

Methods for Treating Electron Correlation

CHEM 430

Electron Correlation Energy

- in the Hartree-Fock approximation, each electron sees the average density of all of the other electrons
- two electrons cannot be in the same place at the same time
- electrons must move to avoid each other, *i.e.* their motion must be correlated
- for a given basis set, the difference between the exact energy and the Hartree-Fock energy is the correlation energy
- ca 20 kcal/mol correlation energy per electron pair

General Approaches

- include r_{12} in the wavefunction
 - suitable for very small systems
 - too many difficult integrals
 - Hylleras wavefunction for helium
- expand the wavefunction in a more convenient set of many electron functions
 - Hartree-Fock determinant and excited determinants
 - very many excited determinants, slow to converge
 - configuration interaction (CI)

Goals for Correlated Methods

- well defined
 - applicable to all molecules with no ad-hoc choices
 - can be used to construct model chemistries
- efficient
 - not restricted to very small systems
- variational
 - upper limit to the exact energy
- size extensive
 - $E(A+B) = E(A) + E(B)$
 - needed for proper description of thermochemistry
- hierarchy of cost vs. accuracy
 - so that calculations can be systematically improved

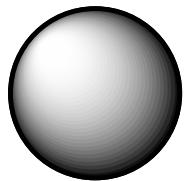
Electron Correlation

How Important is It?

The fundamental approximation of the Hartree-Fock method: interactions between electrons are treated in an *average* way, not an instantaneous way

$$f_i = -\frac{1}{2}\nabla_i^2 - \sum_k^{\text{nuclei}} \frac{Z_k}{r_{ik}} + V_i^{\text{HF}}\{j\}$$

Infinite basis set results

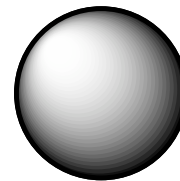


H

One electron

$$E_{\text{HF}} = -0.500\ 00 \text{ a.u.}$$

$$E_{\text{exact}} = -0.500\ 00 \text{ a.u.}$$



He

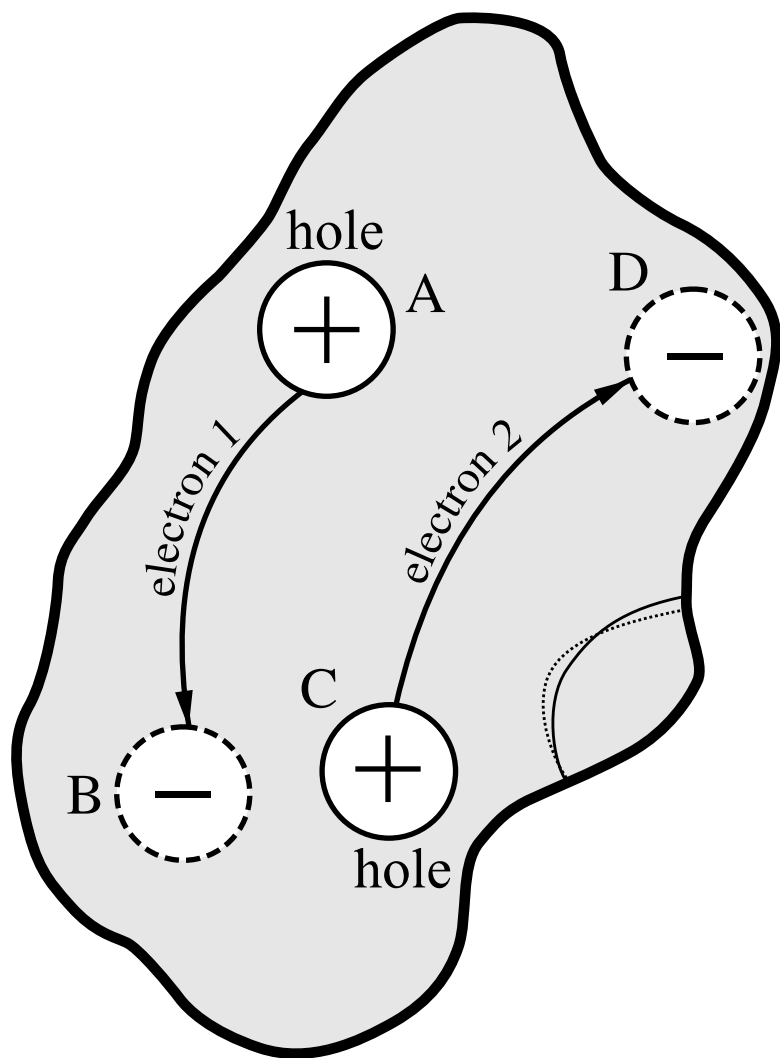
Two electrons

$$E_{\text{HF}} = -2.861\ 68 \text{ a.u.}$$

$$E_{\text{exact}} = -2.903\ 72 \text{ a.u.}$$

Error $\sim 26 \text{ kcal mol}^{-1}$!

Correlated Motion of Pairs of Electrons is of Primary Importance



In order to include the electron correlation, the wave function should somehow reflect the fact electrons avoid each other. Electron 1 jumping from A (an orbital) to B (another orbital) should make 2 escape from C (close to B) to D (close to A).

This is the very essence of electron correlation. The other orbitals play the role of spectators. However, the spectators change upon the excitations described above. These changes are performed by allowing their own excitations. This is how triple, quadruple and higher excitations emerge and contribute to electronic correlation.

Correlated Methods. I. Configuration Interaction

A Hartree-Fock one-electron orbital is expressed as a linear combination of basis functions with expansion coefficients optimized according to a variational principle

$$| \mathbf{F} - E\mathbf{S} | = 0 \quad \longrightarrow \quad \phi = \sum_{i=1}^N a_i \varphi_i$$

The HF many-electron wave function is the Slater determinant formed by occupation of lowest possible energy orbitals, *but, the HF orbitals are not "perfect" because of the HF approximation*

So, one way to improve things would be to treat the different Slater determinants that can be formed from *any occupation of HF orbitals* to *themselves* be a basis set to be used to create an improved many-electron wave function

$$| \mathbf{H} - E\mathbf{S} | = 0 \quad \longrightarrow \quad \Psi = a_0 \Psi_{\text{HF}} + \sum_i^{\text{occ.}} \sum_r^{\text{vir.}} a_i^r \Psi_i^r + \sum_{i < j}^{\text{occ.}} \sum_{r < s}^{\text{vir.}} a_{ij}^{rs} \Psi_{ij}^{rs} + \dots$$

Excited Slater Determinants from a HF Reference

—	—	—	—	↓	↑↓	↑
—	—	↑	—	—	↓	↑↓
—	↑	—	↑↓	↑	—	↓
↑↓	↓	↑↓	—	↑	↑	↑
↑↓	↑↓	↑	↑↓	↓	—	—
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↓
HF	S-type	S-type	D-type	D-type	T-type	Q-type

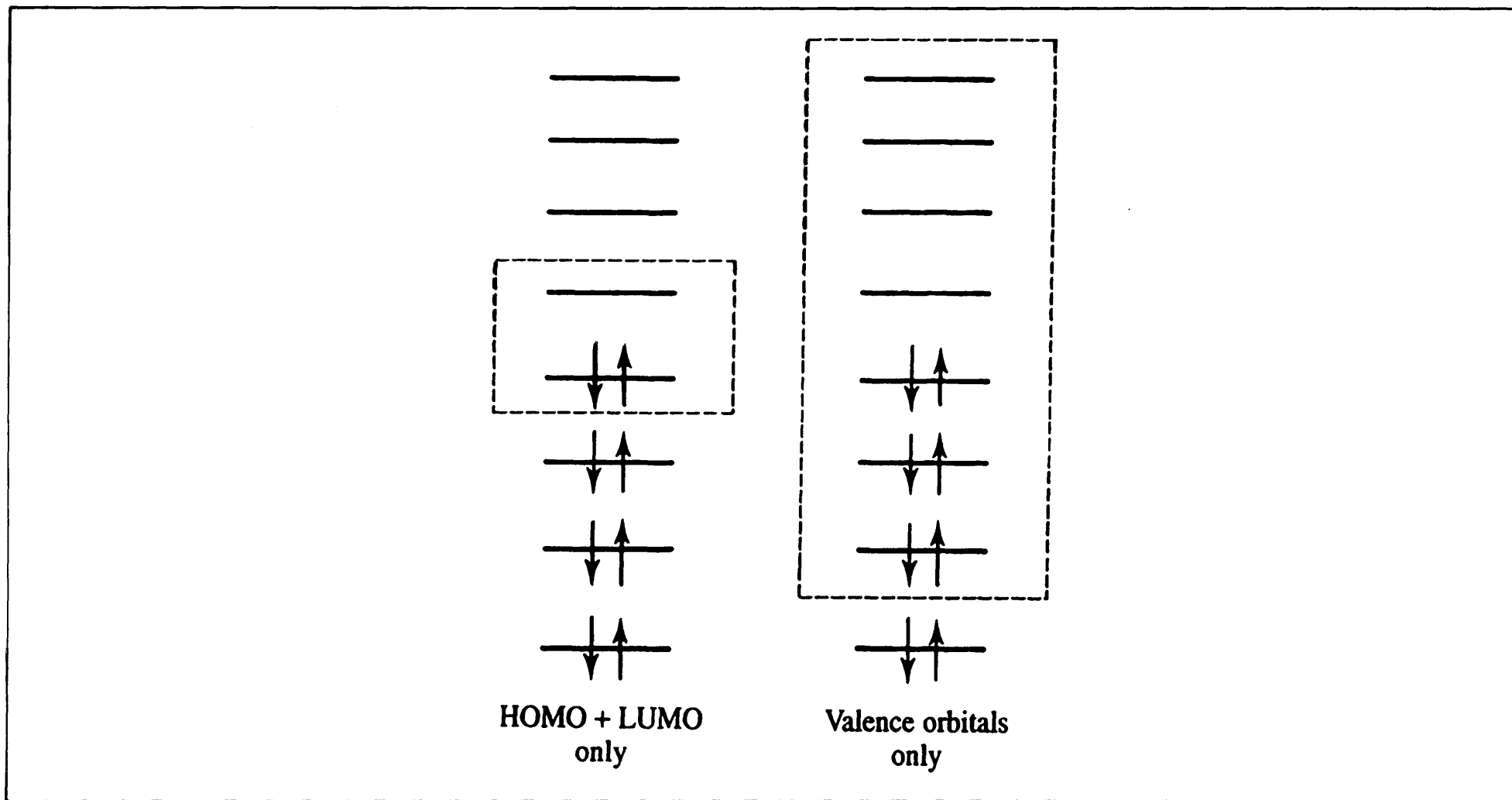


Fig. 3.3: Some of the ways in which excited-state wavefunctions can be included in a configuration interaction calculation.

Number of Slater Determinants (CSFs) by Excitation Level for Water in the 6-31G* Basis

Excitation level	n	Number of nth excited CSF	Total number of CSFs
1		71	71
2		2485	2556
3		40040	42596
4		348530	391126
5		1723540	2114666
6		5033210	7147876
7		8688680	15836556
8		8653645	24490201
9		4554550	29044751
10		1002001	30046752

Configuration Interaction

- determine CI coefficients using the variational principle

$$\Psi = \Psi_0 + \sum_{ia} t_i^a \Psi_i^a + \sum_{ijab} t_{ij}^{ab} \Psi_{ij}^{ab} + \sum_{ijkabc} t_{ijk}^{abc} \Psi_{ijk}^{abc} + \dots$$

minimize $E = \int \Psi^* \hat{H} \Psi d\tau / \int \Psi^* \Psi d\tau$ with respect to t

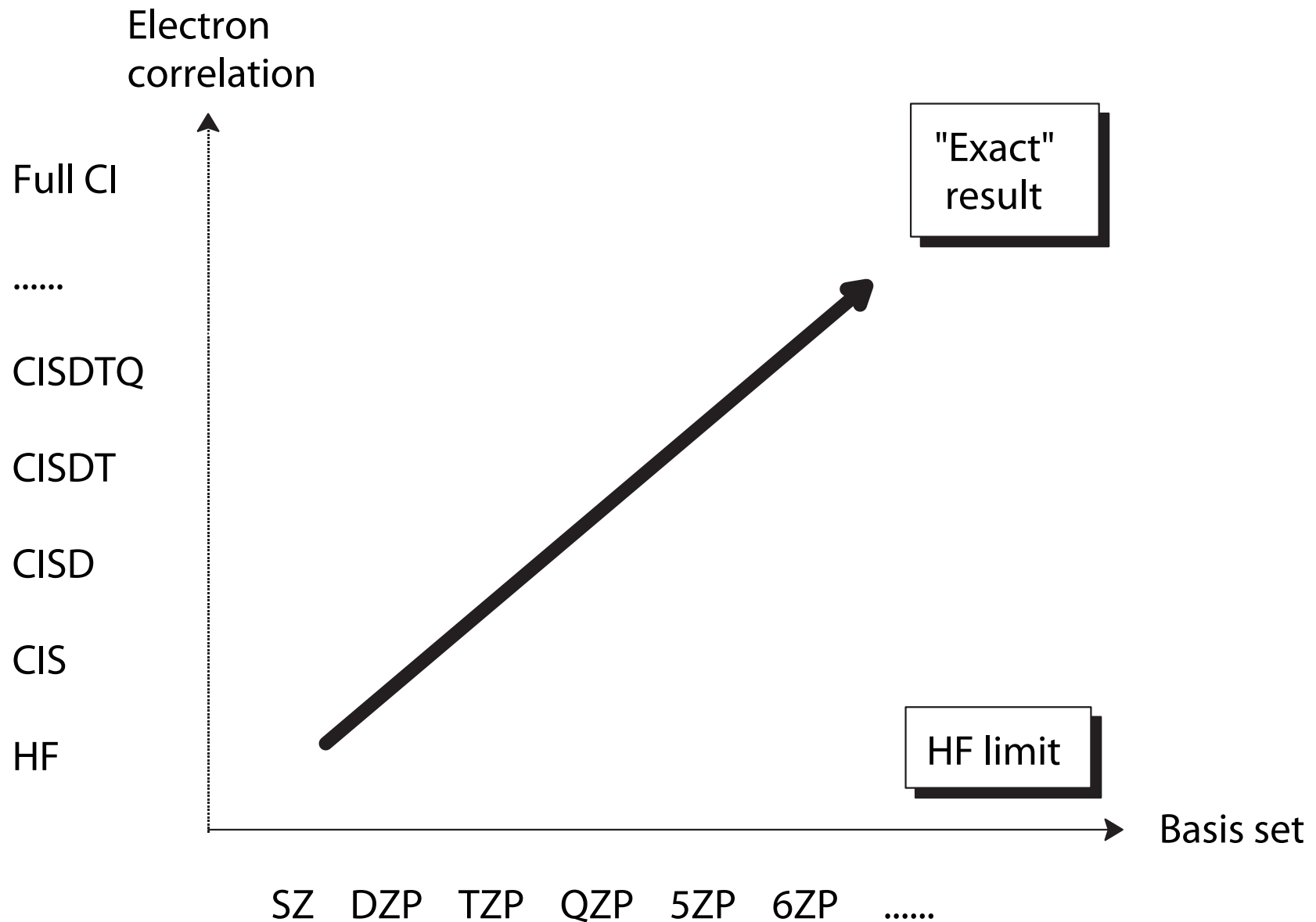
- CIS – include all single excitations
 - useful for excited states, but not for correlation of the ground state
- CISD – include all single and double excitations
 - most useful for correlating the ground state
 - O^2V^2 determinants (O=number of occ. orb., V=number of unocc. orb.)
- CISDT – singles, doubles and triples
 - limited to small molecules, ca O^3V^3 determinants
- Full CI – all possible excitations
 - $((O+V)!/O!V!)^2$ determinants
 - exact for a given basis set
 - limited to ca. 14 electrons in 14 orbitals

Configuration Interaction

$$\mathbf{H} \mathbf{t} = E \mathbf{t}$$

- very large eigenvalue problem, can be solved iteratively
- only linear terms in the CI coefficients
- gives upper bound to the exact energy (~~is~~ variational), but not size extensive
- applicable to excited states
- gradients simpler than for non-variational methods

Full CI in a Complete Basis Set Gives the “Exact” Energy



Sum of CI Weights by Excitation Level for the Neon Atom

Excitation level	Weight
0	9.6×10^{-1}
1	9.8×10^{-4}
2	3.4×10^{-2}
3	3.7×10^{-4}
4	4.5×10^{-4}
5	1.9×10^{-5}
6	1.7×10^{-6}
7	1.4×10^{-7}
8	1.1×10^{-9}

The Incorrect Dissociation Limit of RHF Wavefunctions has Many Consequences

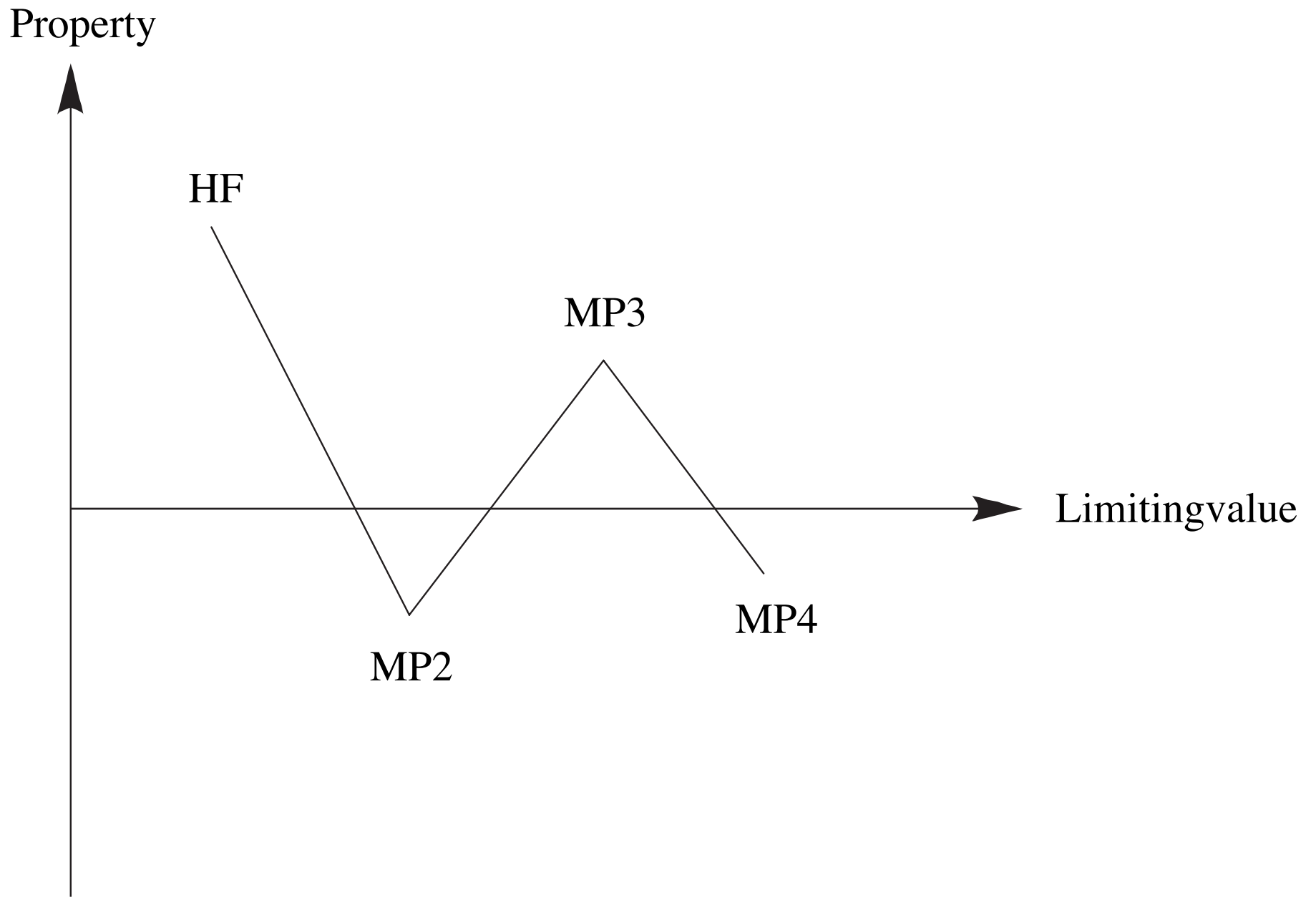
- [1] Energy of stretched bonds is too high, meaning transition states with partial bonds are too high
- [2] Energy increases too rapidly as bonds stretch, so the minimum on the PE curve is too “early” and RHF equilibrium bond lengths are too short
- [3] Energy increases too steeply, so RHF vibrational frequencies are typically too high
- [4] RHF wavefunctions are too “ionic”, resulting in atomic partial charges and dipole moments that are generally too large

Correlated Methods. II. Many-body Perturbation Theory

- Rayleigh-Schrödinger perturbation theory maps an inexact operator with known eigenfunctions to an exact operator with increasing orders of accuracy
- Møller and Plesset (MP) first suggested mapping from the zeroth-order Fock operator to the correct Hamiltonian (the “perturbation” is the entire electron repulsion energy...)
- MP0 double-counts electron repulsion, MP1 = HF, MP2 captures a “good” amount of correlation energy at low cost, higher orders available (up to about MP6 in modern codes—becomes expensive rapidly)
- Multireference options available: CASPT2, RASPT2, and analogs
- No guarantee of convergent behavior—pathological cases occur with unpleasant frequency

Møller-Plesset Perturbation Theory

- size extensive at every order
- MP2 - second order relatively cheap (requires only double excitations)
- 2nd order recovers a large fraction of the correlation energy when Hartree-Fock is a good starting point
- practical up to fourth order (single, doubly, triple and quadruple excitations)
- MP4 order recovers most of the rest of the correlation energy
- series tends to oscillate (even orders lower)
- convergence poor if serious spin contamination or if Hartree-Fock not a good starting point



Typical oscillating behaviour of results obtained with the MP method

Correlated Methods. III. Coupled Cluster

CI adopts a linear ansatz to improve upon the HF reference

$$\Psi = a_0 \Psi_{\text{HF}} + \sum_i^{\text{occ.}} \sum_r^{\text{vir.}} a_i^r \Psi_i^r + \sum_{i < j}^{\text{occ.}} \sum_{r < s}^{\text{vir.}} a_{ij}^{rs} \Psi_{ij}^{rs} + \dots$$

Coupled cluster proceeds from the idea that accounting for the interaction of one electron with more than a single other electron is unlikely to be important. Thus, to the extent that “many-electron” interactions are important, it will be through simultaneous pair interactions, or so-called “disconnected clusters”

An exponential ansatz can accomplish this in an elegant way. If we define excitation operators, e.g., the double excitation operator as

$$\mathbf{T}_2 \Psi_{\text{HF}} = \sum_{i < j}^{\text{occ.}} \sum_{a < b}^{\text{vir.}} t_{ij}^{ab} \Psi_{ij}^{ab}$$

Then the full CI wave function for n electrons can be generated from the action of $1 + \mathbf{T} = 1 + \mathbf{T}_1 + \mathbf{T}_2 + \dots + \mathbf{T}_n$ on the HF reference

Correlated Methods. III. Coupled Cluster (cont.)

More importantly, if we consider the action of $e^{\mathbf{T}}$ on the HF reference, restricting ourselves for the moment to just $\mathbf{T} = \mathbf{T}_2$

$$\begin{aligned}\Psi_{\text{CCD}} &= e^{\mathbf{T}_2} \Psi_{\text{HF}} \\ &= \left(1 + \mathbf{T}_2 + \frac{\mathbf{T}_2^2}{2!} + \frac{\mathbf{T}_2^3}{3!} + \dots \right) \Psi_{\text{HF}}\end{aligned}$$

Note that repeated applications of \mathbf{T}_2 (which is what is implied in squared, cubed, etc. terms) generates the desired “disconnected clusters”

Like CID, an iterative solution to coupled equations can be undertaken

$$\langle \Psi_{\text{HF}} | \mathbf{H} | e^{\mathbf{T}_2} \Psi_{\text{HF}} \rangle = E_{\text{corr}} \left\langle \Psi_{\text{HF}} \left| \left(\Psi_{\text{HF}} + \sum_{A < B, I < J} c_{ab}^{ij} \Psi_{ab}^{ij} \right) \right. \right\rangle = E_{\text{corr}}$$

$$\langle \Psi_{ab}^{ij} | \mathbf{H} | e^{\mathbf{T}_2} \Psi_{\text{HF}} \rangle = \left\langle \Psi_{ab}^{ij} | \mathbf{H} \left| \left(1 + \mathbf{T}_2 + \frac{1}{2} \mathbf{T}_2^2 \right) \Psi_{\text{HF}} \right. \right\rangle = t_{ab}^{ij} E_{\text{corr}}$$

Correlated Methods. III. Coupled Cluster (cont.)

The math is somewhat tedious, but the CC equations can be shown to be size-extensive for any level of excitation

CCSD (single and double excitations) is convenient but addition of disconnected triples (CCSDT) is very expensive. A perturbative estimate of the effect of triple excitations defines the CCSD(T) method, sometimes called the “gold standard” of modern single-reference WFT

Post-HF levels: Price/Performance

HF < MP2 ~ MP3 ~ CCD < CISD

< MP4SDQ ~ QCISD ~ CCSD < MP4 < QCISD(T) ~ CCSD(T) < ...

Scaling behavior	Method(s)
N^4	HF
N^5	MP2
N^6	MP3, CISD, MP4SDQ, CCSD, QCISD
N^7	MP4, CCSD(T), QCISD(T)
N^8	MP5, CISDT, CCSDT
N^9	MP6
N^{10}	MP7, CISDTQ, CCSDTQ

Table 11.7 % electron correlation recovered by different methods in the cc-pVDZ basis

Method	% EC
MP2	94.0
MP3	97.0
MP4	99.5
MP5	99.8
CCSD	98.3
CCSD(T)	99.7
CISD	94.5
CISDT	95.8
CISDTQ	99.9

Table 11.8 Total energy (+76 a.u.) as a function of basis set and electron correlation (valence only)

Method	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV6Z	cc-pV ∞ Z
HF	-0.02677	-0.05713	-0.06479	-0.06704	-0.06735	-0.0676
MP2	-0.22844	-0.31863	-0.34763	-0.35860	-0.36264	-0.368
MP3	-0.23544	-0.32275	-0.34939	-0.35815	-0.36094	-0.364
MP4	-0.24067	-0.33302	-0.36104	-0.37051	-0.37357	-0.377
MP5	-0.24120	-0.33159				
CCSD	-0.23801	-0.32455	-0.35080	-0.35952		-0.366
CCSD(T)	-0.24104	-0.33219	-0.35979	-0.36904		-0.376
CISD	-0.22997	-0.31384	-0.33922	-0.34765		-0.354

Table 11.9 Total energy (+76 a.u.) as a function of basis set and electron correlation (all electrons)

Method	cc-pCVDZ	cc-pCVTZ	cc-pCVQZ	cc-pCV5Z	cc-pCV ∞ Z (%EC)
HF	-0.02718	-0.05731	-0.06490	-0.06706	-0.0677 (0.0)
MP2	-0.26855	-0.37486	-0.40758	-0.41939	-0.430 (97.4)
MP3	-0.27638	-0.37984	-0.41012	-0.41978	-0.430 (97.4)
MP4	-0.28194	-0.39079	-0.42240	-0.43268	-0.440 (100.0)
MP5	-0.28239	-0.38907			
CCSD	-0.27897	-0.38154	-0.41144	-0.42104	-0.428 (96.9)
CCSD(T)	-0.28226	-0.38978	-0.42096	-0.43105	-0.438 (99.5)
CISD	-0.26898	-0.36799	-0.39675	-0.40599	-0.412 (92.6)

Table 11.1. H₂O geometry as a function of basis set at the HF level of theory

Basis	$R_{\text{OH}} (\text{\AA})$	α_{HOH}
cc-pVDZ	0.9463	104.61
cc-pVTZ	0.9406	106.00
cc-pVQZ	0.9396	106.22
cc-pV5Z	0.9396	106.33
cc-pV6Z	0.9396	106.33

Table 11.2 H₂O geometry as a function of basis set at the MP2 level of theory

Basis	$R_{\text{OH}} (\text{\AA})$	α_{HOH}	$\Delta R_{\text{OH}} (\text{\AA})$	$\Delta \alpha_{\text{HOH}}$
cc-pVDZ	0.9649	101.90	0.0186	-2.71
cc-pVTZ	0.9591	103.59	0.0185	-2.48
cc-pVQZ	0.9577	104.02	0.0181	-2.20
cc-pV5Z	0.9579	104.29	0.0184	-2.04
cc-pV6Z	0.9581	104.36	0.0185	-1.97

Table 11.20 Bond distance (\AA) in FOOF. Experimental values are 1.217 and 1.575 \AA

	cc-pVDZ	R _{OO} DZP	TZ(2d)	cc-pVDZ	R _{FO} DZP	TZ(2d)
HF	1.304	1.308	1.301	1.368	1.362	1.361
MP2	1.210	1.266	1.140	1.581	1.521	1.728
MP3	1.302	1.320	1.301	1.455	1.449	1.450
CCSD	1.276	1.307	1.278	1.494	1.474	1.482
CCSD(T)	1.216	1.261	1.216	1.637	1.571	1.614
CISD	1.304	1.316	1.301	1.416	1.412	1.407
SVWN	1.202	1.222	1.186	1.556	1.536	1.573
BLYP	1.224	1.243	1.207	1.622	1.604	1.643
BPW91	1.211	1.231	1.119	1.612	1.589	1.623
B3LYP	1.240	1.264	1.222	1.523	1.502	1.540
B3PW91	1.229	1.254	1.217	1.517	1.491	1.524

Table 11.20 sourced from Ref. 15.

Table 11.10 H₂O dipole moment (Debye) as a function of theory (valence correlation only), experimental value is 1.847 D

Basis	HF	MP2	CCSD(T)
cc-pVDZ	2.057	1.964	1.936
cc-pVTZ	2.026	1.922	1.903
cc-pVQZ	2.008	1.904	1.890
cc-pV5Z	2.003	1.895	
cc-pV6Z	1.990		
aug-cc-pVDZ	2.000	1.867	1.848
aug-cc-pVTZ	1.984	1.852	1.839
aug-cc-pVQZ	1.982	1.858	1.848
aug-cc-pV5Z	1.982	1.861	

Table 11.11 H₂O dipole moment (Debye) as a function of theory (all electrons)

Basis	HF	MP2	CCSD(T)
aug-cc-pCVDZ	2.001	1.868	1.849
aug-cc-pCVTZ	1.983	1.857	1.843

Table 11.12 H₂O dipole moment (Debye) as a function of DFT functional and basis set; the experimental value is 1.847 D

Basis	SVWN	BLYP	BPW91	B3LYP	B3PW91
aug-cc-pVDZ	1.853	1.796	1.803	1.855	1.859
aug-cc-pVTZ	1.857	1.799	1.800	1.854	1.854
aug-cc-pVQZ	1.855	1.798	1.797	1.854	1.852
aug-cc-pV5Z	1.856	1.799	1.798	1.855	1.852

Table 11.21 Dipole moment (Debye) for CO; the experimental value is 0.122 D

	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z
HF	-0.255	-0.263	-0.265	-0.265
MP2	0.296	0.280	0.275	0.273
MP3	0.076	0.047	0.036	0.032
MP4	0.220	0.222	0.216	0.214
CCSD	0.097	0.070	0.059	0.055
CCSD(T)	0.141	0.127	0.118	0.115
CISD	0.050	0.023	0.011	
SVWN	0.232	0.226	0.229	
BLYP	0.187	0.184	0.185	
BPW91	0.221	0.217	0.218	
B3LYP	0.091	0.086	0.087	
B3PW91	0.119	0.114	0.116	