Quantum Chemistry Methods

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- The electronic Schrödinger equation
- Hartree–Fock theory
  - self-consistent field theory
  - basis functions and basis sets
- FCI theory
  - electron correlation
- static correlation
  - MCSCF theory
- dynamical correlation
  - coupled-cluster theory
  - perturbation theory

The Schrödinger equation

- The time-independent Schrödinger equation for a system of N electrons:

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

- Field-free, nonrelativistic Hamiltonian operator in atomic units:

$$\hat{H} = -\frac{1}{2}\sum_{i}\nabla_i^2 - \sum_{iI}\frac{Z_I}{r_{iI}} + \sum_{i>j}\frac{1}{r_{ij}} + \sum_{I>J}\frac{Z_I Z_J}{r_{IJ}}$$

- The wave function is a function of the $3N$ Cartesian spatial coordinates r_i and N spin coordinates s_i of the N electrons:

$$\Psi = \Psi\left(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N\right) = \Psi\left(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots \mathbf{r}_N, s_N\right)$$

- In addition, the wave function depends parametrically on the nuclear coordinates (the Born–Oppenheimer approximation).
- In the absence of magnetic fields, the Hamiltonian is spinless. Spin plays an important role because of the symmetry requirements on the wave function.

Some properties of exact and approximate wave functions

- For bound states, the exact wave function is square-integrable:

$$\langle\Psi|\Psi\rangle = \int \Psi^* (\mathbf{x})\, \Psi (\mathbf{x})\, \mathrm{d}\mathbf{x} = 1 \qquad \leftarrow \text{always satisfied}$$

- The exact wave function is antisymmetric in the electron coordinates:

$$P_{ij}\Psi = -\Psi \qquad \leftarrow \text{always satisfied}$$

- The exact wave function is variational (i.e., the energy is stable):

$$\langle\delta\Psi|\Psi\rangle = 0 \quad \Rightarrow \quad \langle\delta\Psi|\hat{H}|\Psi\rangle = 0 \qquad \leftarrow \text{not always satisfied}$$

- The exact nonrelativistic wave function is a spin eigenfunction:

$$\hat{S}^2\Psi = S(S+1)\Psi; \quad \hat{S}_z\Psi = M_S\Psi \qquad \leftarrow \text{not always satisfied}$$

- The exact wave function is size-extensive, implying that:

$$\hat{H} = \textstyle\sum_i \hat{H}_i \quad \Rightarrow \quad E = \textstyle\sum_i E_i \qquad \leftarrow \text{not always satisfied}$$

Noninteracting electronic systems: spin orbitals and orbital energies

- Consider a fictitious system of N noninteracting electrons:

$$\hat{H}_0\Psi = E\Psi; \quad \hat{H}_0 = \sum_i \hat{h}_i; \quad \hat{h}_i = -\tfrac{1}{2}\nabla_i^2 - \sum_I \frac{Z_I}{r_{iI}}$$

- Solving the one-electron eigenvalue problem

$$\hat{h}\phi_i(\mathbf{x}) = \varepsilon_i\phi_i(\mathbf{x}); \quad \langle\phi_i|\phi_j\rangle = \delta_{ij},$$

we obtain the spin orbitals ϕ_i and the orbital energies ε_i.

- The exact N-particle solution may be written in the separated form

$$\Psi = \hat{A}\prod_{i=1}^{N} \underbrace{\phi_i(\mathbf{x}_i)}_{\text{spin orbitals}} \quad ; \quad E = \sum_{i=1}^{N} \varepsilon_i \leftarrow \text{orbital energies}$$

where $\hat{A}$ is the antisymmetrization operator.

- The N-particle problem reduces to N one-particle problems.

Interacting electronic systems: the Hartree–Fock model

- For a system of interacting electrons, the exact wave function cannot be written as an antisymmetrized product of spin orbitals.
- Nevertheless, we may use the antisymmetrized product form as a useful *ansatz* for an approximate electronic wave function:

$$\Phi = \hat{A} \prod_{i=1}^{N} \phi_i(\mathbf{x}_i); \quad \langle \phi_i | \phi_j \rangle = \delta_{ij}; \quad \langle \Phi | \Phi \rangle = 1$$

- To make the most of this *ansatz*, we invoke the variation principle and minimize the expectation value of the energy:

$$E = \min_{\phi_i} \langle \Phi | \hat{H} | \Phi \rangle \geq E_{\text{exact}} \quad \leftarrow \quad \text{Hamiltonian bounded from below}$$

- This is the Hartree–Fock (HF) approximation.
- The HF model is the cornerstone of *ab initio* theory:
  - it constitutes a useful, qualitative model on its own;
  - it forms the starting point for more accurate models.

The Hartree–Fock equations and the Fock operator

- Minimization of the HF energy may be carried out by solving the one-electron Hartree–Fock equations:

$$\hat{F}\phi_p = \varepsilon_p \phi_p \quad \leftarrow \text{ canonical orbitals and orbital energies}$$

- The effective Fock operator depends on its own eigenvectors:

$$\begin{aligned} \hat{F} &= \hat{h} + \hat{\jmath} - \hat{k} \\ \hat{\jmath}\phi_p(\mathbf{x}_1) &= \textstyle\sum_{i=1}^{N} \phi_p(\mathbf{x}_1) \int \frac{\phi_i^*(\mathbf{x}_2)\phi_i(\mathbf{x}_2)}{r_{12}} \, \mathrm{d}\mathbf{x}_2 && \leftarrow \text{Coulomb operator} \\ \hat{k}\phi_p(\mathbf{x}_1) &= \textstyle\sum_{i=1}^{N} \phi_i(\mathbf{x}_1) \int \frac{\phi_i^*(\mathbf{x}_2)\phi_p(\mathbf{x}_2)}{r_{12}} \, \mathrm{d}\mathbf{x}_2 && \leftarrow \text{exchange operator} \end{aligned}$$

- Each electron experiences an averaged field set up by the other electrons.
- The equations are solved iteratively: the self-consistent field (SCF) method.
- The HF wave function is invariant to unitary transformations of the MOs and a sufficient condition for minimum is:

$$\langle \phi_i | \hat{F} | \phi_a \rangle = 0 \quad \leftarrow \phi_i \text{ occupied, } \phi_a \text{ unoccupied}$$

Slater determinants and spin orbitals

- The HF wave function is often written as a Slater determinant:

$$\Phi(\mathrm{x}_1, \mathrm{x}_2, \ldots, \mathrm{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathrm{x}_1) & \phi_2(\mathrm{x}_1) & \cdots & \phi_N(\mathrm{x}_1) \\ \phi_1(\mathrm{x}_2) & \phi_2(\mathrm{x}_2) & \cdots & \phi_N(\mathrm{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathrm{x}_N) & \phi_2(\mathrm{x}_N) & \cdots & \phi_N(\mathrm{x}_N) \end{vmatrix}$$

- Commonly, each spin orbital is written as a product of a spatial orbital and a spin function:

$$\phi_i(\mathbf{x}) = \varphi_{p_i}(\mathbf{r})\sigma_{p_i}(s); \quad \sigma_{p_i}(s) = \alpha(s),\ \beta(s) \qquad \leftarrow \text{alpha and beta spin}$$

- From each $\varphi_p(\mathbf{r})$, we may thus generate two orthogonal spin orbitals:
  - in restricted HF (RHF) theory, the alpha and beta spin orbitals have the same spatial part;
  - in unrestricted HF (UHF) theory, there are no such constraints.

Linear combination of atomic orbitals (LCAO)

- In atomic and diatomic work, the molecular orbitals (MOs) $\varphi_p(\mathbf{r})$ are sometimes represented numerically on a grid.
- In molecular calculations, by contrast, the MOs are invariably expanded in a set of n simple, analytical, square-integrable atomic orbitals (AOs):

$$\varphi_i(\mathrm{r}) = \sum_\mu C_{\mu i}\chi_\mu(\mathrm{r}) \qquad \leftarrow \text{LCAO}$$

- There are two types of AOs in use:
  - Gaussian-type orbitals (GTOs) with the radial form $\exp(-\alpha r_A^2)$;
  - Slater-type orbitals (STOs) with the radial form $\exp(-\alpha r_A)$.
- GTOs are preferred over STOs since they greatly simplify multicenter integral evaluation.
- The optimization of the HF wave function now reduces to the determination of the MO coefficients $C_{\mu i}$.

The Roothaan–Hall SCF equations

- Three- and six-dimensional integrals over AOs:
  - overlap integrals: $S_{\mu\nu} = \int \chi_\mu^*(\mathbf{r})\chi_\nu(\mathbf{r})\,\mathrm{d}\mathbf{r}$
  - one-electron integrals: $h_{\mu\nu} = \int \chi_\mu^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{r_I}\right)\chi_\nu(\mathbf{r})\,\mathrm{d}\mathbf{r}$
  - two-electron integrals: $g_{\mu\nu\rho\sigma} = \iint \frac{\chi_\mu^*(\mathbf{r}_1)\chi_\rho^*(\mathbf{r}_2)\chi_\nu(\mathbf{r}_1)\chi_\sigma(\mathbf{r}_2)}{r_{12}}\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2$
  - integral evaluation is fairly simple with GTOs
- The LCAO RHF Fock equations may now be written in matrix form

$$\begin{aligned} \mathbf{FC} &= \mathbf{SC}\varepsilon && \leftarrow \text{Roothaan–Hall equations} \\ F_{\mu\nu} &= h_{\mu\nu} + \textstyle\sum_{\rho\sigma} D_{\rho\sigma}\left(g_{\mu\nu\rho\sigma} - \frac{1}{2}g_{\mu\sigma\rho\nu}\right) && \leftarrow \text{Fock matrix in AO basis} \end{aligned}$$

  - a new density matrix is constructed at each SCF iteration:

$$D_{\rho\sigma} = 2\sum_{i=1}^{N} C_{\rho i}C_{\sigma i} \qquad \leftarrow \text{one contribution from each occupied orbital}$$

  - a large number of integrals are calculated at each SCF iteration

Solution of the Roothaan–Hall SCF equations

- The iterative solution of the Roothaan–Hall equations is fairly robust:
  - convergence improved by damping techniques such as DIIS;
  - typically 10–20 iterations are needed.
- The solution of the Roothaan–Hall equations produces not only a set of occupied MOs but also a set of unoccupied (virtual) MOs:
  - the virtual MOs are utilized in more accurate, post-HF treatments of electronic structure.
- The bottleneck is the calculation of the Coulomb contribution:
  - formally an n^4 process but screening reduces it to an n^2 process
  - linear scaling achieved by fast summation of Coulomb contributions
- The diagonalization of the Fock matrix scales as n^3:
  - full diagonalization not necessary
  - alternatives are being explored (direct AO density optimization)

Gaussian-type orbitals (GTOs)

- The AOs are usually (fixed linear combinations of) Cartesian GTOs centered on the atoms:

$$\begin{aligned} G_{ijk}(\mathrm{r}_A,\alpha) &= x_A^i y_A^j z_A^k \exp\left(-\alpha r_A^2\right) \\ \mathrm{r}_A &= \mathrm{r}-\mathrm{A} && \leftarrow \text{atom-centered function} \\ \alpha &> 0 && \leftarrow \text{real orbital exponent} \\ i,j,k &= 0,1,2,\ldots && \leftarrow \text{integer quantum numbers} \end{aligned}$$

- Properties of Cartesian GTOs:
  - separability in the Cartesian directions;
  - the Gaussian product rule: a product of two Gaussians is a Gaussian;
  - non-Coulomb integrals may be expressed in closed analytical form;
  - Coulomb integrals may be reduced to one-dimensional integrals:

$$F_n(x) = \int_0^1 \exp(-xt^2)t^{2n}\,\mathrm{d}t \qquad \leftarrow \text{Boys function}$$

Solid-harmonic GTOs

- The GTOs are usually not used in Cartesian form but are linearly combined to solid-harmonic form:

$$\begin{aligned} G_{lm}(\mathbf{r}_A, \alpha) &= S_{lm}(\mathbf{r}_A) \exp\left(-\alpha r_A^2\right); \quad l \geq |m| \geq 0 \\ S_{lm}(\mathbf{r}_A) &= \sum_{ijk} S_{lm}^{ijk} x_A^i y_A^j z_A^k \qquad \leftarrow \text{solid-harmonic function} \end{aligned}$$

- For a given subshell of angular momentum $l \geq 0$, there are $2l + 1$ independent, real-valued solid-harmonic GTOs (ignoring normalization):

$$\begin{aligned} S_{00}(\mathbf{r}_A) &= 1 && \leftarrow 1\ s \text{ function} \\ S_{1m}(\mathbf{r}_A) &= x_A,\ z_A,\ y_A && \leftarrow 3\ p \text{ functions} \\ S_{2m}(\mathbf{r}_A) &= x_A^2 - y_A^2,\ x_A z_A,\ 3z_A^2 - r_A^2,\ y_A z_A,\ x_A y_A && \leftarrow 5\ d \text{ functions} \end{aligned}$$

- The GTOs are always added in full subshells of $2l + 1$ functions.

Contracted GTOs

- The Gaussian radial form of the GTOs is well suited to integration but does not resemble closely the radial form of numerical orbitals.
- In practice, therefore, we mostly use contracted GTOs (CGTOs)—that is, fixed linear combinations of GTOs of the same quantum numbers:

$$\underbrace{G_{lm}^{\text{CGTO}}(\mathbf{r}_A)}_{\text{contracted GTO}} = \sum_i d_i \underbrace{G_{lm}(\mathbf{r}_A, \alpha_i)}_{\text{primitive GTO}}$$

- The orbital exponents α_i and the contraction coefficients d_i are usually determined in atomic calculations in such a way that each CGTO closely resembles an atomic orbital.
- Standard compilations of CGTOs of different size and flexibility exist for each atom in the periodic table.
- The use of such universal standard basis sets ensures that the calculations are well-defined and reproducible.

Gaussian basis sets

- minimal or single-zeta (SZ) basis sets:
  - one CGTO shell for each (partially) occupied atomic shell ($2s1p$)
  - crude description of the electronic system
- double-zeta (DZ) basis sets:
  - two CGTO shells for each (partially) occupied atomic shell ($4s2p$)
  - sufficient for qualitative work
- triple-zeta (TZ), quadruple-zeta (QZ), and higher-zeta basis sets:
  - necessary for quantitative work
- polarization functions:
  - CGTOs of angular momentum l higher than the highest occupied AO
  - necessary for polarization of the electronic charge in a molecular environment
  - DZP: $4s2p1d$, TZP: $6s3p2d1f$, and so on.

Performance of the RHF method: application to H_2O

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	experiment	error
E (E_h)	−76.027	−76.058	−76.066	−76.068	−76.439[a]	−0.5%
AE (kJ/mol)	620	645	650	652	975	−33.1%
R_{OH} (pm)	94.6	94.1	94.0	94.0	95.7	−1.8%
Θ_{HOH} (°)	104.6	106.0	106.2	106.3	104.5	1.7%
μ_{e} (D)	2.04	1.99	1.96	1.96	1.85	5.9%
ω_1 (cm^{-1})	4212	4227	4229	4231	3942	7.3%
ω_2 (cm^{-1})	4114	4127	4130	4131	3832	7.8%
ω_3 (cm^{-1})	1776	1753	1751	1748	1649	6.0%
σ_{O} (ppm)	354	344	340	337	344	−1.9%
σ_{H} (ppm)	31.8	31.5	31.2	31.1	30.1	3.3%
$^1J_{\mathrm{OH}}$ (Hz)	−92.5	−75.1	−94.0	−97.3	−80.6	20.7%
$^2J_{\mathrm{HH}}$ (Hz)	−13.8	−19.7	−16.8	−18.6	−7.1	162.0%

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[a] CCSD(T) energy

The full configuration-interaction (FCI) wave function

- The HF wave function contains a single determinant.
- By contrast, the FCI wave function contains all Slater determinants generated by distributing N electrons among n spin orbitals:

$$\Psi_{\mathrm{FCI}} = \sum_{k=1}^{N_{\mathrm{det}}} c_k \Phi_k \quad \leftarrow \quad \text{all possible determinants } N_{\mathrm{det}}$$

- FCI thus represents the 'exact' solution in a given (limited) AO basis.
- Unfortunately, the number of FCI determinants increases very steeply:

$$N_{\mathrm{det}} = \begin{pmatrix} n \\ N \end{pmatrix}; \quad N_{\mathrm{det}}(n_\alpha = n_\beta = N = 2m) \approx \frac{16^m}{m\pi} \quad (\text{large } m)$$

- Therefore, only very small basis sets can be used, and only very small systems can be studied by this brute-force method.
- Still, FCI is very useful for benchmarking more approximate methods. It represents an invaluable tool for the development of new methods.

The intractability of the FCI model

electrons	orbitals	FCI determinants
2	2	4
4	4	36
6	6	400
8	8	4 900
10	10	63 504
12	12	853 776
14	14	11 778 624
16	16	165 636 900
18	18	2 363 904 400
20	20	34 134 779 536

Optimization of the FCI wave function

- The FCI wave function is obtained by solving the following matrix eigenvalue problem:

$$\mathbf{Hc} = E_{\mathrm{FCI}}\mathbf{c}; \quad H_{\mu\nu} = \langle \Phi_\mu | \hat{H} | \Phi_\nu \rangle$$

- Because of the large dimensions, iterative techniques are used:
  1. $\tilde{\mathbf{c}}_{n+1} = -(\mathbf{H}_0 - E_n\mathbf{I})^{-1}(\mathbf{H} - E_n\mathbf{I})\mathbf{c}_n$ ← the Davidson step
  2. Orthogonalize the trial vectors and diagonalize the FCI subproblem.

- Moreover, efficient, integral-driven direct CI techniques have been developed to calculate directly matrix-vector products

$$\mathbf{b} = \mathbf{Hc}$$

  - Essentially, the contributions of each MO integral to **Hc** are obtained directly, without constructing Hamiltonian matrix elements.

- In this manner, FCI wave functions containing a billion or more Slater determinants have been determined.

Correlation energy

- So far, we have considered two approximations to the exact wave function:

  Hartree–Fock: qualitatively correct, one-determinant method

  FCI: exact in a given AO basis but prohibitively expensive

- We need models more accurate than HF but less expensive than FCI!
- In the development of such models, the concept of correlation energy plays a central role.
- It is defined as the difference between the FCI and HF energies:

$$E_{\mathrm{corr}} = E_{\mathrm{FCI}} - E_{\mathrm{HF}} \qquad \leftarrow \text{typically} < 1\% \text{ but of great chemical significance}$$

- Broadly speaking, there are two types of electron correlation:

  static: arises from (near) degeneracy of determinants

  dynamical: arises from the detailed correlated motion of the electrons

- We shall consider first static correlation and next dynamical correlation.

Static correlation: H_2 in a minimal basis

- In a minimal description, there are two 1s STOs, one on each atom:

$$1s_{\mathrm{A}} = \frac{1}{\sqrt{\pi}} \exp(-r_{\mathrm{A}}); \quad 1s_{\mathrm{B}} = \frac{1}{\sqrt{\pi}} \exp(-r_{\mathrm{B}})$$

- From these AOs, two symmetry-adapted MOs may be constructed:

$$1\sigma_g = 1s_{\mathrm{A}} + 1s_{\mathrm{B}}; \quad 1\sigma_u = 1s_{\mathrm{A}} - 1s_{\mathrm{B}}$$

- At equilibrium, $\varepsilon(1\sigma_g) < \varepsilon(1\sigma_u)$, and H_2 is well described by a single bonding configuration (symmetry-adapted determinant):

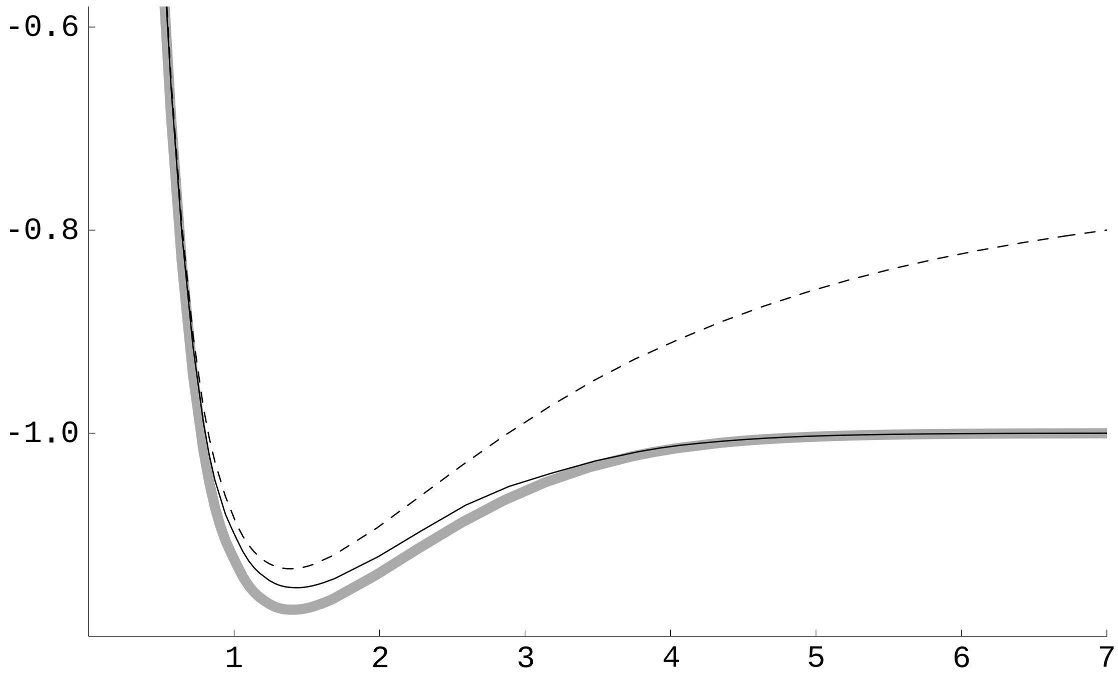
$$|{}^1\Sigma_g^+\rangle = 0.9939|1\sigma_g^2\rangle - 0.1106|1\sigma_u^2\rangle \approx |1\sigma_g^2\rangle$$

- Upon dissociation, $\varepsilon(1\sigma_g) = \varepsilon(1\sigma_u)$, and we can no longer ignore the antibonding configuration:

$$|{}^1\Sigma_g^+\rangle = \frac{1}{\sqrt{2}}|1\sigma_g^2\rangle - \frac{1}{\sqrt{2}}|1\sigma_u^2\rangle$$

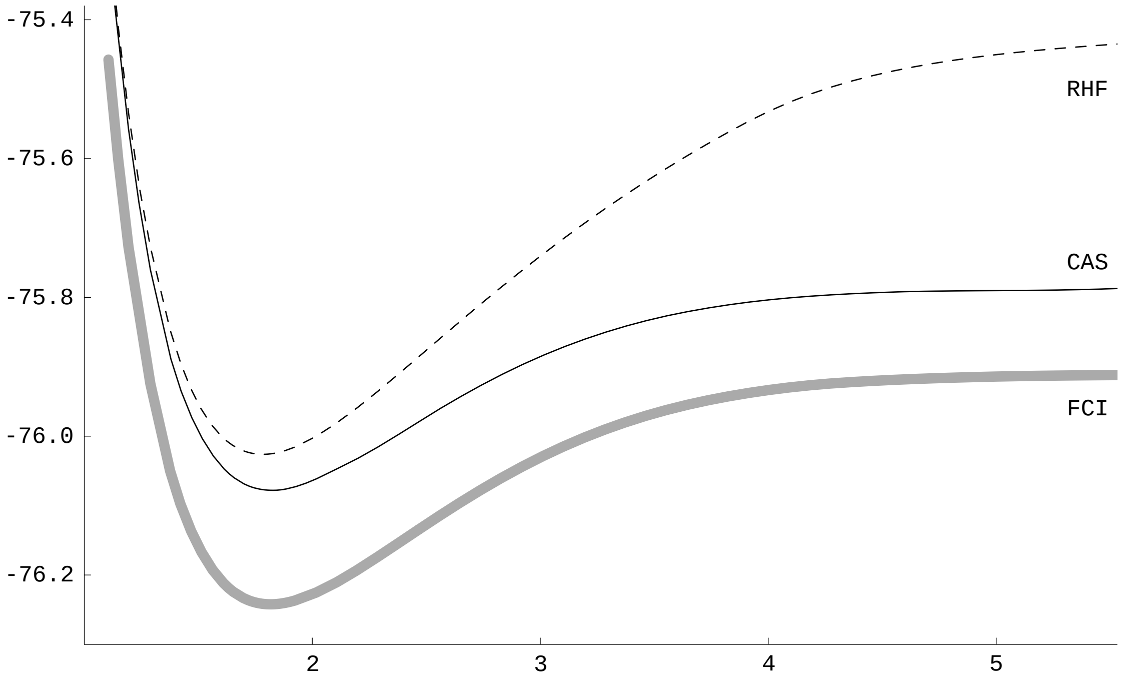
- For a uniform description of the dissociation process, a multiconfigurational treatment is needed at all separations.

Symmetric dissociation of H_2



- Upon dissociation, the single-configuration RHF description deteriorates, resulting in a too high dissociation energy.
- A two-configuration treatment provides a qualitatively correct, uniform description of the dissociation process.

Symmetric dissociation of H_2O



- The difference between the FCI and CAS curves represents the dynamical correlation energy.
- The difference between the CAS and RHF curves represents the static correlation energy.

Multiconfigurational self-consistent field theory

- RHF fails when several configurations have (nearly) the same energy.
- For qualitative agreement with the true wave function, these degenerate or nearly degenerate configurations must all be included.
- The multiconfigurational SCF (MCSCF) model is a generalization of the HF model to several (often many) configurations:

$$|\mathrm{MC}\rangle = \sum_k c_k \det\left[\phi_{k_1}(\mathbf{x}_1)\cdots\phi_{k_N}(\mathbf{x}_N)\right]; \quad \varphi_p(\mathrm{r}) = \sum_\mu C_{\mu p}\chi_\mu(\mathrm{r})$$

- The CI coefficients c_k and the MO coefficients $C_{\mu p}$ are simultaneously variationally determined:
  - for ground states, a minimization is carried out:

$$E_{\mathrm{MC}} = \min_{c_k, C_{\mu p}} \frac{\langle \mathrm{MC}|\hat{H}|\mathrm{MC}\rangle}{\langle \mathrm{MC}|\mathrm{MC}\rangle} \geq E_{\mathrm{exact}}$$

  - for exicted states, a saddle point is determined.
- The correlation recovered at the MCSCF level is referred to as static.

MCSCF configuration spaces

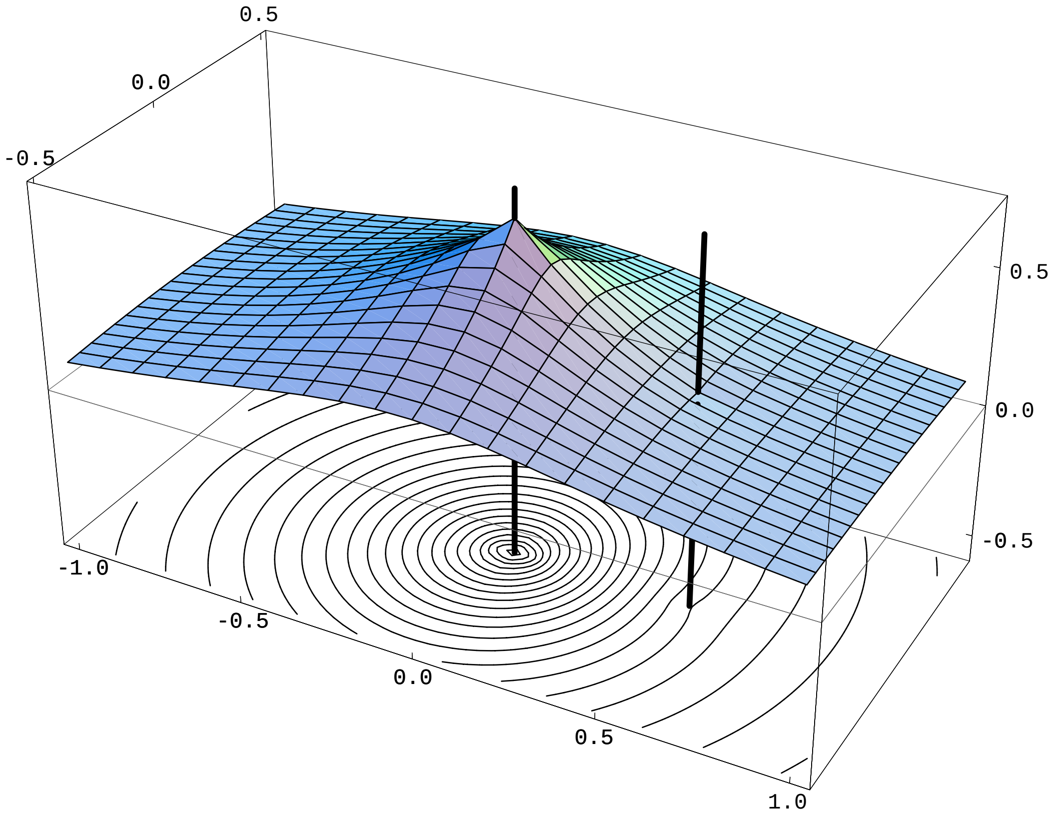
- Individual selection of MCSCF configurations is impractical.
- In complete-active-space (CAS) SCF theory, the configurations are generated by distributing the electrons among orbital subspaces:
  1. inactive (core) orbitals: doubly occupied in all configurations
  2. secondary (virtual) orbitals: unoccupied in all configurations
  3. active (valence) orbitals: all possible occupations
- In a sense, we are carrying out an FCI calculation in a limited (but variationally optimized) active orbital space.
- The MCSCF optimization is more difficult than for FCI or HF, since we optimize both the orbitals and the CI coefficients.
- Second-order (Newton-based) techniques are used.
- More than 16 electrons among 16 active orbitals is currently not possible.
- MCSCF applicable only to rather small systems.

Comparison of Hartree–Fock and CASSCF for N_2

Method	Basis	D_e (kJ/mol)	r_e (pm)	ω_e (cm^{-1})	ν(cm^{-1})
Hartree–Fock	cc-pVDZ	469.3	107.73	2758.3	2735.7
	cc-pVTZ	503.7	106.71	2731.7	2710.3
	cc-pVQZ	509.7	106.56	2729.7	2708.1
	cc-pV5Z	510.6	106.54	2730.3	2708.5
CASSCF	cc-pVDZ	857.8	111.62	2354.3	2325.6
	cc-pVTZ	885.3	110.56	2339.4	2312.1
	cc-pVQZ	890.9	110.39	2339.5	2312.1
	cc-pV5Z	891.9	110.37	2340.4	2313.0
Experiment		956.3	109.77	2358.6	2329.9

The ground-state helium atom

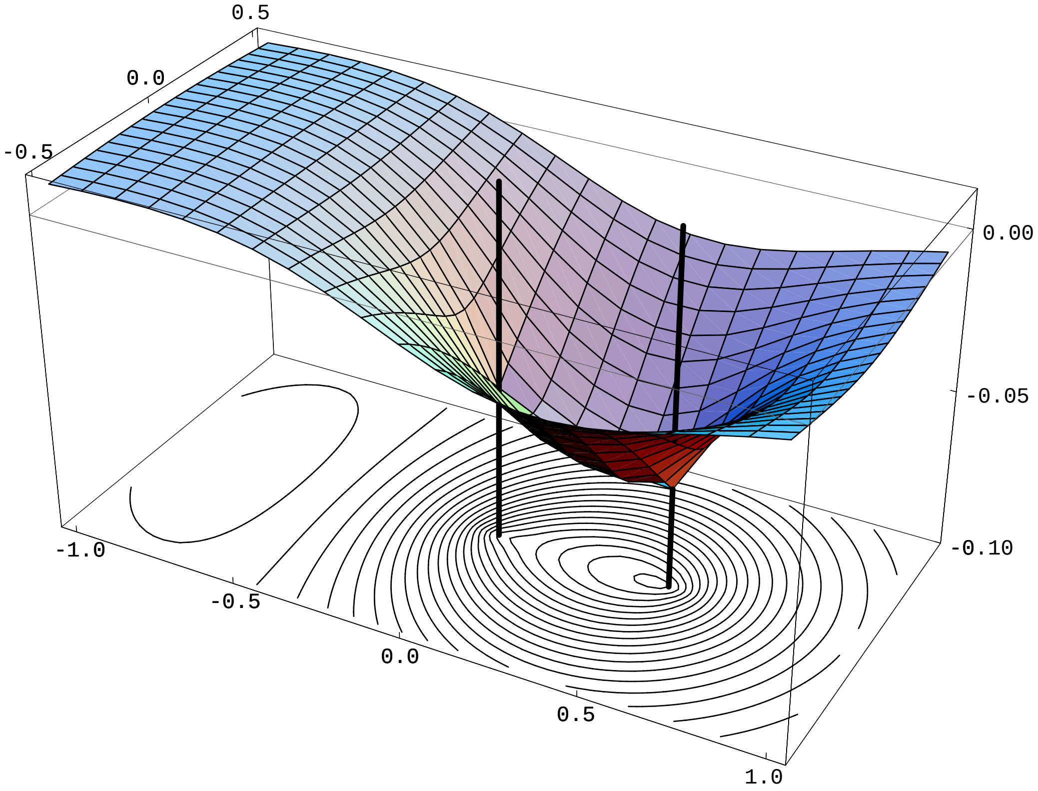
- The Hylleraas ground-state wave function of the helium atom, with one electron fixed at a distance of $0.5a_0$ from the nucleus:



- The wave function is spherically symmetric about the nucleus.
- However, some distortion is noted in the region of coalescence.

The Coulomb hole

- Subtracting the HF wave function from the Hylleraas wave function, we see the Coulomb hole:



- In the ground state, there is a reduced probability of finding the two electrons close to each other.

Dynamical correlation and virtual excitations

- In the HF description, the electrons move independently of one another.
- To improve on this description, we must allow the electrons to interact beyond the mean-field approximation.
- In the orbital picture, such interactions manifest themselves through virtual excitations.
- Consider the following double excitation operator:

$$\hat{X}_{ij}^{ab} = t_{ij}^{ab} a_b^\dagger a_a^\dagger a_i a_j; \quad [a_p, a_q]_+ = 0, \quad [a_p^\dagger, a_q^\dagger]_+ = 0, \quad [a_p, a_q^\dagger]_+ = \delta_{pq}$$

- The amplitude t_{ij}^{ab} represents the probability that the electrons in ϕ_i and ϕ_j will interact and be excited to ϕ_a and ϕ_b.
- By applying $1 + \hat{X}_{ij}^{ab}$ to the HF state, we obtain an improved, correlated description of the electrons:

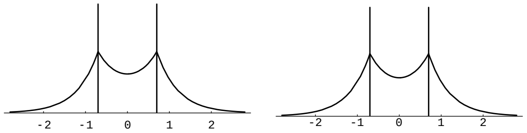
$$|\mathrm{HF}\rangle \rightarrow (1 + \hat{X}_{ij}^{ab})|\mathrm{HF}\rangle$$

Example: dynamical correlation in H_2

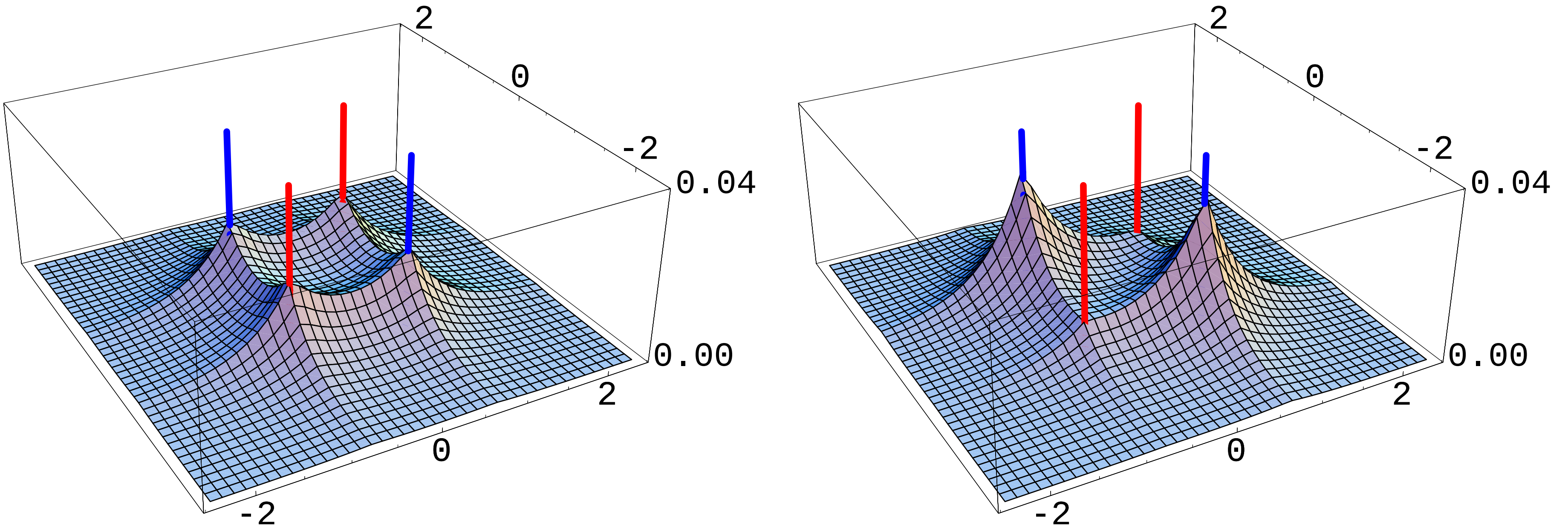
- Consider the effect of a double excitation in the minimal-basis H_2:

$$|1\sigma_g^2\rangle \rightarrow (1+\hat{X}_{gg}^{uu})|1\sigma_g^2\rangle = |1\sigma_g^2\rangle - 0.11|1\sigma_u^2\rangle$$

- The one-electron density $\rho(z)$ is barely affected:



- However, the two-electron density $\rho(z_1, z_2)$ changes dramatically:



One- and two-electron density matrices

- The quality of our description depends on the two-electron as well as on the one-electron density matrix:

$$E = \sum_{\mu\nu} D_{\mu\nu} h_{\mu\nu} + \tfrac{1}{2} \sum_{\mu\nu\rho\sigma} d_{\mu\nu\rho\sigma} g_{\mu\nu\rho\sigma} + h_{\text{nuc}}$$

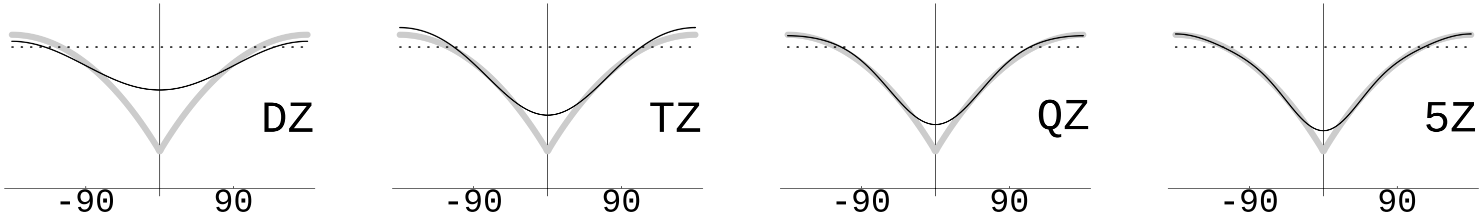
- Basis-set requirements are different for the two density matrices:
  - one-electron density requires relatively few AOs for convergence;
  - two-electron density requires a large number of AOs to describe the Coulomb hole (Coulomb cusp).
- In Hartree–Fock theory, only the one-electron density matrix matters:

$$d^{\text{HF}}_{\mu\nu\rho\sigma} = D^{\text{HF}}_{\mu\nu} D^{\text{HF}}_{\rho\sigma} - \tfrac{1}{2} D^{\text{HF}}_{\mu\sigma} D^{\text{HF}}_{\rho\rho} \qquad \leftarrow \text{HF density matrix factorizes}$$

- Basis-set requirements are thus more stringent for correlated calculations.

Basis-set convergence of the correlation energy

- Orbital-based wave functions are ill suited for describing the Coulomb hole and the two-electron cusp:



- Very large basis sets are required for errors smaller than 1 kJ/mol:

N_2/CCSD	DZ	TZ	QZ	5Z	6Z	limit
corr. energy (mE_h)	-309.3	-371.9	-393.1	-400.6	-403.7	$-408(1)$

- However, the convergence is very smooth:

$$\Delta E_X \approx a X^{-3} \quad \leftarrow X = 2, 3, \ldots \text{ for DZP, TZP, } \ldots$$

- Extrapolations (to within 1 mE_h) are possible.
- Wave functions that contain the interelectronic distances r_{ij} explicitly (explicitly correlated wave functions) converge much faster.

Coupled-cluster theory

- In coupled-cluster (CC) theory, we generate the correlated state from the HF reference state by applying all possible operators $1 + \hat{X}_\mu$:

$$|\mathrm{CC}\rangle = \left[\prod_{ai}\left(1 + \hat{X}_i^a\right)\right]\left[\prod_{abij}\left(1 + \hat{X}_{ij}^{ab}\right)\right]\cdots|\mathrm{HF}\rangle\,; \quad [\hat{X}_\mu, \hat{X}_\nu] = 0$$

- It is reasonable to assume that lower-order excitations are more important than higher-order ones.
- Double excitations are particularly important, arising from pair interactions.
- This classification provides a hierarchy of 'truncated' CC wave functions:
  - CCSD: CC with all single and double excitations
  - CCSDT: CC with all single, double, and triple excitations
- Generalization to multiconfigurational reference states difficult (more complicated algebra).

Connected and disconnected clusters

- Expanding the CCSD product state, we obtain:

$$\begin{aligned} |\mathrm{CCSD}\rangle &= [\prod_{ai}(1+\hat{X}_i^a)][\prod_{abij}(1+\hat{X}_{ij}^{ab})]\,|\mathrm{HF}\rangle \\ &= |\mathrm{HF}\rangle + \sum_{ai}\hat{X}_i^a\,|\mathrm{HF}\rangle + \sum_{abij}(\hat{X}_{ij}^{ab} + \hat{X}_i^a\hat{X}_j^b)\,|\mathrm{HF}\rangle + \cdots . \end{aligned}$$

- The doubly-excited determinants have two distinct contributions:
  - from pure double excitations: connected doubles
  - from products of single excitations: disconnected doubles
- In large systems, the disconnected (i.e., independent) excitations become more important.
- Indeed, without the disconnected excitations, the wave function would not be size-extensive.
- The CCSD wave function contains contributions from *all* FCI determinants, generated by connected and disconnected excitations.

Digression: truncated CI theory

- In truncated CI theory, we retain only the connected exictations:

$$|\mathrm{CI}\rangle = \left(1 + \sum_{ai} \hat{X}_i^a + \sum_{abij} \hat{X}_{ij}^{ab} + \cdots\right) |\mathrm{HF}\rangle$$

- We then obtain the following hierarchy of truncated CI wave functions:
  - CISD: CI with all singly- and doubly-excited determinants
  - CISDT: CI with all singly-, doubly-, and triply-excited determinants
- However, the truncated CI model is not size-extensive:
  1. In CISD, for example, triple and higher excitations are forbidden.
  2. In large systems, high-order (disconnected) excitations dominate.
  3. CISD therefore works best for 10-electron systems.
- The CI model has largely been abandoned in favor of the CC model.
- Nevertheless, the CI model is important for (small) multiconfigurational systems (MRCI), where the application of CC theory is difficult.

The CC exponential ansatz

- The CC wave function is usually written in exponential form:

$$|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{HF}\rangle; \quad \hat{T} = \textstyle\sum_{ai} \hat{X}_i^a + \sum_{abij} \hat{X}_{ij}^{ab} + \cdots$$

- Equivalence with the product form is easily established since, for example:

$$\exp(\hat{X}_i^a) = 1 + \hat{X}_i^a + \tfrac{1}{2}\hat{X}_i^a\hat{X}_i^a + \cdots = 1 + \hat{X}_i^a \quad \Leftarrow \quad \hat{X}_i^a\hat{X}_i^a = 0$$

- For technical reasons, the CC energy is not determined variationally.
- Multiplying the CC Schrödinger equation in the form

$$\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle = E|\mathrm{HF}\rangle \quad \leftarrow \text{similarity-transformed Hamiltonian}$$

from the left by $\langle\mathrm{HF}|$ and the excited determinants $\langle\mu|$, we obtain

$$\begin{aligned} \langle\mathrm{HF}|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle &= E \quad \leftarrow \text{energy (not an upper bound)} \\ \langle\mu|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle &= 0 \quad \leftarrow \text{amplitudes} \end{aligned}$$

- From these equations, the CC energy and amplitudes are determined.

Performance of the CC method: application to H_2O

H_2O	HF	CCSD	CCSD(T)	experiment
AE (kJ/mol)	652	960	976	975
R_{OH} (pm)	94.0	95.4	95.7	95.8
$\Theta_{\mathrm{HOH}}(^\circ)$	106.3	104.5	104.2	104.4
μ_{e} (D)	1.96	1.87	1.85	1.85
ω_1 (cm^{-1})	4231	3998	3958	3942
ω_2 (cm^{-1})	4131	3893	3851	3832
ω_3 (cm^{-1})	1748	1670	1658	1649
σ_{O} (ppm)	337	337	338	344(17)
σ_{H} (ppm)	31.1	30.9	30.9	30.1

The CC hierarchy and its approximations

- The CC hierarchy represents the most successful approach to *ab initio* wave-function quantum chemistry.
- However, whereas the error decreases rapidly with increasing excitation level, the increase in cost is very steep.
- For vibrational frequencies, for example, we observe the following errors:

HF	$\approx 15\%$	cost n^4
CCSD	$\approx 5\%$	cost n^6
CCSDT	$\approx 1\%$	cost n^8
CCSDTQ	$< 1\%$	cost n^{10}

- Clearly, there is a need for more approximate, less expensive treatments.
- Such approximate treatments are based on perturbation theory:
  - MP2: perturbative treatment of doubles at cost n^5
  - CCSD(T): perturbative treatment of triples at cost n^7

Møller–Plesset perturbation theory

- When HF is reasonably accurate, we may improve on it by perturbation theory.
- In Møller–Plesset theory, we use the Fock operator as the zero-order operator and the HF state as the zero-order state:

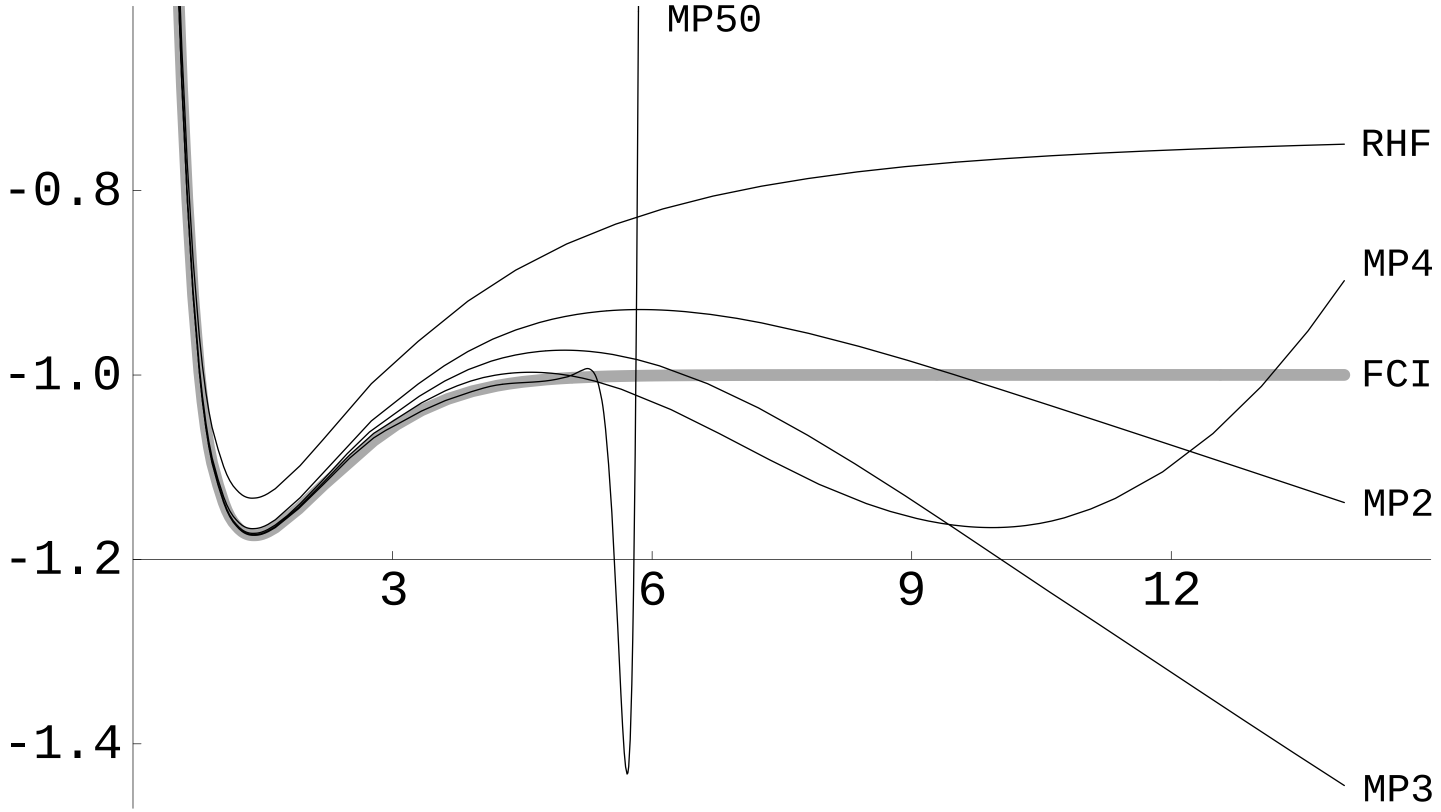
$$\hat{H}^{(0)} = \hat{F}; \quad \hat{F}|\mathrm{HF}\rangle = \textstyle\sum_i \varepsilon_i |\mathrm{HF}\rangle; \quad \hat{V} = \hat{H} - \hat{F}$$

- To first order, we recover the HF energy and to second order we obtain (in the spin-orbital basis):

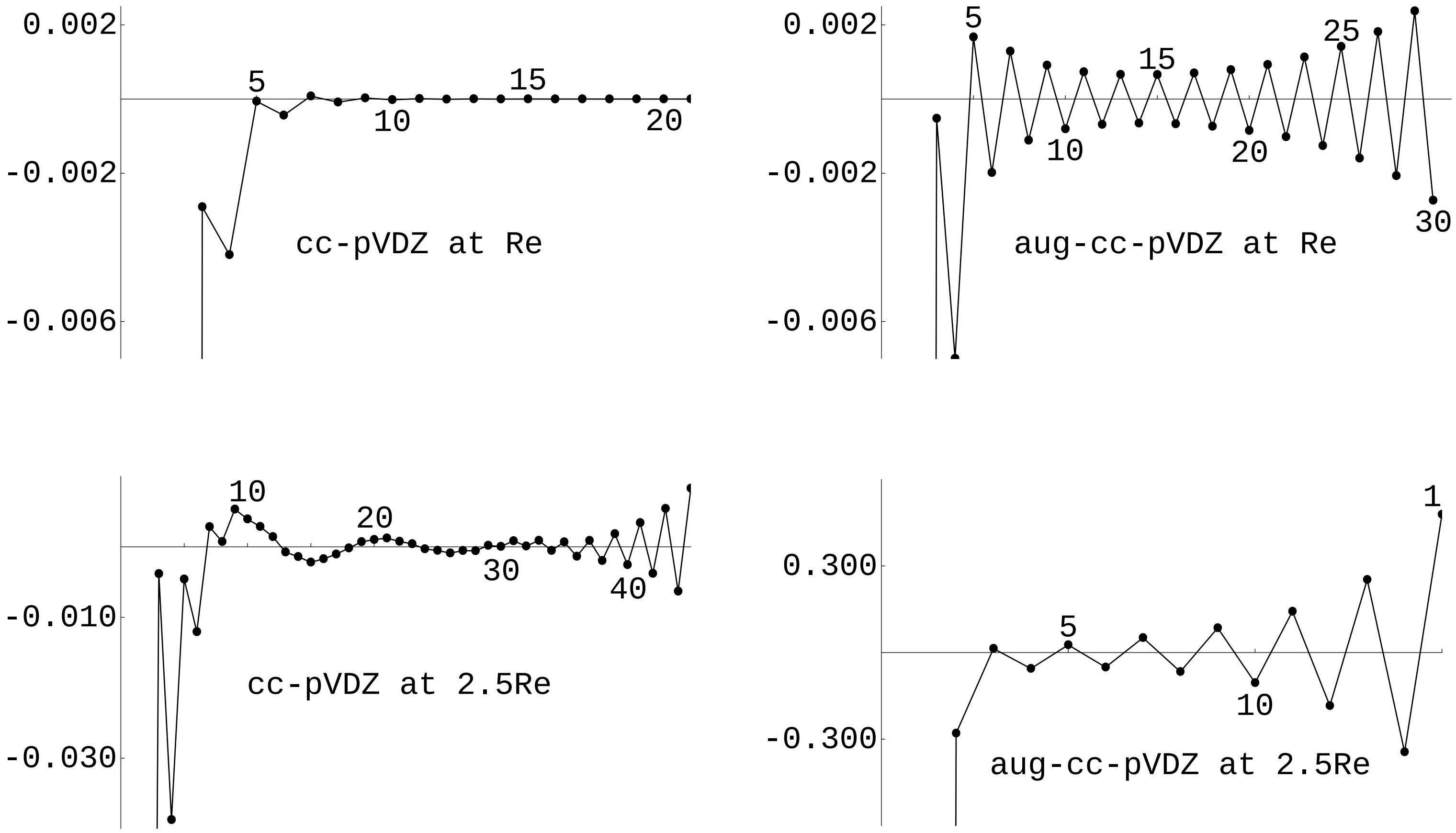
$$E_{\mathrm{MP2}} = E_{\mathrm{HF}} - \textstyle\sum_{a>b,i>j} \frac{|g_{aibj} - g_{ajbi}|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \qquad \leftarrow \text{cost } n^5$$

- The MP2 energy represents a highly successful approximation to the CCSD energy, at a fraction of the cost (noniterative n^5 vs. iterative n^6).
- Higher-order corrections (in particular, MP3 and MP4) may be calculated, but convergence is often poor.
- Indeed, in a sufficiently large basis, the Møller–Plesset series often diverges.

Convergence of the Møller–Plesset series for the H_2 molecule



Convergence of the Møller–Plesset series for the HF molecule



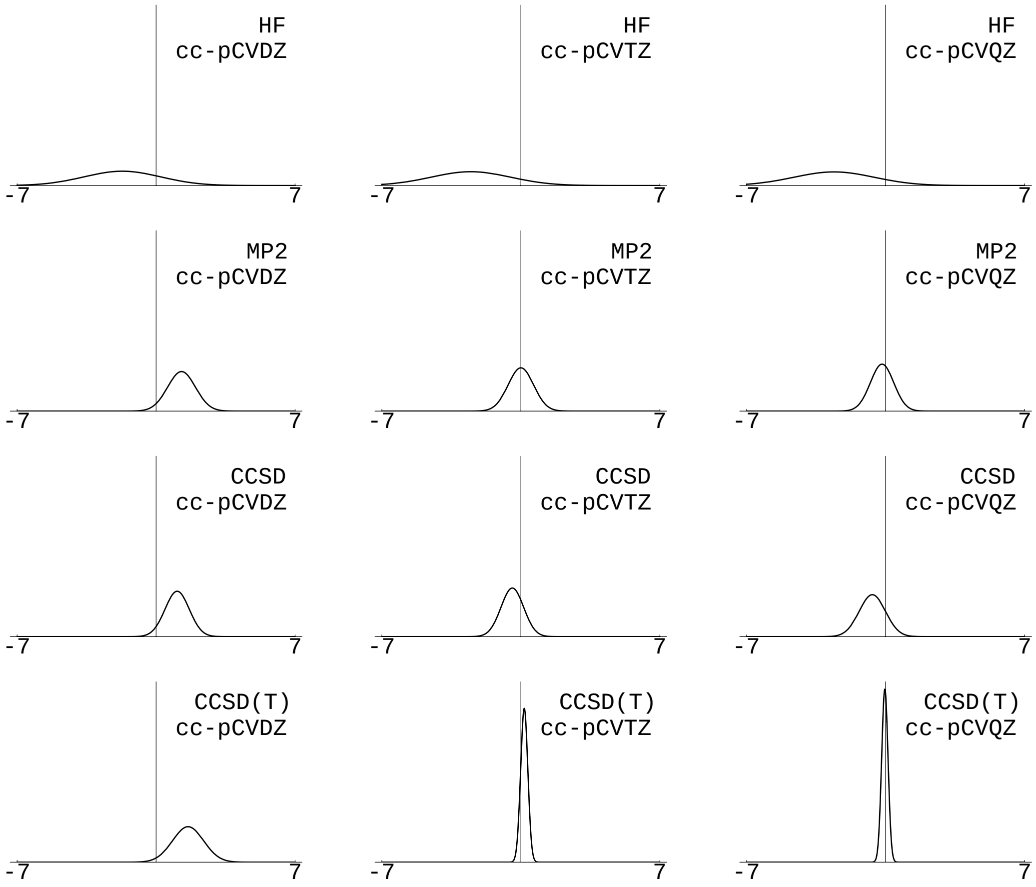
CCSD(T): the most accurate generally applicable *ab initio* model

- Typically, CCSD is not sufficiently accurate and CCSDT is too expensive.
- The CCSD(T) model is then often a useful alternative:
  - the triples correction to CCSD is estimated by perturbation theory;
  - cost is noniterative n^7 rather than iterative n^8;
  - the triples correction is typically overestimated by 5%.
- For many properties, the CCSD(T) model gives results very close to experiment, sometimes rivalling the accuracy of measurements:

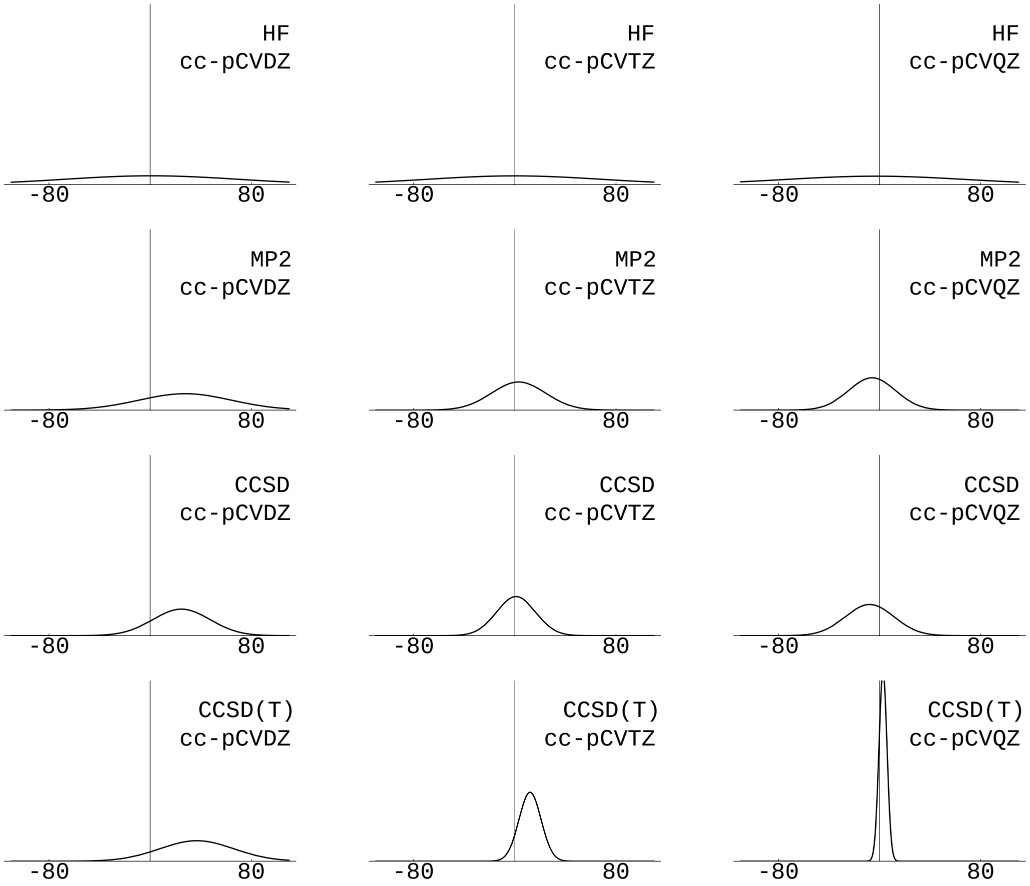
	mean	std. dev.	mean abs.	max
r_{e} (pm)	−0.04	0.16	0.09	0.59
ω_{e} (cm^{-1})	9.8	5.4	9.8	17.0
AE (kJ/mol)	−0.9	2.8	1.4	10.7

- Nevertheless, the CCSD(T) model benefits from error cancellation and is less robust than CCSDT; cf. MP2 and CCSD.

Normal distributions or errors in bond distances (pm)



Normal distributions of errors in reaction enthalpies (kJ/mol)



Conclusions

- We have reviewed the standard models of wave-function based quantum chemistry:
  - the FCI model
  - the HF and MCSCF models
  - the CC models
  - perturbation theory
- Within these models, hierarchies exist of increasing cost and accuracy, allowing the true solution to be approached in a systematic manner.
- An outstanding problem is the treatment of dynamical correlation for multiconfigurational systems.
- For these methods to be applicable to large systems, their cost and in particular the scaling of their cost must be reduced.