Computational Chemistry and Materials Modeling

Lecture 2
Hartree-Fock method and beyond

Sergey Levchenko

Center for Energy Science and Technology (CEST)
Skolkovo Institute of Science and Technology
Moscow, Russia

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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 4*N* variables (spatial + spin)**

- **electrons interact via Coulomb forces**

Ground-state electronic structure problem

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

Ground-state electronic structure problem

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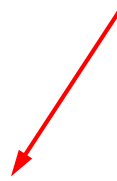
$$V^{\text{ext}}(\{\mathbf{r}\}) = \sum_i v(\mathbf{r}_i)$$

Ground-state electronic structure problem

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

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

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

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

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

Variational principle

$$\hat{H}\Psi = E\Psi$$

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}, \ \langle\Psi|\Psi\rangle \equiv \int \Psi^*(\{\mathbf{r}\},\{\sigma\})\Psi(\{\mathbf{r}\},\{\sigma\})d\{\mathbf{r}\}d\{\sigma\} = 1$$

$$\langle\Psi|\hat{H}|\Psi\rangle \equiv \int \Psi^*(\{\mathbf{r}\},\{\sigma\})\hat{H}\,\Psi(\{\mathbf{r}\},\{\sigma\})d\{\mathbf{r}\}d\{\sigma\}$$

**Observation: minimization of E with respect to Ψ →
Schrödinger equation**

$$\delta E = \frac{\delta E}{\delta \Psi^*}\delta\Psi^* + \frac{\delta E}{\delta\Psi}\delta\Psi = 0 \rightarrow \frac{\delta E}{\delta\Psi^*} = \frac{\delta E}{\delta\Psi} = 0$$

**because $\delta\Psi^*$ and $\delta\Psi$ are _arbitrary_ (complex conjugate of the
same equation, consider only one)**

Variational principle

$$\hat{H}\Psi = E\Psi$$

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}, \ \langle\Psi|\Psi\rangle \equiv \int \Psi^*(\{\mathbf{r}\},\{\sigma\})\Psi(\{\mathbf{r}\},\{\sigma\})d\{\mathbf{r}\}d\{\sigma\} = 1$$

$$\langle\Psi|\hat{H}|\Psi\rangle \equiv \int \Psi^*(\{\mathbf{r}\},\{\sigma\})\hat{H}\,\Psi(\{\mathbf{r}\},\{\sigma\})d\{\mathbf{r}\}d\{\sigma\}$$

**Observation: minimization of *E* with respect to Ψ →
Schrödinger equation**

$$\delta\frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\langle\delta\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} - \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle^2}\langle\delta\Psi|\Psi\rangle = 0$$

$$\langle\delta\Psi|\hat{H} - \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}|\Psi\rangle = 0 \rightarrow \hat{H}\Psi - E\Psi = 0$$

Variational principle

$$\hat{H}\Psi = E\Psi$$

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad \langle \Psi | \Psi \rangle \equiv \int \Psi^*(\{\mathbf{r}\},\{\sigma\})\Psi(\{\mathbf{r}\},\{\sigma\})d\{\mathbf{r}\}d\{\sigma\} = 1$$

$$\langle \Psi | \hat{H} | \Psi \rangle \equiv \int \Psi^*(\{\mathbf{r}\},\{\sigma\})\hat{H}\,\Psi(\{\mathbf{r}\},\{\sigma\})d\{\mathbf{r}\}d\{\sigma\}$$

Another way -- minimization with constraints:

$$L = \langle \Psi | \hat{H} | \Psi \rangle - E\big(\langle \Psi | \Psi \rangle - 1\big)$$

Lagrangian

constraint (normalization)

$$\delta L = \langle \delta\Psi | \hat{H} | \Psi \rangle - E\langle \delta\Psi | \Psi \rangle = 0 \rightarrow (\hat{H} - E)\Psi = 0$$

Hartree approximation

Apply _variational principle_: $\Psi(\{\boldsymbol{r}\}) = \prod_i \psi_i(\boldsymbol{r}_i)$

$$\frac{\delta}{\delta \psi_k^*}\left(\langle \Psi | \hat{H} | \Psi \rangle - \sum_i \varepsilon_i (\langle \psi_i | \psi_i \rangle - 1) \right) = 0$$

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_i \langle \psi_i | \hat{h} | \psi_i \rangle + \sum_{i>j} \int \frac{|\psi_i(\mathbf{r}_i)|^2 |\psi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} d^3 r_i d^3 r_j$$

$$\left(\hat{h} + \sum_{j \neq k} \int \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d^3 r' \right) \psi_k(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r})$$

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

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

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

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

However,

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

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

$\downarrow$

Permutation of two particles cannot change any observable

$\downarrow$

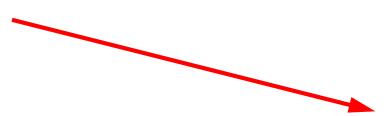**Wavefunction can change only by a phase factor**

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

Permuting again should change the wavefunction back

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

Fermions versus bosons

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

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

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

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

Fermions versus bosons

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

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

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
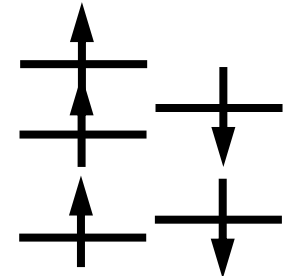
Many-electron wave function

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

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

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,

k – k-point

$$\Psi = \qquad \begin{array}{l} n = 3, \ \mathbf{k} = \mathbf{k}_1, \ \dots, \mathbf{k}_4 \\[2em] n = 2, \ \mathbf{k} = \mathbf{k}_1, \ \dots, \mathbf{k}_4 \\[2em] n = 1, \ \mathbf{k} = \mathbf{k}_1, \ \dots, \mathbf{k}_4 \end{array}$$

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)

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

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

variational principle

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

The Hartree-Fock (HF) approximation

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

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

Fock operator

$$\hat{f}\psi_i = \left(\hat{h} + \sum_k \left(\widehat{U}_k - \hat{J}_k\right)\right)\psi_i = \varepsilon_i\psi_i$$

$$\hat{h}\psi_i = \left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}\right)\psi_i \qquad \widehat{U}_k\psi_i = \int d^3r' \frac{|\psi_k(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|}\psi_i(\boldsymbol{r})$$

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

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

The Hartree-Fock (HF) approximation

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

$$E_{\text{tot}} = \sum_{n=1}^{N} \langle \psi_n | \hat{h} | \psi_n \rangle + \frac{1}{2} \sum_{I=1}^{M} \sum_{J=1}^{M} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' -$$

$$- \frac{1}{2} \sum_{m,n=1}^{N} \int \frac{\psi_m^*(\mathbf{r},\sigma)\psi_n(\mathbf{r},\sigma)\psi_n^*(\mathbf{r}',\sigma')\psi_m(\mathbf{r}',\sigma')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' d\sigma d\sigma'$$
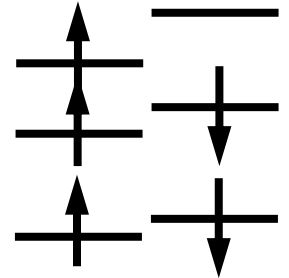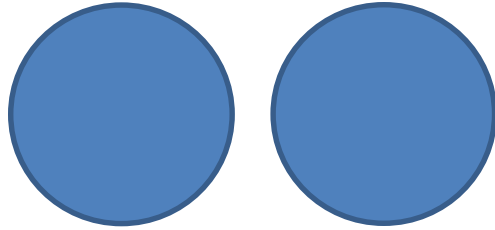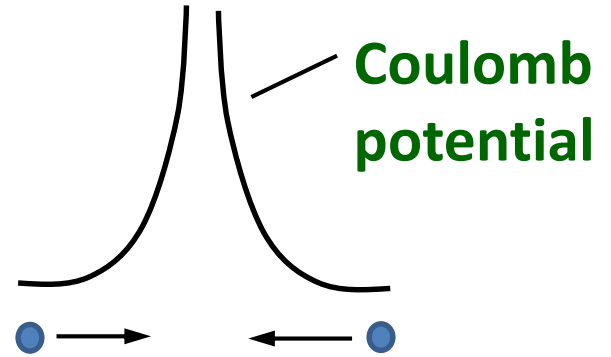
HF (exact) exchange energy

- **No self-interaction**

- **Coulomb mean-field → no dynamic correlation, single determinant → no static correlation**

Two types of correlation

Dynamic correlation:

versus
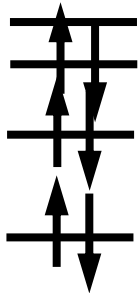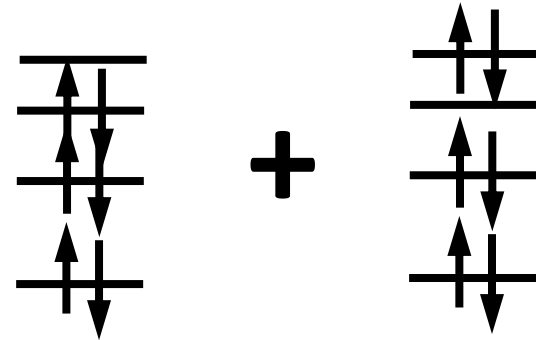
Coulomb potential

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

Non-dynamic (static) correlation:

versus

(quasi)degenerate HOMO-LUMO)

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

Solution of Hartree-Fock equations

Fock operator

$$\hat{f}\psi_i = \left(\hat{h} + \sum_k (\widehat{U}_k - \hat{J}_k)\right)\psi_i = \varepsilon_i\psi_i$$

$$\hat{h}\psi_i = \left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}\right)\psi_i \qquad \widehat{U}_k\psi_i = \int d^3r'\,\frac{|\psi_k(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|}\psi_i(\boldsymbol{r})$$

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

Solution of Hartree-Fock equations

Fock operator

$$\hat{f}\psi_i = \left(\hat{h} + \sum_k (\widehat{U}_k - \hat{J}_k)\right)\psi_i = \varepsilon_i \psi_i$$

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

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

In a given basis set: $\quad \psi_i = \sum_\alpha c_{\alpha i}\phi_\alpha$

$$\hat{f}\psi_i = \sum_\alpha c_{\alpha i}\hat{f}\phi_\alpha = \varepsilon_i\psi_i = \varepsilon_i \sum_\alpha c_{\alpha i}\phi_\alpha$$

Solution of Hartree-Fock equations

In a given basis set: $\psi_i = \sum\limits_{\alpha} c_{\alpha i} \phi_{\alpha}$

$$\hat{f}\psi_i = \sum\limits_{\alpha} c_{\alpha i} \hat{f} \phi_{\alpha} = \varepsilon_i \psi_i = \varepsilon_i \sum\limits_{\alpha} c_{\alpha i} \phi_{\alpha}$$

$$\sum\limits_{\alpha} c_{\alpha i} \langle \phi_{\beta} | \hat{f}[\boldsymbol{c}] | \phi_{\alpha} \rangle = \varepsilon_i \sum\limits_{\alpha} c_{\alpha i} \langle \phi_{\beta} | \phi_{\alpha} \rangle$$

Generalized eigenvalue problem, but the matrix $\langle \phi_{\beta} | \hat{f}[\boldsymbol{c}] | \phi_{\alpha} \rangle$ depends on $c_{\alpha i}$

Need to solve ITERATIVELY!

Self-consistent field (SCF) cycle

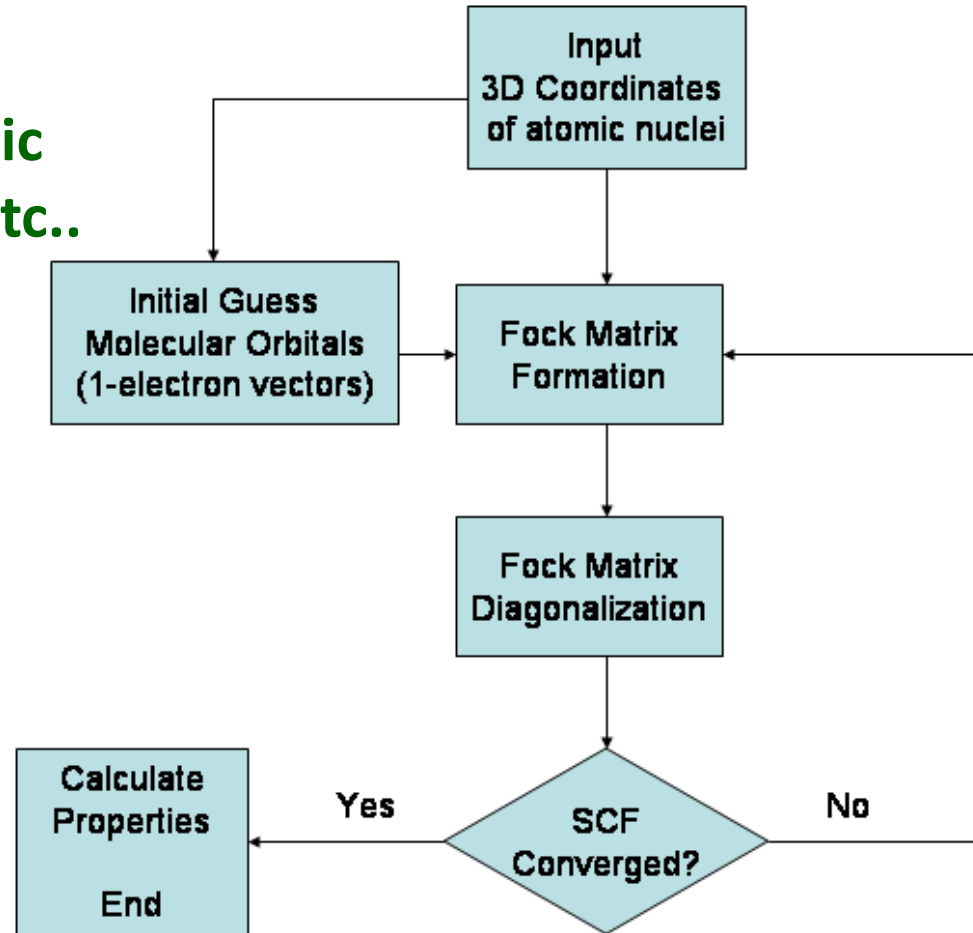Initial guess for $c_{\alpha i}$: random, atomic orbitals, simple models (Hückel), etc..

Convergence criteria: change in energy < ..., change in density < ..., change in forces < ...

If the guess is not good, convergence can be problematic: mix new and previous density matrices: $\widetilde{D}_{\alpha\beta}^{j+1} = \omega D_{\alpha\beta}^{j+1} + (1-\omega)D_{\alpha\beta}^{j}$ (or more - Pulay mixing)

Input
3D Coordinates of atomic nuclei

Initial Guess Molecular Orbitals (1-electron vectors)

Fock Matrix Formation

Fock Matrix Diagonalization

Calculate Properties

End

Yes

SCF Converged?

No

Beyond mean-field approximation

Finite-order perturbation theory

❐ **Rayleigh-Schrödinger perturbation theory (RSPT)**

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

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

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

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

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

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)**

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

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

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

Corrections to ground-state energy:

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

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

Finite-order perturbation theory

☐ **Møller-Plesset perturbation theory (MPn)**

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

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

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

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

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

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

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

Virtual (unoccupied) orbitals

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

The Fock operator has *infinite* number of eigenstates

virtual states

Φ_0

Excited determinants:

Φ_i^a $\qquad$ Φ_{ij}^{ab} $\qquad$ ...
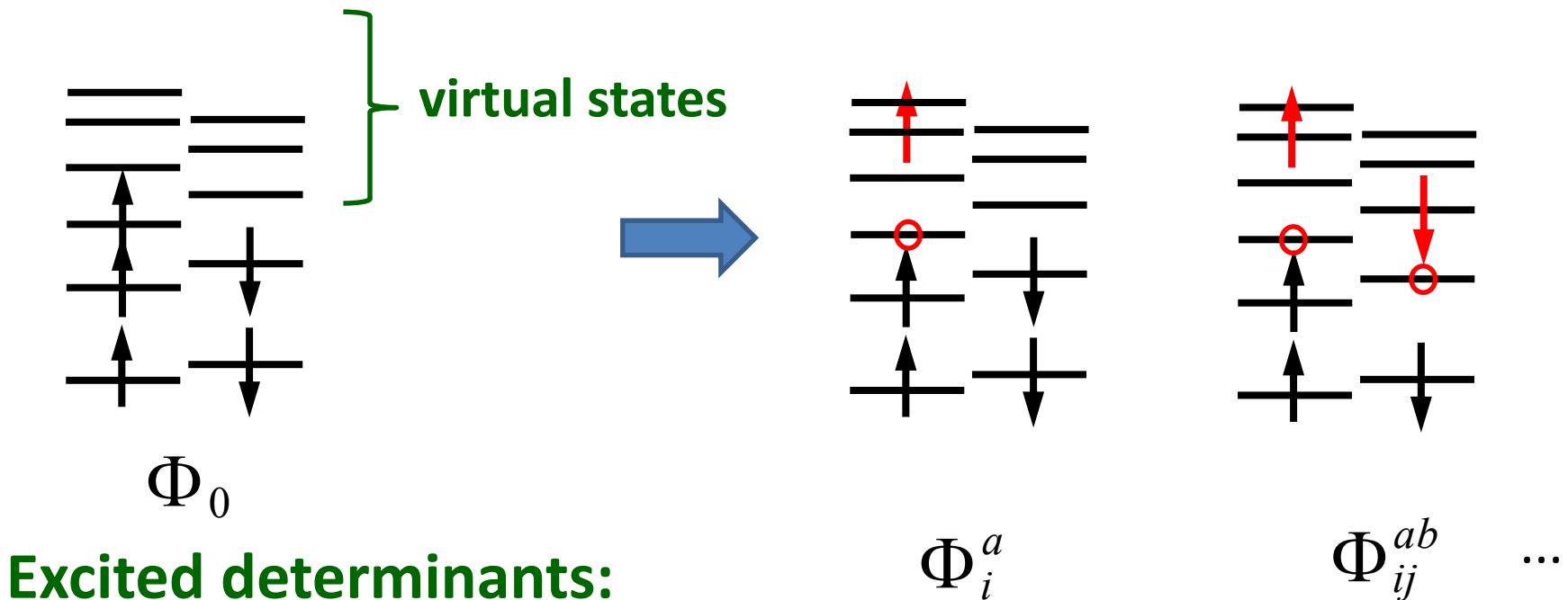
Finite-order perturbation theory

☐ **Møller-Plesset perturbation theory**

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

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

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

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

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

Brillouin's theorem

Finite-order perturbation theory

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Brillouin's theorem

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

Finite-order perturbation theory

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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**

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

Wavefunction first-order correction:

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

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

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

When this is a bad approximation?

Finite-order perturbation theory

☐ **Møller-Plesset perturbation theory**

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

Wavefunction first-order correction:

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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
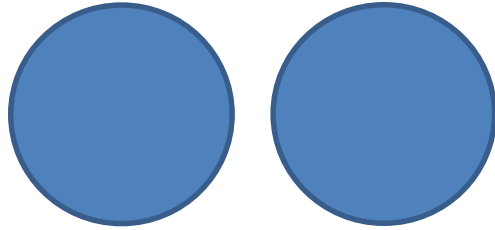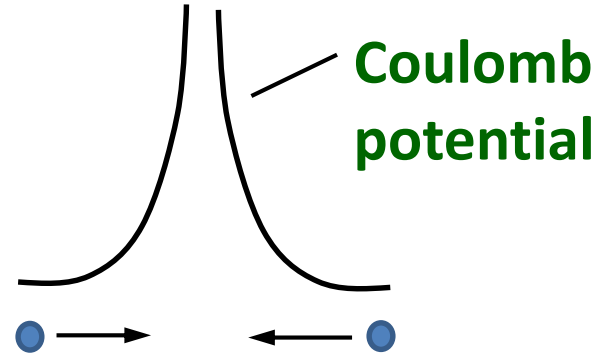
Dynamic correlation:

versus

Coulomb potential

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

Non-dynamic (static) correlation:
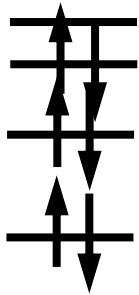
versus
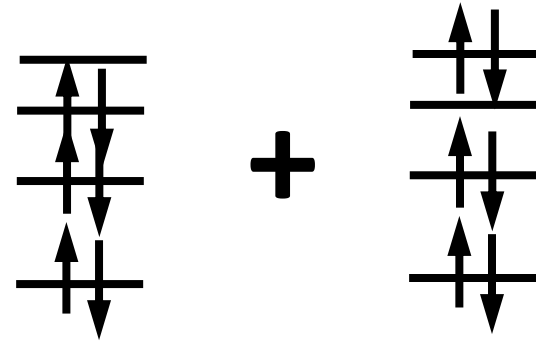
(quasi)degenerate HOMO-LUMO)

Configuration interaction

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

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

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

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

The concept of mixing excitations

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

$$\left| \Phi_0 \right\rangle = \quad , \quad \left| \Phi_1 \right\rangle = \quad + \quad , \quad \left| \Phi_2 \right\rangle = \quad + \quad , \quad \cdots$$
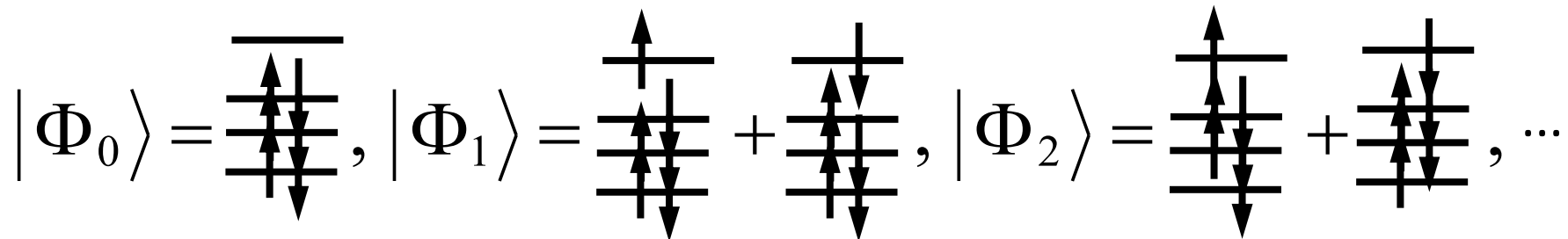
$$\{\Phi_i\}$$ **– a basis set for *N*-electron wave functions**

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

Project onto $\left\langle \Phi_k \right|$ **→ equations for** c_{ij} **:**

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

configuration interaction

Configuration interaction – matrix diagonalization

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

M orbitals

n-tuple excitations

Configuration interaction – matrix diagonalization

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

M orbitals
n-tuple excitations

$$
\begin{array}{c c c c c c c}
 & |\Phi_0\rangle & |S\rangle & |D\rangle & |T\rangle & |Q\rangle & \ldots \\
\langle\Phi_0| & \langle\Phi_0|\hat{H}|\Phi_0\rangle & \langle\Phi_0|\hat{H}|S\rangle & \langle\Phi_0|\hat{H}|D\rangle & 0 & 0 & \ldots \\
\langle S| & \langle S|\hat{H}|\Phi_0\rangle & \langle S|\hat{H}|S\rangle & \langle S|\hat{H}|D\rangle & \langle S|\hat{H}|T\rangle & 0 & \ldots \\
\langle D| & \langle D|\hat{H}|\Phi_0\rangle & \langle D|\hat{H}|S\rangle & \langle D|\hat{H}|D\rangle & \langle D|\hat{H}|T\rangle & \langle D|\hat{H}|Q\rangle & \ldots \\
\langle T| & 0 & \langle T|\hat{H}|S\rangle & \langle T|\hat{H}|D\rangle & \langle T|\hat{H}|T\rangle & \langle T|\hat{H}|Q\rangle & \ldots \\
\langle Q| & 0 & 0 & \langle Q|\hat{H}|D\rangle & \langle Q|\hat{H}|T\rangle & \langle Q|\hat{H}|Q\rangle & \ldots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \\
\end{array}
$$

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)

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: $\dfrac{M!}{(M-N)!\,N!}$

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

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

Truncated CI

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

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

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

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

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(CISD method)

Truncated CI: Properties

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

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

Trancated CI is *variational* ➔ $E \geq E_{\text{exact}}$

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):

$$E_{NA} = NE_A$$

This insures that the error per unit does not increase with system size
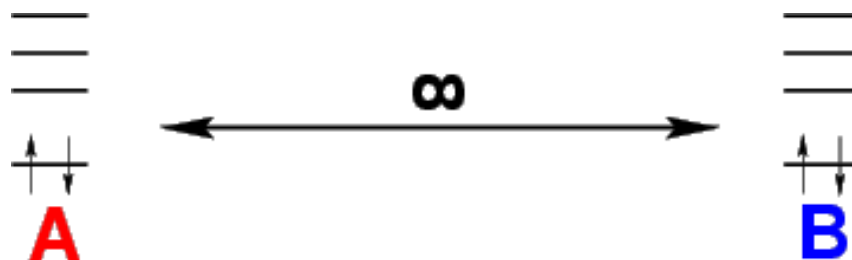
Hartree-Fock is size extensive

Approximate DFT is size extensive

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

Truncated CI is not size-extensive
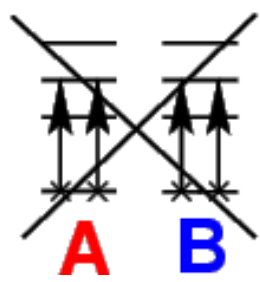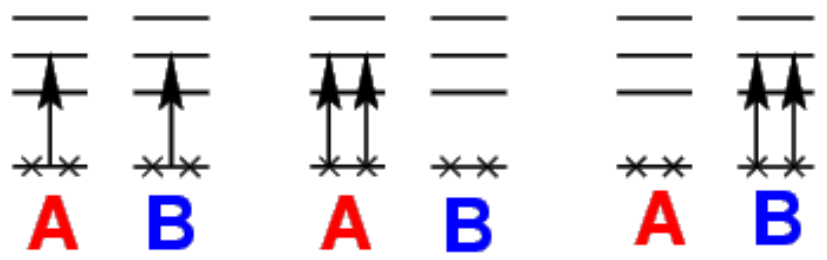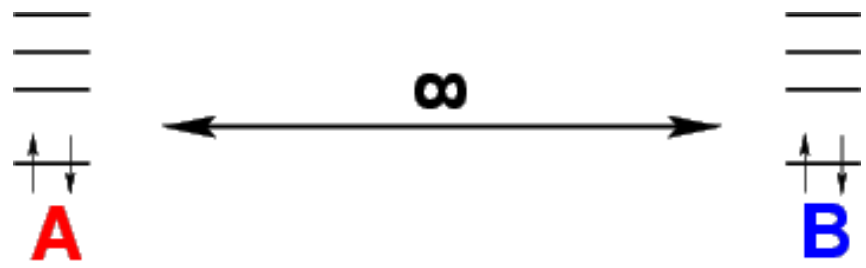
Truncated CI is not size-extensive
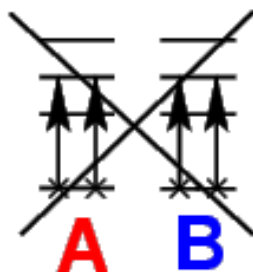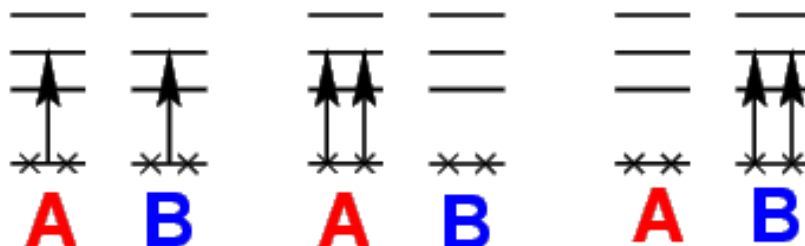
But full CI is size-extensive

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:

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

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

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

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

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

Coupled cluster theory

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

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

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

$$\Psi = (1 + \hat{T}_1 + \hat{T}_2 + \qquad\longleftarrow\qquad \textit{connected } \textbf{terms}$$

$$\frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \qquad \textit{disconnected } \textbf{terms}$$

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

(note: intermediate normalization above)

Formally, all excitations from Φ_0 are present

$t_{ij...}^{ab...}$ **are called *amplitudes***

Coupled-cluster equations

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

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

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

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

Amplitude equations:

$$\big\langle \Phi_i^a \big|\overline{H}\big|\Phi_0\big\rangle = 0,\ \big\langle \Phi_{ij}^{ab} \big|\overline{H}\big|\Phi_0\big\rangle = 0,...$$

-- as many equations as unknown amplitudes

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

Coupled-cluster equations

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

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

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

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

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

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,…)

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

Coupled-cluster
(CCD,CCSD,CCSDT,…)

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

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

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

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

MPm: ~$n N^{m+2}$

CC{m}: ~$n^m N^{m+2}$
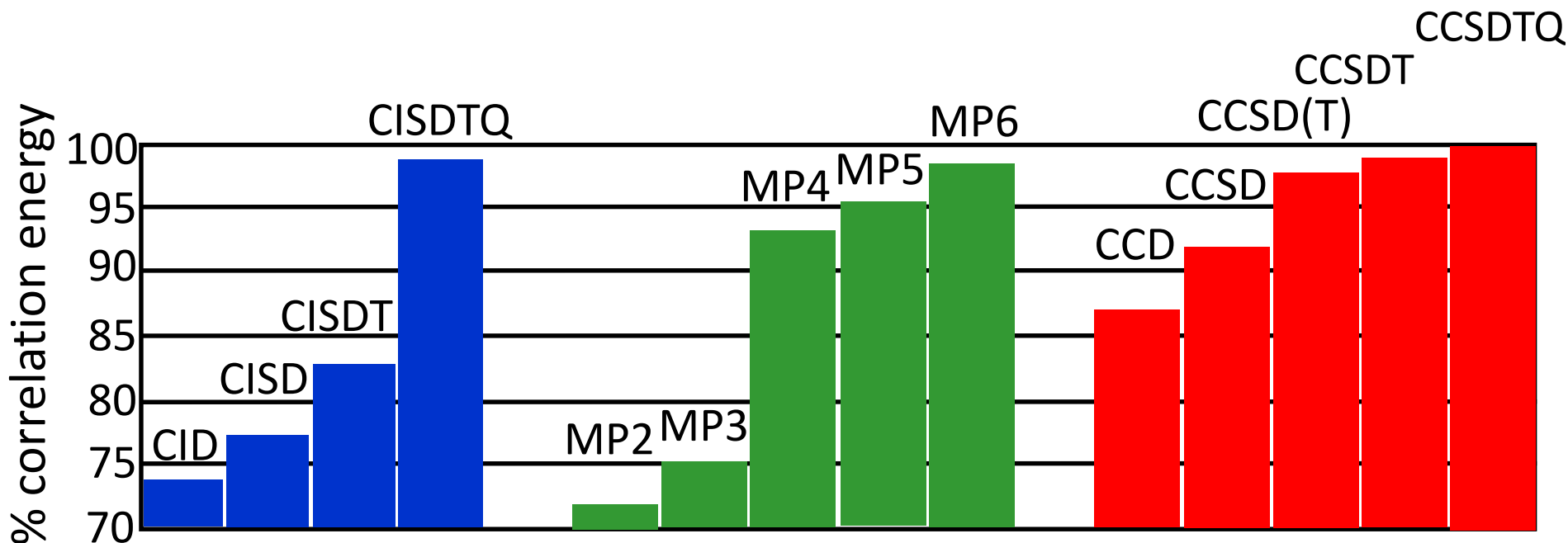
figure courtesy of R.J. Bartlett

The curse of non-dynamic correlation

(A)

$N_2 \rightarrow N + N$
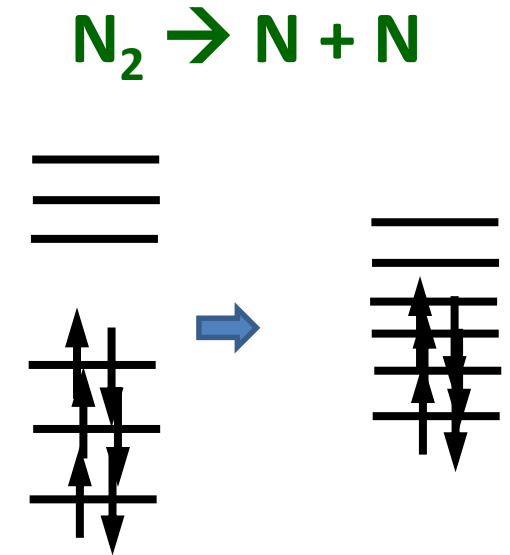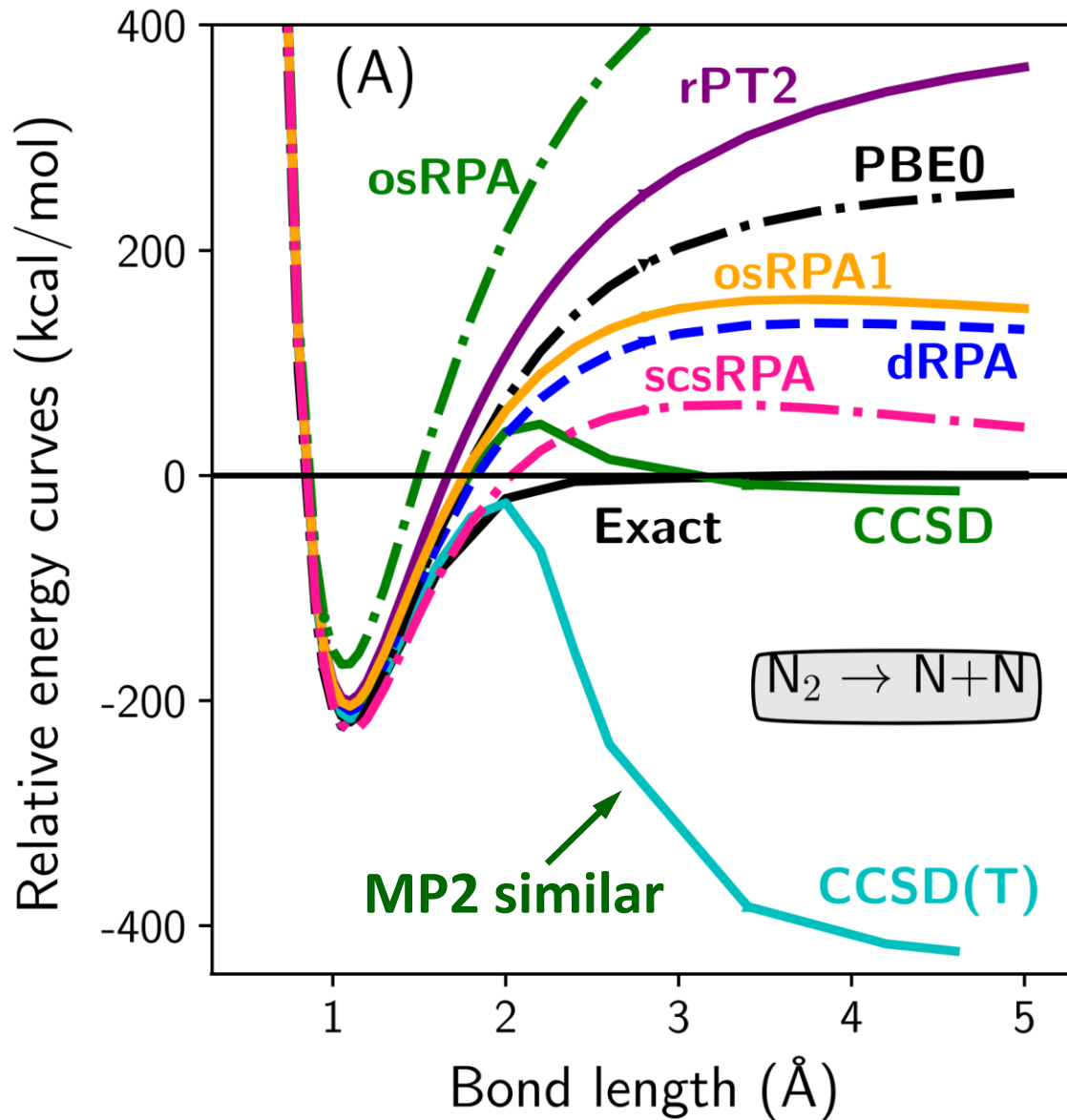
Non-dynamic correlation: reference determinant Φ is not a good starting point!

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

Multireference methods

Idea: include all degenerate determinants as a reference

$$\Psi^{(0)} = \quad C_1 \quad + \quad C_2 \quad + \quad C_3 \quad + \quad C_4$$

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

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

Multireference methods

Idea: include all degenerate determinants as a reference

$$\Psi^{(0)} = C_1 \quad + C_2 \quad + C_3 \quad + C_4$$
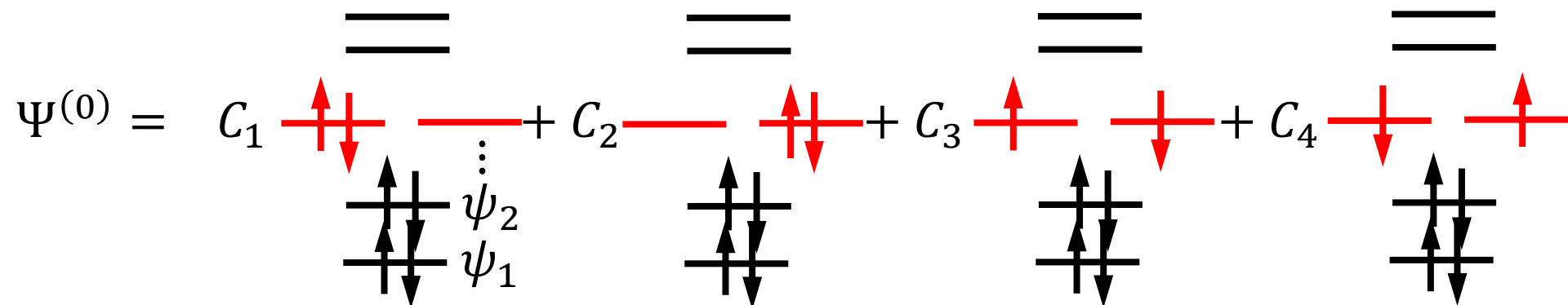
$$\min_{\psi_i, C_I} \frac{\langle \Psi^{(0)} | \widehat{H} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \rightarrow \psi_i, C_I$$

-- 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

$$\Psi^{(0)} = \quad C_1 \quad + \quad C_2 \quad + \quad C_3 \quad + \quad C_4$$
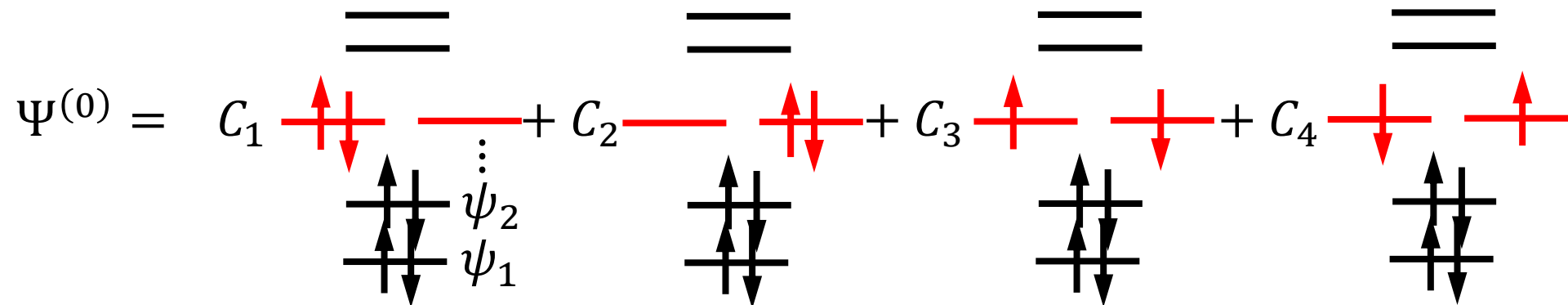
Complete active space SCF (CASSCF): All excitations within "active space"

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

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

MR-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

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

Wave function methods: Summary
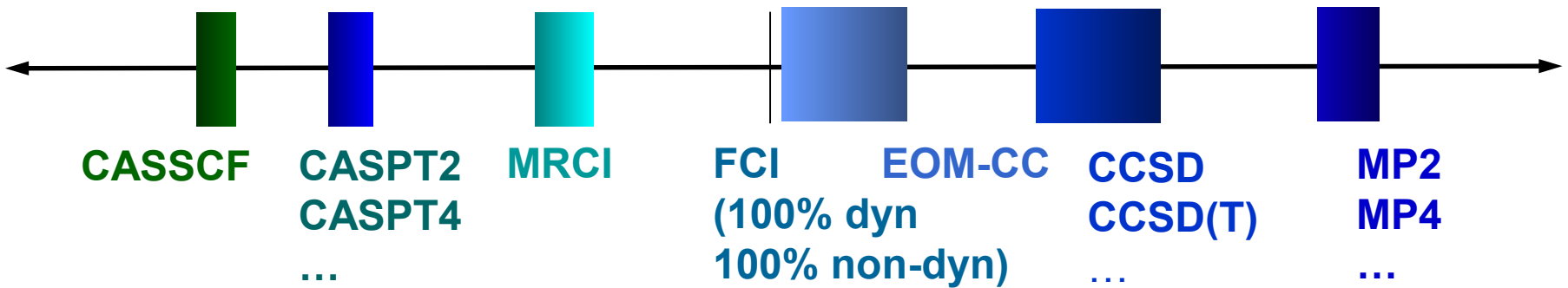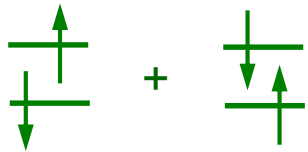
A potential breakthrough:
Wavefunction and other methods
on quantum computers

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)