Quantitative quantum chemistry: Introduction to wave-function methods

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`www.lct.jussieu.fr/pagesperso/toulouse/enseignement/presentation_wft.pdf`

Why and how learning wave-function methods?

Understanding the different **quantum-chemistry wave-function methods** is important for:

- improving them and developing new ones;
- using them in applications in an appropriate way.

Recommended books:

- J.-L. Rivail, *Éléments de chimie quantique à l'usage des chimistes*, EDP Sciences / CNRS Editions, 1999.
- G. Berthier, *Nécessaire de chimie théorique*, Ellipses, 2009.
- **A. Szabo and N. S. Ostlund, Modern Quantum Chemistry, Dover Publications Inc., NY, 1996.**
- T. Helgaker, P. Jørgensen, J. Olsen, *Molecular Electronic-Structure Theory*, Wiley, 2002.

My lecture notes:

- M1 course: `www.lct.jussieu.fr/pagesperso/toulouse/enseignement/introduction_qc.pdf`
- M2 course: `www.lct.jussieu.fr/pagesperso/toulouse/enseignement/introduction_pt_cc.pdf`

Outline

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1. Introduction
   - Quantum many-electron problem
   - The two families of electronic-structure methods

The Hamiltonian and the many-electron wave function

- We consider an N-**electron system** (atom, molecule, solid) in the Born-Oppenheimer and non-relativistic approximations.
- The **electronic Hamiltonian** in the position representation is, in atomic units,

$$\hat{H} = \sum_{i}^{N} \hat{h}(\mathbf{r}_i) + \frac{1}{2} \sum_{i}^{N} \sum_{j \neq i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

  where $\hat{h}(\mathbf{r}_i) = -(1/2)\nabla^2_{\mathbf{r}_i} + v_{\text{ne}}(\mathbf{r}_i)$ is the one-electron Hamiltonian including the nuclei-electron interaction $v_{\text{ne}}(\mathbf{r}_i) = -\sum_\alpha Z_\alpha/|\mathbf{r}_i - \mathbf{R}_\alpha|$.
- Stationary states satisfy the **time-independent Schrödinger equation**

$$\hat{H}\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$$

  where $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$ is a wave function written with space-spin coordinates $\mathbf{x}_i = (\mathbf{r}_i, \omega_i)$ (with $\mathbf{r}_i \in \mathbb{R}^3$ and $\omega_i \in \{\uparrow,\downarrow\}$) and E is the associated energy.
- Because electrons are fermions, the wave function must be **antisymmetric** with respect to the exchange of two space-spin coordinates

$$\Psi(..., \mathbf{x}_i, ..., \mathbf{x}_j, ...) = -\Psi(..., \mathbf{x}_j, ..., \mathbf{x}_i, ...)$$

- Using **Dirac bra-ket notations**, we write

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

The ground-state electronic energy and other properties

- The **ground-state electronic energy** E_0 can be expressed with the **variational principle**

$$\boxed{E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle}$$

  where the minimization is over all N-electron antisymmetric wave functions Ψ normalized to unity $\langle \Psi | \Psi \rangle = 1$, and we recall that

$$\langle \Psi | \hat{H} | \Psi \rangle = \int\int \cdots \int \Psi^*(\mathbf{x}_1, \cdots, \mathbf{x}_N) \hat{H} \Psi(\mathbf{x}_1, \cdots, \mathbf{x}_N) \, \mathrm{d}\mathbf{x}_1 \cdots \mathrm{d}\mathbf{x}_N$$

- Properties (such as dipole moments or optical spectra) can be essentially obtained as **derivatives of the ground-state energy with respect to a perturbation**.

- For systems containing heavy atoms, we need to include **relativistic effects**, e.g. using the four-component Dirac Hamiltonian.

- For photochemistry studies, we sometimes need to go **beyond the Born-Oppenheimer approximation**, e.g. calculating non-adiabatic couplings (or vibronic couplings) between the electronic and nuclear vibrational states.

- We aim at about **1% accuracy** on energy differences and other properties.

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Computational electronic-structure methods

- There are **two main families of computational electronic-structure methods**: **wave-function methods** and **density-functional theory**.

- **Wave-function methods** directly try to approximate the wave function of a state of the system.
    - A hierachy of methods: Hartree-Fock, Configuration interaction, Perturbation theory, Coupled-cluster theory, ...
    - In principle, systematically improvable up to high accuracy
    - But computationally costly

- **Density-functional theory** is based on a reformulation of the problem by expressing the energy as a functional of the one-electron density.
    - A plethora of approximate density functionals
    - Reasonably low computational cost
    - But not systematically improvable

- Both wave-function methods and density-functional theory are **still actively developed** to improve accuracy and/or lower the computational cost.

- We may add a less used yet powerful family of methods known as **quantum Monte Carlo** which use stochastic techniques to solve the Schrödinger equation.

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2 The Hartree-Fock method

- The Hartree-Fock wave function and energy
- The Hartree-Fock equations and orbital energies
- Spin symmetry: UHF and RHF
- RHF calculations in a basis set
- Examples: He atom and H_2 molecule
- The electron correlation energy

The Hartree-Fock wave function

- The Hartree-Fock (HF) method consists in approximating the ground-state wave function Ψ_0 as an antisymmetrized product of N spin orbitals $\{\chi_i(\mathbf{x})\}$, denoted by Φ_0,

$$\Phi_0(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \mathcal{A}\left[\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\cdots\chi_N(\mathbf{x}_N)\right]$$

  with the antisymmetrizer $\mathcal{A} = 1/\sqrt{N!}\sum_{n=1}^{N!}(-1)^{p_n}\,\mathcal{P}_n$ where the sum is over the $N!$ permutations $\mathcal{P}_n$ of the space-spin coordinates $\{\mathbf{x}_1, ..., \mathbf{x}_N\}$ and p_n is the number of pair inversions in $\mathcal{P}_n$.

- $\Phi_0(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$ can be conveniently expressed as a **Slater determinant**

$$\Phi_0(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

- Often, shorthand notations are used: $|\Phi_0\rangle \equiv |\chi_1\ \chi_2\ \cdots\ \chi_N\rangle \equiv |1\ 2\ \cdots\ N\rangle$

- The spin orbitals are usually written as the product a spatial orbital $\psi_i(\mathbf{r})$ and a spin function $\alpha(\omega)$ or $\beta(\omega)$

$$\chi_i(\mathbf{x}) = \psi_i(\mathbf{r})\alpha(\omega) \qquad \text{or} \qquad \chi_i(\mathbf{x}) = \psi_i(\mathbf{r})\beta(\omega)$$

  with $\alpha(\uparrow) = 1$, $\alpha(\downarrow) = 0$ and $\beta(\uparrow) = 0$, $\beta(\downarrow) = 1$.

- The spin orbitals are taken as orthonormal: $\langle\chi_i|\chi_j\rangle = \int \chi_i^*(\mathbf{x})\chi_j(\mathbf{x})\mathrm{d}\mathbf{x} = \delta_{ij}$

The Hartree-Fock energy

- The HF electronic energy is written in terms of integrals over these spin orbitals (using Slater's rules for calculating expectation values over Slater determinants)

$$E_{\mathrm{HF}}[\{\chi_a\}] = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_a^N h_{aa} + \frac{1}{2} \sum_a^N \sum_b^N \langle ab || ab \rangle$$

  where a and b refer to occupied spin orbitals in Φ_0, h_{aa} are the one-electron integrals

$$h_{aa} = \langle \chi_a | \hat{h} | \chi_a \rangle = \int \mathrm{d}\mathbf{x} \; \chi_a^*(\mathbf{x}) \; \hat{h} \; \chi_a(\mathbf{x})$$

  and $\langle ab||ab\rangle = \langle ab|ab\rangle - \langle ab|ba\rangle$ are the antisymmetrized two-electron integrals with

$$\langle ij|kl\rangle = \iint \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \; \frac{\chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

  (in physicists' notation)

- It is important to remember that the antisymmetrized integral $\langle ab||ab\rangle$ includes a **direct** contribution $\langle ab|ab\rangle$ and an **exchange** contribution $\langle ab|ba\rangle$.

- The spin orbitals are determined by minimizing the HF energy subject to the spin-orbital orthonormalization constraints

$$E_{\mathrm{HF}} = \min_{\substack{\{\chi_a\} \\ \langle \chi_a | \chi_b \rangle = \delta_{ab}}} E_{\mathrm{HF}}[\{\chi_a\}]$$

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The Hartree-Fock equations (1/2)

- Using the method of Lagrange multipliers for the constrained minimization, we introduce the Lagrangian

$$L[\{\chi_a\}] = E_{\text{HF}}[\{\chi_a\}] - \sum_{a}^{N} \varepsilon_a \left(\langle \chi_a | \chi_a \rangle - 1\right)$$

  where ε_a is the Lagrange multiplier for the normalization constraint $\langle \chi_a | \chi_a \rangle = 1$.

  Remark: To derive the equations, we can momentarily drop the orthogonality constraints $\langle \chi_a | \chi_b \rangle = 0$ for $a \neq b$.

- The Lagrangian must be stationary with respect to variations of the spin orbitals $\chi_a(\mathbf{x})$

$$\frac{\delta L[\{\chi_a\}]}{\delta \chi_a^*(\mathbf{x})} = 0$$

- Mathematical note: For a functional $L : \chi \mapsto L[\chi]$ of the function $\chi : \mathbf{x} \mapsto \chi(\mathbf{x})$, an infinitesimal variation $\delta\chi$ of χ leads to an infinitesimal variation of L which can be expressed as

$$\delta L[\chi] = \int \frac{\delta L[\chi]}{\delta \chi(\mathbf{x})} \delta\chi(\mathbf{x}) \mathrm{d}\mathbf{x}$$

  This defines the **functional derivative** of $L[\chi]$ with respect to $\chi(\mathbf{x})$: $\dfrac{\delta L[\chi]}{\delta \chi(\mathbf{x})}$

The Hartree-Fock equations (2/2)

- The stationary conditions lead to the (canonical) **HF eigenvalue equations**

$$\hat{f}\chi_i(\mathbf{x}) = \varepsilon_i \chi_i(\mathbf{x})$$

giving occupied and virtual HF spin orbitals $\chi_i(\mathbf{x})$ and associated orbital energies ε_i.

- The **one-electron HF Hamiltonian or Fock operator** is

$$\hat{f} = \hat{h} + \hat{v}_{\text{HF}}$$

where $\hat{v}_{\text{HF}}$ is the **one-electron HF potential operator**

$$\hat{v}_{\text{HF}} = \sum_a^N \hat{J}_a - \hat{K}_a$$

composed of a **Coulomb (or Hartree)** operator and an **exchange (or Fock)** operator

$$\hat{J}_a \chi_i(\mathbf{x}_1) = \int \mathrm{d}\mathbf{x}_2 \frac{\chi_a^*(\mathbf{x}_2)\chi_a(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_i(\mathbf{x}_1) \quad \text{and} \quad \hat{K}_a \chi_i(\mathbf{x}_1) = \int \mathrm{d}\mathbf{x}_2 \frac{\chi_a^*(\mathbf{x}_2)\chi_i(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_a(\mathbf{x}_1)$$

- The HF potential is a **mean-field potential** approximating the effect of the two-electron interaction $(1/2)\sum_i^N \sum_{j\neq i}^N 1/|\mathbf{r}_i - \mathbf{r}_j|$ in an average way.
- Since the HF potential depends the spin orbitals, the HF equations are a set of nonlinear integro-differential equations that must be solved iteratively.
- The HF method is also called **self-consistent field**.

The Hartree-Fock orbital energies

- The (canonical) HF (occupied or virtual) orbital energies are

$$\varepsilon_i = \langle \chi_i | \hat{f} | \chi_i \rangle = \int \chi_i^*(\mathbf{x}) \; \hat{f} \; \chi_i(\mathbf{x}) \mathrm{d}\mathbf{x} = h_{ii} + \sum_{a}^{N} \langle ia || ia \rangle$$

- To find the meaning of ε_i, let us remove an electron from the occupied spin orbital c. Without relaxation of the orbitals, the new Slater determinant is

$$|\Phi_c^{N-1}\rangle = \hat{a}_c |\Phi_0\rangle = |1 \; \cdots (c-1) \;\; (c+1) \; \cdots \;\; N\rangle$$

  where $\hat{a}_c$ is the annihilation operator of spin orbital c.

- The **HF ionization potential (IP)** for spin orbital c is then found to be

$$\begin{aligned} \mathrm{IP}_c &= \langle \Phi_c^{N-1} | \hat{H} | \Phi_c^{N-1} \rangle - E_{\mathrm{HF}} = \sum_{a \neq c}^{N} h_{aa} + \frac{1}{2} \sum_{a \neq c}^{N} \sum_{b \neq c}^{N} \langle ab || ab \rangle - E_{\mathrm{HF}} \\ &= -h_{cc} - \frac{1}{2} \sum_{a \neq c}^{N} \langle ac || ac \rangle - \frac{1}{2} \sum_{b \neq c}^{N} \langle cb || cb \rangle = -h_{cc} - \sum_{a}^{N} \langle ac || ac \rangle \end{aligned}$$

- We arrive at **Koopmans' theorem** for an occupied spin orbital c: $\mathrm{IP}_c = -\varepsilon_c$

- Similarly, Koopmans' theorem states that the **HF electron affinity (EA)** for the virtual spin orbital r, i.e. $\mathrm{EA}_r = E_{\mathrm{HF}} - \langle \Phi_r^{N+1} | \hat{H} | \Phi_r^{N+1} \rangle$ with $|\Phi_r^{N+1}\rangle = \hat{a}_r^\dagger |\Phi_0\rangle$ where $\hat{a}_r^\dagger$ is the creation operator for r, is given by

$$\mathrm{EA}_r = -\varepsilon_r$$

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Spin symmetry

- For an N-electron system, the total spin operator is $\hat{\mathbf{S}} = \sum_i^N \hat{\mathbf{s}}_i$, where $\hat{\mathbf{s}}_i$ is the spin operator for electron i.
- The spin operators $\hat{S}_z$ and $\hat{S}^2$ commute with the nonrelativistic Hamiltonian, $[\hat{H}, \hat{S}_z] = 0$ and $[\hat{H}, \hat{S}^2] = 0$, i.e. $\hat{S}_z$ and $\hat{S}^2$ represent symmetries of the system.
- This implies that we can choose the eigenstates $|\Psi\rangle$ of H as simultaneously eigenstates of $\hat{S}_z$ and $\hat{S}^2$:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad \text{and} \quad \hat{S}_z|\Psi\rangle = M_S|\Psi\rangle \quad \text{and} \quad \hat{S}^2|\Psi\rangle = S(S+1)|\Psi\rangle$$

- So far, we have considered a HF Slater determinant of the form $|\Phi_0^{\text{UHF}}\rangle = |\chi_1\chi_2\cdots\chi_N\rangle$ where each spin orbital is of the form $\chi_i = \psi_i\alpha$ or $\chi_i = \psi_i\beta$ but **without any restrictions on the spatial orbitals of different spins**.

$\Longrightarrow$ This is called **(spin-)unrestricted Hartree-Fock (UHF)**.

- The UHF Slater determinant is an eigenstate of $\hat{S}_z$, but in general not an eigenstate of $\hat{S}^2$

$$\hat{S}_z|\Phi_0^{\text{UHF}}\rangle = M_S|\Phi_0^{\text{UHF}}\rangle \quad \text{and} \quad \hat{S}^2|\Phi_0^{\text{UHF}}\rangle \neq S(S+1)|\Phi_0^{\text{UHF}}\rangle$$

- Thus, with UHF we generally have **spin-symmetry breaking** and the quantity $\langle\Phi_0^{\text{UHF}}|\hat{S}^2|\Phi_0^{\text{UHF}}\rangle - S(S+1)$ measures **spin contamination** (for a state of exact spin S).

Restricted Hartree-Fock for closed-shell states (1/2)

- In **(spin-)restricted Hartree-Fock (RHF)** for **closed-shell** states, the RHF Slater determinant is

  $$|\Phi_0^{\text{RHF}}\rangle = |\psi_1\alpha\ \psi_1\beta\ \psi_2\alpha\ \psi_2\beta \cdots \psi_{N/2}\alpha\ \psi_{N/2}\beta\rangle \equiv |1\ \bar{1}\ 2\ \bar{2} \cdots N/2\ \overline{N/2}\rangle$$

  i.e., we have $N/2$ pairs of spin orbitals sharing the same spatial orbital.

- This RHF determinant is a proper eigenstate of both $\hat{S}_z$ and $\hat{S}^2$

  $$\hat{S}_z|\Phi_0^{\text{RHF}}\rangle = M_S|\Phi_0^{\text{RHF}}\rangle \quad \text{and} \quad \hat{S}^2|\Phi_0^{\text{RHF}}\rangle = S(S+1)|\Phi_0^{\text{RHF}}\rangle$$

  with $M_S = 0$ and $S = 0$, i.e. it is a **spin singlet**.

- By summing over the spin coordinates, we find the **closed-shell RHF energy**

  $$E_{\text{RHF}} = 2\sum_a^{N/2} h_{aa} + \sum_a^{N/2}\sum_b^{N/2}\left(2\underbrace{\langle ab|ab\rangle}_{J_{ab}} - \underbrace{\langle ab|ba\rangle}_{K_{ab}}\right)$$

  where now a and b refer to occupied spatial orbitals, and we use the same notation as before for the one-electron and two-electron integrals now in terms of the spatial orbitals

  $$h_{aa} = \int d\mathbf{r}\ \psi_a^*(\mathbf{r})\ \hat{h}\ \psi_a(\mathbf{r}) \quad \text{and} \quad \langle ij|kl\rangle = \iint d\mathbf{r}_1 d\mathbf{r}_2\ \frac{\psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\psi_k(\mathbf{r}_1)\psi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

- Note that chemists' notation is also often used: $(ik|jl) = \langle ij|kl\rangle$

- $J_{ab} = \langle ab|ab\rangle$ and $K_{ab} = \langle ab|ba\rangle$ are the Coulomb and exchange integrals, respectively.

Restricted Hartree-Fock for closed-shell states (2/2)

- The closed-shell RHF equations are

$$\boxed{\hat{f}\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})}$$

where $\hat{f}$ is now the **closed-shell Fock operator**

$$\boxed{\hat{f} = \hat{h} + \sum_{a}^{N/2} 2\hat{J}_a - \hat{K}_a}$$

and $\hat{J}_a$ and $\hat{K}_a$ are the Coulomb and exchange operators in terms of spatial orbitals

$$\boxed{\hat{J}_a\psi_i(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{\psi_a^*(\mathbf{r}_2)\psi_a(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\psi_i(\mathbf{r}_1)} \quad \text{and} \quad \boxed{\hat{K}_a\psi_i(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{\psi_a^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\psi_a(\mathbf{r}_1)}$$

- The (canonical) closed-shell RHF orbital energies are

$$\boxed{\varepsilon_i = \langle\psi_i|\hat{f}|\psi_i\rangle = \int \psi_i^*(\mathbf{r})\ \hat{f}\ \psi_i(\mathbf{r})d\mathbf{r} = h_{ii} + \sum_{a}^{N/2} 2J_{ia} - K_{ia}}$$

- Remark: for open-shell states, if we still use pairs of spin-orbitals sharing the same spatial orbital, we obtain **(spin-)restricted open-shell Hartree-Fock (ROHF)**.

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RHF calculations in a basis set

- The spatial orbitals are expanded on a **basis set** $\{\phi_\mu(\mathbf{r})\}_{\mu=1,\ldots,K}$

$$\psi_i(\mathbf{r}) = \sum_\mu^K C_{\mu i}\phi_\mu(\mathbf{r})$$

- In the basis, the RHF equations take the form a **self-consistent generalized eigenvalue matrix equation**

$$\mathbf{F}\,\mathbf{C}_i = \varepsilon_i\,\mathbf{S}\,\mathbf{C}_i$$

  where $F_{\mu\nu} = \int \phi_\mu^*(\mathbf{r})\ \hat{f}\ \phi_\nu(\mathbf{r})\mathrm{d}\mathbf{r}$ are the elements of the closed-shell Fock matrix and $S_{\mu\nu} = \int \phi_\mu^*(\mathbf{r})\phi_\nu(\mathbf{r})\mathrm{d}\mathbf{r}$ are the elements of the overlap matrix.

- The elements of the **closed-shell Fock matrix** are

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_\lambda^K \sum_\sigma^K P_{\lambda\sigma}\left(\langle\mu\sigma|\nu\lambda\rangle - \frac{1}{2}\langle\mu\sigma|\lambda\nu\rangle\right)$$

  where $H_{\mu\nu}^{\text{core}} = \int \phi_\mu^*(\mathbf{r})\hat{h}\phi_\nu(\mathbf{r})\mathrm{d}\mathbf{r}$ are the elements of the one-electron Hamiltonian and $P_{\lambda\sigma} = 2\sum_a^{N/2} C_{\lambda a}C_{\sigma a}^*$ are the elements of **closed-shell density matrix**.

- In practice, we use atom-centered **Gaussian-type orbital (GTO) basis sets**

$$\phi_\mu(\mathbf{r}) = \sum_p d_{p\mu}\ g_p(\mathbf{r}) \quad \text{with} \quad g_p(\mathbf{r}) = N_p\ r^{\ell_p}\ e^{-\alpha_p r^2}\ Y_{\ell_p}^{m_p}(\theta,\phi)$$

  using spherical coordinates $\mathbf{r} = (r,\theta,\phi)$ around the nucleus center.

- In a straightforward implementation, the computational time of HF scales as $\mathcal{O}(K^4)$.

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Example of the He atom

- The ground-state RHF wave function of He atom is $|\Phi_0^{\mathrm{RHF}}\rangle = |1\,\bar{1}\rangle$, i.e. there is only one spatial (1s) orbital $\psi_1(\mathbf{r})$ doubly occupied by two electrons of opposite spins.
- The ground-state RHF energy is

$$E_{\mathrm{RHF}} = 2h_{11} + 2J_{11} - K_{11} = 2h_{11} + J_{11}$$

  where we have used $K_{11} = J_{11} = \langle 11|11\rangle = (11|11)$.
- The occupied (1s) orbital energy is

$$\varepsilon_1 = h_{11} + 2J_{11} - K_{11} = h_{11} + J_{11}$$

  and the first virtual (2s) orbital energy is

$$\varepsilon_2 = h_{22} + 2J_{12} - K_{12}$$

- In the complete basis set (CBS) limit, the RHF energy is

$$E_{\mathrm{RHF}} = -2.8617... \quad > \quad E_{\mathrm{exact}} = -2.9037... \text{ hartree}$$

  $\Longrightarrow$ we are missing dynamic (or weak) **electron correlation**.

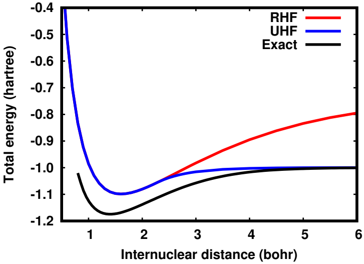
  and the occupied (1s) orbital energy is

$$\varepsilon_1 = -0.9180... \qquad \text{vs} \qquad \mathrm{IP}_{\mathrm{exact}} = 0.9037... \text{ hartree}$$

  $\Longrightarrow$ we are missing **electron correlation** for He and **orbital relaxation** for He$^+$.

Example of the H_2 molecule (1/2)

- We consider the H_2 molecule with a distance R between the two protons H_a and H_b.
- We work in a minimal basis set $\{\phi_a(\mathbf{r}), \phi_b(\mathbf{r})\}$, composed of two identical 1s functions centered on H_a and H_b, respectively.
- The ground-state RHF wave function is $|\Phi_0^{\text{RHF}}\rangle = |1\,\bar{1}\rangle \equiv |\sigma_g \overline{\sigma_g}\rangle$ where $\psi_1(\mathbf{r}) \equiv \psi_{\sigma_g}(\mathbf{r})$ is the doubly occupied σ_g bonding orbital.
- The ground-state UHF wave function is $|\Phi_0^{\text{UHF}}\rangle = |\psi_1\alpha\, \psi_2\beta\rangle$ where $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$ are allowed to be different.
- Comparison RHF vs. UHF:



  - Around the equilibrium, RHF = UHF and we are missing dynamic (or weak) correlation.
  - At dissociation, $E_{\text{UHF}} < E_{\text{RHF}}$, and RHF is missing static (or strong) correlation.

Example of the H_2 molecule (2/2)

- In the dissociation limit ($R \to \infty$), we have

$$\psi_{\sigma_\mathrm{g}}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\phi_a(\mathbf{r}) + \phi_b(\mathbf{r})\right)$$

and so the RHF wave function becomes

$$|\Phi_0^{\mathrm{RHF}}\rangle = |\sigma_\mathrm{g}\overline{\sigma_\mathrm{g}}\rangle = \frac{1}{2}\Bigg(\underbrace{|a\bar{b}\rangle + |b\bar{a}\rangle}_{\text{correct neutral terms}} + \underbrace{|a\bar{a}\rangle + |b\bar{b}\rangle}_{\text{spurious ionic terms}}\Bigg)$$

and the RHF energy goes to

$$E_{\mathrm{RHF}}(\mathrm{H}\cdots\mathrm{H}) = \underbrace{2h_{aa}}_{2E_{\mathrm{RHF}}(\mathrm{H})} + \underbrace{\frac{1}{2}J_{aa}}_{\text{static correlation error}}$$

- In the dissociation limit ($R \to \infty$), the UHF wave function becomes

$$|\Phi_0^{\mathrm{UHF}}\rangle = |a\bar{b}\rangle \text{ or } |\Phi_0^{\mathrm{UHF}}\rangle = |b\bar{a}\rangle$$

and the UHF energy correctly goes to

$$E_{\mathrm{UHF}}(\mathrm{H}\cdots\mathrm{H}) = 2h_{aa} = 2E_{\mathrm{UHF}}(\mathrm{H})$$

but we have spin contamination

$$\langle\Phi_0^{\mathrm{UHF}}|\hat{S}^2|\Phi_0^{\mathrm{UHF}}\rangle = 1 \neq 0$$

due to spin-symmetry breaking of the UHF wave function which is a combination of a singlet state and a triplet state.

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The electron correlation energy

- Let us repeat that the HF potential $\hat{v}_{\text{HF}}$ is an one-electron **mean-field potential** approximating the effect of the two-electron interaction $(1/2)\sum_{i}^{N}\sum_{j\neq i}^{N} 1/|\mathbf{r}_i - \mathbf{r}_j|$ in an average way.
- The effect of the electron-electron interaction beyond the HF approximation is called **electron correlation**. The difference between the exact ground-state energy E_0 and the HF energy E_{HF} is called the **correlation energy**

$$\boxed{E_{\text{c}} = E_0 - E_{\text{HF}}}$$

- Even though E_{c} is usually a small percentage of the total energy, it very often makes a large and crucial contribution to **energy differences** (such as reaction energies, reaction barrier heights, ...). It is therefore important to go beyond the HF approximation and calculate the value of the correlation energy, which is the goal of the **post-HF methods**.

Outline

3. Overview of post-Hartree-Fock methods
    - Full configuration interaction
    - Single-reference post-HF methods
    - Multi-reference post-HF methods

A straightforward post-HF method: Full configuration interaction (FCI)

- In FCI, **the wave function is expanded in terms of the HF determinant Φ_0, the singly excited determinants Φ_a^r, the doubly excited determinants Φ_{ab}^{rs}, and so on up to N-fold excited determinants**:

  $$|\Psi_{\text{FCI}}\rangle = c_0|\Phi_0\rangle + \sum_{a}^{\text{occ}}\sum_{r}^{\text{vir}} c_a^r|\Phi_a^r\rangle + \sum_{a<b}^{\text{occ}}\sum_{r<s}^{\text{vir}} c_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \sum_{a<b<c}^{\text{occ}}\sum_{r<s<t}^{\text{vir}} c_{abc}^{rst}|\Phi_{abc}^{rst}\rangle + \cdots$$

  and the coefficients $\mathbf{c} = (c_0, c_a^r, c_{ab}^{rs}, c_{abc}^{rst}, ...)$ are found by minimizing the FCI energy $E_{\text{FCI}} = \min_{\mathbf{c}}\langle\Psi_{\text{FCI}}|\hat{H}|\Psi_{\text{FCI}}\rangle$ (with the normalization constraint $\langle\Psi_{\text{FCI}}|\Psi_{\text{FCI}}\rangle = 1$), which corresponds to diagonalizing $\hat{H}$ in the space spanned by all determinants.

- In a finite basis set, FCI gives an upper bound to the exact ground-state energy: $E_{\text{FCI}} \geq E_0$. In the limit of a **complete basis set** ($K \to \infty$), **FCI becomes exact**: $E_{\text{FCI}} = E_0$.

- The **correlation energy** $E_{\text{c}} = E_0 - E_{\text{HF}}$ has a **slow convergence with the basis size**: the error on E_{c} typically decreases as $\mathcal{O}\left(K^{-1}\right)$.

- **Combinatorial explosion of number of determinants**: $N_{\text{det}} = \binom{2K}{N} = \mathcal{O}\left((2K)^N\right)$
  $\implies$ necessity to find low-power-scaling approximations

- To develop approximations to FCI, we identify **two regimes of electron correlation**: **dynamic (or weak) correlation** and **static (or strong) correlation**.

Outline

3 Overview of post-Hartree-Fock methods

- Full configuration interaction
- Single-reference post-HF methods
- Multi-reference post-HF methods

Post-HF methods for dynamic/weak correlation: single-reference methods

- **Correlation is called "dynamic" or "weak" if** $c_a^r, c_{ab}^{rs}, \ldots \ll c_0$
  $\Longrightarrow$ HF is a good starting point
- This corresponds to situations with a **large HOMO-LUMO HF gap**.
  Example: He atom, H_2 molecule at equilibrium distance.
- ⚠ Even if each coefficient is small, their total contribution can be large.
- For dynamic correlation, one considers **"single-reference" methods** which are approximations to FCI **assuming the predominance of the single HF determinant**.
- Three main families of single-reference post-HF methods:
  - **Truncated configuration interaction (CI)**
  - **Møller-Plesset (MP) perturbation theory (PT)**
  - **Coupled-cluster (CC) theory**

Single-reference truncated configuration interaction (CI)

- The FCI wave function is **truncated at a given excitation level**, e.g. keeping only single and double excitations (CISD):

$$|\Psi_{\text{CISD}}\rangle = c_0|\Phi_0\rangle + \sum_{a}^{\text{occ}}\sum_{r}^{\text{vir}} c_a^r|\Phi_a^r\rangle + \sum_{a<b}^{\text{occ}}\sum_{r<s}^{\text{vir}} c_{ab}^{rs}|\Phi_{ab}^{rs}\rangle$$

- The coefficients $\mathbf{c} = (c_0, c_a^r, c_{ab}^{rs})$ corresponding to the ground-state wave function are found by minimizing the CISD energy (with the constraint of the normalization of the wave function)

$$E_{\text{CISD}} = \min_{\mathbf{c}}\langle\Psi_{\text{CISD}}|\hat{H}|\Psi_{\text{CISD}}\rangle$$

  which, according to the variational principle, gives $E_{\text{CISD}} \geq E_{\text{FCI}}$.

- The CISD computational cost scales as $\mathcal{O}\left(K^6\right)$.

- **Serious shortcoming of truncated CI: it is not size-consistent**.

- We prefer methods that satisfy the **size-consistency property**: the energy of a system composed of two non-interacting fragments A and B is equal to the sum of the energies of the separate fragments:

$$E(A \;\cdots B) = E(A) + E(B)$$

  This property is important in chemistry. There is also the related **size-extensity property**: $E(N) \propto N$ for $N \to \infty$ which is important for extended systems.

Single-reference Møller-Plesset (MP) perturbation theory

- **Perturbation theory starting from the HF Hamiltonian**: $\hat{H} = \hat{F} + \hat{V}$
- The first-order wave function includes only doubly excited determinants:

$$|\Psi^{(1)}\rangle = \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} c_{ab}^{rs,(1)} |\Phi_{ab}^{rs}\rangle \qquad \text{with} \qquad c_{ab}^{rs,(1)} = -\frac{\langle rs||ab\rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}$$

- The second-order energy gives the **MP2 correlation energy**:

$$E_{\text{c}}^{\text{MP2}} = \langle \Phi_0 | \hat{V} | \Psi^{(1)} \rangle = -\sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}$$

- **MP2 is not variational** (E_{MP2} can be lower than E_{FCI}) **but is size-consistent**.
- The MP2 computational cost scales as $\mathcal{O}\left(K^5\right)$.
- **MP2 is a simple largely used post-HF method that often reasonably accounts for dynamic/weak correlation**.
- However, **accuracy is limited by missing higher-order terms**.
  Including higher-order terms (MP3, MP4, etc...) can be computationally costly and the series does not generally converge!

Single-reference coupled-cluster (CC) theory

- In CC, the wave function is taken as **an exponential of a truncated excitation expansion**, e.g. with single and double excitations (CCSD):

$$\boxed{|\Psi_{\text{CCSD}}\rangle = e^{\hat{T}_1+\hat{T}_2}|\Phi_0\rangle}$$

  where $\hat{T}_1 = \sum_{a}^{\text{occ}} \sum_{r}^{\text{vir}} t_a^r \, \hat{a}_r^\dagger \hat{a}_a$ and $\hat{T}_2 = \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} t_{ab}^{rs} \, \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_b \hat{a}_a$ are operators generating singly and doubly excited determinants when acting on the HF wave function $|\Phi_0\rangle$.
- **The CCSD wave function contains all excited determinants of the FCI wave function**, but the coefficients of triply, quadruply, etc.. excited determinants are (antisymmetrized) products of the coefficients of singly and doubly excited determinants.
- **The amplitudes t_a^r and t_{ab}^{rs} are found by projecting the Schrödinger equation** $\hat{H}|\Psi_{\text{CCSD}}\rangle = E|\Psi_{\text{CCSD}}\rangle$ onto $\langle\Phi_a^r|$ and $\langle\Phi_{ab}^{rs}|$.
- **CCSD is not variational** (E_{CCSD} can be lower than E_{FCI}) **but is size-consistent**.
- The CCSD computational cost scales as $\mathcal{O}\left(K^6\right)$.
- **CCSD is more accurate than MP2** because it contains higher-order terms.
- Possibility to perturbatively add the triple-excitation operator $\hat{T}_3$ in the expansion $\Longrightarrow$ **CCSD(T) which is often considered as the gold standard for dynamic/weak correlation** with computational cost scaling as $\mathcal{O}\left(K^7\right)$.

Outline

3 Overview of post-Hartree-Fock methods

- Full configuration interaction
- Single-reference post-HF methods
- Multi-reference post-HF methods

Post-HF methods for static/strong correlation: multi-reference methods

- **Correlation is called "static" or "strong" if there are some coefficients in the FCI expansion that are not small compared to c_0** $\Longrightarrow$ HF is NOT a good starting point
- This corresponds to situations with a **small HOMO-LUMO HF gap**.
  Example: Be atom, H_2 molecule at dissociation, transition metals (Fe, Cu, etc...).
- **Single-reference methods give too much importance to the HF determinant and tend to fail for static/strong correlation** (e.g., MP2 diverges for zero HOMO-LUMO HF gap).
- Instead of HF, we use now the **multiconfiguration self-consistent field (MCSCF) method** which is a multideterminant extension of HF:

  $$E_{\text{MCSCF}} = \min_{\{c_n,\chi_i\}} \langle \Psi_{\text{MCSCF}} | \hat{H} | \Psi_{\text{MCSCF}} \rangle \qquad \text{with} \qquad |\Psi_{\text{MCSCF}}\rangle = \sum_n c_n |\Phi_n\rangle$$

  Usually, we include all determinants $|\Phi_n\rangle$ that can be generated from a small orbital subspace, called **complete active space (CAS)** $\Longrightarrow$ accounts for static/strong correlation but combinatorial explosion with the size of the active space!
- Starting from MCSCF, remaining dynamic/weak correlation can be added with **multi-reference (MR) methods**:
  - **MRCI** (e.g., MRCISD): not size-consistent but used for very small systems
  - **MRPT** (e.g., CASPT2, NEVPT2): fairly used but requires large enough CAS
  - **MRCC**: several proposed methods but no consensual method yet

Outline

4 Configuration interaction

- General configuration interaction
- Configuration interaction singles doubles
- Examples: He atom and H_2 molecule
- Lack of size-consistency of truncated configuration interaction

General configuration interaction (1/2)

- **Configuration interaction** is a general post-HF method consists in expanding the wave function in a set of Slater determinants:

$$|\Psi_{\text{CI}}\rangle = \sum_{I=1}^{N_{\text{det}}} c_I |\Phi_I\rangle$$

- The coefficients $\{c_I\}$ for the ground state are determined by minimizing the CI energy with the normalization constraint $\langle \Psi_{\text{CI}} | \Psi_{\text{CI}} \rangle = \sum_{I=1}^{N_{\text{det}}} |c_I|^2 = 1$

$$E_{\text{CI}} = \min_{\substack{\{c_I\} \\ \sum_{I=1}^{N_{\text{det}}} |c_I|^2 = 1}} \langle \Psi_{\text{CI}} | \hat{H} | \Psi_{\text{CI}} \rangle$$

- The corresponding Lagrangian is

$$\begin{aligned} L[\{c_I\}] &= \langle \Psi_{\text{CI}} | \hat{H} | \Psi_{\text{CI}} \rangle - E_{\text{CI}} \Big(\langle \Psi_{\text{CI}} | \Psi_{\text{CI}} \rangle - 1 \Big) \\ &= \sum_{I=1}^{N_{\text{det}}} \sum_{J=1}^{N_{\text{det}}} c_I^* c_J \langle \Phi_I | \hat{H} | \Phi_J \rangle - E_{\text{CI}} \Big(\sum_{I=1}^{N_{\text{det}}} |c_I|^2 - 1 \Big) \end{aligned}$$

where E_{CI} acts as the Lagrange multiplier for the normalization constraint.

General configuration interaction (2/2)

- The stationary condition on the Lagrangian L

  $$\frac{\partial L}{\partial c_I^*} = 0$$

  leads to the CI eigenvalue equation

  $$\sum_{J=1}^{N_{\text{det}}} \langle \Phi_I | \hat{H} | \Phi_J \rangle c_J = E_{\text{CI}}\, c_I$$

- In matrix form, the CI eigenvalue equation is

  $$\begin{pmatrix} \langle \Phi_1 | \hat{H} | \Phi_1 \rangle & \langle \Phi_1 | \hat{H} | \Phi_2 \rangle & \cdots & \langle \Phi_1 | \hat{H} | \Phi_{N_{\text{det}}} \rangle \\ \langle \Phi_2 | \hat{H} | \Phi_1 \rangle & \langle \Phi_2 | \hat{H} | \Phi_2 \rangle & \cdots & \langle \Phi_2 | \hat{H} | \Phi_{N_{\text{det}}} \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \Phi_{N_{\text{det}}} | \hat{H} | \Phi_1 \rangle & \langle \Phi_{N_{\text{det}}} | \hat{H} | \Phi_2 \rangle & \cdots & \langle \Phi_{N_{\text{det}}} | \hat{H} | \Phi_{N_{\text{det}}} \rangle \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_{N_{\text{det}}} \end{pmatrix} = E_{\text{CI}} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_{N_{\text{det}}} \end{pmatrix}$$

  where the matrix elements $\langle \Phi_I | \hat{H} | \Phi_J \rangle$ can be expressed in terms of one-electron and two-electron integrals.

- Solutions of the CI eigenvalue equation give approximations to the ground and excited states.

Spin/spatial symmetries in configuration interaction

- Slater determinants generally do not satisfy the spin and spatial symmetries of the state considered.

- To impose spin/spatial symmetry and simplify the calculation, one can form **configuration state functions (CSFs)** $\{|\Psi_I\rangle\}$, i.e. fixed linear combinations of a few Slater determinants having the spin and spatial symmetries of the state considered

  $$|\Psi_I\rangle = \sum_J d_{J,I} |\Phi_J\rangle$$

  and use them to expand the CI wave function

  $$|\Psi_{\text{CI}}\rangle = \sum_{I=1}^{N_{\text{CSF}}} c_I |\Psi_I\rangle$$

- For example, for a closed-shell state, the singly excited determinants $|\Phi_a^r\rangle$ and $|\Phi_{\bar{a}}^{\bar{r}}\rangle$ (where a and r refer to spatial orbitals) are eigenstates of $\hat{S}_z$ but not of $\hat{S}^2$. One can form a spin-singlet adapted CSF as

  $$|{}^1\Psi_a^r\rangle = \frac{1}{\sqrt{2}} \left(|\Phi_a^r\rangle + |\Phi_{\bar{a}}^{\bar{r}}\rangle \right)$$

  which is an eigenstate of $\hat{S}^2$ with eigenvalue 0.

Outline

4 Configuration interaction

- General configuration interaction
- Configuration interaction singles doubles
- Examples: He atom and H_2 molecule
- Lack of size-consistency of truncated configuration interaction

Configuration interaction singles doubles (1/2)

- Ideally, one would like to perform CI using all Slater determinants that can be generated with the considered basis set, i.e. **full configuration interaction (FCI)** which gives the exact wave function within the basis set.
- But the total number of determinants explodes combinatorially: $N_{\text{det}} = \binom{2K}{N} = \mathcal{O}\left((2K)^N\right)$
- For the vast majority of cases, one has thus to select a subset of determinants. This can be done either on-the-fly for each system (**selected CI**) or according to a predetermined truncation pattern (e.g., excitation levels).
- The most common truncation is to keep only singly and doubly excited determinants, known as **configuration interaction singles doubles (CISD)**:

$$|\Psi_{\text{CISD}}\rangle = c_0|\Phi_0\rangle + \sum_{a}^{\text{occ}}\sum_{r}^{\text{vir}} c_a^r|\Phi_a^r\rangle + \sum_{a<b}^{\text{occ}}\sum_{r<s}^{\text{vir}} c_{ab}^{rs}|\Phi_{ab}^{rs}\rangle$$

and again the coefficients $(c_0, c_a^r, c_{ab}^{rs})$ for the ground state are found by minimizing the CISD energy $E_{\text{CISD}} = \langle\Psi_{\text{CISD}}|\hat{H}|\Psi_{\text{CISD}}\rangle$ (with the constraint of the normalization of the wave function).

Configuration interaction singles doubles (2/2)

- We obtain a CISD eigenvalue equation with the following block structure:

$$\left(\begin{array}{c|c|c} \langle\Phi_0|\hat{H}|\Phi_0\rangle & \langle\Phi_0|\hat{H}|\Phi_a^r\rangle & \langle\Phi_0|\hat{H}|\Phi_{ab}^{rs}\rangle \\ \hline \langle\Phi_{a'}^{r'}|\hat{H}|\Phi_0\rangle & \langle\Phi_{a'}^{r'}|\hat{H}|\Phi_a^r\rangle & \langle\Phi_{a'}^{r'}|\hat{H}|\Phi_{ab}^{rs}\rangle \\ \hline \langle\Phi_{a'b'}^{r's'}|\hat{H}|\Phi_0\rangle & \langle\Phi_{a'b'}^{r's'}|\hat{H}|\Phi_a^r\rangle & \langle\Phi_{a'b'}^{r's'}|\hat{H}|\Phi_{ab}^{rs}\rangle \end{array}\right) \left(\begin{array}{c} c_0 \\ \hline c_a^r \\ \hline c_{ab}^{rs} \end{array}\right) = E_{\text{CISD}} \left(\begin{array}{c} c_0 \\ \hline c_a^r \\ \hline c_{ab}^{rs} \end{array}\right)$$

- A well-known simplication: when using HF orbitals, the matrix element between the HF determinant and any singly determinant vanishes

  $$\langle\Phi_0|\hat{H}|\Phi_a^r\rangle = \langle\Phi_{a'}^{r'}|\hat{H}|\Phi_0\rangle = 0$$

  This is known as **Brillouin's theorem**.

- The proof of Brillouin's theorem is immediate:

  $$\langle\Phi_0|\hat{H}|\Phi_a^r\rangle \quad = \quad h_{ar} + \sum_b^{\text{occ}} \langle ab||rb\rangle = f_{ar} = 0$$

  since f_{ar} is an off-diagonal matrix element of the Fock operator.

- **Doubly excited determinants make the most important contribution to the correlation energy**. Singly excited determinants still contribute a little via their interaction with the doubly excited determinants.

Outline

4. Configuration interaction
   - General configuration interaction
   - Configuration interaction singles doubles
   - Examples: He atom and H_2 molecule
   - Lack of size-consistency of truncated configuration interaction

Example of the He atom

- For the He atom, since there are only two electrons, CISD = FCI.
- **FCI ground-state energy using a family of basis sets of increasing size** denoted by cc-pVXZ where X =D,T,Q,5,6:

	Total energy (hartree)
cc-pVDZ	-2.8876...
cc-pVTZ	-2.9002...
cc-pVQZ	-2.9024...
cc-pV5Z	-2.9032...
cc-pV6Z	-2.9034...
Exact	**-2.9037...**

- The FCI total energy has a **slow power-law convergence** as $\mathcal{O}(X^{-3}) = \mathcal{O}(K^{-1})$.

Example of the H_2 molecule (1/2)

- For the H_2 molecule, again since there are only two electrons, CISD = FCI.
- We work in a minimal basis set $\{\phi_a(\mathbf{r}), \phi_b(\mathbf{r})\}$, composed of two identical 1s functions centered on H_a and H_b, respectively. This leads to two RHF molecular orbitals:
  - the bonding orbital: $\psi_1(\mathbf{r}) \equiv \psi_{\sigma_\mathrm{g}}(\mathbf{r})$
  - the antibonding orbital: $\psi_2(\mathbf{r}) \equiv \psi_{\sigma_\mathrm{u}}(\mathbf{r})$
- In this basis, due to spatial symmetry, only two determinants contribute to the FCI ground-state wave function, i.e. the RHF determinant $|\Phi_0\rangle = |1\,\bar{1}\rangle$ and the doubly excited determinant $|\Phi_{1\,\bar{1}}^{2\,\bar{2}}\rangle = |2\,\bar{2}\rangle$,

$$\boxed{|\Psi_\mathrm{FCI}\rangle = c_1|1\,\bar{1}\rangle + c_2|2\,\bar{2}\rangle}$$

- The FCI 2×2 matrix eigenvalue equation is

$$\begin{pmatrix} \langle 1\,\bar{1}|\hat{H}|1\,\bar{1}\rangle & \langle 1\,\bar{1}|\hat{H}|2\,\bar{2}\rangle \\ \langle 2\,\bar{2}|\hat{H}|1\,\bar{1}\rangle & \langle 2\,\bar{2}|\hat{H}|2\,\bar{2}\rangle \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E_\mathrm{FCI} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

with matrix elements:

$\langle 1\,\bar{1}|\hat{H}|1\,\bar{1}\rangle = E_\mathrm{RHF} = 2h_{11} + J_{11}$ and $\langle 2\,\bar{2}|\hat{H}|2\,\bar{2}\rangle = E_2 = 2h_{22} + J_{22}$

and $\langle 1\,\bar{1}|\hat{H}|2\,\bar{2}\rangle = \langle 2\,\bar{2}|\hat{H}|1\,\bar{1}\rangle = \langle 1\,\bar{1}||2\,\bar{2}\rangle = \langle 1\,\bar{1}|2\,\bar{2}\rangle = \langle 1\,1|2\,2\rangle = K_{12}$

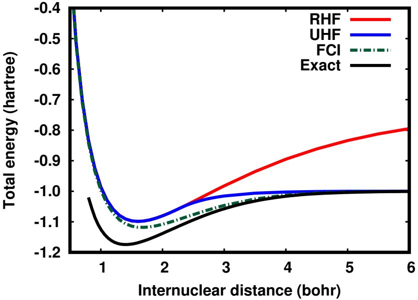
Example of the H_2 molecule (2/2)

- In the minimal basis, the FCI ground-state energy is

$$\begin{aligned} E_{\mathrm{FCI}} &= \frac{1}{2}\left(E_{\mathrm{RHF}} + E_2 - \sqrt{(E_2 - E_{\mathrm{RHF}})^2 + 4K_{12}^2}\right) \\ &= E_{\mathrm{RHF}} + \Delta - \sqrt{\Delta^2 + K_{12}^2} \end{aligned}$$

  where $\Delta = (E_2 - E_{\mathrm{RHF}})/2$

- FCI energy curve in the minimal basis:



  - FCI corrects RHF at dissociation by including static (or strong) correlation
  - Around the equilibrium distance, we are still missing some dynamic (or weak) correlation due to the minimal basis

Outline

4. Configuration interaction
   - General configuration interaction
   - Configuration interaction singles doubles
   - Examples: He atom and H_2 molecule
   - Lack of size-consistency of truncated configuration interaction

Lack of size-consistency of truncated configuration interaction (1/2)

- We say that a method is **size-consistent** if the calculated energy of a system composed of two non-interacting fragments A and B is equal to the sum of the calculated energies of the separate fragments:

$$E(A \cdots B) = E(A) + E(B)$$

- **The most serious drawback of truncated CI methods is that they are not size-consistent.**

- Let us show this on the example of two H_2 molecules in a minimal basis set separated by an infinite distance:

$$\underbrace{\mathrm{H}_2}_{\text{fragment } A} \quad \cdots\cdots \quad \underbrace{\mathrm{H}_2}_{\text{fragment } B}$$

- We have two spatial RHF orbitals located on A, denoted by 1_A and 2_A, and two spatial RHF orbitals located on B, denoted by 1_B and 2_B. The RHF wave function of the total system is $|\Phi_{\mathrm{RHF}}^{A\cdots B}\rangle = |1_A\, \bar{1}_A\, 1_B\, \bar{1}_B\rangle$.

- The CISD wave function of the total system is

$$|\Psi_{\mathrm{CISD}}^{A\cdots B}\rangle = c_1|1_A\, \bar{1}_A\, 1_B\, \bar{1}_B\rangle + c_2|2_A\, \bar{2}_A\, 1_B\, \bar{1}_B\rangle + c_3|1_A\, \bar{1}_A\, 2_B\, \bar{2}_B\rangle$$

  - all single excitations do not contribute by symmetry
  - all other double excitations (e.g., $|2_A\, \bar{2}_B\, 1_B\, \bar{1}_B\rangle$) do not contribute because they give zero matrix elements

Lack of size-consistency of truncated configuration interaction (2/2)

- The CISD 3×3 matrix eigenvalue equation is
$$\begin{pmatrix} 2E_{\text{RHF}}^{A} & K_{12} & K_{12} \\ K_{12} & E_{\text{RHF}}^{A} + E_{2}^{A} & 0 \\ K_{12} & 0 & E_{\text{RHF}}^{A} + E_{2}^{A} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = E_{\text{CISD}}^{A\cdots B} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$
where $E_{\text{RHF}}^{A} = E_{\text{RHF}}^{B} = 2h_{11} + J_{11}$ is the RHF energy of one fragment, $E_2^A = E_2^B = 2h_{22} + J_{22}$ is the energy of a double excitation of one fragment, and $K_{12} = \langle 12|12\rangle$ is the interaction integral between the orbitals 1 and 2 of one fragment.

- The CISD ground-state energy is
$$\begin{aligned} E_{\text{CISD}}^{A\cdots B} &= \frac{1}{2}\left(3E_{\text{RHF}}^{A} + E_2^A - \sqrt{(E_2^A - E_{\text{RHF}}^{A})^2 + 8K_{12}^2}\right) \\ &= 2E_{\text{RHF}}^{A} + \Delta - \sqrt{\Delta^2 + 2K_{12}^2} \end{aligned}$$
where $\Delta = (E_2^A - E_{\text{RHF}}^{A})/2$

- It is **not** equal to twice the CISD ground-state energy of one fragment
$$E_{\text{CISD}}^{A\cdots B} \neq 2E_{\text{CISD}}^{A} = 2E_{\text{RHF}}^{A} + 2\Delta - 2\sqrt{\Delta^2 + K_{12}^2}$$
so **CISD is not size-consistent**.

- To recover size-consistency, one would need to add quadruple excitations in the calculation of $A\cdots B$.

Outline

5. Perturbation theory
   - General Rayleigh-Schrödinger perturbation theory
   - Møller-Plesset perturbation theory

General Rayleigh-Schrödinger perturbation theory (1/3)

- Consider a Hamiltonian $\hat{H}^{\lambda}$ depending on a coupling constant λ
$$\hat{H}^{\lambda} = \hat{H}^{(0)} + \lambda \hat{V}$$
where $\hat{H}^{(0)}$ is a zeroth-order Hamiltonian operator and $\hat{V}$ is a perturbation operator. The "physical" Hamiltonian corresponds to $\lambda = 1$, i.e. $\hat{H} = \hat{H}^{\lambda=1}$.
- $\hat{H}^{(0)}$ is chosen such that its eigenstates Φ_n and associated eigenvalues $E_n^{(0)}$ are known
$$\hat{H}^{(0)}|\Phi_n\rangle = E_n^{(0)}|\Phi_n\rangle$$
and the eigenstates are chosen to be orthonormal, i.e. $\langle\Phi_n|\Phi_m\rangle = \delta_{n,m}$.
- We want to determine the eigenstates Ψ_n^{λ} and associated eigenvalues E_n^{λ} of the Hamiltonian $\hat{H}^{\lambda}$, e.g. for the ground state
$$\hat{H}^{\lambda}|\Psi_0^{\lambda}\rangle = E_0^{\lambda}|\Psi_0^{\lambda}\rangle$$
- We assume that E_0^{λ} and Ψ_0^{λ} can be expanded in powers of λ
$$E_0^{\lambda} = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \cdots \quad \text{and} \quad |\Psi_0^{\lambda}\rangle = |\Psi_0^{(0)}\rangle + \lambda|\Psi_0^{(1)}\rangle + \lambda^2|\Psi_0^{(2)}\rangle + \cdots$$
where $\Psi_0^{(0)} = \Phi_0$.
- It is convenient to choose the so-called **intermediate normalization** for Ψ_0^{λ}:
$$\langle\Phi_0|\Psi_0^{\lambda}\rangle = 1 \text{ for all } \lambda \implies \langle\Phi_0|\Psi_0^{(i)}\rangle = 0 \text{ for all } i \geq 1$$

General Rayleigh-Schrödinger perturbation theory (2/3)

- Insertion of the expansion of Ψ_0^{λ} and E_0^{λ} into the eigenvalue equation gives

$$\left(\hat{H}^{(0)} + \lambda \hat{V}\right)\left(|\Phi_0\rangle + \lambda|\Psi_0^{(1)}\rangle + \lambda^2|\Psi_0^{(2)}\rangle + \cdots\right)$$
$$= \left(E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \cdots\right)\left(|\Phi_0\rangle + \lambda|\Psi_0^{(1)}\rangle + \lambda^2|\Psi_0^{(2)}\rangle + \cdots\right)$$

- Looking at this equation order by order in λ, we recover at **zeroth order**

$$\hat{H}^{(0)}|\Phi_0\rangle = E_0^{(0)}|\Phi_0\rangle$$

- At **first order**, we obtain

$$\boxed{\hat{H}^{(0)}|\Psi_0^{(1)}\rangle + \hat{V}|\Phi_0\rangle = E_0^{(0)}|\Psi_0^{(1)}\rangle + E_0^{(1)}|\Phi_0\rangle}$$

- Projecting this equation on the bra state $\langle\Phi_0|$ gives the **first-order energy correction**

$$\boxed{E_0^{(1)} = \langle\Phi_0|\hat{V}|\Phi_0\rangle}$$

- Projecting now on the bra states $\langle\Phi_n|$ for $n \neq 0$ gives

$$\boxed{E_n^{(0)}\langle\Phi_n|\Psi_0^{(1)}\rangle + \langle\Phi_n|\hat{V}|\Phi_0\rangle = E_0^{(0)}\langle\Phi_n|\Psi_0^{(1)}\rangle}$$

leading to the **first-order wave-function correction**

$$\langle\Phi_n|\Psi_0^{(1)}\rangle = -\frac{\langle\Phi_n|\hat{V}|\Phi_0\rangle}{E_n^{(0)} - E_0^{(0)}} \Longrightarrow \boxed{|\Psi_0^{(1)}\rangle = -\sum_{n\neq 0}\frac{\langle\Phi_n|\hat{V}|\Phi_0\rangle}{E_n^{(0)} - E_0^{(0)}}|\Phi_n\rangle}$$

General Rayleigh-Schrödinger perturbation theory (3/3)

- Similarly, at **second order**, we obtain

$$\hat{H}^{(0)}|\Psi_0^{(2)}\rangle + \hat{V}|\Psi_0^{(1)}\rangle = E_0^{(0)}|\Psi_0^{(2)}\rangle + E_0^{(1)}|\Psi_0^{(1)}\rangle + E_0^{(2)}|\Phi_0\rangle$$

- Projecting this equation on the bra state $\langle\Phi_0|$ gives the **second-order energy correction**

$$E_0^{(2)} = \langle\Phi_0|\hat{V}|\Psi_0^{(1)}\rangle = -\sum_{n\neq 0}\frac{|\langle\Phi_0|\hat{V}|\Phi_n\rangle|^2}{E_n^{(0)} - E_0^{(0)}}$$

- Note that $E_0^{(2)}$ diverges if there is a state Φ_n (with $n \neq 0$) of energy $E_n^{(0)}$ equals to $E_0^{(0)}$, i.e. if the zeroth-order Hamiltonian $\hat{H}^{(0)}$ has a degenerate ground state. In this case, one must instead diagonalize the Hamiltonian in the degenerate space before applying perturbation theory, which is known as degenerate perturbation theory.

- Similarly, one can show that the **third-order energy correction** has the following expression

$$\begin{aligned} E_0^{(3)} &= \langle\Phi_0|\hat{V}|\Psi_0^{(2)}\rangle \\ &= \sum_{n,m\neq 0}\frac{\langle\Phi_0|\hat{V}|\Phi_n\rangle\langle\Phi_n|\hat{V}|\Phi_m\rangle\langle\Phi_m|\hat{V}|\Phi_0\rangle}{(E_n^{(0)} - E_0^{(0)})(E_m^{(0)} - E_0^{(0)})} - E_0^{(1)}\sum_{n\neq 0}\frac{|\langle\Phi_0|\hat{V}|\Phi_n\rangle|^2}{(E_n^{(0)} - E_0^{(0)})^2} \end{aligned}$$

Outline

5 Perturbation theory

- General Rayleigh-Schrödinger perturbation theory
- Møller-Plesset perturbation theory

Møller-Plesset perturbation theory (1/5)

- Møller-Plesset (MP) perturbation theory is a particular case of Rayleigh-Schrödinger perturbation theory for which the zeroth-order Hamiltonian is chosen to be the Hartree-Fock (sometimes also simply called Fock) Hamiltonian

$$\hat{H}^{(0)} = \hat{F}$$

- The expression of $\hat{F}$ in the position representation is

$$F(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \sum_{i}^{N} f(\mathbf{x}_i)$$

- The corresponding perturbation operator $\hat{V}$ is thus the difference between the electron-electron Coulomb interaction and the HF potential

$$V(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \frac{1}{2} \sum_{i}^{N} \sum_{i \neq j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i}^{N} v_{\text{HF}}(\mathbf{x}_i)$$

Møller-Plesset perturbation theory (2/5)

- The **zeroth-order ground-state energy** is given by the sum of occupied orbital energies

$$E_0^{(0)} = \langle \Phi_0 | \hat{F} | \Phi_0 \rangle = \sum_a^{\text{occ}} \varepsilon_a$$

- The **first-order energy correction** is the expectation value of the HF determinant over the perturbation operator

$$E_0^{(1)} = \langle \Phi_0 | \hat{V} | \Phi_0 \rangle$$

  Therefore, the sum of the zeroth-order energy and first-order energy correction just gives back the HF energy

$$E_0^{(0)} + E_0^{(1)} = \langle \Phi_0 | \hat{F} + \hat{V} | \Phi_0 \rangle = E_{\text{HF}}$$

- The **second-order energy correction**, also called the **second-order Møller-Plesset (MP2) correlation energy**, is

$$E_0^{(2)} = E_{\text{c}}^{\text{MP2}} = - \sum_{n \neq 0} \frac{|\langle \Phi_0 | \hat{V} | \Phi_n \rangle|^2}{E_n^{(0)} - E_0^{(0)}}$$

  where Φ_n can be *a priori* single, double, triple, ... excited determinants.

Møller-Plesset perturbation theory (3/5)

- In fact, since $\hat{V}$ is at most a two-body operator, according to Slater's rules, triple and higher excitations with respect to Φ_0 give vanishing matrix elements $\langle \Phi_0 | \hat{V} | \Phi_n \rangle$.
- In addition, it turns out that single excitations only give a vanishing contribution

$$\langle \Phi_0 | \hat{V} | \Phi_a^r \rangle = \sum_b^{\text{occ}} \langle ab || rb \rangle - \langle a | \hat{v}_{\text{HF}} | r \rangle = \sum_b^{\text{occ}} \langle ab || rb \rangle - \sum_b^{\text{occ}} \langle ab || rb \rangle = 0$$

- It thus remains only the double excitations, $\Phi_n = \Phi_{ab}^{rs}$. Only the two-body part of the perturbation operator gives a non-zero matrix element

$$\langle \Phi_0 | \hat{V} | \Phi_{ab}^{rs} \rangle = \langle ab || rs \rangle$$

and the zeroth-order energy corresponding to the doubly-excited determinants Φ_{ab}^{rs} is

$$E_n^{(0)} = E_{ab}^{rs,(0)} = E_0^{(0)} + \varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b$$

- We arrive at the following expression for the MP2 correlation energy

$$E_{\text{c}}^{\text{MP2}} = - \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b} = -\frac{1}{4} \sum_{a,b}^{\text{occ}} \sum_{r,s}^{\text{vir}} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}$$

where we have used the antisymmetry property of the integrals, i.e. $\langle ab || rs \rangle = -\langle ab || sr \rangle = -\langle ba || rs \rangle$.

Møller-Plesset perturbation theory (4/5)

- The MP2 correlation energy is always negative.
- It diverges to $-\infty$ if one energy denominator $\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b$ is zero. This happens for systems with zero HF HOMO-LUMO gap, in which case MP perturbation theory cannot be applied.
- The MP2 energy is

$$\boxed{E_{\text{MP2}} = E_{\text{HF}} + E_{\text{c}}^{\text{MP2}}}$$

Since it is not a variational theory, E_{MP2} is not necessarily above E_{FCI}.

- Similarly, it can be shown, after much work, that the third-order Møller-Plesset (MP3) energy correction has the following expression

$$\begin{aligned} E_0^{(3)} &= \frac{1}{8}\sum_{a,b,c,d}^{\text{occ}}\sum_{r,s}^{\text{vir}} \frac{\langle ab||rs\rangle\langle rs||cd\rangle\langle cd||ab\rangle}{(\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b)(\varepsilon_r+\varepsilon_s-\varepsilon_c-\varepsilon_d)} \\ &+\frac{1}{8}\sum_{a,b}^{\text{occ}}\sum_{r,s,t,u}^{\text{vir}} \frac{\langle ab||rs\rangle\langle rs||tu\rangle\langle tu||ab\rangle}{(\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b)(\varepsilon_t+\varepsilon_u-\varepsilon_a-\varepsilon_b)} \\ &+\sum_{a,b,c}^{\text{occ}}\sum_{r,s,t}^{\text{vir}} \frac{\langle ab||rs\rangle\langle cs||tb\rangle\langle rt||ac\rangle}{(\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b)(\varepsilon_r+\varepsilon_t-\varepsilon_a-\varepsilon_c)} \end{aligned}$$

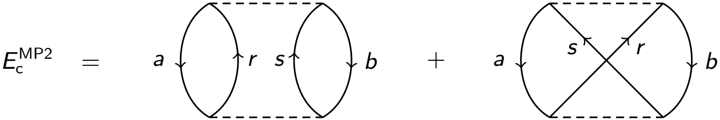
The calculation of the third- or higher-order terms is often considered as not worthwhile in comparison with coupled-cluster methods for example.

Møller-Plesset perturbation theory (5/5)

- The MP2 correlation energy can be rewritten as the sum of a **direct** and **exchange** term

$$E_c^{\text{MP2}} = -\frac{1}{2}\sum_{a,b}^{\text{occ}}\sum_{r,s}^{\text{vir}}\frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b} + \frac{1}{2}\sum_{a,b}^{\text{occ}}\sum_{r,s}^{\text{vir}}\frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b}$$

- These terms can be represented by **Feynman diagrams** (also called **Goldstone diagrams** in quantum chemistry)



- When starting from an unrestricted HF calculation, MP perturbation theory is correctly **size consistent** at each order. In terms of diagrams, this comes from the fact that each diagram contributing to the perturbative expansion of the energy is made of a single linked piece. Unlinked diagrams do not contribute. This is known as the **linked-cluster theorem**.

Outline

6 Coupled-cluster theory

- The exponential ansatz
- Truncation of the cluster operator
- The coupled-cluster energy and the coupled-cluster equations
- Example: coupled-cluster doubles
- Coupled-cluster methods in practice

The exponential ansatz (1/5)

- In **coupled-cluster (CC)** theory, one starts by an exponential ansatz for the CC wave function

  $$|\Psi_{\text{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle$$

  where $|\Phi_0\rangle$ is the HF wave function, and $\hat{T}$ is the **cluster (excitation) operator** which is the sum of cluster operators of different excitation levels

  $$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_N$$

- $\hat{T}_1$ is the cluster operator for the **single excitations**

  $$\hat{T}_1 = \sum_a^{\text{occ}} \sum_r^{\text{vir}} t_a^r \; \hat{a}_r^\dagger \hat{a}_a$$

  where t_a^r are the **single-excitation cluster amplitudes** to be determined.

  We have used the **second-quantization formalism**:

  - $\hat{a}_a$ is the **annihilation operator** of the spin orbital a
  - $\hat{a}_r^\dagger$ is the **creation operator** of the spin orbital r
  - When the operator $\hat{a}_r^\dagger \hat{a}_a$ acts on the HF single determinant $|\Phi_0\rangle$, it generates the single-excited determinant $|\Phi_a^r\rangle = \hat{a}_r^\dagger \hat{a}_a|\Phi_0\rangle$

The exponential ansatz (2/5)

- Similarly, $\hat{T}_2$ is the cluster operator for the **double excitations**

$$\hat{T}_2 = \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} t_{ab}^{rs} \, \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_b \hat{a}_a$$

  where t_{ab}^{rs} are the **double-excitation cluster amplitudes** to be determined.

  When the operator $\hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_b \hat{a}_a$ acts on the HF single determinant $|\Phi_0\rangle$, it generates the double-excited determinant $|\Phi_{ab}^{rs}\rangle = \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_b \hat{a}_a |\Phi_0\rangle$.

- And so on up to the $\hat{T}_N$ cluster operator for N-fold excitations.

The exponential ansatz (3/5)

- To understand the action of the operator $e^{\hat{T}}$ on the HF wave function $|\Phi_0\rangle$, one can expand the exponential and rearrange the operators in terms of excitation levels

$$e^{\hat{T}} = \hat{1} + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots + \frac{\hat{T}^N}{N!} = \hat{1} + \hat{C}_1 + \hat{C}_2 + \cdots + \hat{C}_N$$

where the operator $\hat{C}_1$ generates single excitations, $\hat{C}_2$ generates double excitations, etc.

- Noting that the cluster operators $\hat{T}_1$, $\hat{T}_2$, ..., $\hat{T}_N$ commute with each other, we find for example for the first four excitation operators

$$\hat{C}_1 = \hat{T}_1$$

$$\hat{C}_2 = \hat{T}_2 + \frac{1}{2}\hat{T}_1^2$$

$$\hat{C}_3 = \hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3$$

$$\hat{C}_4 = \hat{T}_4 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{24}\hat{T}_1^4$$

and so on.

The exponential ansatz (4/5)

- The **CC wave function** has thus the same form as the FCI wave function (with intermediate normalization, i.e. $c_0 = 1$)

$$
\begin{aligned}
|\Psi_{\mathrm{CC}}\rangle =& |\Phi_0\rangle + \sum_{a}^{\mathrm{occ}} \sum_{r}^{\mathrm{vir}} c_a^r |\Phi_a^r\rangle + \sum_{a<b}^{\mathrm{occ}} \sum_{r<s}^{\mathrm{vir}} c_{ab}^{rs} |\Phi_{ab}^{rs}\rangle \\
&+ \sum_{a<b<c}^{\mathrm{occ}} \sum_{r<s<t}^{\mathrm{vir}} c_{abc}^{rst} |\Phi_{abc}^{rst}\rangle + \sum_{a<b<c<d}^{\mathrm{occ}} \sum_{r<s<t<u}^{\mathrm{vir}} c_{abcd}^{rstu} |\Phi_{abcd}^{rstu}\rangle + \cdots
\end{aligned}
$$

with coefficients related to the cluster amplitudes by

$$c_a^r = t_a^r$$

$$c_{ab}^{rs} = t_{ab}^{rs} + t_a^r * t_b^s$$

$$c_{abc}^{rst} = t_{abc}^{rst} + t_a^r * t_{bc}^{st} + t_a^r * t_b^s * t_c^t$$

$$c_{abcd}^{rstu} = t_{abcd}^{rstu} + t_a^r * t_{bcd}^{stu} + t_{ab}^{rs} * t_{cd}^{tu} + t_a^r * t_b^s * t_{cd}^{tu} + t_a^r * t_b^s * t_c^t * t_d^u$$

and so on.

Here, $*$ means an **antisymmetric product** with respect to exchange of indices:

$$t_a^r * t_b^s = t_a^r t_b^s - t_b^r t_a^s$$

$$t_a^r * t_{bc}^{st} = t_a^r t_{bc}^{st} - t_b^r t_{ac}^{st} + t_c^r t_{ab}^{st} - t_a^s t_{bc}^{rt} + t_b^s t_{ac}^{rt} - t_c^s t_{ab}^{rt} + t_a^t t_{bc}^{rs} - t_b^t t_{ac}^{rs} + t_c^t t_{ab}^{rs}$$

$$t_a^r * t_b^s * t_c^t = t_a^r t_b^s t_c^t - t_a^r t_c^s t_b^t - t_b^r t_a^s t_c^t - t_c^r t_b^s t_a^t + t_c^r t_a^s t_b^t + t_b^r t_c^s t_a^t$$

and so on.

The exponential ansatz (5/5)

- Thus, the CC wave function contains **all excited determinants**, just as the FCI wave function.
- If the cluster operator $\hat{T}$ is not truncated, the CC wave function is just a **nonlinear reparametrization of the FCI wave function** with the same number of parameters. Optimizing the cluster amplitudes $\mathbf{t} = (t_a^r, t_{ab}^{rs}, t_{abc}^{rst}, ...)$ so as to minimize the total energy would lead to the FCI wave function.
- The interest of the CC approach only appears when the cluster operator is **truncated**.

Outline

6 Coupled-cluster theory

- The exponential ansatz
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Truncation of the cluster operator

- For example, let us consider **coupled-cluster singles doubles (CCSD)**

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

- The expansion of $e^{\hat{T}}$ gives

$$e^{\hat{T}} = \hat{1} + \hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right) + \left(\hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3\right) + \left(\frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{24}\hat{T}_1^4\right) + \cdots$$

- The CCSD wave function has the same form as the FCI wave function, i.e. it contains **all excited determinants**, but with coefficients now given by

$$c_a^r = t_a^r$$

$$c_{ab}^{rs} = t_{ab}^{rs} + t_a^r * t_b^s$$

$$c_{abc}^{rst} = t_a^r * t_{bc}^{st} + t_a^r * t_b^s * t_c^t$$

$$c_{abcd}^{rstu} = t_{ab}^{rs} * t_{cd}^{tu} + t_a^r * t_b^s * t_{cd}^{tu} + t_a^r * t_b^s * t_c^t * t_d^u$$

and so on.

- The coefficients of the triple excitations c_{abc}^{rst} are now only **approximated by products** of single- and double-excitation amplitudes t_a^r and t_{bc}^{st}, and similarly for all higher-level excitations.
- In comparison with the CISD wave function, the CCSD wave function has many more excited determinants but the **same number of free parameters** $\mathbf{t} = (t_a^r, t_{ab}^{rs})$ to optimize!

Truncation of the cluster operator: size-consistency

- Contrary to truncated CI, **truncated CC is size-consistent**, which directly stems from the **exponential form** of the CC wave function.
- Proof: consider a system composed of two infinitely separated (and thus non-interacting) fragments A and B:

$$\hat{H} = \hat{H}_A + \hat{H}_B$$

  - If the HF calculation is size-consistent, the HF wave function is multiplicatively separable: $|\Phi_0^{A\cdots B}\rangle = |\Phi_0^A\rangle \otimes |\Phi_0^B\rangle$ (where $\otimes$ is the antisymmetric tensor product)
  - Because the orbitals of each fragments do not overlap, the cluster operator of the system is additively separable: $\hat{T}^{A\cdots B} = \hat{T}^A + \hat{T}^B$
  - We can then show that the **CC wave function is multiplicatively separable**:

$$\begin{aligned}
|\Psi_{\text{CC}}^{A\cdots B}\rangle =& e^{\hat{T}^{A\cdots B}}|\Phi_0^{A\cdots B}\rangle \\
=& e^{\hat{T}^A+\hat{T}^B}|\Phi_0^A\rangle \otimes |\Phi_0^B\rangle \\
=& e^{\hat{T}^A}|\Phi_0^A\rangle \otimes e^{\hat{T}^B}|\Phi_0^B\rangle \\
=& |\Psi_{\text{CC}}^A\rangle \otimes |\Psi_{\text{CC}}^B\rangle
\end{aligned}$$

  - This implies that the **CC energy is additively separable**:

$$\begin{aligned}
E_{\text{CC}}(A\cdots B) =& \langle\Psi_{\text{CC}}^{A\cdots B}|\hat{H}_A + \hat{H}_B|\Psi_{\text{CC}}^{A\cdots B}\rangle \\
=& \langle\Psi_{\text{CC}}^A|\hat{H}_A|\Psi_{\text{CC}}^A\rangle\langle\Psi_{\text{CC}}^B|\Psi_{\text{CC}}^B\rangle + \langle\Psi_{\text{CC}}^A|\Psi_{\text{CC}}^A\rangle\langle\Psi_{\text{CC}}^B|\hat{H}_B|\Psi_{\text{CC}}^B\rangle \\
=& E_{\text{CC}}(A) + E_{\text{CC}}(B)
\end{aligned}$$

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6 Coupled-cluster theory

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The coupled-cluster energy and the coupled-cluster equations (1/4)

- We consider in all the following an arbitrary truncation level of the cluster operator.
- The most natural way to calculate the CC amplitudes **t** and CC energy would be by using the **variational method**:

  $$E_{\text{CC}}^{\text{var}} = \min_{\mathbf{t}} \langle \Psi_{\text{CC}} | \hat{H} | \Psi_{\text{CC}} \rangle$$

  with the constraint $\langle \Psi_{\text{CC}} | \Psi_{\text{CC}} \rangle = 1$.

  However, the CC wave function includes all excited determinants up to N-fold excitations which contribute to the expectation value, giving too complex equations to be efficiently solved.
- A more convenient approach for obtaining the CC amplitudes and CC energy is the **projection method**: we require that Ψ_{CC} satisfies the Schrödinger equation

  $$(\hat{H} - E_{\text{CC}}) | \Psi_{\text{CC}} \rangle = 0$$

  projected onto the space spanned by $\langle \Phi_0 |$, $\langle \Phi_a^r |$, $\langle \Phi_{ab}^{rs} |$, $\langle \Phi_{abc}^{rst} |$,...

  $$\langle \Phi_0 | (\hat{H} - E_{\text{CC}}) | \Psi_{\text{CC}} \rangle = 0$$

  $$\langle \Phi_a^r | (\hat{H} - E_{\text{CC}}) | \Psi_{\text{CC}} \rangle = 0$$

  $$\langle \Phi_{ab}^{rs} | (\hat{H} - E_{\text{CC}}) | \Psi_{\text{CC}} \rangle = 0$$

  $$\langle \Phi_{abc}^{rst} | (\hat{H} - E_{\text{CC}}) | \Psi_{\text{CC}} \rangle = 0 \qquad \text{and so on.}$$

The coupled-cluster energy and the coupled-cluster equations (2/4)

- Remember the expansion of $|\Psi_{\text{CC}}\rangle$ in terms of determinants

$$|\Psi_{\text{CC}}\rangle = |\Phi_0\rangle + \sum_{a}^{\text{occ}}\sum_{r}^{\text{vir}} c_a^r |\Phi_a^r\rangle + \sum_{a<b}^{\text{occ}}\sum_{r<s}^{\text{vir}} c_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \sum_{a<b<c}^{\text{occ}}\sum_{r<s<t}^{\text{vir}} c_{abc}^{rst}|\Phi_{abc}^{rst}\rangle + \cdots$$

  with intermediate normalization, i.e. $\langle\Phi_0|\Psi_{\text{CC}}\rangle = 1$.

- We see that the first projected equation, $\langle\Phi_0|(\hat{H} - E_{\text{CC}})|\Psi_{\text{CC}}\rangle = 0$, gives the **CC energy**

$$E_{\text{CC}} = \langle\Phi_0|\hat{H}|\Psi_{\text{CC}}\rangle = \langle\Phi_0|\hat{H}|\Phi_0\rangle + \sum_{a}^{\text{occ}}\sum_{r}^{\text{vir}} c_a^r\langle\Phi_0|\hat{H}|\Phi_a^r\rangle + \sum_{a<b}^{\text{occ}}\sum_{r<s}^{\text{vir}} c_{ab}^{rs}\langle\Phi_0|\hat{H}|\Phi_{ab}^{rs}\rangle$$

  in which, according to Slater's rules, triple and higher excitations do not contribute.

- It turns out that the single-excitation term does not contribute thanks to **Brillouin's theorem** $\langle\Phi_0|\hat{H}|\Phi_a^r\rangle = 0$. We thus obtain the **CC correlation energy**

$$E_{\text{c}}^{\text{CC}} = E_{\text{CC}} - E_{\text{HF}} = \sum_{a<b}^{\text{occ}}\sum_{r<s}^{\text{vir}} c_{ab}^{rs}\langle\Phi_0|\hat{H}|\Phi_{ab}^{rs}\rangle = \sum_{a<b}^{\text{occ}}\sum_{r<s}^{\text{vir}}(t_{ab}^{rs} + t_a^r * t_b^s)\langle ab||rs\rangle$$

- Except in the uninteresting case where the cluster operator $\hat{T}$ is not truncated, the CC energy obtained with the projection method is **not identical** to the one that would have been obtained with the variational method: $E_{\text{CC}} \neq E_{\text{CC}}^{\text{var}}$.

The coupled-cluster energy and the coupled-cluster equations (3/4)

- The other projected equations determine the **CC amplitudes**

$$\langle \Phi_a^r | (\hat{H} - E_{\mathrm{CC}}) e^{\hat{T}} | \Phi_0 \rangle = 0$$

$$\langle \Phi_{ab}^{rs} | (\hat{H} - E_{\mathrm{CC}}) e^{\hat{T}} | \Phi_0 \rangle = 0$$

$$\langle \Phi_{abc}^{rst} | (\hat{H} - E_{\mathrm{CC}}) e^{\hat{T}} | \Phi_0 \rangle = 0 \qquad \text{and so on.}$$

  which are known as the **unlinked CC amplitude equations**.

- They represent a system of **coupled nonlinear equations** for the amplitudes t_a^r, t_{ab}^{rs}, t_{abc}^{rst}, etc.

- To have the same number of equations as the number of unknown amplitudes, the projection space must correspond to the truncation level of the cluster operator. For example, for determining the CCSD amplitudes, one needs to consider projection onto single- and double-excited determinants only.

The coupled-cluster energy and the coupled-cluster equations (4/4)

- In practice, it is often more convenient to write the CC amplitude equations is a different way, by first multiplying from the left by the operator $e^{-\hat{T}}$ in the Schrödinger equation before projecting on the excited determinants

$$\langle \Phi_a^r | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0$$

$$\langle \Phi_{ab}^{rs} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0$$

$$\langle \Phi_{abc}^{rst} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0 \qquad \text{and so on.}$$

  which are known as the **linked CC amplitude equations**.

- Although equivalent to the unlinked equations, the linked equations have the advantage of leading to more compact expressions which are **manifestly size-consistent** and **at most quartic** in the amplitudes (at any truncation level).

- This last feature comes from the fact that the Baker-Campbell-Hausdorff (BCH) expansion of $e^{-\hat{T}} \hat{H} e^{\hat{T}}$ exactly terminates at fourth order because $\hat{H}$ contains at most a two-electron operator:

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{3!}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{4!}[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}]$$

Outline

Example: coupled-cluster doubles (1/3)

- As an example, we now write down the complete equations in the case of **coupled-cluster doubles (CCD)**.
- In this case, the cluster operator only contains **double excitations**

$$\hat{T} = \hat{T}_2$$

- The **CCD wave function** thus contains double-excited determinants, quadruple-excited determinants, ...

$$|\Psi_{\mathrm{CCD}}\rangle = |\Phi_0\rangle + \sum_{a<b}^{\mathrm{occ}} \sum_{r<s}^{\mathrm{vir}} t_{ab}^{rs} |\Phi_{ab}^{rs}\rangle + \sum_{a<b<c<d}^{\mathrm{occ}} \sum_{r<s<t<u}^{\mathrm{vir}} (t_{ab}^{rs} * t_{cd}^{tu}) |\Phi_{abcd}^{rstu}\rangle + \cdots$$

  where the coefficients of the quadruple excitations are given by the antisymmetrized product of the coefficients of the double excitations, and so on.

- The **CCD correlation energy** is given by

$$E_{\mathrm{c}}^{\mathrm{CCD}} = \sum_{a<b}^{\mathrm{occ}} \sum_{r<s}^{\mathrm{vir}} t_{ab}^{rs} \langle ab||rs\rangle$$

Example: coupled-cluster doubles (2/3)

- The **double-excitation amplitudes** t_{ab}^{rs} can be determined from the unlinked CC amplitude equations:

$$\langle \Phi_{ab}^{rs} | (\hat{H} - E_{\mathrm{CCD}}) | \Psi_{\mathrm{CCD}} \rangle = 0$$

- After expanding Ψ_{CCD}, we get:

$$\langle \Phi_{ab}^{rs} | \hat{H} | \Phi_0 \rangle + \sum_{c<d}^{\mathrm{occ}} \sum_{t<u}^{\mathrm{vir}} \langle \Phi_{ab}^{rs} | \hat{H} - E_{\mathrm{CCD}} | \Phi_{cd}^{tu} \rangle t_{cd}^{tu} + \sum_{c<d}^{\mathrm{occ}} \sum_{t<u}^{\mathrm{vir}} \langle \Phi_{ab}^{rs} | \hat{H} | \Phi_{abcd}^{rstu} \rangle (t_{ab}^{rs} * t_{cd}^{tu}) = 0$$

- Using $\langle \Phi_{ab}^{rs} | \hat{H} | \Phi_0 \rangle = \langle rs || ab \rangle$ and $\langle \Phi_{ab}^{rs} | \hat{H} | \Phi_{abcd}^{rstu} \rangle = \langle cd || tu \rangle$,
and inserting $E_{\mathrm{CCD}} = E_{\mathrm{HF}} + E_{\mathrm{c}}^{\mathrm{CCD}}$ gives

$$\langle rs || ab \rangle + \sum_{c<d}^{\mathrm{occ}} \sum_{t<u}^{\mathrm{vir}} \langle \Phi_{ab}^{rs} | \hat{H} - E_{\mathrm{HF}} | \Phi_{cd}^{tu} \rangle t_{cd}^{tu} + \sum_{c<d}^{\mathrm{occ}} \sum_{t<u}^{\mathrm{vir}} \langle cd || tu \rangle (t_{ab}^{rs} * t_{cd}^{tu} - t_{ab}^{rs} t_{cd}^{tu}) = 0$$

- The remaining matrix element is more complicated to calculate, but can be done with a bit of method and patience. We get:

$$\begin{aligned} \langle \Phi_{ab}^{rs} | \hat{H} - E_{\mathrm{HF}} | \Phi_{cd}^{tu} \rangle \quad = \quad & (\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b) \delta_{a,c} \delta_{b,d} \delta_{r,t} \delta_{s,u} \\ & + \langle rs || tu \rangle \delta_{a,d} \delta_{b,d} + \langle cd || ab \rangle \delta_{r,t} \delta_{s,u} \\ & + \langle ds || ub \rangle \delta_{a,c} \delta_{r,t} - \langle cs || ub \rangle \delta_{a,d} \delta_{r,t} \\ & - \langle ds || tb \rangle \delta_{a,c} \delta_{r,u} + \langle cs || tb \rangle \delta_{a,d} \delta_{r,u} \end{aligned}$$

Example: coupled-cluster doubles (3/3)

- The final **CCD amplitude equations** are:

$$\begin{aligned} &\langle rs||ab\rangle + (\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b) t_{ab}^{rs} + \sum_{t<u}^{\text{vir}} \langle rs||tu\rangle t_{ab}^{tu} + \sum_{c<d}^{\text{occ}} \langle cd||ab\rangle t_{cd}^{rs} \\ &+ \sum_{d}^{\text{occ}} \sum_{u}^{\text{vir}} \langle ds||ub\rangle t_{ad}^{ru} - \sum_{c}^{\text{occ}} \sum_{u}^{\text{vir}} \langle cs||ub\rangle t_{ca}^{ru} - \sum_{d}^{\text{occ}} \sum_{t}^{\text{vir}} \langle ds||tb\rangle t_{ad}^{tr} + \sum_{c}^{\text{occ}} \sum_{t}^{\text{vir}} \langle cs||tb\rangle t_{ca}^{tr} \\ &+ \sum_{c<d}^{\text{occ}} \sum_{t<u}^{\text{vir}} \langle cd||tu\rangle (t_{ab}^{rs} * t_{cd}^{tu} - t_{ab}^{rs} t_{cd}^{tu}) = 0 \end{aligned}$$

  which are **quadratic equations for t to be solved iteratively**.

- Let us consider now the expansion of the amplitudes in powers of the electron-electron interaction: $t_{ab}^{rs} = t_{ab}^{rs,(1)} + t_{ab}^{rs,(2)} + \cdots$. The **first-order amplitudes** are given by

$$\langle rs||ab\rangle + (\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b) t_{ab}^{rs,(1)} = 0 \implies t_{ab}^{rs,(1)} = -\frac{\langle rs||ab\rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}$$

  Inserting this expression of $t_{ab}^{rs,(1)}$ in the expression of the correlation energy, we get:

$$\sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} t_{ab}^{rs,(1)} \langle ab||rs\rangle = -\sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b} = E_{\text{c}}^{\text{MP2}}$$

  Thus, **CCD correctly reduces to MP2 at second order in the e-e interaction**.

Outline

6 Coupled-cluster theory

- The exponential ansatz
- Truncation of the cluster operator
- The coupled-cluster energy and the coupled-cluster equations
- Example: coupled-cluster doubles
- Coupled-cluster methods in practice

Coupled-cluster methods in practice: CCSD and CCSD(T)

- The first level of CC approximation commonly used is **coupled-cluster singles doubles (CCSD)**:

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

  - CCSD is correct up to third order in the e-e interaction
  - The CCSD computational cost scales as $\mathcal{O}(N_{\mathrm{occ}}^2 N_{\mathrm{vir}}^4)$

- To obtain more accurate results, it is important to add the effect of the triple-excitation operator $\hat{T}_3$ perturbatively, which is known as **coupled-cluster singles doubles and perturbative triples (CCSD(T))**:
  - The second-order triple-excitation amplitudes $t_{abc}^{rst,(2)}$ are calculated non-iteratively from the CCSD double-excitation amplitudes t_{ab}^{rs}
  - Parts of the fourth-order and fifth-order energy corrections involving the triple-excitation amplitudes are calculated and added to the CCSD energy

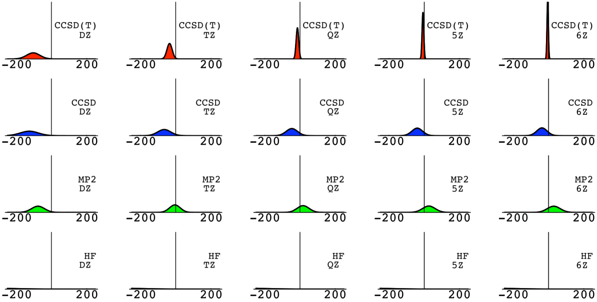
$$E_{\mathrm{CCSD(T)}} = E_{\mathrm{CCSD}} + E_{\mathrm{T}}^{(4)} + E_{\mathrm{ST}}^{(5)}$$

  - The CCSD(T) computational cost scales as $\mathcal{O}(N_{\mathrm{occ}}^3 N_{\mathrm{vir}}^4)$

Benchmark on atomization energies

Atomization energies (in kJ/mol) of 16 small molecules: H_2, CH_2, CH_4, H_2O, NH_3, HF, N_2, F_2, CO, HCN, C_2H_2, C_2H_4, CH_2O, HNO, CO_2, O_3

Normal **distribution of errors** for HF, MP2, CCSD, and CCSD(T) with different basis sets (DZ, TZ, QZ, 5Z, 6Z):



With largest basis set (6Z):	HF	MP2	CCSD	CCSD(T)
Mean error (in kJ/mol)	-423.1	29.7	-37.3	-4.7
Standard deviation (in kJ/mol)	179.3	36.8	29.4	3.8

From T. Helgaker, *High-Accuracy Quantum Chemistry*, Lecture at UPMC, 2012 and T. Helgaker, P. Jørgensen, J. Olsen, *Molecular Electronic-Structure Theory*, Wiley, 2002.

Benchmark on reaction enthalpies

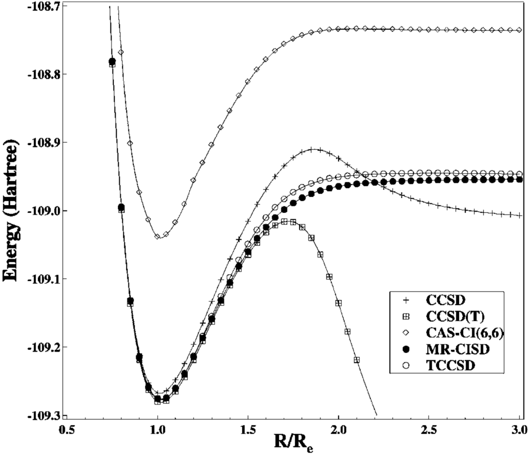
Reaction enthalpies and their errors (in kJ/mol) of 14 reactions for B3LYP and CCSD(T):

	B3LYP		CCSD(T)		Exp.
$CH_2 + H_2 \rightarrow CH_4$	-543	1	-543	1	-544(2)
$C_2H_2 + H_2 \rightarrow C_2H_4$	-208	-5	-206	-3	-203(2)
$C_2H_2 + 3H_2 \rightarrow 2CH_4$	-450	-4	-447	-1	-446(2)
$CO + H_2 \rightarrow CH_2O$	-34	-13	-23	-2	-21(1)
$N_2 + 3H_2 \rightarrow 2NH_3$	-166	-2	-165	-1	-164(1)
$F_2 + H_2 \rightarrow 2HF$	-540	23	-564	-1	-563(1)
$O_3 + 3H_2 \rightarrow 3H_2O$	-909	24	-946	-13	-933(2)
$CH_2O + 2H_2 \rightarrow CH_4 + H_2O$	-234	17	-250	1	-251(1)
$H_2O_2 + H_2 \rightarrow 2H_2O$	-346	19	-362	3	-365(2)
$CO + 3H_2 \rightarrow CH_4 + H_2O$	-268	4	-273	-1	-272(1)
$HCN + 3H_2 \rightarrow CH_4 + NH_3$	-320	0	-321	-1	-320(3)
$HNO + 2H_2 \rightarrow H_2O + NH_3$	-429	15	-446	-2	-444(1)
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-211	33	-244	0	-244(1)
$2CH_2 \rightarrow C_2H_4$	-845	-1	-845	-1	-844(3)

From T. Helgaker, *High-Accuracy Quantum Chemistry*, Lecture at UPMC, 2012 and
T. Helgaker, P. Jørgensen, J. Olsen, *Molecular Electronic-Structure Theory*, Wiley, 2002.

Benchmark on the dissociation energy curve of N_2

Dissociation energy curve of N_2 with cc-pVDZ basis set (with respect to the relative internuclear distance R/R_e where $R_e = 2.074$ bohr):



From T. Kinoshita, O. Hino, and R. J. Bartlett, Journal of Chemical Physics **123**, 074106 (2005) or R. J. Bartlett, WIREs Computational Molecular Science **2**, 126 (2012).

Outline

7. Appendix
   - Slater's rules for matrix elements
   - Gaussian basis sets
   - The formalism of second quantization

Slater's rules for matrix elements

Matrix elements where Φ_0 is a reference Slater determinant, Φ_a^r is a single-excited determinant, and Φ_{ab}^{rs} is a double-excited determinant made of **spin orbitals** $\{|i\rangle\}$ which are **orthonormal** $\langle i|j\rangle = \delta_{i,j}$:

- **Zero-electron operator (overlap)**:

$$\langle \Phi_0|\Phi_0\rangle = 1 \qquad \langle \Phi_0|\Phi_a^r\rangle = 0 \qquad \langle \Phi_0|\Phi_{ab}^{rs}\rangle = 0$$

- **One-electron operator**: $\hat{O}_1 = \sum_i^N \hat{h}(\mathbf{x}_i)$

$$\langle \Phi_0|\hat{O}_1|\Phi_0\rangle = \sum_a^{\text{occ}} \langle a|\hat{h}|a\rangle \qquad \langle \Phi_0|\hat{O}_1|\Phi_a^r\rangle = \langle a|\hat{h}|r\rangle \qquad \langle \Phi_0|\hat{O}_1|\Phi_{ab}^{rs}\rangle = 0$$

- **Two-electron operator**: $\hat{O}_2 = \sum_i^N \sum_{j>i}^N 1/r_{ij}$

$$\langle \Phi_0|\hat{O}_2|\Phi_0\rangle = \frac{1}{2}\sum_a^{\text{occ}}\sum_b^{\text{occ}} \langle ab||ab\rangle \qquad \langle \Phi_0|\hat{O}_2|\Phi_a^r\rangle = \sum_b^{\text{occ}} \langle ab||rb\rangle$$

$$\langle \Phi_0|\hat{O}_2|\Phi_{ab}^{rs}\rangle = \langle ab||rs\rangle$$

All matrix elements between Φ_0 and triple- or higher-excited determinants are zero.

Outline

7 Appendix

- Slater's rules for matrix elements
- Gaussian basis sets
- The formalism of second quantization

Gaussian basis sets

In quantum chemistry, we usually use **Gaussian-type orbital (GTO) basis sets**.

- The atom-centered Gaussian **primitive functions** are of the form

$$g_p(\mathbf{r}) = N_p \; r^{\ell_p} \; e^{-\alpha_p r^2} \; Y_{\ell_p}^{m_p}(\theta,\phi)$$

  using spherical coordinates $\mathbf{r} = (r,\theta,\phi)$ around the nucleus center.

- The basis functions are generally **fixed linear combinations** (called **contractions**) of primitive functions:

$$\phi_\mu(\mathbf{r}) = \sum_p d_{p\mu} \; g_p(\mathbf{r})$$

- Many such GTO basis sets have been optimized for each atom. Widely used for wave-function calculations is the family of **Dunning's correlation-consistent polarized valence basis sets** denoted by cc-pVXZ where X =D,T,Q,5,6.
  - Example for the C atom:

Basis set	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV6Z
Core basis functions	1s	1s	1s	1s	1s
Valence basis functions	2s+2p	3s+3p	4s+4p	5s+5p	6s+6p
Polarization basis functions	1d	2d+1f	3d+2f+1g	4d+3f+2g+1h	5d+4f+3g+2h+1i
Total number of basis functions ($K \propto X^3$)	14	30	55	91	140

  - There are also basis sets **augmented with diffuse basis functions**: aug-cc-pVXZ
  - There are also basis sets with more **core basis functions** for core correlation: cc-pCVXZ

Outline

7. Appendix
   - Slater's rules for matrix elements
   - Gaussian basis sets
   - The formalism of second quantization

The formalism of second quantization (1/2)

Second quantization is a very convenient formalism for dealing with many-body quantum systems. In particular, for electrons, it allows one to incorporate the antisymmetry property of the wave functions directly into an algebra of operators.

We consider a set of **spin orbitals** $\{|i\rangle\}$ which are **orthonormal**, $\langle i|j\rangle = \delta_{i,j}$.

- **Vaccum state**:
  We define a **vaccum state** $|\text{vac}\rangle$ containing zero electron and normalized to one: $\langle\text{vac}|\text{vac}\rangle = 1$.
- **Creation and annihilation operators**:
  At each spin orbital i, we associate a **creation operator** $\hat{a}_i^\dagger$ which acts on $|\text{vac}\rangle$ to create the state $|i\rangle$ corresponding to one electron in the spin orbital i

  $$\hat{a}_i^\dagger|\text{vac}\rangle = |i\rangle$$

  At each spin orbital i, we also associate an **annihilation operator** $\hat{a}_i$ which gives back the vaccum state $|\text{vac}\rangle$ when acting on the state $|i\rangle$

  $$\hat{a}_i|i\rangle = |\text{vac}\rangle$$

  The creation operator $\hat{a}_i^\dagger$ is the adjoint of the annihilation operator $\hat{a}_i$, and vice versa.

  If we try to create a spin orbital that has already been created, we get zero: $\hat{a}_i^\dagger|i\rangle = 0$.
  If we try to annihilate a spin orbital that has not been created, we get zero: $\hat{a}_i|\text{vac}\rangle = 0$.

The formalism of second quantization (2/2)

- **Many-electron states**:
  A **many-electron state** is created by acting sucessively with several creation operators on the vaccum state. For example, acting with the creation operator $\hat{a}_1^\dagger$, $\hat{a}_2^\dagger$, ..., $\hat{a}_N^\dagger$ gives a state corresponding to a Slater determinant with N electrons occupying the spin orbitals labeled by 1, 2, ...,N:

$$\hat{a}_1^\dagger \hat{a}_2^\dagger \cdots \hat{a}_N^\dagger |\text{vac}\rangle = |1\ 2\ \cdots\ N\rangle = |\Phi_0\rangle$$

- **Excitation operators**:
  Excited determinants can be conveniently expressed as **excitation operators** acting on the reference determinant $|\Phi_0\rangle$. For example, the operator $\hat{a}_r^\dagger \hat{a}_a$ generates a single excitation and the operator $\hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_b \hat{a}_a$ generates a double excitation:

$$\hat{a}_r^\dagger \hat{a}_a |\Phi_0\rangle = |\Phi_a^r\rangle \quad \text{and} \quad \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_b \hat{a}_a |\Phi_0\rangle = |\Phi_{ab}^{rs}\rangle \quad \text{and so on.}$$

- **Fermionic anticommutation rules**:
  The previous rules imply that the creation and annihilation operators obey the **fermionic anticommutation relations**:

$$\{\hat{a}_i^\dagger, \hat{a}_j^\dagger\} = \hat{a}_i^\dagger \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i^\dagger = 0$$

$$\{\hat{a}_i, \hat{a}_j\} = \hat{a}_i \hat{a}_j + \hat{a}_j \hat{a}_i = 0$$

$$\{\hat{a}_i, \hat{a}_j^\dagger\} = \hat{a}_i \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i = \delta_{i,j}$$