

Electron correlation in quantum chemistry

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Electronic Schrödinger equation

$$\hat{\mathbf{H}}\Psi(r_1, \dots, r_N) = E\Psi(r_1, \dots, r_N)$$

- **Target:** Solve the electronic Schrödinger equation for a many electron (N) problem
- The exact solutions are arbitrary functions depending on $3N$ coordinates
- How can we approximate these solutions?

Hartree product

$$\Psi_H(r_1, \dots, r_N) = \phi_1(r_1)\phi_2(r_2)\dots\phi_N(r_N)$$

- write the many electron function as a product of one electron functions (MOs)
 - MOs typically formed as linear combinations of atomic basis functions (AOs)
- electrons in this case are completely statistically independent „uncorrelated“
- **problem:** this form violates the Pauli principle for Fermions – the wave function has to be antisymmetric

Hartree-Fock

$$\begin{aligned}\Psi_{HF}(r_1, \dots, r_N) &= \hat{\mathbf{A}}\Psi_H(r_1, \dots, r_N) = \\ &= \hat{\mathbf{A}}\phi_1(r_1)\dots\phi_N(r_N) \\ &= \frac{1}{\sqrt{N!}} \sum_{\pi \in S_n} \text{sgn}(\pi) \phi_{\pi(1)}(r_1)\dots\phi_{\pi(N)}(r_N)\end{aligned}$$

- antisymmetrize the Hartree product and form a Slater determinant
- in other words: the antisymmetric wave function is constructed as a sum of Hartree products

Hartree-Fock

- Pauli principle fulfilled
- but: very stiff functional form
 - there is no reason to assume that the exact solution has this product form
 - in particular no correlation between electrons is included

Configuration interaction

- Natural extension: include virtual orbitals into wave function
 - create excited determinants to improve the wave function

$$\Psi_i^b = \hat{\mathbf{a}}_b^T \hat{\mathbf{a}}_i \Psi_{HF} = \hat{\mathbf{A}} \phi_1 \dots \phi_{i-1} \phi_b \phi_{i+1} \dots \phi_N$$

$$\Psi_{ij}^{bc} = \hat{\mathbf{a}}_b^T \hat{\mathbf{a}}_c^T \hat{\mathbf{a}}_j \hat{\mathbf{a}}_i \Psi_{HF}$$

Configuration interaction

- New wave function ansatz
 - wave function written as a sum of excited determinants
 - d coefficients have to be determined
 - truncation at some excitation level
- Example CISD

$$\Psi_{CISD} = d_0 \Psi_{HF} + \sum_{\substack{i \in O \\ b \in U}} d_i^b \Psi_i^b + \sum_{\substack{i, j \in O \\ b, c \in U}} d_{ij}^{bc} \Psi_{ij}^{bc}$$

Configuration interaction

- Computational procedure
 - diagonalize the CI matrix
 - usually iterative procedure to find the lowest root(s)

CI matrix

Matrix with elements of the form

$$\langle \Psi_k | \hat{H} | \Psi_l \rangle$$

where Ψ_k and Ψ_l are any Slater determinants used in the expansion

the matrix elements can be evaluated from MO-integrals

Perturbation theory

- Perturbation theory
 - general strategy in computational chemistry and physics
 - split the Hamiltonian into $\hat{\mathbf{H}} = \hat{\mathbf{H}}_0 + \lambda\hat{\mathbf{H}}'$
where solutions to \mathbf{H}_0 are available
 - total solution approximated as a Taylor series in λ
 - approximation given to any given order in this Taylor series

Moller-Plesset PT

- Choice for \mathbf{H}_0
 - non-interacting Hartree-Fock Hamiltonian (some of Fock operators)
- first correction at second order
 - MP2
 - widely used efficient ground state method
- higher orders also sometimes used
 - MP3, MP4

Moller-Plesset PT

- Energy expression
 - quadruple sum over MO integrals

$$E^{(2)} = \frac{1}{4} \sum_{\substack{i>j \in O \\ b>c \in U}} \frac{\left| \left\langle \phi_i(r_1)\phi_j(r_2) \left| \frac{1}{r_{12}} \right| \phi_b(r_1)\phi_c(r_2) - \phi_c(r_1)\phi_b(r_2) \right\rangle \right|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_b - \varepsilon_c}$$

Coupled Cluster

- Define excitation operators

$$\hat{\mathbf{T}} = \hat{\mathbf{1}} + \hat{\mathbf{T}}_1 + \hat{\mathbf{T}}_2 + \dots$$

$$\hat{\mathbf{T}}_1 = \sum_{\substack{i \in O \\ b \in U}} d_i^b \hat{\mathbf{a}}_b^T \hat{\mathbf{a}}_i$$

$$\hat{\mathbf{T}}_2 = \sum_{\substack{i, j \in O \\ b, c \in U}} d_{ij}^{bc} \hat{\mathbf{a}}_b^T \hat{\mathbf{a}}_c^T \hat{\mathbf{a}}_j \hat{\mathbf{a}}_i$$

Coupled Cluster

- Use an exponential ansatz
 - provides „disconnected“ higher excitations
 - size consistent, extensive

$$\Psi_{CI} = \hat{\mathbf{T}}\Psi_{HF}$$

$$\Psi_{CC} = \exp(\hat{\mathbf{T}})\Psi_{HF}$$

Coupled Cluster

- Energy expression

$$E_{CC} = E_0 + \sum_{\substack{i < j \in O \\ b < c \in U}} \left(d_{ij}^{bc} + d_i^b d_j^c - d_i^c d_j^b \right) \left(\langle \phi_i(r_1) \phi_j(r_2) | \frac{1}{r_{12}} | \phi_b(r_1) \phi_c(r_2) - \phi_c(r_1) \phi_b(r_2) \rangle \right)$$

similar to MP2, but with different amplitudes

Coupled Cluster

- Amplitudes derived from projection equations
 - solved iteratively
 - non-variational procedure

$$\langle \Psi_{i\dots}^{b\dots} | \exp(-\mathbf{T}) \mathbf{H} \exp(\mathbf{T}) | \Psi_{HF} \rangle = 0$$

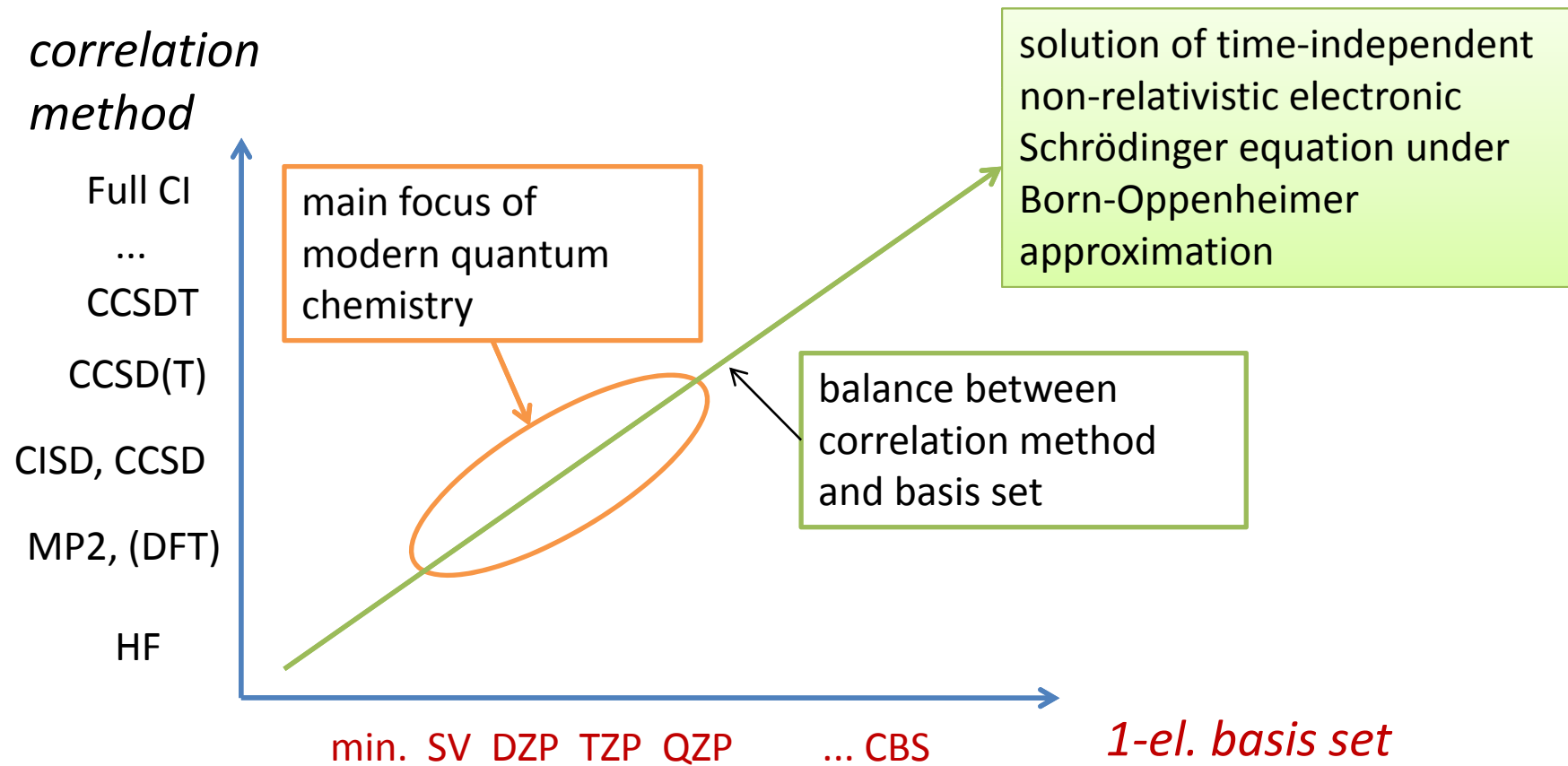
Summary of methods

Scaling	CI method	MP method	CC method
M^3, M^4	<i>HF, DFT</i>		
M^5	CIS	MP2	CC2
M^6	CISD	MP3	CCSD
M^7		MP4	CC3, CCSD(T)
M^8	CISDT	MP5	CCSDT
M^9		MP6	
M^{10}	CISDTQ	MP7	CCSDTQ

at the same level: CC methods usually longer than CI by a constant factor

combinations of CC and perturbation theory as steps between full CC methods

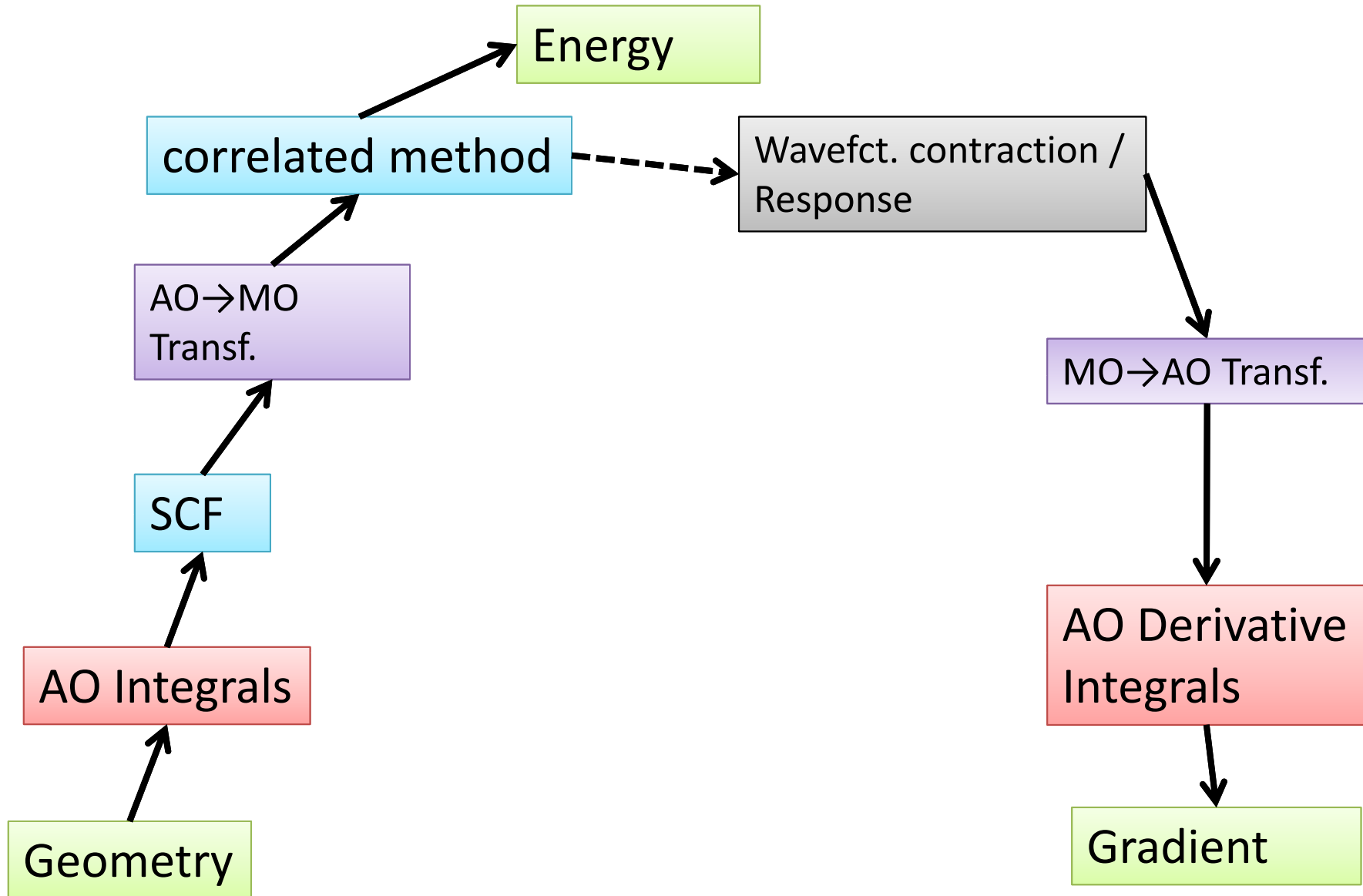
Comparison of methods



Extensions:

1. relativistic effects
2. dynamical effects (including post Born-Oppenheimer couplings)

General calculation scheme



Literature

- „Introduction to Computational Chemistry“, Frank Jensen, 2007, Wiley.