QUANTUM CHEMISTRY APPROACHES TO ELECTRON CORRELATION

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Major challenges in theoretical chemistry

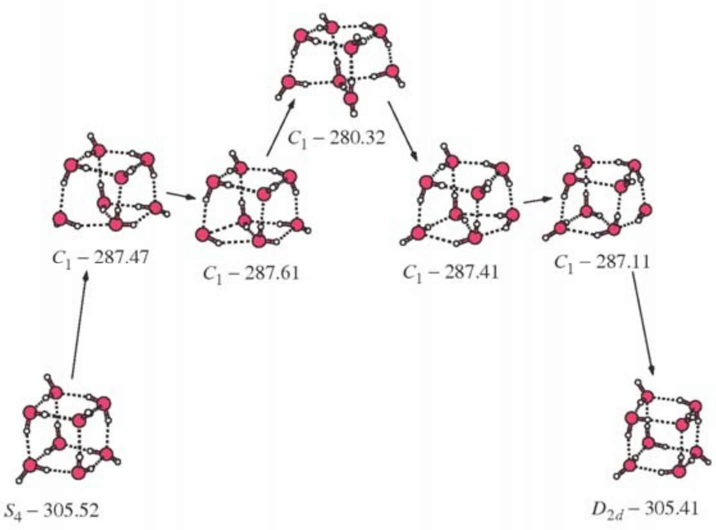
- Treating heterogeneous systems
  1. Catalysis on surfaces (often defect dominated)
  2. Electrochemistry (water, electrodes, various ions)
  3. Biological processes (water, ions, long-time scales)
  4. Photochemical processes in the condensed phase and at interfaces (excited states, non-adiabatic dynamics)
- Bridging time and length scales (e.g., protein folding may occur on msec or longer time scale)
- Sampling structures (e.g., locating polymorphs of crystals, transition states, minimum energy pathways)

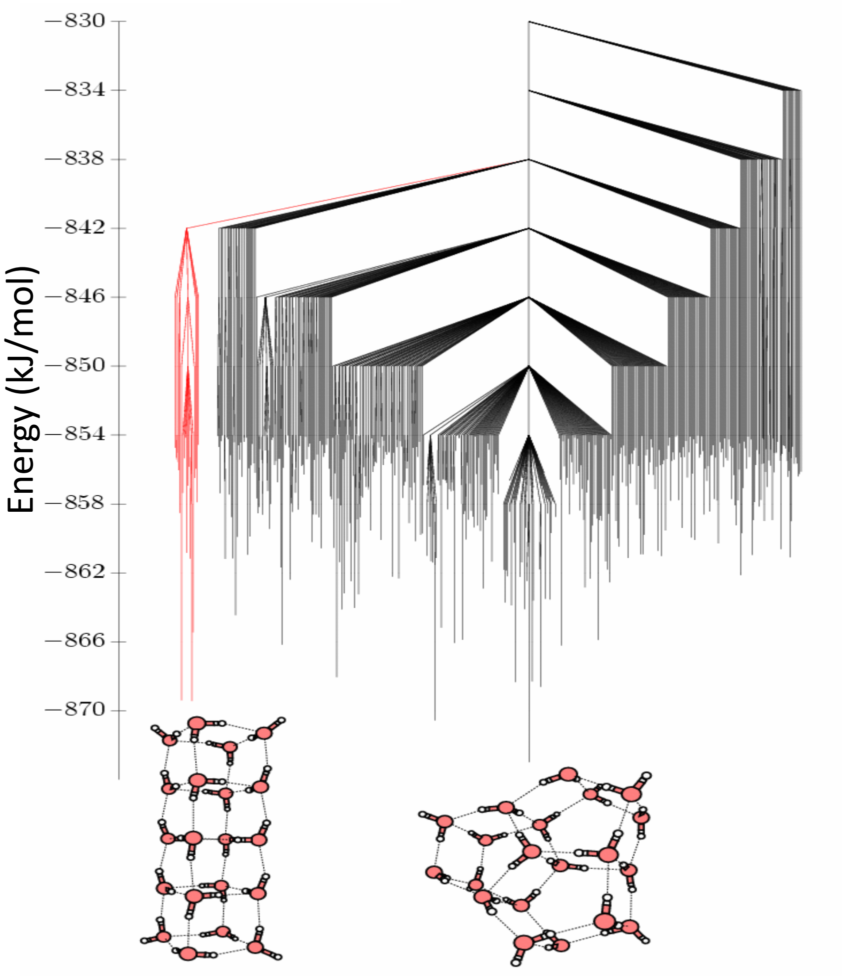
Even a cluster as small as $(H_2O)_{20}$ has a huge number of isomers[1]

Disconnectivity diagram[1] shows only the minima within 17 kJ/mol of the global minimum

The dodecahedral form of $(H_2O)_{20}$, in isolation, is about 47 kJ/mol less stable than the global minimum

Each rearrangement pathway can be quite complex as shown below for $(H_2O)_8$ (again from Wales)





[1] D. J. Wales and M. P. Hodges, Chem. Phys. Lett., 286, 65-72 (1998)

Approaches/Tools

- **Electronic structure theory**
  - ✓ Wave function based methods
  - ✓ DFT
- **QM/MM**: Embedded electronic structure (MM = molecular mechanics = force field)

  Applicable when the changes in electronic structure are localized
- **Thermodynamics and dynamics simulations**
  - ✓ Monte Carlo (equilibrium properties)
  - ✓ Molecular dynamics (equilibrium + non equilibrium
  - ✓ Generally carried out with force fields, but for small systems or short time scales simulations can be done using QM energies/forces
  - ✓ Nuclear quantum effects can be included by path integral methods

Schrödinger equation

$$H\psi = E\psi$$

$$E = T_e + T_N + V_{eN} + V_{NN} + V_{ee}$$

Born-Oppenheimer approximation

Separate electronic + nuclear degrees of freedom

$$E = E_{el} + E_{nucl}$$

$$H_{el}\psi_{el} = E_{el}\psi_{el}$$

$$E_{e\ell} = T_e + V_{eN} + V_{NN} + V_{ee}$$

$E_{e\ell}\left(\tilde{R}\right) =$ potential energy surface

governs motion of the nuclei (atoms)

used in molecular dynamics simulations and in calculation of vibrational spectroscopy

What makes solving the electronic Schrödinger equation difficult are the V_{ee} terms

Many approximations have been introduced

The Hartree-Fock method is the simplest **ab initio** approximation

$$\psi = \left|\varphi_1(r_1)\varphi_2(r_2)\ldots\varphi_N(r_N)\right| \longleftarrow$$

Slater determinant: builds in antisymmetry of wavefunction

To solve for the HF energy and orbitals, one introduces a basis set

Atom-centered functions (Gaussians or numerical)

$$1s, 2s, 2s', 2p, 2p', 3d, etc.$$

But other choices (e.g., plane waves or grid-based) are possible

One of the most widely used GTO basis sets are Dunning’s correlation consistent basis sets

cc-pVDZ	(3s2p1d)	(14)
cc-pVTZ	(4s3p2d1f)	(30)
cc-pVQZ	(5s4p3d2f1g)	(55)
cc-pV5Z	(6s5p4d3f2g1h)	(91)

To accurately describe polarization, van der Waals interactions, and anions: need to augment these basis sets with a diffuse function of each angular momentum type

Dunning’s aug-cc-pVTZ basis set for O

```
S   8   1.00
 15330.0000000          0.0005080
  2299.0000000          0.0039290
   522.4000000          0.0202430
   147.3000000          0.0791810
    47.5500000          0.2306870
    16.7600000          0.4331180
     6.2070000          0.3502600
     0.6882000         -0.0081540
S   8   1.00
 15330.0000000         -0.0001150
  2299.0000000         -0.0008950
   522.4000000         -0.0046360
   147.3000000         -0.0187240
    47.5500000         -0.0584630
    16.7600000         -0.1364630
     6.2070000         -0.1757400
     0.6882000          0.6034180
S   1   1.00
     1.7520000          1.0000000
S   1   1.00
     0.2384000          1.0000000
S   1   1.00
     0.0737600          1.0000000
```

```
P   3   1.00
   34.4600000          0.0159280
    7.7490000          0.0997400
    2.2800000          0.3104920
P   1   1.00
    0.7156000          1.0000000
P   1   1.00
    0.2140000          1.0000000
P   1   1.00
    0.0597400          1.0000000
D   1   1.00
    2.3140000          1.0000000
D   1   1.00
    0.6450000          1.0000000
D   1   1.00
    0.2140000          1.0000000
F   1   1.00
    1.4280000          1.0000000
F   1   1.00
    0.5000000          1.0000000
```

The inner functions are contracted: i.e., represented by several primitive Gaussian functions with fixed coefficients

Number of primitives greatly exceeds number of contracted functions

As far as solving SCF equations or doing post HF calculations, it is the number of contracted functions that matters

Diffuse “aug” functions indicated in blue

Vary orbitals to minimize $\langle\psi|H|\psi\rangle$,
subject to keeping orbitals orthonormal

Gives the Fock equation

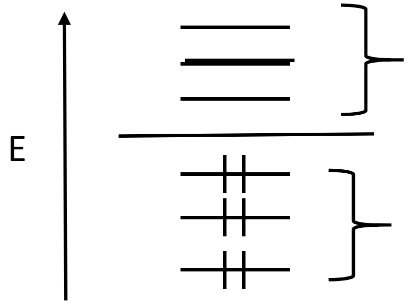
$$\mathcal{F}\,\phi_i = \varepsilon_i\phi_i \quad : \quad \mathcal{F} = T_e + V_{eN} + \langle\psi|V_{ee}|\psi\rangle$$

Fock operator

each electron moves in the average potential of the other electrons
(a mean-field method)

The effective potential depends on the orbitals that we are trying to determine

Solve iteratively (SCF)



empty (virtual) orbitals

filled orbitals

Koopmans' theorem (KT)

$IP_j^{KT} \approx -\varepsilon_j$ ("*j*" an occupied orbital)

$EA_a^{KT} \simeq -\varepsilon_a$ ("*a*" an empty orbital)

Only meaningful if the empty orbital is bound

For most neutral molecules, all virtual orbitals are at positive energy

Virtual orbitals are appropriate for N+1 electron system

Empty valence orbitals "dissolve" in the continuum with large basis sets

Electron correlation energy (neglecting relativistic effects)

$$E^{corr} = E^{exact} - E^{HF}$$ (assuming basis set large enough to reach HF limit)

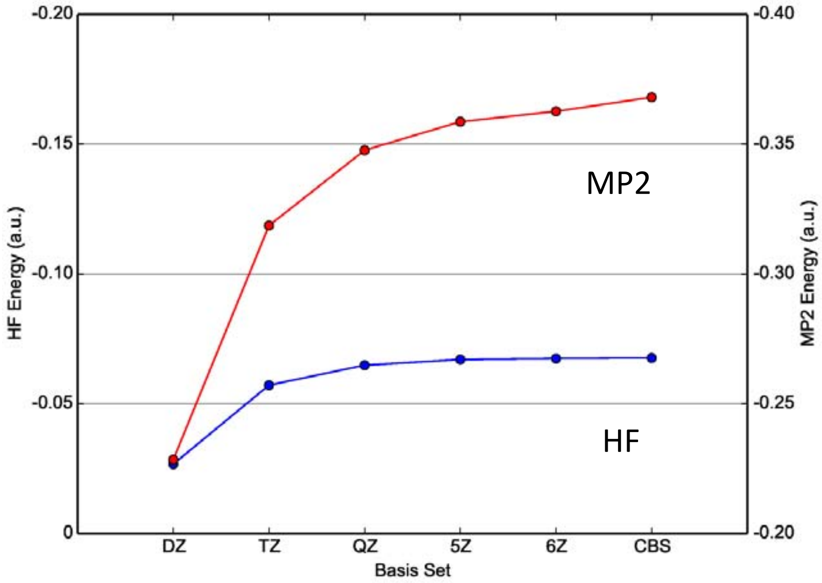
Electron correlation effects are described by excitations from filled to empty orbitals

Slowly convergent expansion, requiring high angular momentum basis functions due to the difficulty of describing in the cusp in terms of $\phi_a(r_i)\phi_b(r_j)$ products as $r_{ij} \to 0$

There are two (related) problems caused by the basis sets

One needs a very large basis to describe the cusps which, in turn, increases the number of virtual orbitals

Due to the virtualorbitals corresponding to the N+1 electron system and the presence of the continuum, one cannot simply excite into only the low-lying orbitals



HF energy converges much more quickly with increasing basis set size than does the energy from calculations including electron correlation. (Results for H_20*; shifted energy scales.)*

CCSD(T) results for N_2

Basis set	Tot. E (a.u.)	BE (kcal/mol)
cc-pVDZ	-109.2765	200.6
cc-pVTZ	-109.3739	216.5
cc-pVQZ	-109.4044	222.9
Expt.		228.9

1 eV difference

6.4 kcal/mol difference

To reach the complete basis set limit (CBS) MP2 or CCSD(T) results requires extrapolating along sequence of the basis sets (e.g., aug-dz, aug-tz, aug-qz)

Not as bleak as it sounds: explicitly correlated methods that introduce explicit r12 dependence in the wave function can achieve the CBS limit with smaller basis sets.

2nd-order Møller-Plesset PT (MP2) is the simplest correction to Hartree-Fock

$$E^{MP2} = E^{HF} + \frac{1}{4}\sum_{i,j,a,b} \frac{\left\langle \psi_{HF} \left| \widehat{V} \right|{}^{ab}_{ij} \right\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

Coulomb and exchange contributions

$$\widehat{H} = \mathcal{F} + \widehat{V}, \quad \widehat{V} = \widehat{H} - \hat{\mathcal{F}}$$

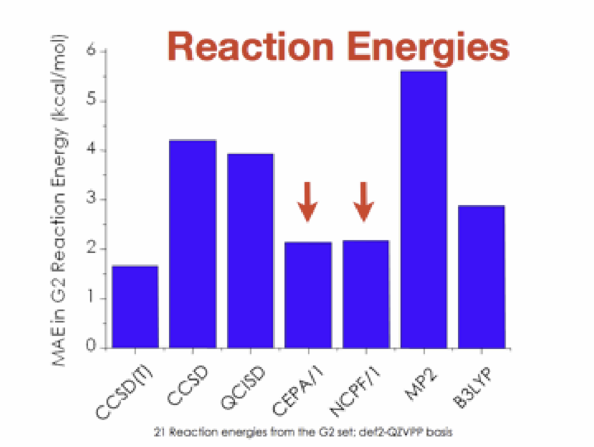
$\widehat{V}$ involves the bare r_{ij}^{-1} minus the average of r_{ij}^{-1} .

Pros of MP2

- Typically recovers 95-105% of the correlation energy
- Describes dispersion intersections
- Can be made linear-scaling by use of localized orbitals

Cons of MP2

- Not applicable when there is a near degeneracy (strong static correlation)
- In general, does not meet the target accuracy of 1 kcal/mol for reaction and activation energies
- Can overestimate dispersion
- Often performs poorer than DFT, which is computationally faster



From F. Neese's talk at Trieste2013 DFT and Beyond meeting

More sophisticated wavefunction-based procedures

Configuration interaction (from HF reference)

$$\Psi = C_o\Phi_{HF} + \sum_{ia} C_i^a \left|{}_i^a\right\rangle + \frac{1}{4}\sum C_{ij}^{ab}\left|{}_{ij}^{ab}\right\rangle + \frac{1}{36}\sum C_{ijk}^{abi}\left|{}_{ijk}^{abc}\right\rangle + \ldots \quad \Bigg| \quad \left|{}_i^a\right> = a_a^+ a_i\,|0\rangle, \quad \text{etc.}$$

The coefficients $\{C_x^y\}$ are determined variationally $\rightarrow$ matrix eigenvalue problem

Structure of CI matrix

$$\begin{pmatrix} E_{HF} & \langle 0|V|S\rangle & \langle 0|V|D\rangle & 0 & 0 \\ \langle S|H|0\rangle & \langle S|H|S\rangle & \langle S|V|D\rangle & \langle S|V|T\rangle & 0 \\ \langle D|V|0\rangle & \langle D|V|S\rangle & \langle D|H|D\rangle & \langle D|V|T\rangle & \langle D|V|Q\rangle \\ 0 & \langle T|V|S\rangle & \langle T|V|D\rangle & \langle T|H|T\rangle & \langle T|V|Q\rangle \\ 0 & 0 & \langle Q|V|D\rangle & \langle Q|V|T\rangle & \langle Q|H|Q\rangle \end{pmatrix} \ddots$$

<0|H|T>, etc. = 0 since H involves at most double excitations

<0|H|S> = 0: Brillouin's theorem: Holds only if |0> = |HF>

Double excitations most important

2^{nd} order PT: doubles

3^{rd} order PT: doubles

4^{th} order PT: singles, doubles, triples, quadruples

Single-plus-double-excitation CI (CISD) used to be quite common

Truncated CI's not size extensive (i.e., E^{corr} does not scale with number of particles)

Consider two He atoms at long distance

SDCI "exact" for He atom

E(He ·····He) $\neq$ 2E(He)

Also while a full CI does not depend on the choice of 0^{th}-order wavefunction, a truncated CI does

Truncated CI calculations based on a single reference configuration fail for near degeneracy problems

Full CI (applicable to only small systems, e.g., H_2O)

Nesbet's theorem: $C_O E^{corr} = \frac{1}{4}\sum C_{ij}^{ab} < ij \| ab >$

If we knew exact C_{ij}^{ab} $\Rightarrow$ would know exact correlation energy

However, C_{ij}^{ab} depend on C_i^a, C_{ijk}^{abc}, C_{ijkl}^{abcd}, etc.

3rd, and 4rth-order MP perturbation theory

Implemented in codes somewhat after MP2

Sometimes perform better than MP2, but sometimes not

  In fact, the perturbation expansion of the energy often diverges

Relatively little used now

Coupled-cluster methods

Basic ideas can be traced back to papers of Coester and Kummel (1957, 1960)

  Applications to nuclear structure

Brought over to electronic structure applications by Cizek, Paldus and Shavitt

  Nesbitt and Sinanoglu introduced approximate coupled cluster theories

Implemented in efficient codes by the Bartlett and Pople groups

Now implemented in nearly all codes that are wave-function based and use GTOs

$$|\psi\rangle = e^{T}|\psi^{HF}\rangle,\quad \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots$$

$$\hat{T}_1 = \sum t_i^a a_a^+ a_i$$

$$\hat{T}_2 = \frac{1}{4}\sum t_{ij}^{ab} a_a^+ a_b^+ a_j a_i$$

$E^{A+B} = e^{A}e^{B}$, so automatically size extensive

CCSD: $T = T_1 + T_2$, scales as $O\left(N^6\right)$

$$e^{\left(\hat{T}_1+\hat{T}_2\right)} = 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \dots$$

CCSDT: $T = T_1 + T_2 + T_3$, scales as $O\left(N^8\right)$

CCSD(T): triples evaluated perturbatively using t_2 amplitudes from CSSD, scales as $\left[O\left(N^7\right)\right]$

CCSD)(T) quantum chemistry “gold standard”

- achieves chemical accuracy (except in near degeneracy cases)
  multireference coupled cluster theories exist,
  but there are no computationally fast implementations
- N^7 scaling restricts the size system that can be treated

How does one solve the coupled-cluster equations?

$$H\left|\psi\right\rangle = H\left|e^T\Phi_0\right\rangle = E\,|\,e^T\,\Phi_0\rangle$$

$$E =< \Phi_0\,|\,H\,|\,e^T\Phi_0 >$$

$$E =< \Phi_0\,|\,H\,|\,\Phi_0 > + < \Phi_0\,|\,H\,|\,T\Phi_0 >$$

$$\left\langle {}^{ab}_{ij}\right|H\left|e^T\Phi_0\right\rangle = E\left\langle {}^{ab}_{ij}\right|e^T\Phi_0\rangle$$

Let $T = T_2$

$$E = E_{HF} + \left\langle\Phi_0\right|H\left|T_2\Phi_0\right\rangle$$

$$\left\langle {}^{ab}_{ij}\right|H\left|1+T_2+\frac{T_2^2}{2}\,\right|\Phi_0\left.\right\rangle = E\left\langle {}^{ab}_{ij}\right|T_2\Phi_0\rangle$$

$$\left\langle {}^{ab}_{ij}\right|H\left|1+T_2+\frac{T_2^2}{2}\,\right|\Phi_0\left.\right\rangle = \left(E_{HF} + \left\langle\Phi_0\right|H\left|T_2\Phi_0\right\rangle\right)\left\langle {}^{ab}_{ij}\right|T_2\Phi_0\rangle$$

Solve for the amplitudes t_{ij}^{ab}

Equations are nonlinear

Delving a bit further:

$\widetilde{H} = e^{-T}He^{T}$ (similarity transform)

Baker-Campbell-Hausdorff (BCH) expansion

$$\widetilde{H} = e^{-T}He^{T} = [H,T] + \frac{1}{2}[[H,T],T] + \frac{1}{6}[[[H,\mathrm{T}],\mathrm{T}],\mathrm{T}] + \frac{1}{24}[[[[H,\mathrm{T}],\mathrm{T}],\mathrm{T}],\mathrm{T}]$$

Truncates exactly after 4 commutators

$$E = E_{HF} + \langle HF \,|[H,T_2]|\, \mathrm{HF}\rangle + \langle HF \,|[[H,T_1],\mathrm{T}_1]|\, \mathrm{HF}\rangle$$

Only T_1 and T_2 terms enter, but they are coupled to higher order terms through the coefficients

Ways of reducing computational effort

- use localized orbitals (“linear scaling)

  Requires sizable HOMO/LUMO gap
- truncate virtual orbital space (most effectively done using natural orbitals)
- use with explicit correlation (e.g., F12 method)

  Reduces the size of the GTO basis by ~3x

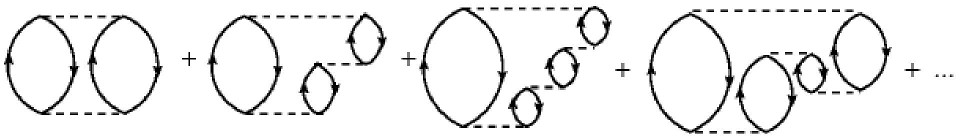
E.g., generate NO’s from MP2, and truncate space before CCSD(T) calculation

Connection with the RPA method

The RPA method has been around since the early 1950’s (Bohn and Pines)

So why the recent interest?

- Adiabatic connection fluctuation-dissipation: natural extension of DFT
- New algorithms give $O\left(N^3\right)$ scaling
- Direct RPA $\approx$ CCD (with ring diagrams)



See Ren et al., Phys. Rev. B 88, 035120 (2013)

Advantages of RPA method over DFT (GGA, hybrid, etc)

- Self-interaction problem largely removed
- Correctly describes long-range dispersion
- “Systematically” improvable

Problems

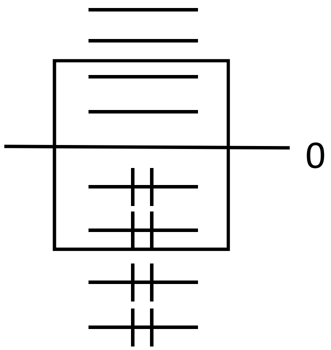
- Neglects second and higher-order exchange interactions
- Neglects ladder diagrams
- Underestimates net correlation energies

RPA with periodic boundary conditions now supported in the VASP and CP2K codes.

Multiconfigurational SCF Methods

CASSCF: all arrangements of electrons in a specified (active) orbital space

- Both CI coefficients and orbitals are optimized
- CASSCF ideal for treating static (near-degeneracy) correlation effects
  - Can properly dissociate bonds
  - Can be used as references for multi-reference MP2 (CASMP2)



Illustrates a CAS (4,4) (4 electrons in 4 orbitals) active space

However, largest possible CAS is (18,18) and that is very expensive

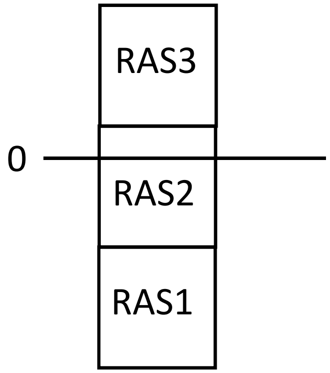
Recently density matrix renormalization group (DMRG) methods have been developed that can account for near degeneracy effects in ~50 or so orbitals

Restricted active space (RAS) methods are very flexible

E.g., could allow at most 2 electrons excited from RAS1, at most 2 electrons in RAS3, and all arrangements in RAS2 space.

Allows more active orbitals than CASSCF

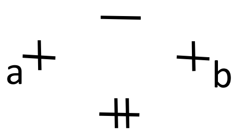
But can be challenging to “correctly” choose the spaces and excitation restrictions



Examples where one needs to use multiconfigurational wavefunctions

1. To dissociate H_2 to atoms: $c_1 |1\sigma_g^2\rangle - c_2 |1\sigma_u^2\rangle$

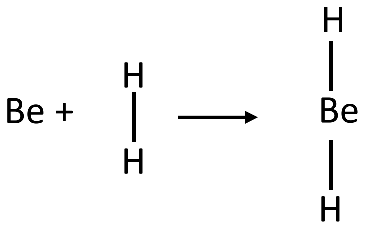
2. Singlet state of square H_4 requires two configurations

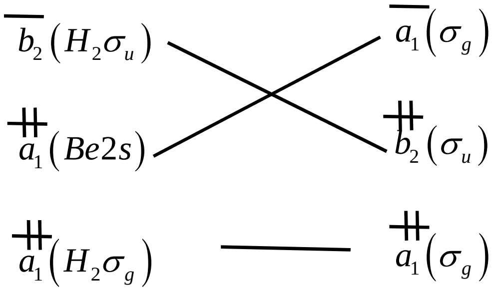


$(a^2 - b^2)$ or $(ab + ba)$

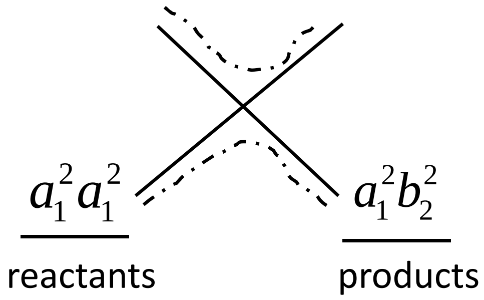
depending on whether one is using localized or delocalized orbitals

3. Insertion of Be into H_2





reactants   product



Symmetry labels: C_{2v} point group

Strong configuration mixing near transition state on reaction pathway

Summary of methods

Method	Correl	Scaling
HF	---	N^4
MP2	2nd order (dynamic)	N^5
CCSD	∞ order (dynamic)	N^6
CCSD(T)	∞ order (dynamic)	N^7
CASSCF	near deg. (static)	See full CI, below
CASMP2 (MR-MP2)	near deg. (static) + dynamic	See full CI, below
CISD	∞ order (dynamic)	$N^2 n_v^4 \sim N^6$
CISDTQ	∞ order (dynamic)	$N^4 n_v^6 \sim N^{10}$
Full CI	Exact in basis set	$N_{\text{det}} N^2 n_v^2$, $N_{\det} \sim \frac{1}{(m!)^2} N^m n_v^m$

N= # orbitals, n_v= # virtuals, m = exc. level

CAS and RAS can be used as reference spaces for multconfigurational CI (MRCI) and multiconfigurational PT (e.g., MRPT2, CASPT2)

Can be used to characterize electronically excited states

EOM-CCSD for IPs, EAs, excitation energies

$$\widetilde{H} = e^{-T} H e^{T}$$

$$|\psi_{ex}\rangle = R|\psi_g\rangle, \qquad R = R_o + R_1 + R_2 + \ldots$$

$$\psi_g = e^{T}\,|0>$$

$$HR|g >= HRe^{T}\,|0>= ERe^{T}\,|0>$$

$$e^{-T} He^{T} R|0>= ER|0>$$

$$\left(e^{-T} He^{T} R - ER\right)|0>= 0$$

$$\left(\widetilde{H} - E\right) R|0>= 0$$

level of excitation

ground state: $R = R_0 = 1$

EA: $R = a_a^{+},\ a_a^{+} a_b^{+} a_i$

IP: $R = a_i,\ a_a^{+} a_i a_j$

Exc. energy: $R = a_a^{+} a_i,\ a_a^{+} a_b^{+} a_i a_j$

IPs, EAs, excitation energies: matrix eigenvalue problem of configurations using $\widetilde{H}$ and above operators.

In general, very accurate IPs, EAs., excitation energies (except where ground state not well described by CCSD)

For some systems, EOM-MP2 is viable

use to amplitudes from MP2 rather than from CSSD to generate

$$\widetilde{H}$$

Some timings

IP of Au_{13}^-: PP with $5s^2 5p^6 5d^{10} 6s$ electrons treated explicitly

6s5p3d1f basis set

248 electrons, 559 basis functions

EOM-MP2: 1.5 hours on 3 cores

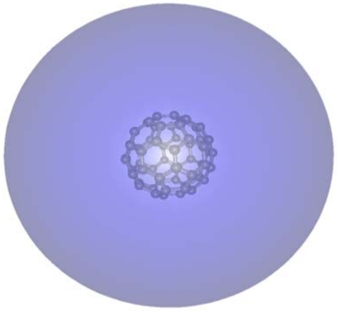
EOM-CCSD: 62 hours on 3 cores

EA of C_{60}: 360 correlated electrons, ~1400 basis functions

EOM-CCSD: ~ 240 hours on 1 core

Calculations carried out using a disk-based code (CFOUR)

Lots of room for improved performance (e.g., density fitting not implemented)



Used to demonstrate that C_{60} has an s-type anion bound by ~130 meV

Electron bound by long-range correlation effects

Counterpart to an image potential state of a metal surface