

Electron Correlation Summary

Hartree-Fock single determinant
One (spin)-orbital one electron
No electron correlation

$$\Psi_{\text{HF}} = |\psi_1(1) \cdots \psi_n(n)|$$

$$\Psi_{\text{MB}} = t_0 \Psi_{\text{HF}} + \sum_{ia} t_i^a \Psi_i^a + \cdots$$

Introduce correlation with many-body
wavefunction
Add excited state determinants to H-F
ground state

Add a handful of excited
configurations

Add all configurations
of a given excitation
type

Add configurations of a
given perturbation
order

MCSCF
CASSCF

Variational
Not size-consistent
Good for describing static
correlation—bond breaking
Not so good for quantitative
energies

CIS
CISD
Full CI

Variational
Not size-consistent
Good for describing excited
states and spectroscopy
Not so good for quantitative
energies

MPn/MBPTn
Coupled-cluster (CC..)
Quadratic CI (QCI..)

Size consistent
Not variational

Good general purpose methods
Excellent structures/energies for
“normal” things