

Computational Chemistry and Materials Modeling

Hartree-Fock method and beyond

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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 $4N$ variables (spatial + spin)
- electrons interact via Coulomb forces

Ground-state electronic structure problem

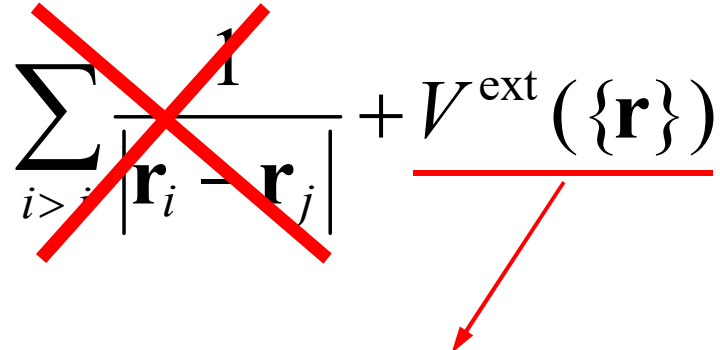
$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} - \sum_i \sum_J \frac{Z_J}{|\mathbf{r}_i - \mathbf{R}_J|} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + V^{\text{ext}}(\{\mathbf{r}\})$$

Ground-state electronic structure problem

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

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

Ground-state electronic structure problem

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


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



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

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

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

Variational principle

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



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

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

**Observation: minimization of E with respect to $\Psi \rightarrow$
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

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



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

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

**Observation: minimization of E with respect to $\Psi \rightarrow$
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:

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

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: $\Psi(\{\mathbf{r}\}) = \prod_i \psi_i(\mathbf{r}_i)$

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

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



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

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

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

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

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

However,

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

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:
can occupy the same
quantum state

Fermions versus bosons

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

fermions:
*cannot occupy the same
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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)



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

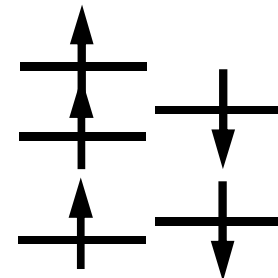
$$\Psi(\{\mathbf{r}\}, \{\sigma\}) = \frac{1}{\sqrt{N!}} \sum_{\mathbf{q}} (-1)^{n(\mathbf{q})} \hat{P}_{\mathbf{q}} \left[\prod_i \psi_i(\mathbf{r}_{q_i}) s_i(\sigma_{q_i}) \right]$$



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

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

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

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

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

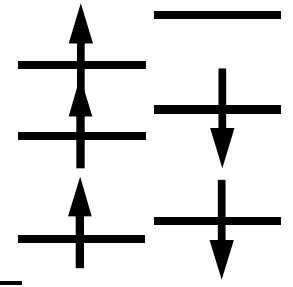
$$\hat{h}\psi_i = \left(-\frac{1}{2} \nabla^2 + V_{\text{ext}} \right) \psi_i \quad \hat{U}_k \psi_i = \int d^3r' \frac{|\psi_k(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r})$$

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

The Hartree-Fock (HF) approximation

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

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

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


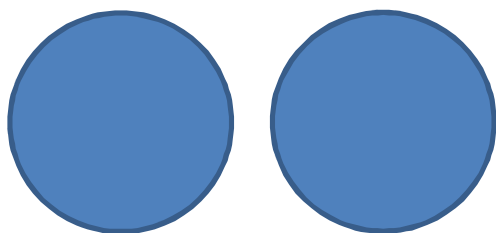
The diagram shows two vertical columns of three horizontal lines representing energy levels. The left column has three upward-pointing arrows (↑) on each level. The right column has three downward-pointing arrows (↓) on each level. This represents a spin-up and spin-down configuration for each of the three energy levels.

HF (exact) exchange energy

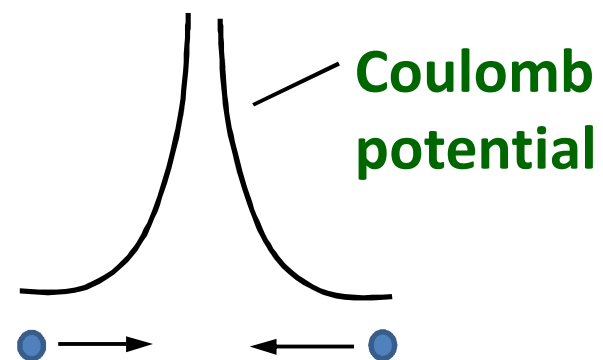
- No self-interaction
- Coulomb mean-field → no dynamic correlation, single determinant → no static correlation

Two types of correlation

Dynamic correlation:

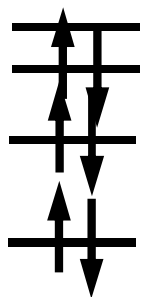


versus

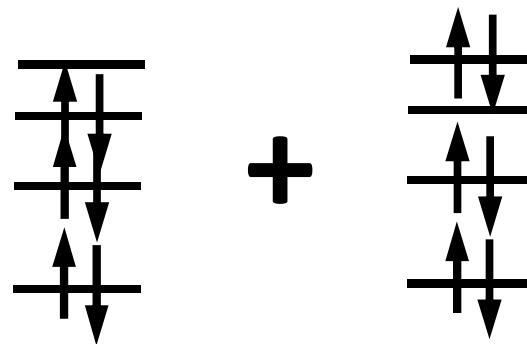


smaller e density, large $\partial\psi / \partial\mathbf{r}$

Non-dynamic (static) correlation:



versus



(quasi)degenerate HOMO-LUMO

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

Solution of Hartree-Fock equations

Fock operator

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

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

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

Solution of Hartree-Fock equations

Fock operator

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

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

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

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

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

Approximations to the electronic problem: Basis set

Idea: represent all unknown functions ($\rho(\mathbf{r})$, $\psi_i(\mathbf{r})$) as a linear combination of known functions with well-defined properties:

$$\psi_i(\mathbf{r}) = \sum_p C_{ip} \varphi_p(\mathbf{r})$$

Widely used basis sets:

gaussians $x^i y^j z^k \exp(-\alpha r^2)$ (localized, analytic integrals)

plane waves $\exp(i\mathbf{k} \cdot \mathbf{r})$ (delocalized, analytic integrals)

Slater-type $x^i y^j z^k \exp(-\alpha r)$ (localized, nuclear cusp)

grid-based $\delta(\mathbf{r} - \mathbf{r}_i)$ (localized, analytic integrals)

Core electrons are often treated separately
(pseudopotentials, plane-wave + localized basis)

Solution of Hartree-Fock equations

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

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



$$\sum_{\alpha} c_{\alpha i} \langle \phi_{\beta} | \hat{f}[\mathbf{c}] | \phi_{\alpha} \rangle = \varepsilon_i \sum_{\alpha} c_{\alpha i} \langle \phi_{\beta} | \phi_{\alpha} \rangle$$

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



Need to solve ITERATIVELY!

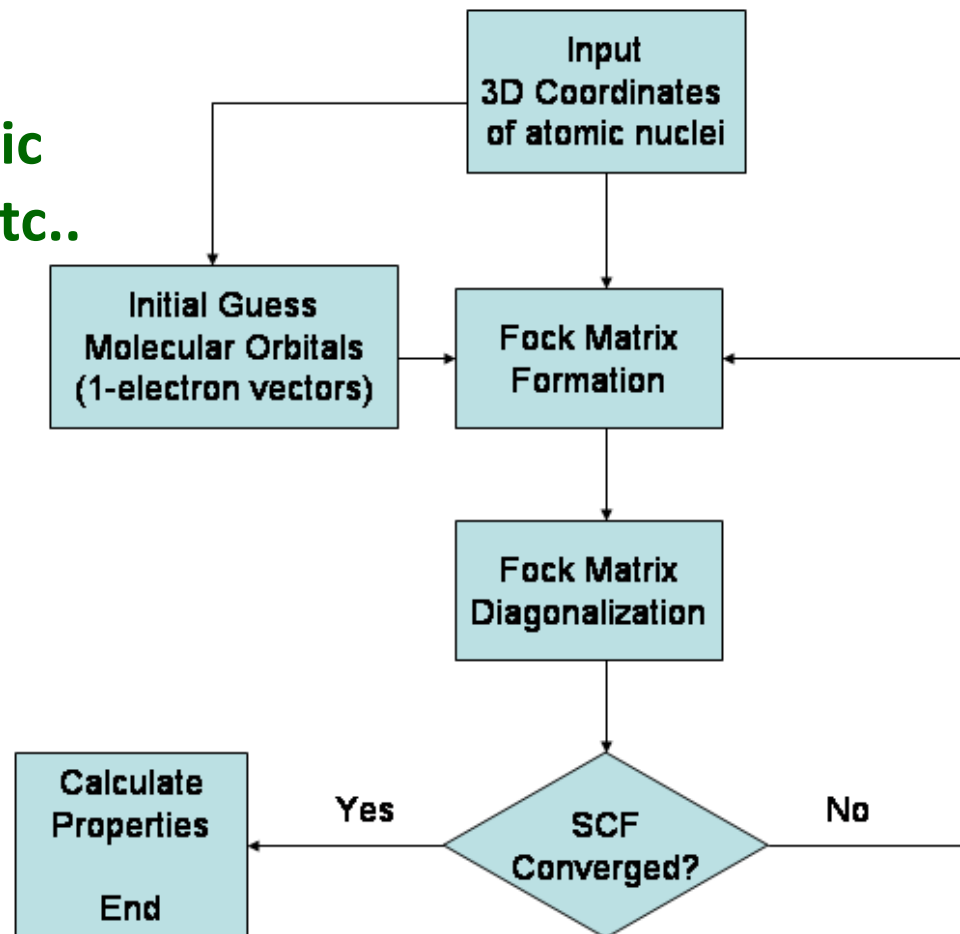
Self-consistent field (SCF) cycle

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

Convergence criteria: change in energy $< \dots$, change in density $< \dots$, change in forces $< \dots$

If the guess is not good, convergence can be problematic: mix new and previous density

matrices: $\tilde{D}_{\alpha\beta}^{j+1} = \omega D_{\alpha\beta}^{j+1} + (1 - \omega) D_{\alpha\beta}^j$ (or more - Pulay mixing)



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:

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

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

Finite-order perturbation theory

□ Møller-Plesset perturbation theory (MP n)

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

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

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

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

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

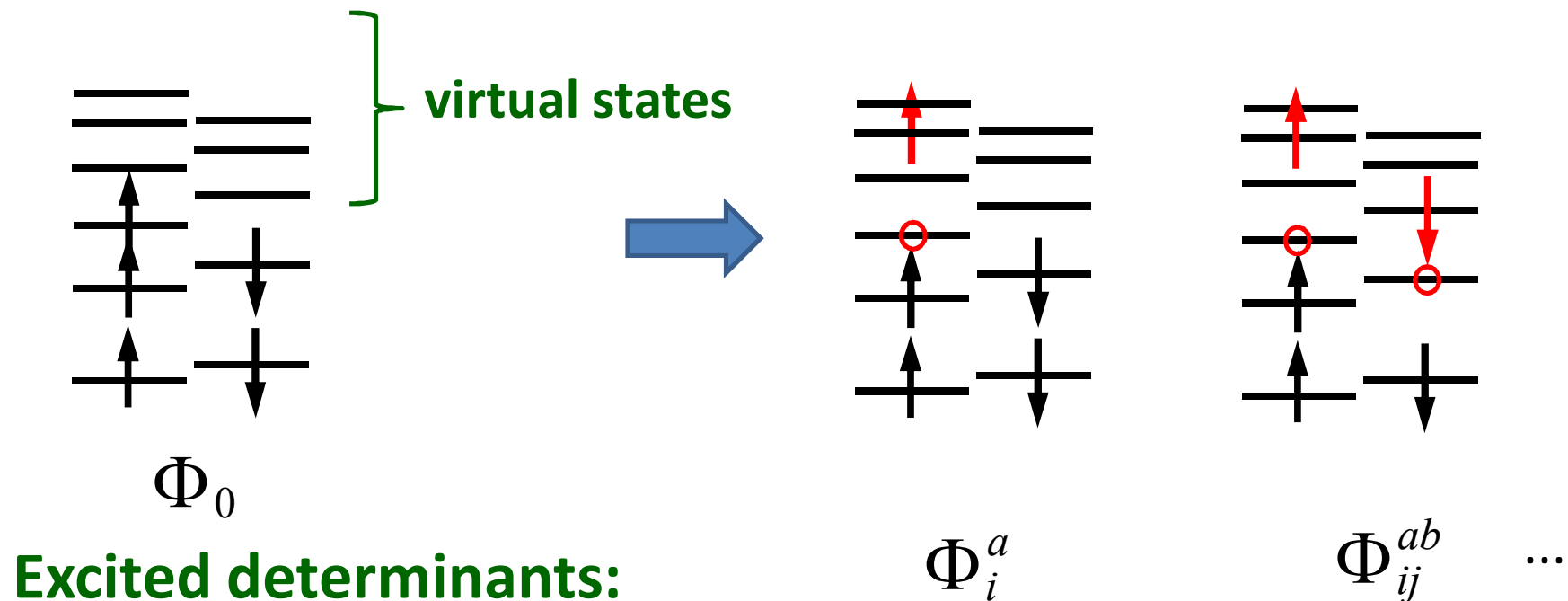
$$\longrightarrow E_0^{(0)} + E_0^{(1)} = \langle \Phi | \hat{H} | \Phi \rangle \text{ -- Hartree-Fock energy}$$

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

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

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

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



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

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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

Finite-order perturbation theory

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Brillouin's theorem

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

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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

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



$$E^{(2)} = \frac{1}{4} \sum_{ij,ab} \frac{|\langle \Phi | \hat{H} | \Phi_{ij}^{ab} \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \text{MP2 energy correction}$$

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

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

When this is a bad approximation?

Finite-order perturbation theory

□ Møller-Plesset perturbation theory

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

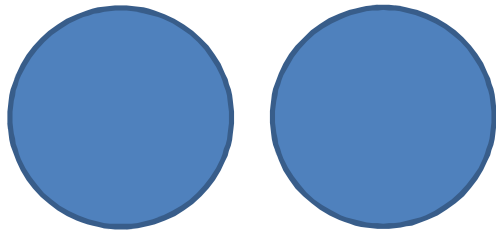
Wavefunction first-order correction:

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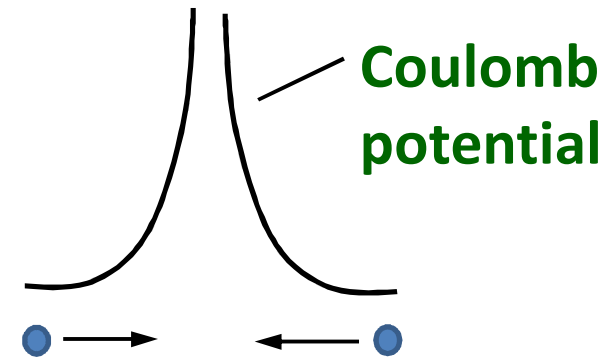
- 1) A linear combination of determinants
- 2) Single excitations do not contribute at first order (Brillouin's theorem), but they do contribute at higher orders
- 3) Higher excitations at higher orders
- 4) Fails when HOMO and LUMO are close -- higher-order terms are needed, wavefunction is not a single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

Two types of correlation

Dynamic correlation:

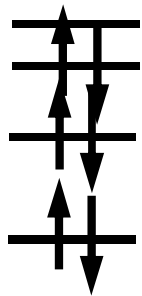


versus

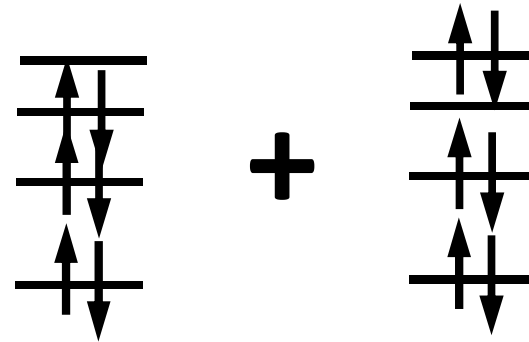


smaller e density, large $\partial\psi / \partial\mathbf{r}$

Non-dynamic (static) correlation:



versus



(quasi)degenerate HOMO-LUMO

Configuration interaction

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

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

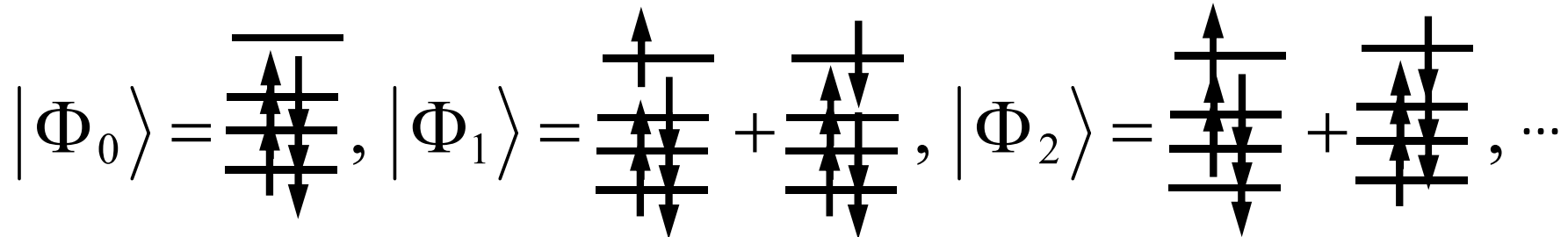
$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \rightarrow \min \Rightarrow \frac{\partial E}{\partial\{C\}} = 0$$



$$\mathbf{HC} = \mathbf{EC}$$

The concept of mixing excitations

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



$\{\Phi_i\}$ – 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 $\langle \Phi_k | \rightarrow$ 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

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

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

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

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

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):

$$E_{NA} = NE_A$$

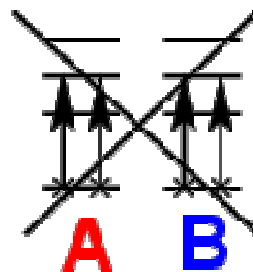
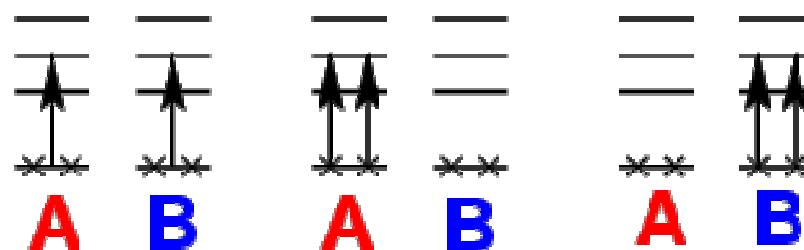
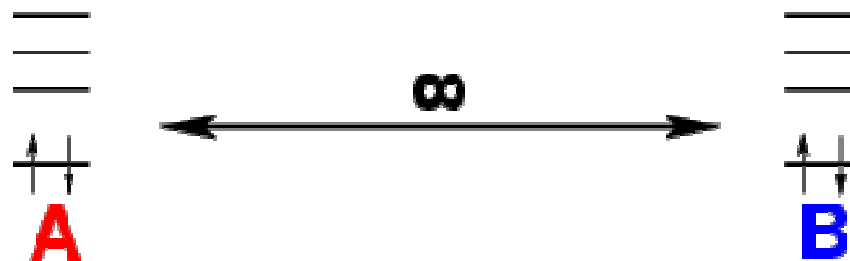
This insures that the error per unit does not increase with system size

Hartree-Fock is size extensive

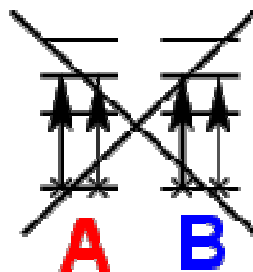
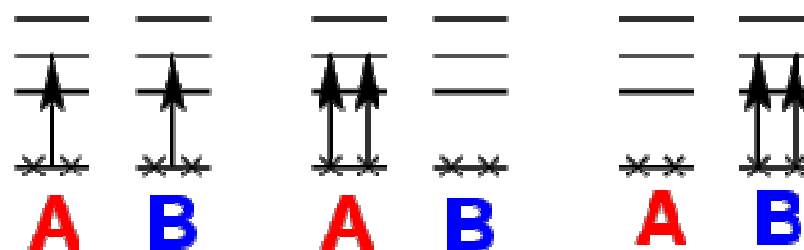
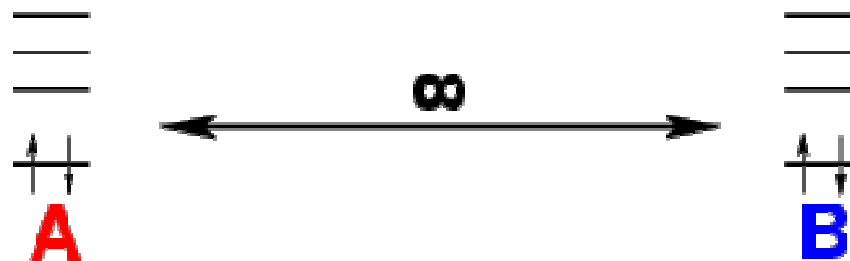
Approximate DFT is size extensive

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

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
 \leftarrow
 \hat{T}_2

$$\Psi = (1 + \hat{T}_1 + \hat{T}_2 + \leftarrow \text{connected terms}$$

$$\frac{1}{2} \hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 + \rightarrow \text{disconnected terms}$$

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

(note: intermediate normalization above)

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

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

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

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

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

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

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,...)

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

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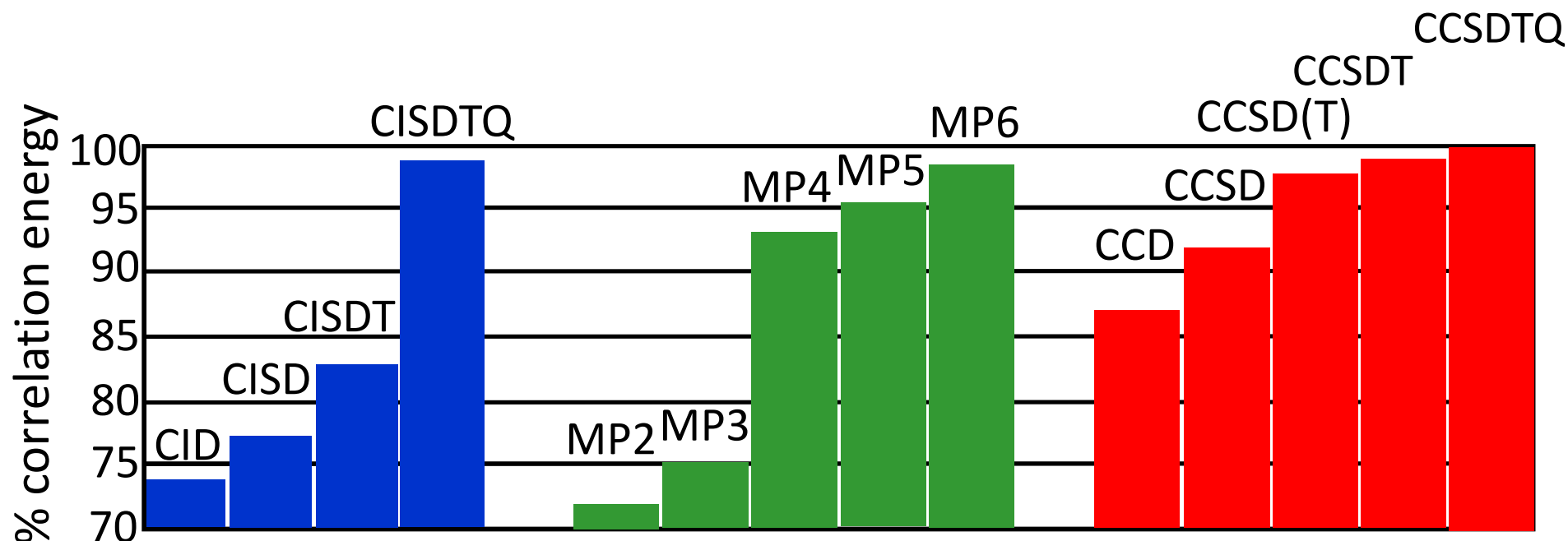
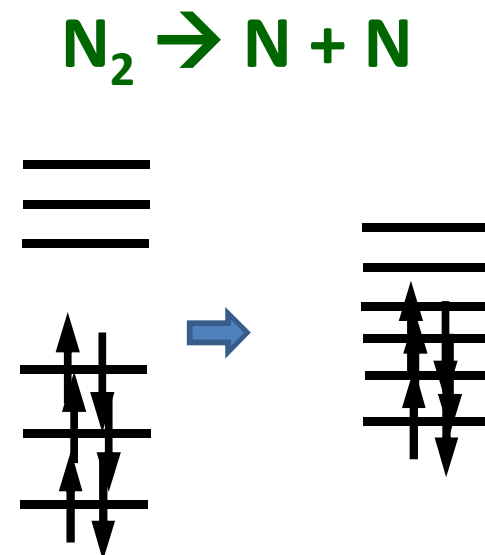
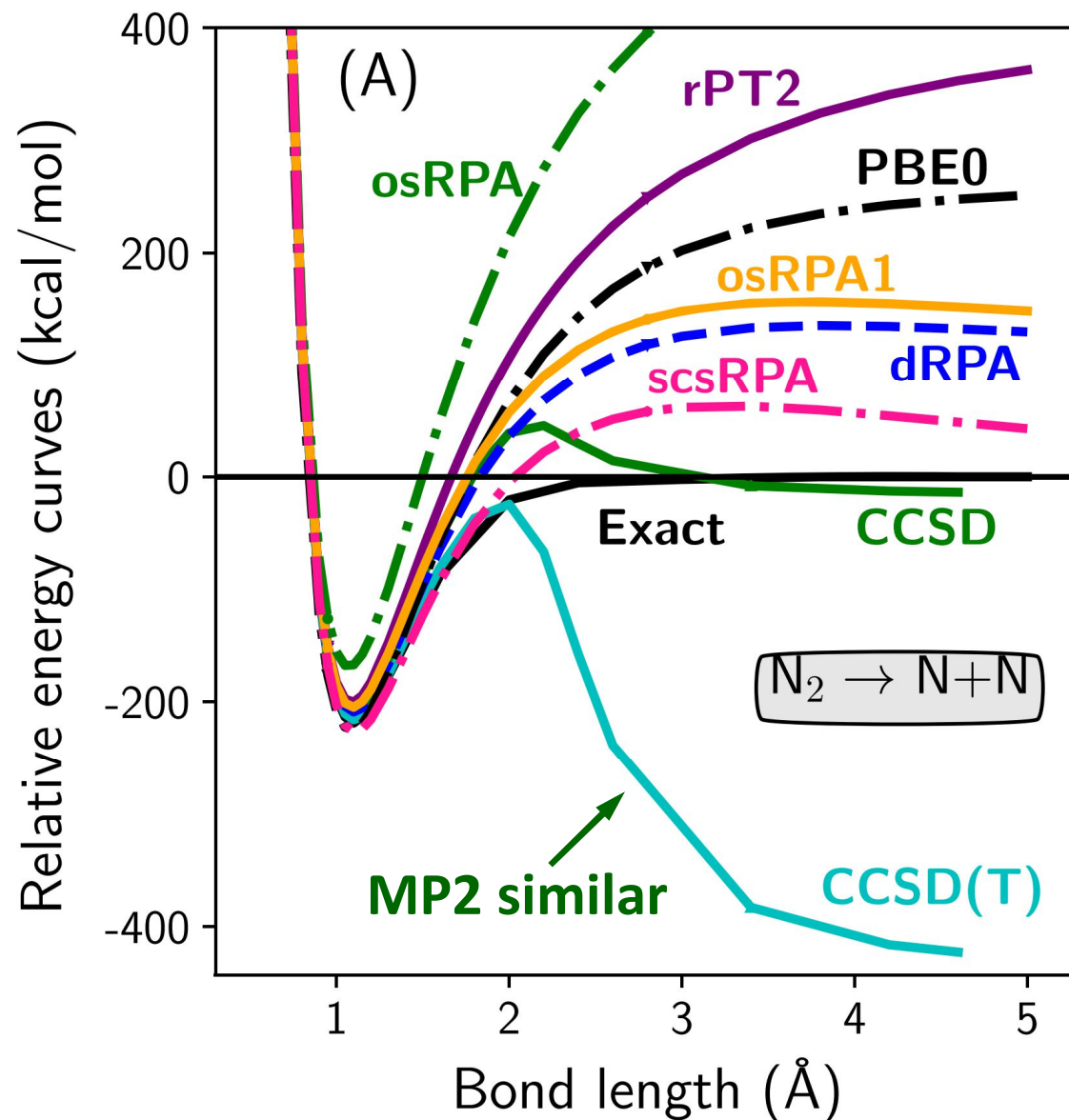


figure courtesy of R.J. Bartlett

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

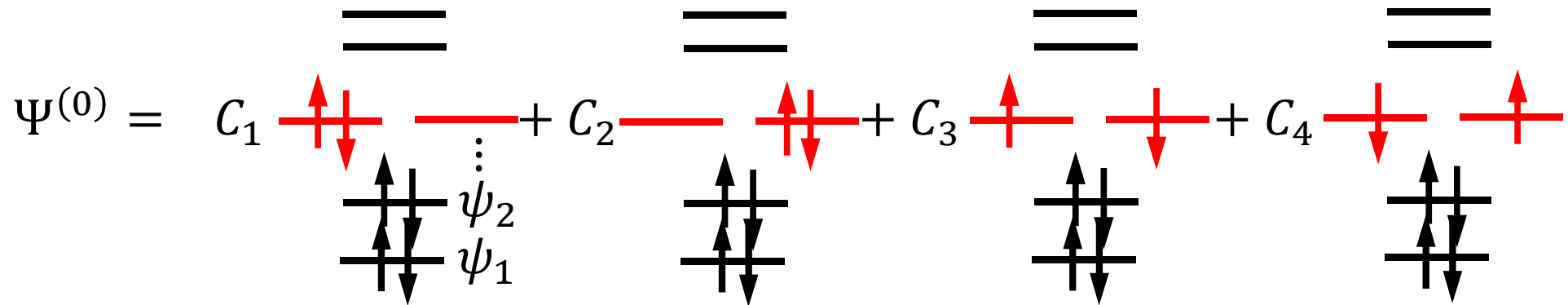
$$\Psi^{(0)} = C_1 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \vdots \\ \uparrow \downarrow \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \psi_2 \\ \uparrow \downarrow \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \psi_1 \end{array} + C_2 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \vdots \\ \uparrow \downarrow \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \psi_2 \\ \uparrow \downarrow \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \psi_1 \end{array} + C_3 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \vdots \\ \uparrow \downarrow \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \psi_2 \\ \uparrow \downarrow \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \psi_1 \end{array} + C_4 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \vdots \\ \uparrow \downarrow \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \psi_2 \\ \uparrow \downarrow \\ \text{---} \\ \uparrow \downarrow \\ \text{---} \\ \psi_1 \end{array}$$

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

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

Multireference methods

Idea: include all degenerate determinants as a reference



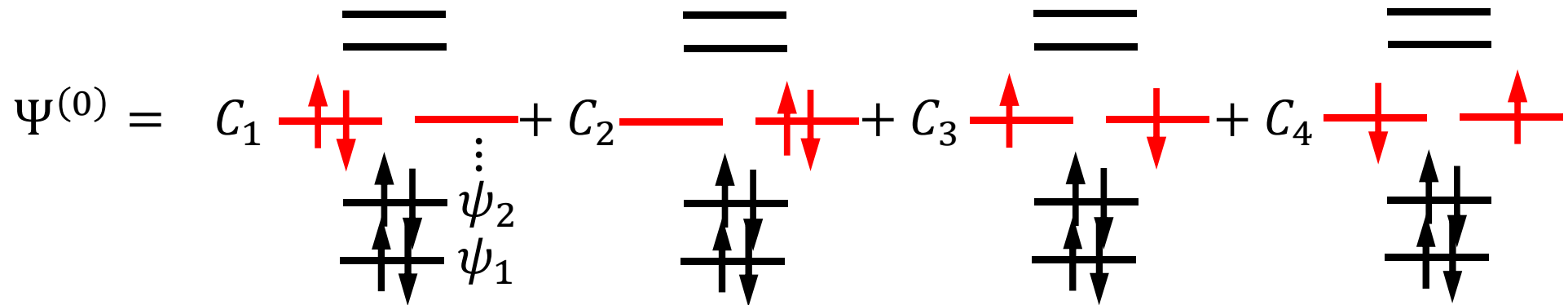
$$\min_{\psi_i, C_I} \frac{\langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \rightarrow \psi_i, C_I$$

-- 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: 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)

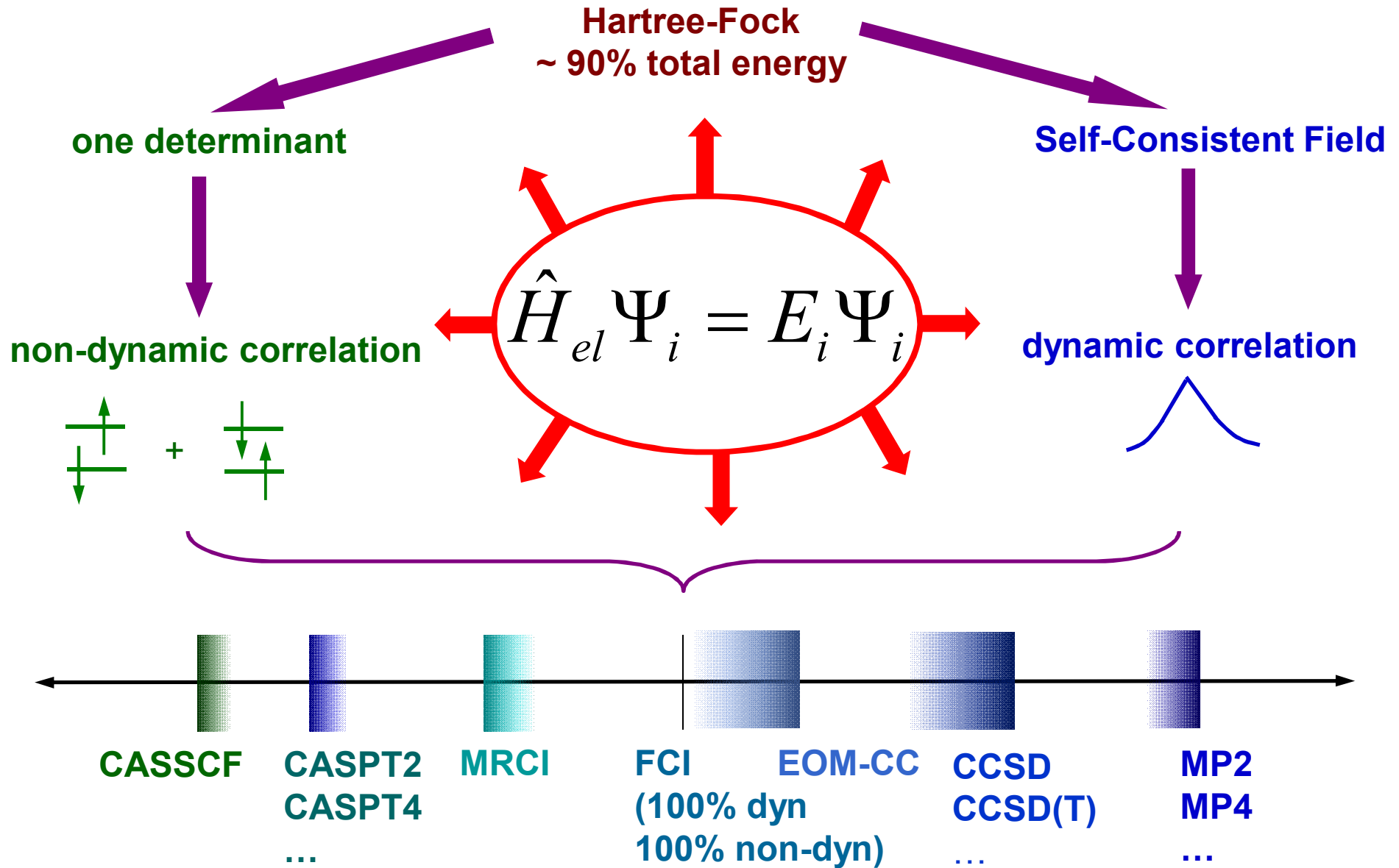
Free:

CP2K (MP2)

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

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

Wave function methods: Summary



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)**