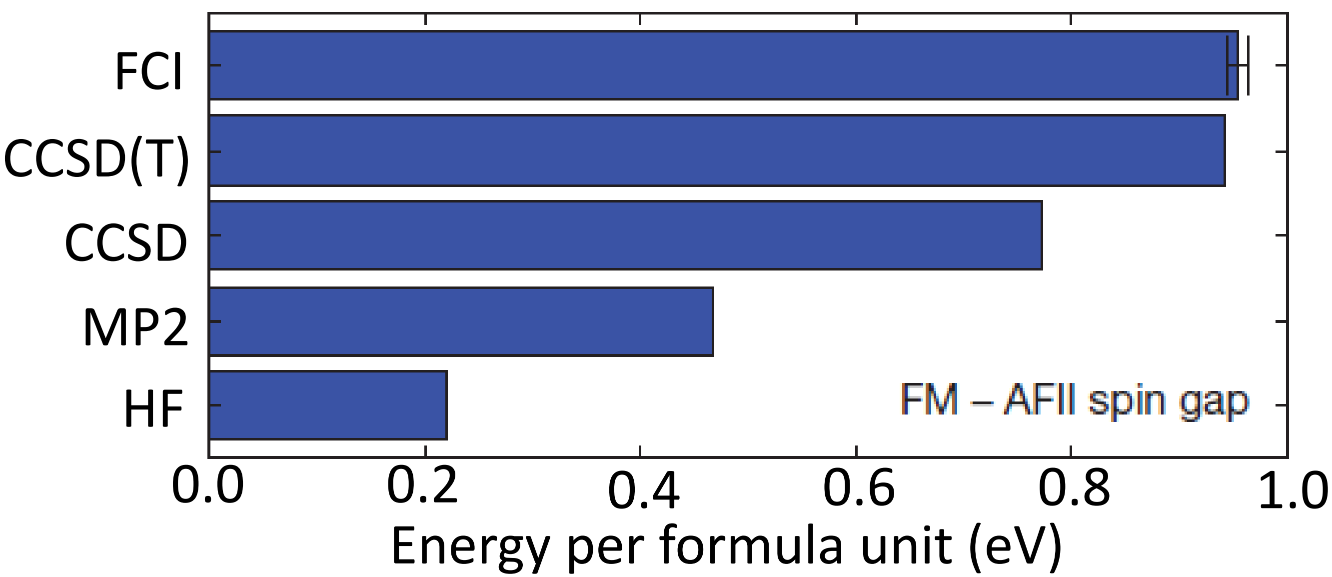
Timing example: diamond, 4x4x4 k-points – 25,000 CPU hours, ±20 meV per atom remaining error in correlation energy

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

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

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

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

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

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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

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

(CISD method)

Truncated CI: Properties

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

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

Trancated CI is *variational* → $E \geq E_{\mathbf{exact}}$

MP*n* is not variational

Size-extensivity

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

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

$$E_{N\mathrm{A}} = N E_{\mathrm{A}}$$

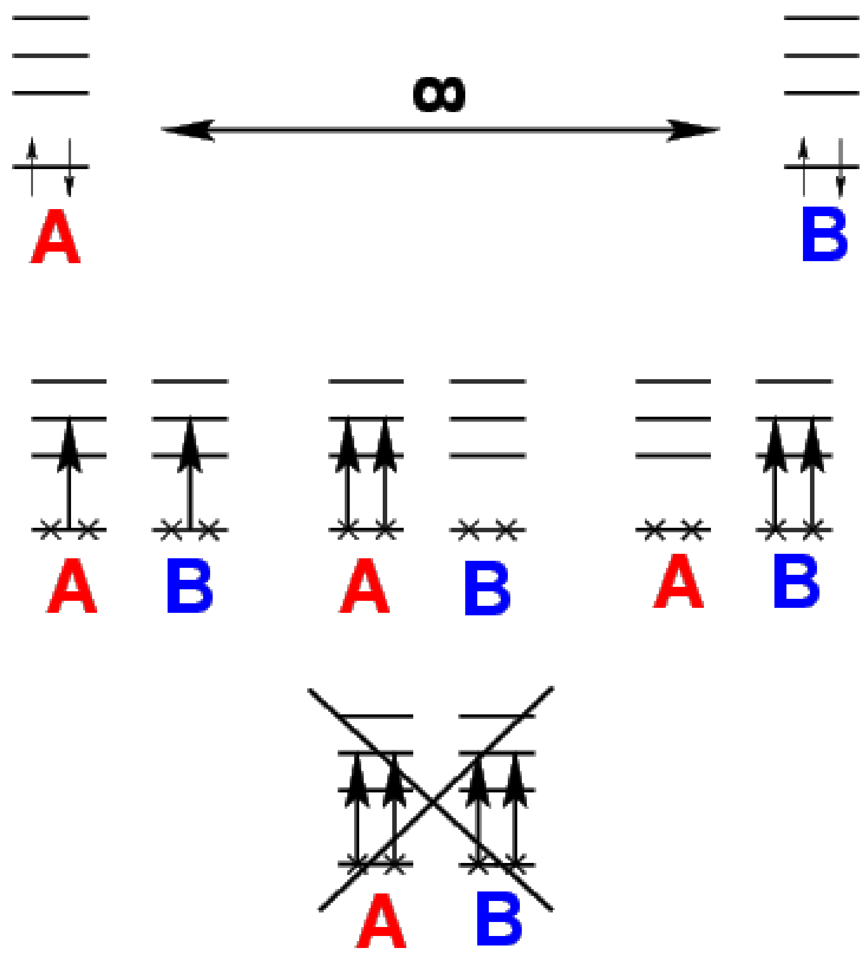
This insures that the error per unit does not increase with system size

Hartree-Fock is size extensive

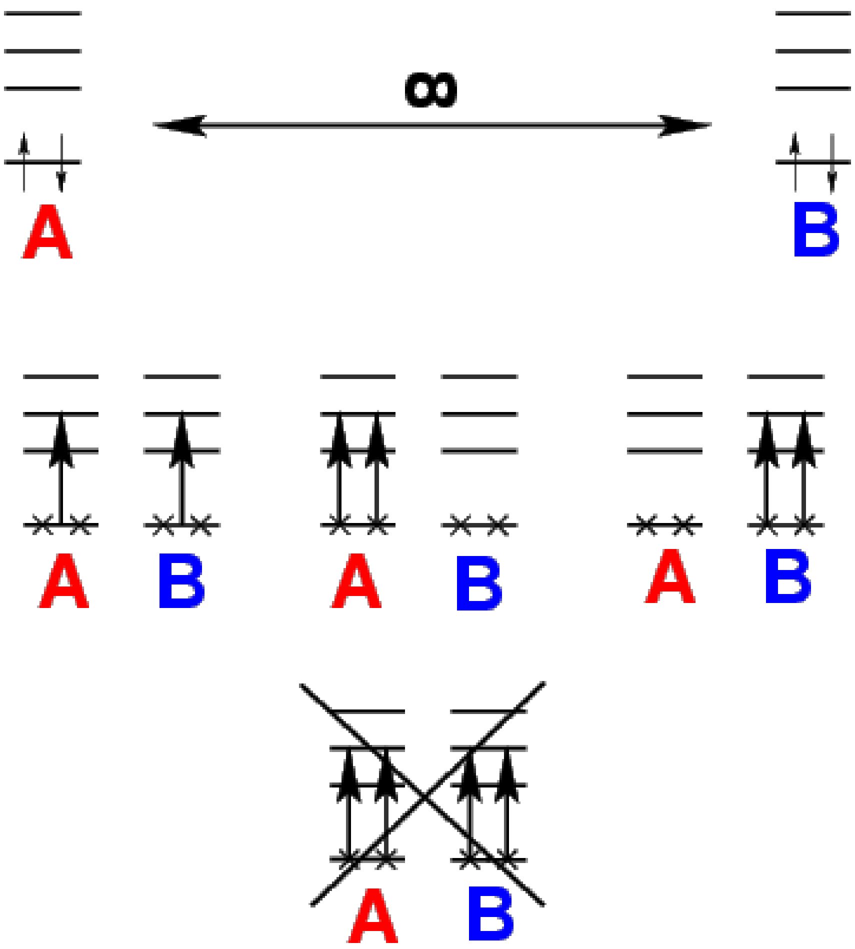
Approximate DFT is size extensive

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

Truncated CI is not size-extensive



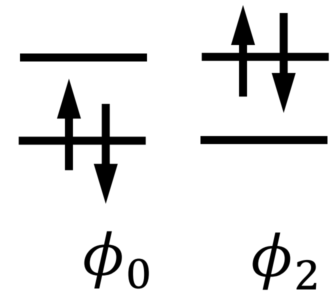
Truncated CI is not size-extensive



But full CI is size-extensive

FCI: The role of higher excitations

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



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

$$\Psi = \mathcal{A}[(\phi_0^1 + c\phi_2^1)(\phi_0^2 + c\phi_2^2)\ \ldots\ (\phi_0^N + c\phi_2^N)]$$

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

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

doubles: $\sim Nc^2$**, quadruples:** $\sim \dfrac{N^2c^4}{2!}$**, sextuples:** $\sim \dfrac{N^3c^6}{3!}$**, …**

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

FCI: The role of higher excitations

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

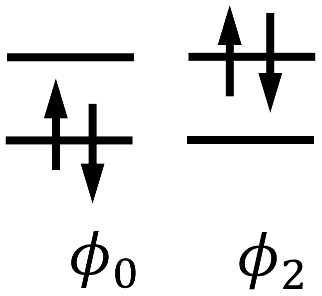
No matter how small c is, there is *N* that makes higher excitations important

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

I. Shavitt and R. Bartlett, *Many-body methods in chemistry and physics*, Cambridge University Press (2009)

Coupled cluster theory

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



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

$$\Psi = \mathsf{A}[(\phi_0^1 + c\phi_2^1)(\phi_0^2 + c\phi_2^2) \ldots (\phi_0^N + c\phi_2^N)]$$

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

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

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

Coupled cluster theory

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

For two non-interacting subsystems:

$$\left|\Phi_0(\mathrm{A}\cdots\mathrm{B})\right\rangle = \left|\Phi_0(\mathrm{A})\Phi_0(\mathrm{B})\right\rangle,\ \hat{T}(\mathrm{A}\cdots\mathrm{B}) = \hat{T}(\mathrm{A}) + \hat{T}(\mathrm{B})$$

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

$$\hat{H}\left|\Psi\right\rangle = (\hat{H}_\mathrm{A} + \hat{H}_\mathrm{B})\left|\Psi(\mathrm{A})\Psi(\mathrm{B})\right\rangle = [E(A) + E(B)]\left|\Psi\right\rangle$$

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

For RSPT, $\left|\Psi\right\rangle \neq \left|\Psi(\mathrm{A})\Psi(\mathrm{B})\right\rangle$**, but the energy is size-extensive**

Coupled cluster theory

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

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

$\hat{T}_1$ $\hat{T}_2$

$$\Psi = (1 + \hat{T}_1 + \hat{T}_2 +$$ ← ***connected*** **terms**

$$\frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 +$$ ← ***disconnected*** **terms**

$$\frac{1}{6}\hat{T}_1^3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{2}\hat{T}_1\hat{T}_2^2 + \frac{1}{6}\hat{T}_2^3 + \ldots)\Phi_0$$

(note: intermediate normalization above)

Formally, all excitations from Φ_0 **are present**

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

Coupled-cluster equations

$$\hat{H}\,\mathrm{e}^{\hat{T}}\left|\Phi_0\right\rangle = E\,\mathrm{e}^{\hat{T}}\left|\Phi_0\right\rangle$$

$$\mathrm{e}^{-\hat{T}}\,\hat{H}\,\mathrm{e}^{\hat{T}}\left|\Phi_0\right\rangle = \overline{H}\left|\Phi_0\right\rangle = E\left|\Phi_0\right\rangle$$

$\overline{H} = \mathrm{e}^{-\hat{T}}\,\hat{H}\,\mathrm{e}^{\hat{T}}$ -- ***similarity-transformed*** **hamiltonian**

$$E = \left\langle\Phi_0\right|\overline{H}\left|\Phi_0\right\rangle$$

Amplitude equations:

$$\left\langle\Phi_i^a\right|\overline{H}\left|\Phi_0\right\rangle = 0,\ \left\langle\Phi_{ij}^{ab}\right|\overline{H}\left|\Phi_0\right\rangle = 0,\ldots$$

-- as many equations as unknown amplitudes

$\overline{H}$ **is non-Hermitian, energy is non-variational (variational CC is intractable)**

Coupled-cluster equations

$$\hat{H}\,\mathrm{e}^{\hat{T}}\left|\Phi_0\right\rangle = E\,\mathrm{e}^{\hat{T}}\left|\Phi_0\right\rangle$$

$$\mathrm{e}^{-\hat{T}}\,\hat{H}\,\mathrm{e}^{\hat{T}}\left|\Phi_0\right\rangle = \overline{H}\left|\Phi_0\right\rangle = E\left|\Phi_0\right\rangle$$

$\overline{H} = \mathrm{e}^{-\hat{T}}\,\hat{H}\,\mathrm{e}^{\hat{T}}$ -- ***similarity-transformed* hamiltonian**

$$E = \left\langle\Phi_0\right|\overline{H}\left|\Phi_0\right\rangle$$

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

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,…)

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

CI{*m*}: ~$n^m N^{m+2}$

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

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

MP*m*: ~nN^{m+2}

Coupled-cluster (CCD,CCSD,CCSDT,…)

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

CC{*m*}: ~$n^m N^{m+2}$

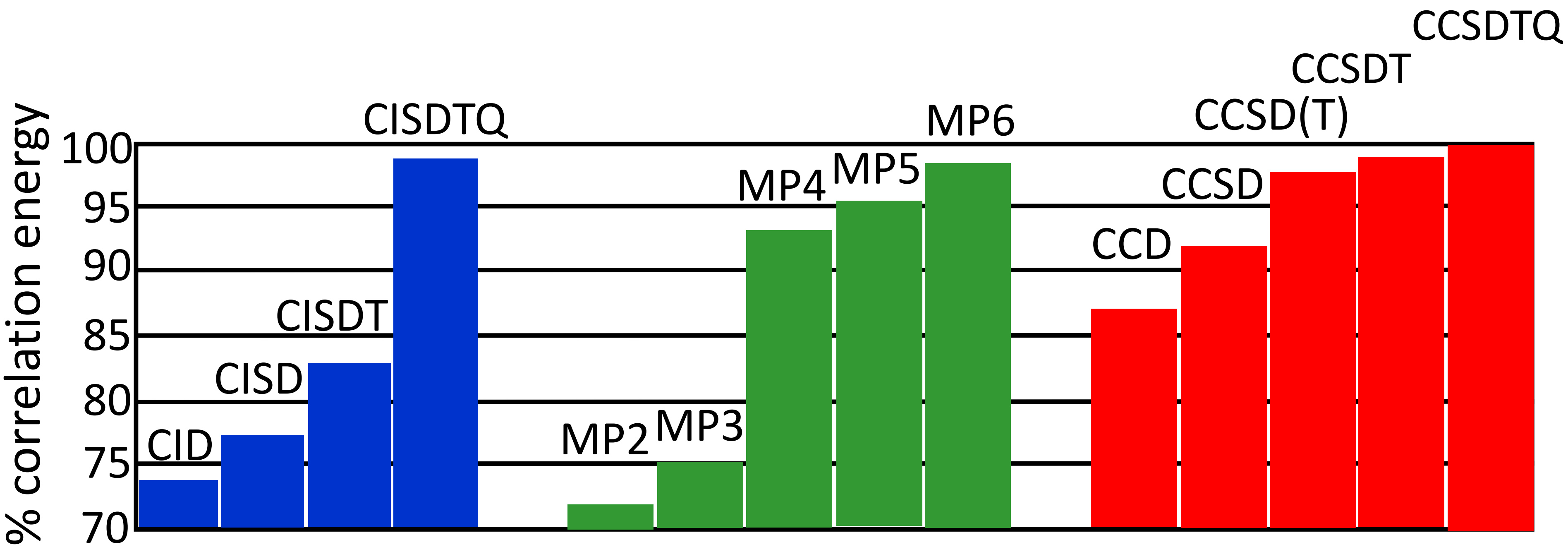
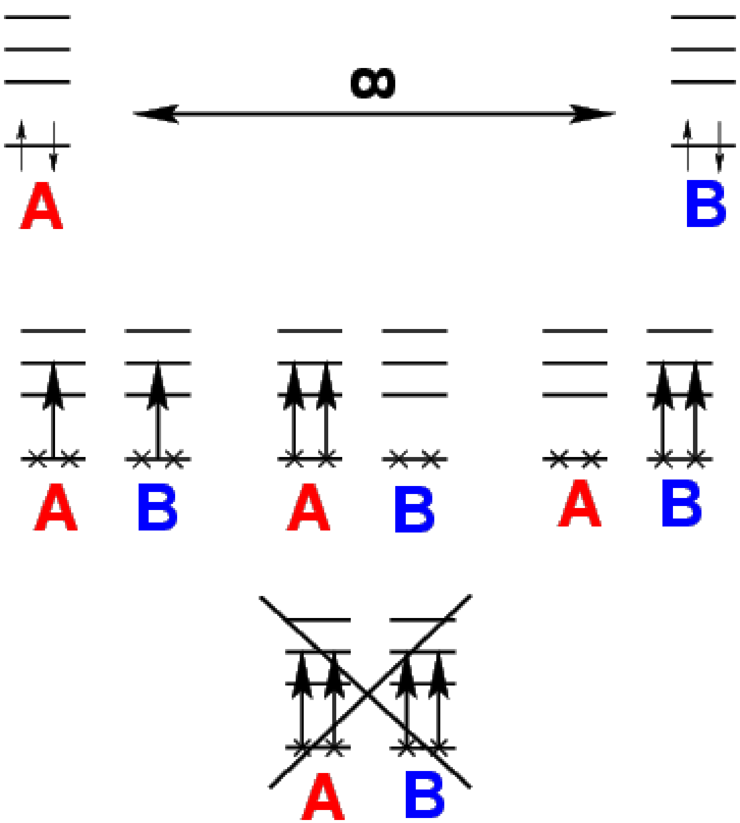


figure courtesy of R.J. Bartlett

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

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

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

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

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

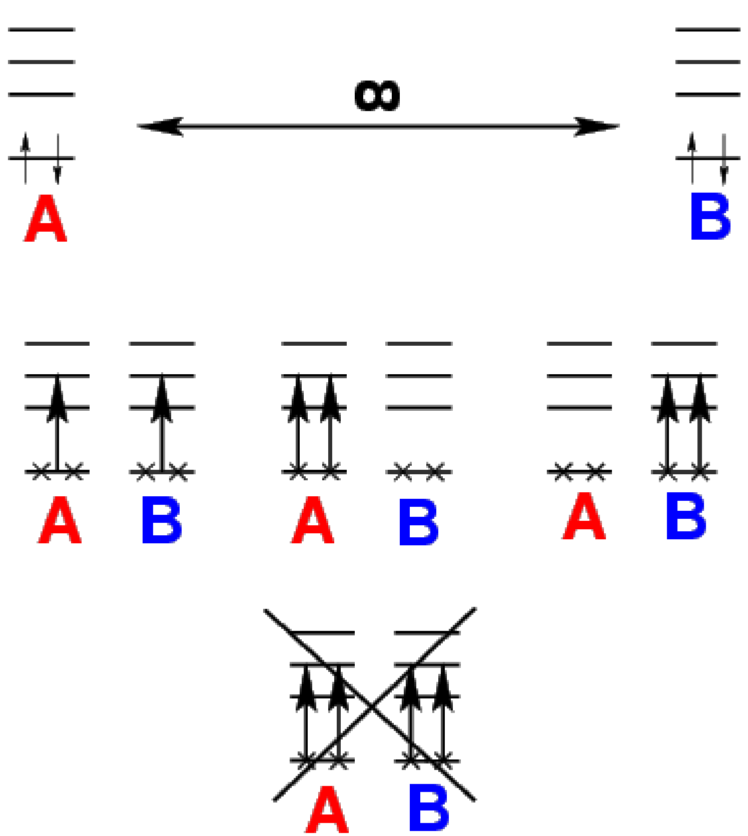
$$[\hat{T},\hat{R}] = 0$$

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

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

Equation-of-motion CC methods

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

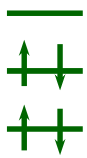
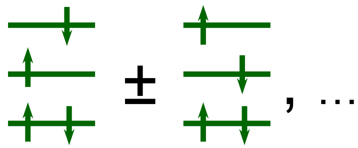
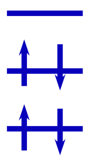
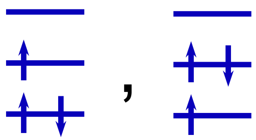
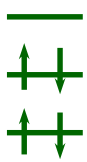
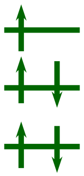
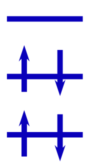
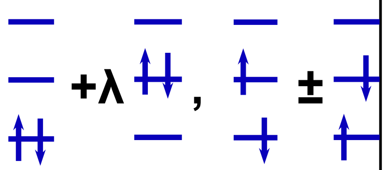
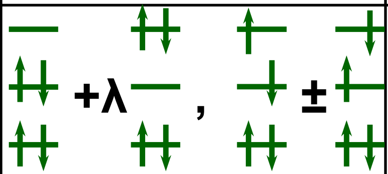
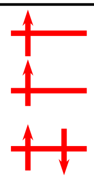
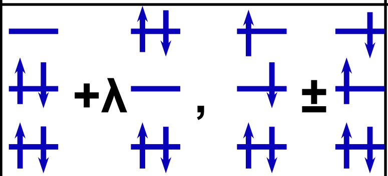


Ground-state energy (CC) is size-extensive

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

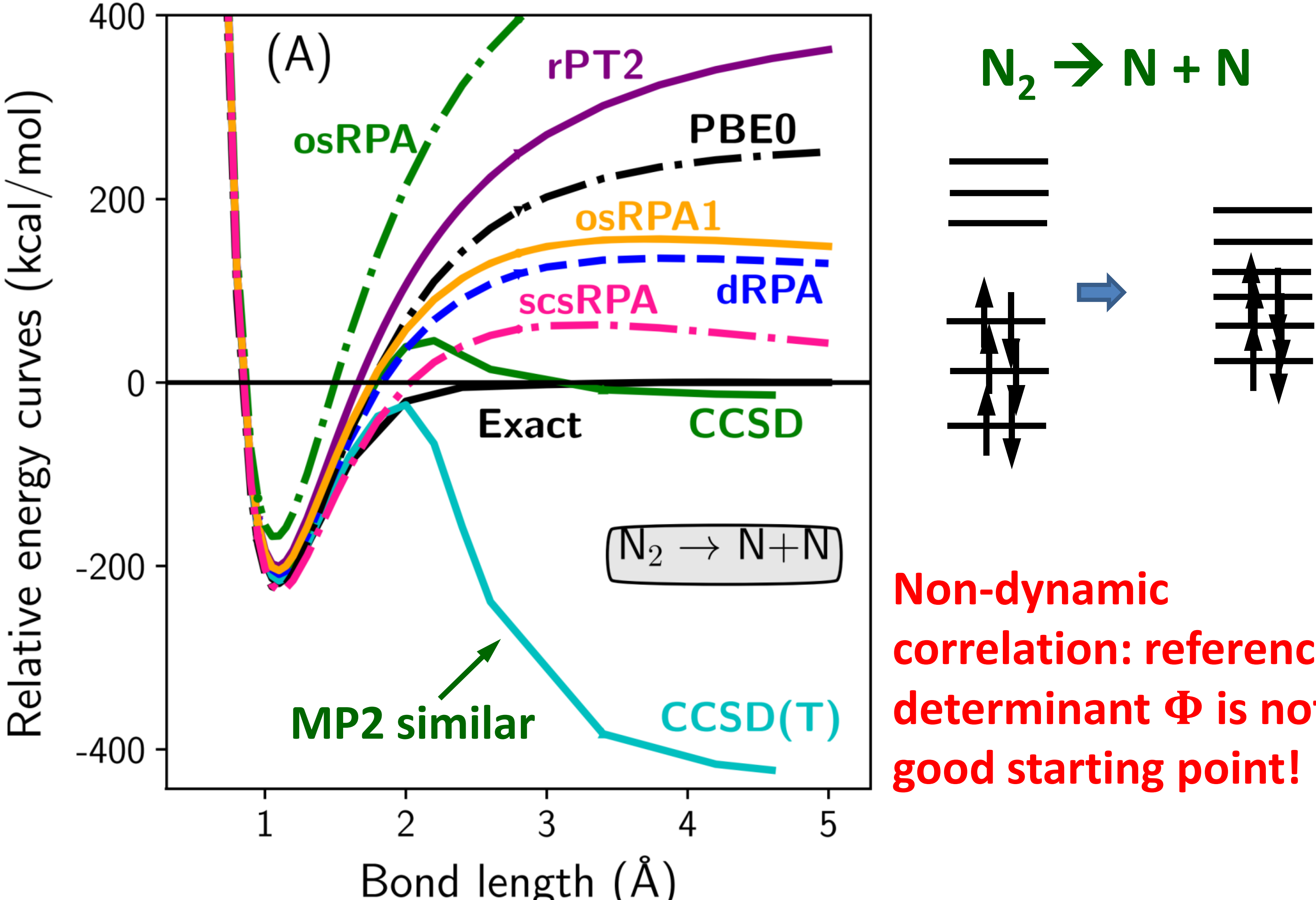
EOM-CC excitation energies on both A and B simultaneously are not size-extensive

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 SVL&AIK, JCP ***120***, 175 (2004)			-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

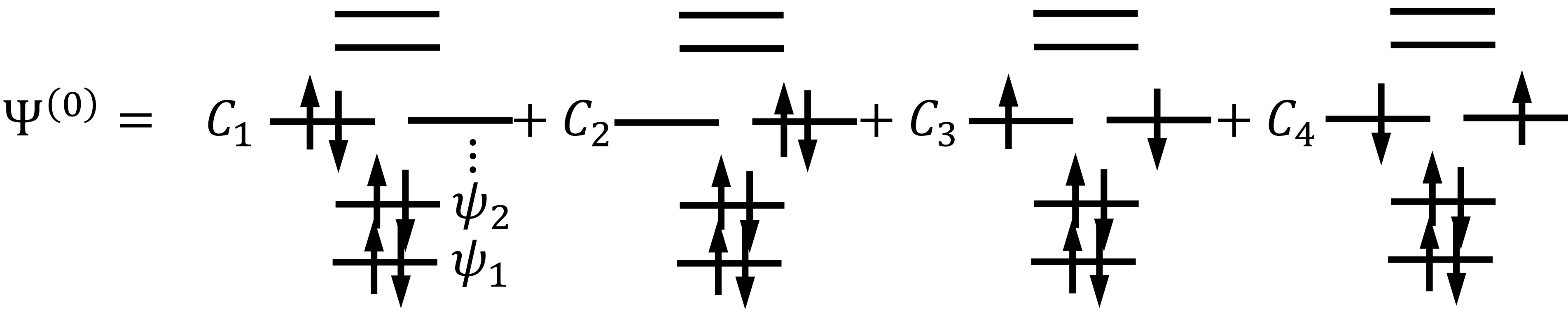


Non-dynamic correlation: reference determinant Φ is not a good starting point!

I.Y. Zhang, X. Xu, J. Phys. Chem. Lett. 2019, 10, 2617

Multireference methods

Idea: include all degenerate determinants as a reference

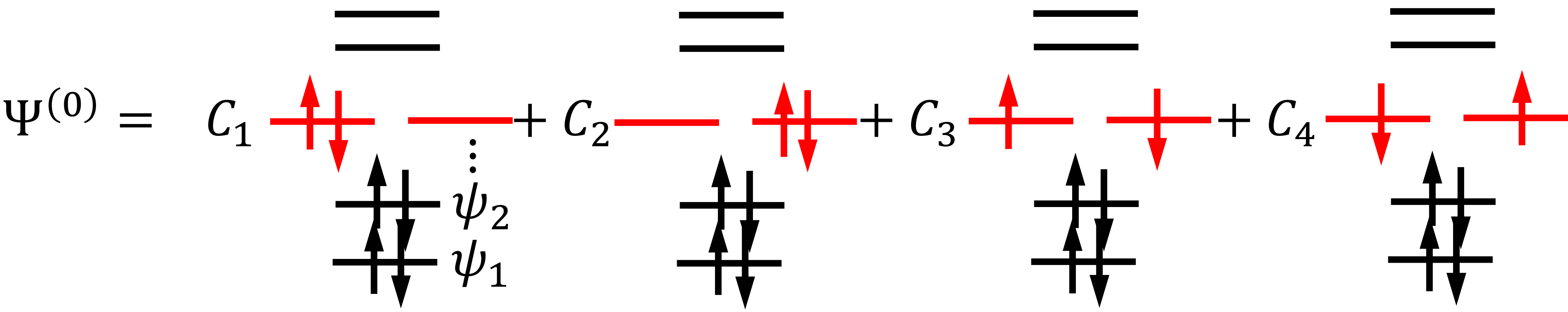


$$\min_{\psi_i, C_I} \frac{\langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \rightarrow \psi_i, C_I$$

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

Multireference methods

Idea: include all degenerate determinants as a reference



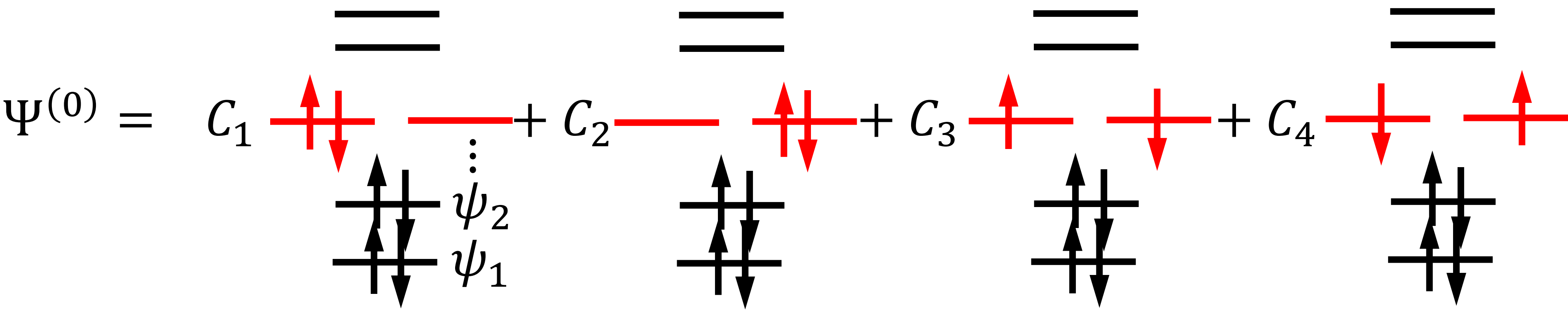
$$\min_{\psi_i, C_I} \frac{\langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \rightarrow \psi_i, C_I$$

-- 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



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

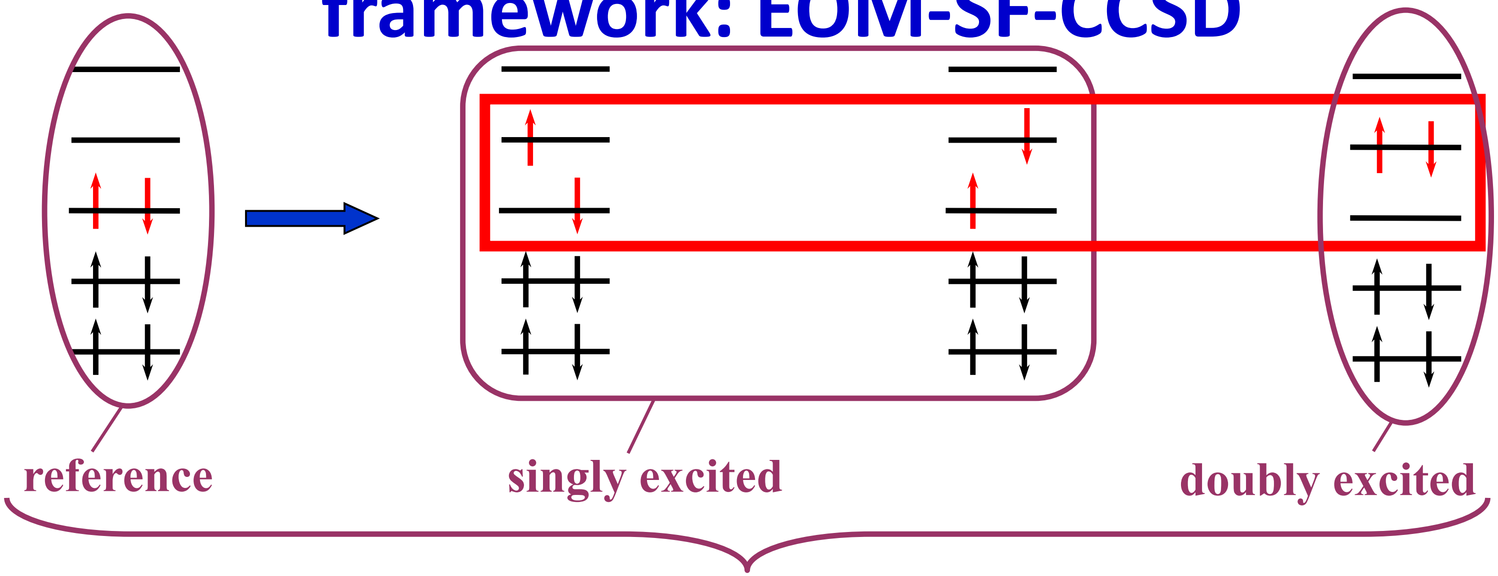
Multireference methods: Problems

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

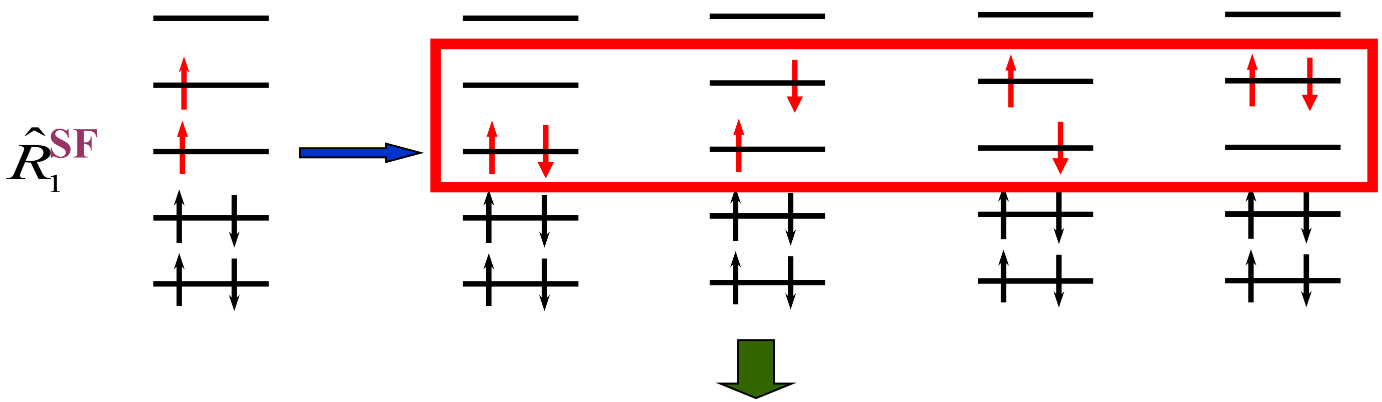
Choice of active space can have a strong effect on the results

Truncated MRCI is not size-extensive

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



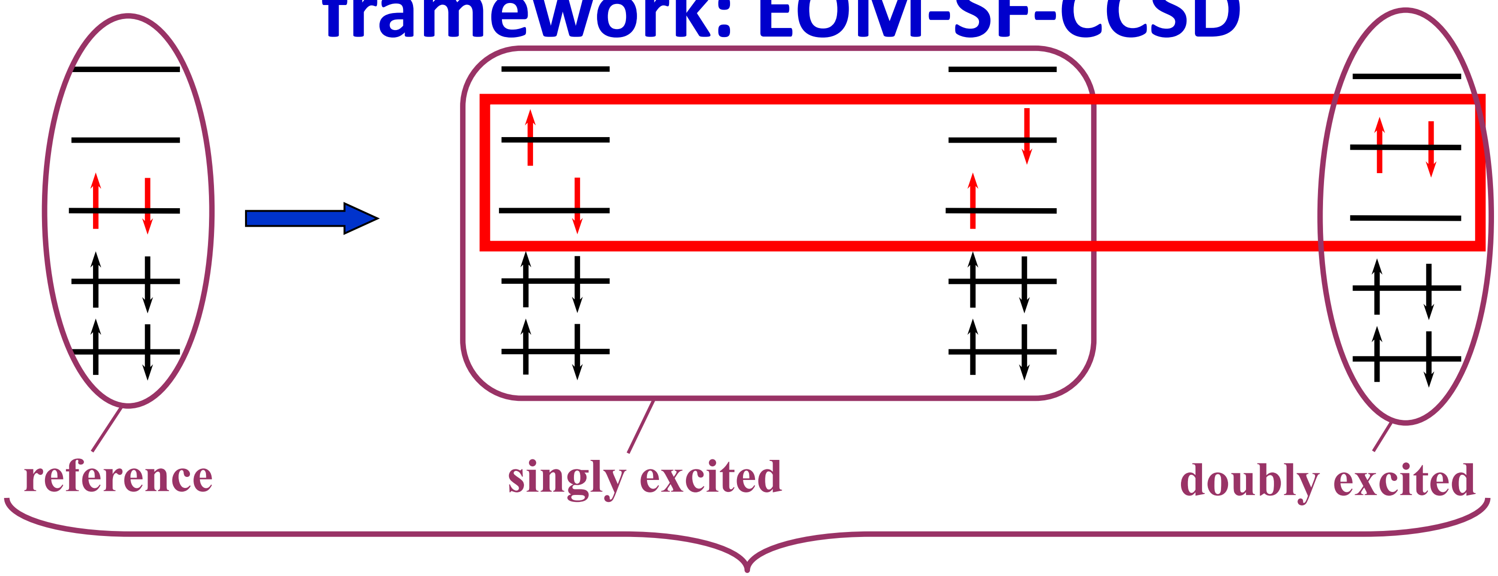
no balance – bad in case of degeneracy (diradicals)



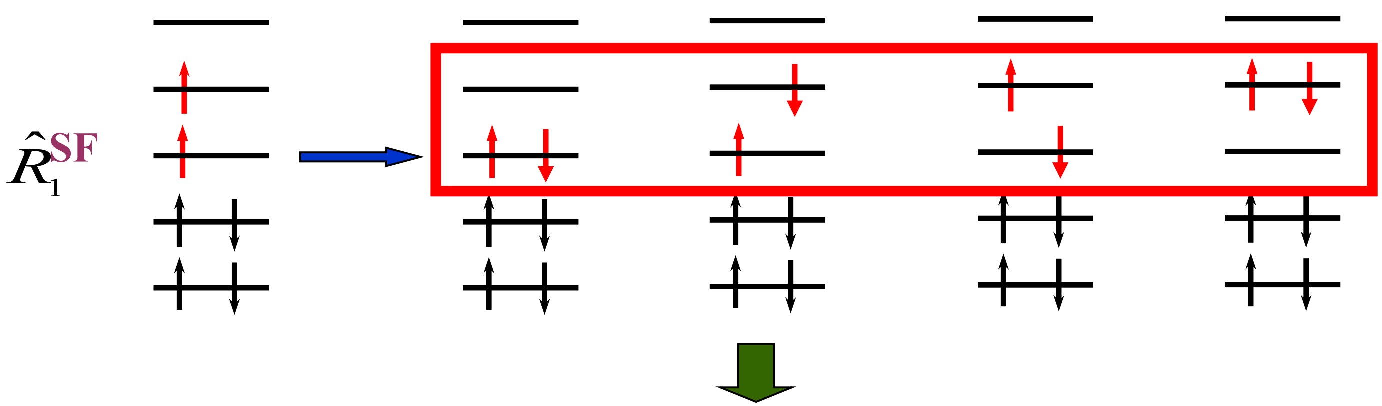
Balanced description -- all quasidegenerate M_S=0 determinants are treated on equal footing

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

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



no balance – bad in case of degeneracy (diradicals)



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)

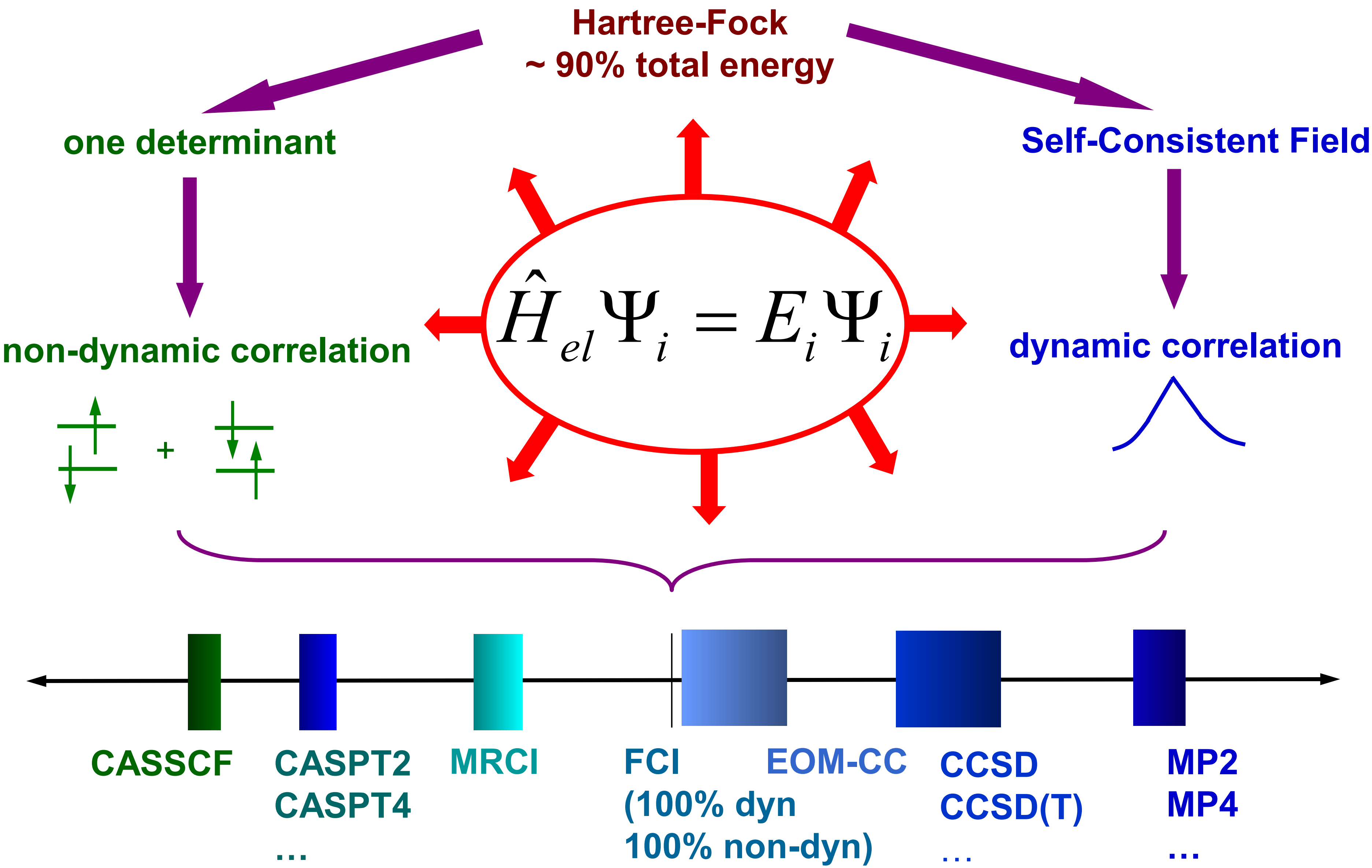
Free: GAMESS, NWChem (parallel), ORCA, ACES III (parallel)

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)