

Theoretical methods

Hartree-Fock (RHF, ROHF, UHF)

MP2 (2nd order PT)

CCSD (coupled cluster singles and doubles)

CCSD(T) (CCSD with perturbative triples)

CI (configuration interaction)

$$|\Psi_{\text{CCSD}}\rangle = \exp(T_1 + T_2)|0\rangle = (1 + T_1 + T_2 + T_2^2 + \dots)|0\rangle$$

Scaling with system (basis) size: HF (N^4), MP2 (N^5), CCSD (N^6), CCSD(T) (N^7), fullCI ($\exp(N)$)

Basis set	H atom	O atom	
STO-3G	1s	2s1p	(5)
6-31G	2s	3s2p	(9)
6-31G(d)	2s	3s2p1d	(14)
cc-pVDZ	2s1p	3s2p1d	(14)
cc-pVTZ	3s2p1d	4s3p2d1f	(30)
cc-pVQZ	4s3p2d1f	5s4p3d2f1g	(55)
aug-cc-pVDZ	3s2p	4s3p2d	(23)
aug-cc-pVTZ	4s3p2d	5s4p3d2f	(46)

HF, MP2, CCSD(T), DFT all perform poorly when there is strong configuration mixing (e.g., when there is a small HOMO/LUMO gap)

Full CI is free of this problem but is applicable only to small molecules

Complete active space SCF (CASSCF) and multiconfigurational SCF (MCSCF) are applicable to near degeneracy problems.

In these approaches one optimizes both the CI coefficients and the orbitals (making this a non-linear variational approach)

Examples: H₂: CAS(2,2), 2 electrons in 2 orbitals

Be: CAS(2,4): 2 electrons in 4 orbitals

Benzene: CAS(6,6): 6 electrons in 6 orbitals (the valence pi/pi* space)

CAS can be followed up by multireference MP2 (CASMP2 or CASPT2))

Truncated CI methods

SDCI: does not scale correctly with the number of electrons

$E(\text{two He atoms at large distance}) \neq 2 \times E(\text{He})$

CAS and CI methods can also be used to characterize excited states.

CIS (configuration interaction singles) uses orbitals of ground state

Essentially of HF quality, but also applicable to singlet excited states

Equation of motion (EOM) methods directly calculate IPs, EAs, excitation energies without doing separate calculations on the ground and excited states

Density functional theory (DFT)

The energy can be obtained from the electron density (ρ) alone

This is important since ρ depends only on r , while the wave function depends on r_1, r_2, \dots, r_n , where n is the number of electrons

In Kohn-Sham DFT, one introduces a Slater determinant of orbitals in order to evaluate the KE

Coulomb interactions are calculated just as in HF

Exchange and correlation treated through a functional of ρ

Many exchange-correlation functionals have been introduced

Those that have no contribution from exact exchange (e.g., BLYP, PBE) scale as $O(N^3)$

Those that include some fraction of exact exchange (e.g., B3LYP, PBE0) scale as $O(N^4)$

Issues:

Because exchange is not treated exactly, the self-Coulomb interaction is not fully cancelled

Error smaller when some exact exchange is included

In general, DFT does not include long-range correlation effects such as dispersion

A common way of addressing this is to add atom-atom C_{ij}/R_{ij}^6 correction terms (e.g., B3LYP+D3)

Convergence of energies with increasing flexibility of the basis set

Larger basis sets are required to converge post-HF wave function methods than HF or DFT

Consider the He atom – to converge the HF or DFT energies we need only s functions, but to converge the MP2 or CCSD energies we need, s, p, d, f, ... functions.

There exist 2- and 3-point extrapolation procedures to extrapolate energies to the complete basis set (CBS) limit

E.g., extrapolate aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ to CBS

F12 methods: account explicitly for r¹² dependence

Density fitting, (e.g., DF-MP2 (or RI-MP2)) can be an order of magnitude faster than regular MP2

Basis set superposition error (BSSE)

Atom A can use the basis functions on atom B to lower its energy

Leads to an artificial lowering of the energy

Counterpoise correction illustrated for water dimer – do calculation on each monomer in the presence of the Basis functions on both monomers.