Modern Electronic Structure Methods:
2. Wavefunction-based theories.

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Outline

1. **Overview of standard wavefunction-based methods**
    - Mean field, perturbation theory, coupled cluster theory
2. Fast methods for dynamic correlations
3. Fast methods for static correlations (with applications)

Complexity

- Many-body Schrödinger equation is a partial differential equation in 3n unknowns– the positions of the electrons.
    - Exact (brute force) solution will scale approximately exponentially with the number of electrons.
- When done in a given basis of 1-electron expansion functions, this is “full configuration interaction” (FCI).
    - Largest FCI’s involve many-body expansions containing billions of terms, for molecules with 2 or 3 of atoms (!).
- Approximations are imperative. Accuracy vs feasibility.

Fundamental approximations

- (1) The one-body problem (“atomic orbital basis”)
    - One-electron functions are expanded in a finite basis.
    - We use atom-centered functions with some maximum angular momentum (L) on atoms of a given period.
    - Standardized basis sets of increasing L are available.
- (2) The n-body problem (“electron correlation method”)
    - More about this in a minute… mean field is the simplest possible treatment.
- Well-defined electronic structure models are completely specified by these two approximations.

Branches of the family tree

- Wavefunction-based electronic structure theory:
    - Minimize the energy by varying the wavefunction
    - Tremendously complicated unknown function: $\Psi = \Psi(r_1, r_2, \ldots, r_n)$
    - Modeling the wavefunction yields “model chemistries”
- Density functional theory
    - The unknown is very simple: $\rho = \rho(r)$
    - Hohenberg-Kohn theorem guarantees that: $E = E\{\rho(r)\}$
    - True functional is unknown and probably unknowable
    - Modeling the functional gives DFT model chemistries.

Wave function approaches to electronic structure

- Hartree-Fock (MO) theory (mean field): A^3-A^4 cost.
    - HF: 99%! “Correlation energy” is roughly 1 eV per pair.
- Perturbative treatment of the electron correlations: A^5
    - MP2: 80% of the last 1%. “Pair correlations” (doubles).
- Treat single & double substitutions self-consistently: A^6
    - CCSD: 95% of the last 1%.
- Correct for the triple substitutions perturbatively: A^7
    - CCSD(T): > 99% of the last 1%. Chemical accuracy.

State of the art thermochemistry

- Up to 4 first row atoms: ± 0.3 kcal/mol
  - Martin, Taylor, Dunning, Helgaker, Klopper…
  - include relativistic effects, core correlation, anharmonicity
  - CCSD(T) with extrapolation to the complete basis set limit
  - limited by (?): extrapolation, sometimes CCSD(T) itself.
- Up to 10 or 15 first row atoms: ± 1 kcal/mol
  - Curtiss, Raghavachari, Pople: G2/G3 methods
  - "CBS" methods of Petersson et al
  - based on methods like CCSD(T), with either additivity corrections for basis set, or extrapolation.

Mean field (Hartree-Fock) theory

- Each electron moves in the average field of all others
  - Wavefunction is an antisymmetrized product of "orbitals"

$$\left|\Psi_{HF}\right\rangle = \det\left(\phi_1\phi_2\cdots\phi_n\right)$$

  - The energy is minimized with respect to variations of the orbitals, giving the Hartree-Fock equations:

$$\hat{f}\phi_i = \varepsilon_i\phi_i$$

  - F is the Fock operator, which is a one-particle Hamiltonian with electron-repulsions averaged:

$$f_{\mu\nu} = h_{\mu\nu} + \sum_j \left(\mu j \| \nu j\right)$$

Chemistry with the Hartree-Fock model

- Size-consistent; exact for isolated electrons
- Absolute energies: about 99% of exact
  - The remaining energy is the "correlation energy"
- Atomization energies: a disaster…
  - The correlation energy of all separated electrons is the error
  - Thus roughly 1eV error (ie. 100 kJ mol) per separated pair
- Optimized molecular geometries: are reasonable…
  - Bondlengths are systematically slightly too short
  - Vibrational frequencies are systematically about 10% high

Dodging the correlation bullet

- Look at energy changes where correlation errors cancel.
- Energy change for isogyric reactions: a bit better
  - Isogyric reactions conserve the total number of electron pairs
  - Example: $H_2 + Cl \longrightarrow HCl + H$
- Energy change for isodesmic reactions: much better!
  - Isodesmic reactions conserve numbers of each type of electron pair (different bond pairs, lone pairs, etc)
  - Example: $H_2C{=}CH{-}CH_3 + CH_4 \longrightarrow H_2C{=}CH_2 + C_2H_6$

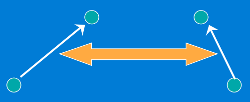
Schematic view of the Hamiltonian matrix

- Group determinants by substitution level from HF
  - 0, s(ingles), d(oubles), t(riples), etc…
- Look at the coupling of HF (0) to higher substitutions
  - HF orbitals are optimized to zero coupling to singles
  - HF wavefunction cannot couple to triples (or higher)
- Double substitutions are the leading correction to HF

$$\mathbf{H} = \begin{bmatrix} E_{HF} & 0 & H_{0d} & 0 \\ 0 & H_{ss} & H_{sd} & H_{st} \\ H_{d0} & H_{ds} & H_{dd} & H_{dt} \\ 0 & H_{ts} & H_{ts} & H_{tt} \end{bmatrix}$$

Double substitutions describe pair correlations

- Correlated fluctuations of 2 electrons
- In general, they are quartic in number.
  - Empty levels
  - Occupied levels



- Correlations decay rapidly with separation.
  - Exponentially between functions of the same electron
  - Algebraically (R^{-3}) between the 2 electrons (→dispersion)

Truncated configuration interaction

- The exact (full CI) wavefunction is a linear superposition

$$\left|\Psi_{exact}\right\rangle = \left(\hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \ldots + \hat{C}_n\right)\left|\Phi_{HF}\right\rangle$$

  - As discussed before, this is exponentially expensive!
- Truncated configuration for electron correlation?
  - For instance include all single + double substitutions (CISD)
- Not useful because it fails to be *size-consistent*
  - CISD is exact for 1 H_2 molecule (only 2 electrons)
  - But is *not* exact for 2 H_2's (that would require CISDTQ)

Møller-Plesset perturbation theory

- Apply perturbation theory to electronic structure, with:

$$\hat{H} = \hat{F}^{(0)} + \lambda \hat{V}^{(1)} \qquad \left(\lambda = 1\right)$$

  - The zero order Hamiltonian is the Fock operator:

$$\hat{F}^{(0)} = \sum_{i=1}^{n} \hat{f}\left(i\right)$$

  - Since the canonical MO's are eigenvectors of f:

$$\hat{f}\phi_i = \varepsilon_i \phi_i$$

  - Then the zero order problem is:

$$\hat{F}^{(0)}\left|\Psi^{(0)}\right\rangle = E^{(0)}\left|\Psi^{(0)}\right\rangle$$

$$\left|\Psi^{(0)}\right\rangle = \left|\Psi_{HF}\right\rangle \qquad E^{(0)} = \sum_{i=1}^{n} \varepsilon_i$$

1st and 2nd order expansions

- Expansion to first order gives the Hartree-Fock energy

$$E^{(0)} + E^{(1)} = \left\langle \Psi^{(0)} \middle| \hat{H}^{(0)} \middle| \Psi^{(0)} \right\rangle + \left\langle \Psi^{(0)} \middle| \hat{V}^{(1)} \middle| \Psi^{(0)} \right\rangle$$

$$= \left\langle \Psi^{(0)} \middle| \hat{H} \middle| \Psi^{(0)} \right\rangle = E_{HF}$$

- Leading estimate of correlation energy is from 2nd order:

$$E^{(2)} = \left\langle \Psi^{(0)} \middle| \hat{V}^{(1)} \middle| \Psi^{(1)} \right\rangle$$

$$\hat{H}^{(0)}\left|\Psi^{(1)}\right\rangle + \hat{V}^{(1)}\left|\Psi^{(0)}\right\rangle = E^{(0)}\left|\Psi^{(1)}\right\rangle + E^{(1)}\left|\Psi^{(0)}\right\rangle$$

  - Recall from the Hamiltonian that the coupling is just doubles

MP2 correlation energy expression

- The 2nd order expression in terms of doubles (d) is:

$$E_{MP2} = -\sum_{d} \frac{\left|\left\langle \Psi_d \middle| \hat{V}^{(1)} \middle| \Psi^{(0)} \right\rangle\right|^2}{\left(E_d^{(0)} - E^{(0)}\right)}$$

- Or in terms of the occupied (i,j) and empty (a,b) orbitals:

$$E_{MP2} = -\frac{1}{4}\sum_{ijab} \frac{\left(ij \| ab\right)^2}{\left(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j\right)}$$

  - MP2 correlation energy is negative definite
  - Computational complexity is 5th order in molecule size.

MP2 as a theoretical model chemistry

- MP2 is size-consistent. Proper treatment of dispersion.
- For closed shell molecules, accuracy is much better than HF
  - Bond lengths are (properly) longer, frequencies lower.
  - Directly reflects role of antibonding orbitals
- For open shell molecules, accuracy is erratic.
  - MP2 is sensitive to spin-contamination in UHF.
- Efficient computational algorithms are available:
  - Cubic memory (OVN), (larger) cubic disk space
  - Cost is asymptotically 5th order, but often lower.

Higher order corrections: MP3 and MP4

- MP3 energy introduces coupling between doubles:

$$E^{(3)} = \left\langle \Psi^{(1)} \middle| \hat{V}^{(1)} \middle| \Psi^{(1)} \right\rangle$$

  - MP3 is A^6 in computational complexity
- MP4 includes singles, doubles, triples & quadruples:

$$\hat{H}^{(0)}\left|\Psi^{(2)}\right\rangle + \hat{V}^{(1)}\left|\Psi^{(1)}\right\rangle = E^{(0)}\left|\Psi^{(2)}\right\rangle + E^{(1)}\left|\Psi^{(1)}\right\rangle + E^{(2)}\left|\Psi^{(0)}\right\rangle$$

$$E^{(4)} = \left\langle \Psi^{(1)} \middle| \hat{V}^{(1)} \middle| \Psi^{(2)} \right\rangle$$

  - The MP4 triples are A^7 to compute
  - The triples energy contribution is "chemically significant"
  - MP3 and MP4 energies are erratic in accuracy

Coupled cluster theory

- The exact wavefunction may be written as the *exponential* of the sum of substitution operators

$$\left|\Psi_{exact}\right\rangle = \exp\left(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots + \hat{T}_n\right)\left|\Phi\right\rangle$$

- Truncation of T defines limited coupled cluster models.
  - Simplest models are CCD (doubles) and CCSD

$$\left|\Psi_{CCSD}\right\rangle = \exp\left(\hat{T}_1 + \hat{T}_2\right)\left|\Phi\right\rangle$$

  - Truncated CC models are clearly size-consistent: e.g.

$$\left|\Psi_{CCD}^{A\oplus B}\right\rangle = \exp\left(\hat{T}_2^{A\oplus B}\right)\left|\Phi\right\rangle$$

$$= \exp\left(\hat{T}_2^{A} + \hat{T}_2^{B}\right)\left|\Phi\right\rangle = \exp\left(\hat{T}_2^{A}\right)\exp\left(\hat{T}_2^{B}\right)\left|\Phi\right\rangle$$

Finding the coupled cluster amplitudes

- Variational CC energy is *intractable* (can you see why?)

$$E_{VCC} = \left\langle \exp\left(\hat{T}\right)\Phi\right|\hat{H}\left|\exp\left(\hat{T}\right)\Phi\right\rangle \Big/ \left\langle \exp\left(\hat{T}\right)\Phi\middle|\exp\left(\hat{T}\right)\Phi\right\rangle$$

- Instead we define CC equations by *subspace projection*:
  - Project with reference (0), and all substitutions in T, to give enough equations to determine the energy, and T amplitudes.

$$\left\langle \Phi_p\right|\left(\hat{H} - E\right)\left|\exp\left(\hat{T}\right)\Phi\right\rangle = 0$$

- This gives *tractable* equations, but the resulting energy *does not obey a variational bound.*
  - The quality of the results will be best for cases when the single reference is the dominant part of the wavefunction

Energy & amplitude equations for CCSD

- Project with the reference (0) to determine the energy

$$\left\langle \Phi\right|\left(\hat{H} - E\right)\left|\exp\left(\hat{T}\right)\Phi\right\rangle = 0$$

$$\Rightarrow E = \left\langle \Phi\right|\hat{H}\left|\exp\left(\hat{T}\right)\Phi\right\rangle = \left\langle \Phi\right|\hat{H}\left|\left(1 + \hat{T}_1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2\right)\Phi\right\rangle$$

- Project with singles (s) & doubles (d) for amplitudes:

$$\left\langle \Phi_s\right|\hat{H}\left|\left(1 + \hat{T}_1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \tfrac{1}{3!}\hat{T}_1^3\right)\Phi\right\rangle_C = 0$$

$$\left\langle \Phi_d\right|\hat{H}\left|\left(1 + \hat{T}_1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \tfrac{1}{3!}\hat{T}_1^3 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_2 + \tfrac{1}{4!}\hat{T}_1^4\right)\Phi\right\rangle_C = 0$$

  - Non-linear equations with A^6 computational complexity.

CCSD as a theoretical model chemistry

- Exact for a pair of electrons
- Size-consistent
- Analysis in terms of the Moller-Plesset series:
  - Complete in second order
  - Complete in third order
  - Missing the triples in fourth order
  - Contains some fifth and higher order terms
- A significant improvement over MP2 for problem cases (radicals!)
  - Not much improvement for closed shell molecules
  - Occasional non-variational pathologies (E.g. stretched bonds)
- Not chemically accurate for relative energies
  - Reflects the fact that the triples are chemically significant

Accounting for the triples in coupled cluster theory

- CCSDT is the next complete truncation
  - Solving for the triples requires A^6 storage (vs A^4 for CCSD)
  - And A^8 computation (vs A^6 for CCSD).
- Hence it is tempting to develop a perturbative approach
  - MP4 triples require A^4 storage and A^7 computation…
- The best standard method for this is CCSD(T)
  - First solve iteratively for CCSD (A^6 computation, A^4 storage)
  - Then non-iteratively account for triples (one A^7 step)

What is CCSD(T)?

- Begin with the MP4 triples expression:

$$E_{MP4T} = \left\langle \Psi_T^{(2)}\right|\hat{V}^{(1)}\left|\Psi^{(1)}\right\rangle$$

$$\left\langle \Psi_t\right|\left(\hat{H}^{(0)} - E^{(0)}\right)\left|\Psi_T^{(2)}\right\rangle + \left\langle \Psi_t\right|\hat{V}^{(1)}\left|\Psi^{(1)}\right\rangle = 0$$

- Simplest correction to CCSD is to just add it on…
- Better is to use converged doubles: $\left|\Psi^{(1)}\right\rangle \rightarrow \left|\hat{T}_2\Psi_{HF}\right\rangle$
- Best is to use converged S+D: $\left|\Psi^{(1)}\right\rangle \rightarrow \left|\left(\hat{T}_1 + \hat{T}_2\right)\Psi_{HF}\right\rangle$
  - The energy expression is chosen to get the effect of singles on triples correct in 5th order (cf doubles on triples in 4th order)
  - This defines the CCSD(T) method

CCSD(T) as a model chemistry

- The “gold standard” of modern quantum chemistry for closed shell molecules!
  - Structures accurate to about 0.002 Å
  - Vibrational frequencies accurate to about 2%
  - Chemical accuracy (< 2 kcal/mol error) in bond energies!!)
- Reducing the need for large basis sets
  - G2 and G3 methods use energy additivity approximations
  - Dunning cc-pVnZ basis sets can be extrapolated towards the basis set limit using 2 point fits. Useful for energies.

Limitations of CCSD(T)

- Can be erratic for radicals (reflects problems of HF)
  - Reduce by using optimized orbitals (or even KS orbitals)
- Exhibits pathologies in bond-breaking
  - Do not use restricted orbitals when they are unstable!
- Succeeds partly by cancellation of errors
  - Slightly overestimates the triples, which compensates for neglect of connected quadruples.
- Computational cost is high.

Wave function approaches to electronic structure

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Outline

1. Overview of standard wavefunction-based methods
2. **Fast methods for dynamic correlations**
   - Auxiliary basis expansions
   - Local correlation methods
   - Opposite-spin second order correlation
   - Towards linear scaling
3. Fast methods for static correlations (with applications)

Auxiliary basis expansions

- Early contributions by Whitten, Dunlap, Baerends, Almlof, others.
  - Auxiliary basis or “resolution of the identity” (RI) or “density fitting” (DF)
- Popularized by Ahlrichs and co-workers for DFT, MP2.
  - Demonstrated efficiency
  - Developed standardized auxiliary basis sets: 3-4 times the AO basis size.
- Replace 4-center integrals by (inexact) expansions:

$$\langle ia|jb\rangle \approx \sum_{KL} C_{ia}^{K} \langle K|L\rangle C_{jb}^{L} = \sum_{K} B_{ia}^{K} B_{jb}^{K}$$

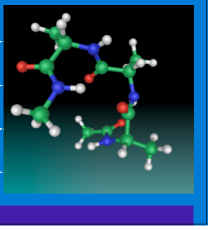
- Coefficients C minimize the Coulomb deviation of the fit:

$$C_{ia}^{K} = \sum_{L} \langle ia|L\rangle \langle L|K\rangle^{-1} \qquad B_{ia}^{K} = \sum_{L} \langle ia|L\rangle \langle L|K\rangle^{-1/2}$$

Benefits of RI-MP2

- The prefactor of the MP2 calculation is greatly reduced.
  - Far fewer integrals & better scaling with angular momentum.
  - The asymptotic rate-determining step is actually more expensive!
- Timings for alanine tetrapeptides on 2 GHz G5. Tight cutoffs (12/9).

	cc-pVDZ	cc-pVQZ
SCF (min)	55	714
MP2 (min)	63	902
RI-MP2 (min)	4	30



Accuracy of the auxiliary basis expansions

- (1) G2 dataset
  - Atomization energies of 148 neutral molecules: MP2 vs RI-MP2
    - RMS deviation = 0.10 kcal/mol
    - Max deviation = 0.27 kcal/mol
- (2) Relative conformational energies of the tetrapeptide
  - 27 conformations. Compare MP2 and RI-MP2
    - RMS deviation = 0.003 kcal/mol
    - Max deviation = 0.007 kcal/mol
- Errors are chemically insignificant at the MP2 level.

"Large molecule" regime for RI-MP2

- When SCF cost is smaller than RI-MP2.
  - M^2 (or less) cost for SCF vs M^5 for RI-MP2
- DZP basis sets: 30-50 non-H atoms & up
  - depends on globularity, AO basis, cutoffs, etc.
- cc-pVDZ alanine polypeptides;
  - 2GHz G5; tight cutoffs (12/9).

	tetrapeptide	octapeptide	hexadecapeptide
SCF (min)	55	390	1779
RI-MP2 (min)	4	120	3935

What is a local correlation model?

- A local correlation model approximates a standard correlation method (we'll look at MP2), computing only some of the amplitudes, based on spatial truncation.
- Convention wavefunction-based models. One can
  - (1) Make models for the correlation energy, stopping at some order in excitations (CCSD) or perturbation theory (MP2).
  - (2) Or, could select retained excitations based on some cutoff criterion… such methods are today not widely used.
- A similar choice will confront us in local correlation

Local correlation methods as model chemistries

- Local correlation models involve strong approximations.
  - Often recover 98 or 99% of the correlation energy
- Local correlation models thus define modified theoretical model chemistries that must be tested.
- They should have the features of a good theoretical model chemistry (not all do, however!).
  - Efficient (a good tradeoff between accuracy and cost)
  - Size-consistent
  - No molecule-dependent adjustable parameters
  - Continuous potential energy surfaces, etc.

Pulay-Szabo Local Electron Correlation Method

- First and most widely used approach to reduce the unphysically high cost of wavefunction-based methods:
  - P.Pulay, Chem. Phys. Lett. 100, 151 (1983).
  - S.Saebo & P.Pulay, Ann. Rev. Phys. Chem. 44, 213 (1993)
- Successfully adopted and extended by other groups:
  - Murphy, Friesner et al, JCP 103, 1481 (1995).
  - Reynolds, Martinez, Carter, JCP 105, 6455 (1996).
  - Schutz, Hetzer, Werner, JCP 111, 5691 (1999).

Pulay-Szabo local model for double substitutions

(1) Localize the occupied orbitals

- symmetry-equivalent atoms may ***not*** be equivalent: benzene

(2) Project atomic orbitals into the virtual space

(3) Allow only substitutions from a pair of occupied orbitals into all pairs of virtual orbitals that strongly overlap one or the other of the occupied orbitals.

- potential energy surfaces will ***not*** be strictly continuous.

- Computational complexity is greatly reduced.
- 98% (or more) of correlation energy is recovered.

Status of the Pulay-Saebo model

- Linear scaling achieved with the work of Schutz/Werner
  - Long-range dispersion truncated
- Extension to CCSD and triples completed.
  - CCSD is used for “strong pairs”, MP2 for “weak pairs”
  - Very weak pairs are further approximated or truncated.
- Some drawbacks for chemical applications due to:
  - Discontinuous potential energy surfaces
  - Use of adjustable numerical parameters
  - Failure for delocalized electronic structure

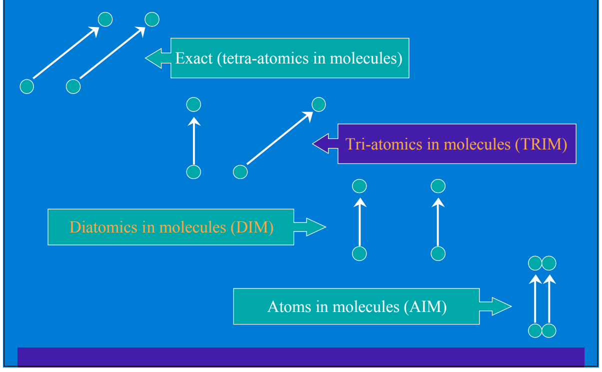
Atomic local correlation models

- We re-examined the 2 steps to make local correlation models:

(1) Choose suitable local 1 particle representations
  - Make them atom centered!
  - A minimal atom-centered basis for occupied space
  - Projected atomic orbitals for the virtual space

(2) Truncate the n-particle spaces in a physical way.
  - Satisfy model chemistry criteria with atomic truncations
  - Parameter free models, continuous potential surfaces

TRIM local correlation model



Exact (tetra-atomics in molecules)

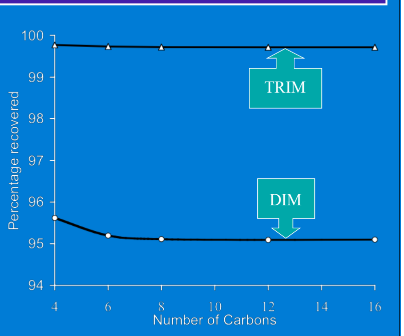
Tri-atomics in molecules (TRIM)

Diatomics in molecules (DIM)

Atoms in molecules (AIM)

Fractional correlation recovery in linear alkanes

- 6-31G* basis.
- TRIM yields 99.7% of correlation energy
- DIM yields 95% of correlation energy



Torsional barriers via local MP2 methods

- 12 conjugated ethylene and benzene derivatives
  - R-OH, R-CHO, R-C_2H_3, R-CFO, R-NH_2, RNO_2
- Delocalization and barriers are tests for local correlation
- 6-311G** basis, frozen core.
- Deviations from untruncated MP2 (in kcal/mol)
  - (magnitude of barriers ranges from 1 to 8 kcal/mol)

	TRIM-MP2	DIM-MP2	Null
RMS Error	0.031	0.252	1.022
Max Error	0.083	0.662	2.316

TRIM-MP2 energy

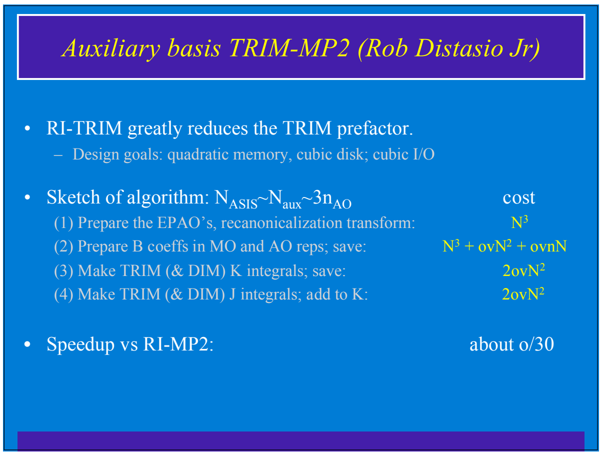
- The working expression for the TRIM energy is:

$$E_{TRIM-MP2} = -\sum_{Pai} \frac{I_{Pai} II_{Pai}}{E_P + \varepsilon_a - \varepsilon_i} - E_{DIM-MP2}$$

- where the DIM energy itself is:

$$E_{DIM-MP2} = -\frac{1}{2} \sum_{PQ} \frac{I_{PQ} II_{PQ}}{E_P + E_Q}$$

- Indices *i*,*a* represent canonical occupieds and virtuals
- Indices *P*,*Q* are recanonicalized atomic single substitutions, with corresponding excitation energies E_P
- TRIM reduces the number of doubles to cubic.
  - Rate-determining steps are 4th order, not 5th order

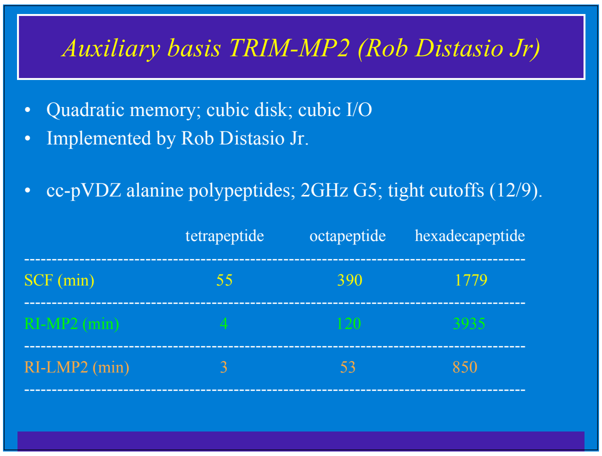


Auxiliary basis TRIM-MP2 (Rob Distasio Jr)

- RI-TRIM greatly reduces the TRIM prefactor.
  - Design goals: quadratic memory, cubic disk; cubic I/O
- Sketch of algorithm: $N_{ASIS} \sim N_{aux} \sim 3n_{AO}$ cost

	cost
(1) Prepare the EPAO's, recanonicalization transform:	N^3
(2) Prepare B coeffs in MO and AO reps; save:	$N^3 + ovN^2 + ovnN$
(3) Make TRIM (& DIM) K integrals; save:	$2ovN^2$
(4) Make TRIM (& DIM) J integrals; add to K:	$2ovN^2$

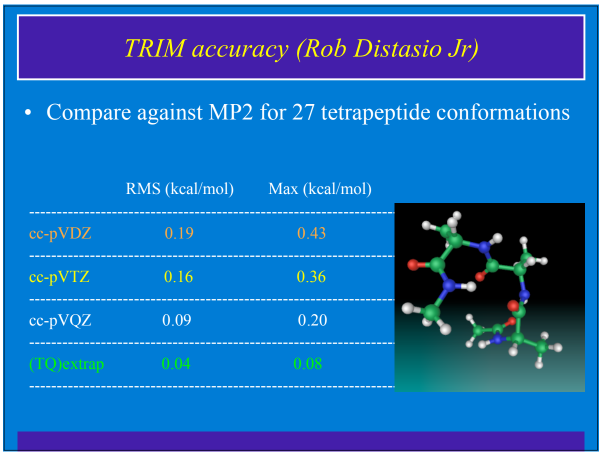
- Speedup vs RI-MP2: about o/30



Auxiliary basis TRIM-MP2 (Rob Distasio Jr)

- Quadratic memory; cubic disk; cubic I/O
- Implemented by Rob Distasio Jr.
- cc-pVDZ alanine polypeptides; 2GHz G5; tight cutoffs (12/9).

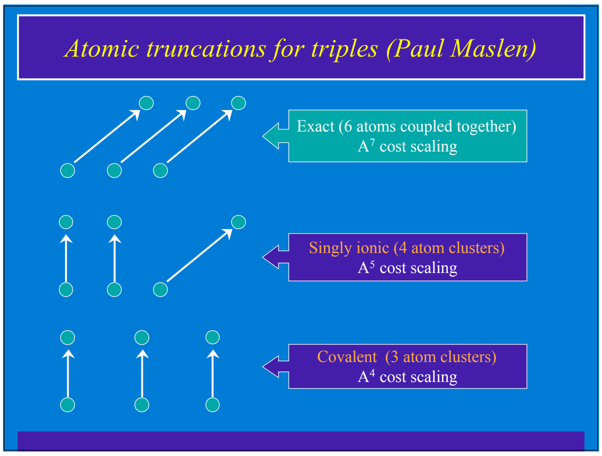
	tetrapeptide	octapeptide	hexadecapeptide
SCF (min)	55	390	1779
RI-MP2 (min)	4	120	3935
RI-LMP2 (min)	3	53	850



TRIM accuracy (Rob Distasio Jr)

- Compare against MP2 for 27 tetrapeptide conformations

	RMS (kcal/mol)	Max (kcal/mol)
cc-pVDZ	0.19	0.43
cc-pVTZ	0.16	0.36
cc-pVQZ	0.09	0.20
(TQ)extrap	0.04	0.08

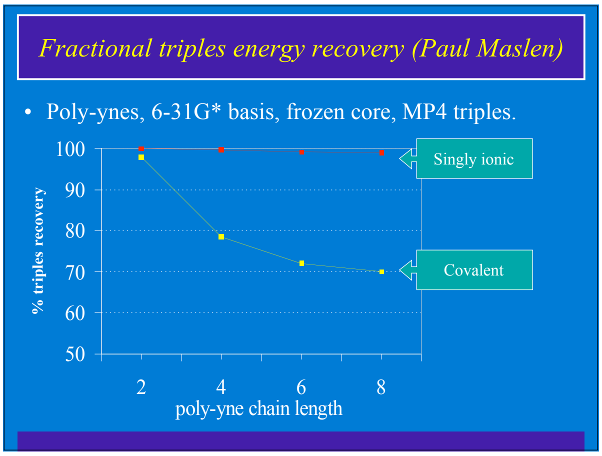


Atomic truncations for triples (Paul Maslen)

Exact (6 atoms coupled together)
A^7 cost scaling

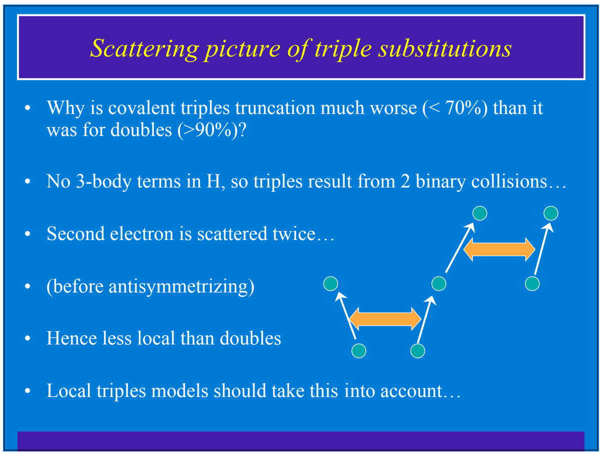
Singly ionic (4 atom clusters)
A^5 cost scaling

Covalent (3 atom clusters)
A^4 cost scaling



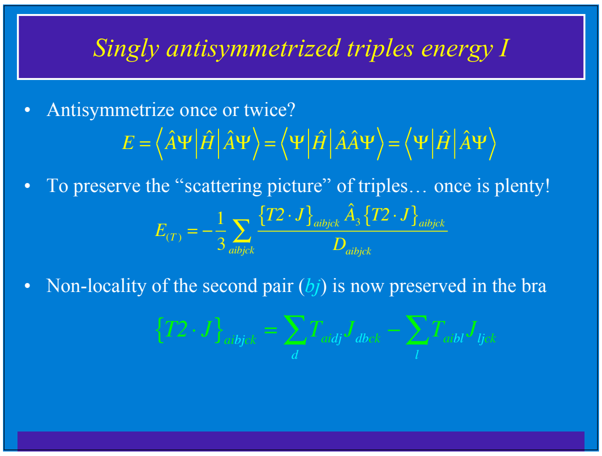
Fractional triples energy recovery (Paul Maslen)

- Poly-ynes, 6-31G* basis, frozen core, MP4 triples.



Scattering picture of triple substitutions

- Why is covalent triples truncation much worse (< 70%) than it was for doubles (>90%)?
- No 3-body terms in H, so triples result from 2 binary collisions…
- Second electron is scattered twice…
- (before antisymmetrizing)
- Hence less local than doubles
- Local triples models should take this into account…



Singly antisymmetrized triples energy I

- Antisymmetrize once or twice?

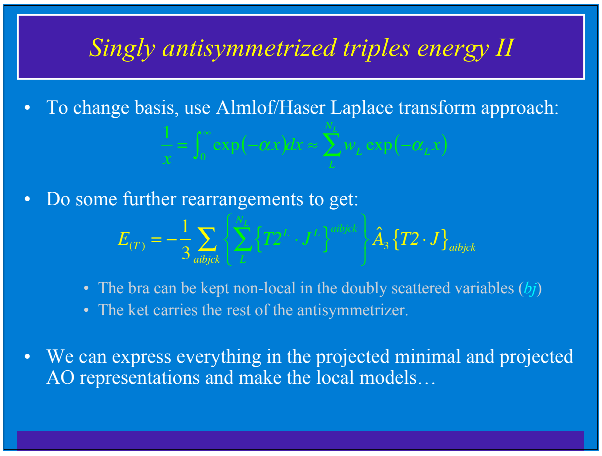
$$E = \left\langle \hat{A}\Psi \middle| \hat{H} \middle| \hat{A}\Psi \right\rangle = \left\langle \Psi \middle| \hat{H} \middle| \hat{A}\hat{A}\Psi \right\rangle = \left\langle \Psi \middle| \hat{H} \middle| \hat{A}\Psi \right\rangle$$

- To preserve the “scattering picture” of triples… once is plenty!

$$E_{(T)} = -\frac{1}{3}\sum_{aibjck} \frac{\{T2 \cdot J\}_{aibjck}\, \hat{A}_3 \{T2 \cdot J\}_{aibjck}}{D_{aibjck}}$$

- Non-locality of the second pair (*bj*) is now preserved in the bra

$$\{T2 \cdot J\}_{aibjck} = \sum_d T_{aidj} J_{dbck} - \sum_l T_{aibl} J_{ljck}$$



Singly antisymmetrized triples energy II

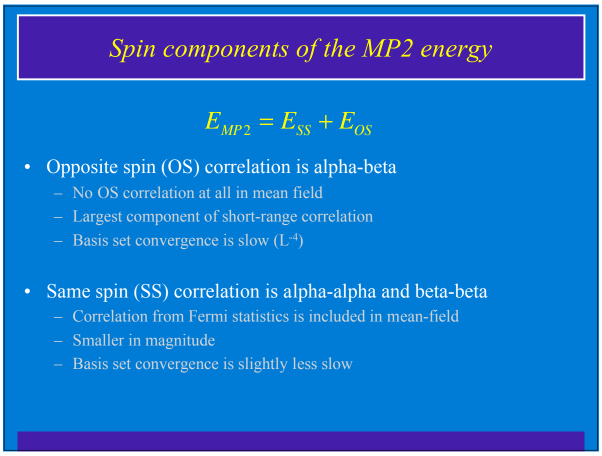
- To change basis, use Almlof/Haser Laplace transform approach:

$$\frac{1}{x} = \int_0^\infty \exp(-\alpha x) dx \approx \sum_L^{N_L} w_L \exp(-\alpha_L x)$$

- Do some further rearrangements to get:

$$E_{(T)} = -\frac{1}{3}\sum_{aibjck} \left\{ \sum_L^{N_L} \left\{ T2^L \cdot J^L \right\}^{aibjck} \right\} \hat{A}_3 \{T2 \cdot J\}_{aibjck}$$

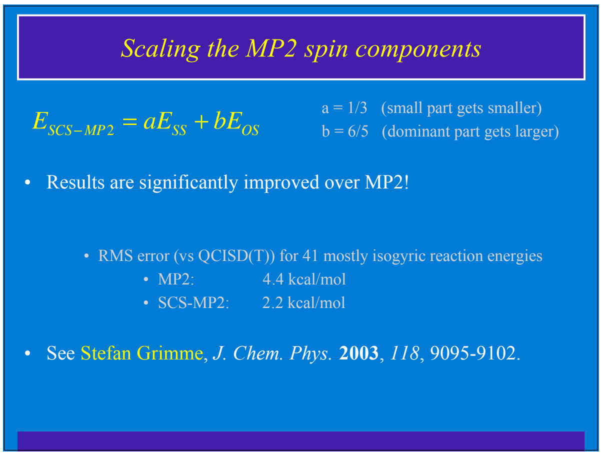
  - The bra can be kept non-local in the doubly scattered variables (*bj*)
  - The ket carries the rest of the antisymmetrizer.
- We can express everything in the projected minimal and projected AO representations and make the local models…



Spin components of the MP2 energy

$$E_{MP2} = E_{SS} + E_{OS}$$

- Opposite spin (OS) correlation is alpha-beta
  - No OS correlation at all in mean field
  - Largest component of short-range correlation
  - Basis set convergence is slow (L^{-4})
- Same spin (SS) correlation is alpha-alpha and beta-beta
  - Correlation from Fermi statistics is included in mean-field
  - Smaller in magnitude
  - Basis set convergence is slightly less slow

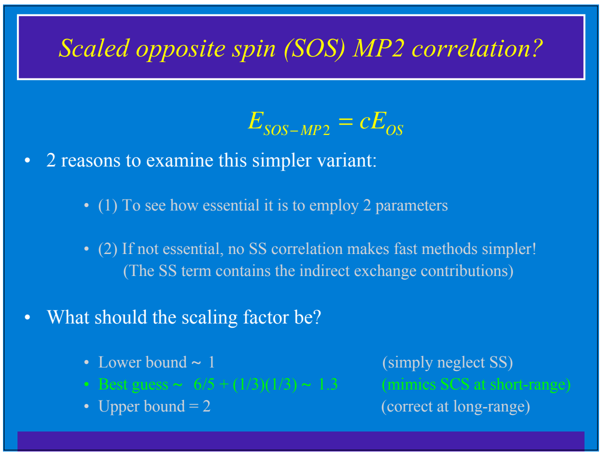


Scaling the MP2 spin components

$$E_{SCS-MP2} = aE_{SS} + bE_{OS}$$

a = 1/3 (small part gets smaller)
b = 6/5 (dominant part gets larger)

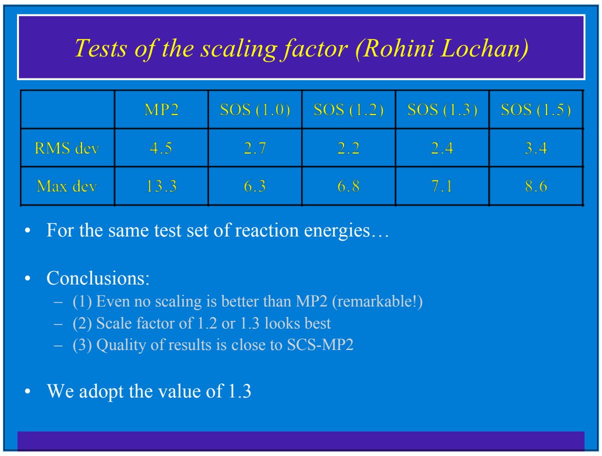
- Results are significantly improved over MP2!
  - RMS error (vs QCISD(T)) for 41 mostly isogyric reaction energies
    - MP2: 4.4 kcal/mol
    - SCS-MP2: 2.2 kcal/mol
- See Stefan Grimme, *J. Chem. Phys.* **2003**, *118*, 9095-9102.



Scaled opposite spin (SOS) MP2 correlation?

$$E_{SOS-MP2} = cE_{OS}$$

- 2 reasons to examine this simpler variant:
  - (1) To see how essential it is to employ 2 parameters
  - (2) If not essential, no SS correlation makes fast methods simpler! (The SS term contains the indirect exchange contributions)
- What should the scaling factor be?
  - Lower bound ~ 1 (simply neglect SS)
  - Best guess ~ 6/5 + (1/3)(1/3) ~ 1.3 (mimics SCS at short-range)
  - Upper bound = 2 (correct at long-range)



Tests of the scaling factor (Rohini Lochan)

	MP2	SOS (1.0)	SOS (1.2)	SOS (1.3)	SOS (1.5)
RMS dev	4.5	2.7	2.2	2.4	3.4
Max dev	13.3	6.3	6.8	7.1	8.6

- For the same test set of reaction energies…
- Conclusions:
  - (1) Even no scaling is better than MP2 (remarkable!)
  - (2) Scale factor of 1.2 or 1.3 looks best
  - (3) Quality of results is close to SCS-MP2
- We adopt the value of 1.3

Fast evaluation of the opposite spin MP2 energy

- Using an auxiliary basis, the SOS-MP2 energy can be evaluated with no 5th order steps.
- This is done using the Laplace formulation in an auxiliary basis. No other approximation (e.g. local model) is required.
- The working equations are: (with rate-determining step ovN^2)

$$E_{MP2}^{OS} = -\frac{1}{2}\sum_z w_z \sum_{IJ}^{occ}\sum_{AB}^{vir}\overline{\left(IA\,|\,JB\right)}^2 \qquad \bar{Y}_{KL} = \sum_{ia}\bar{C}_{ia}^{K}\bar{C}_{ia}^{L}$$

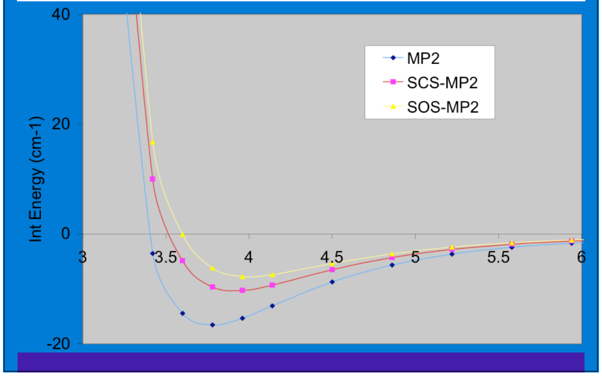
$$= -\frac{1}{2}\sum_z w_z \sum_{KL}^{aux}\sum_{MN}^{aux}\bar{Y}_{KM}\left\langle K\middle|L\right\rangle\bar{Y}_{LN}\left\langle M\middle|N\right\rangle$$

Timing comparison (Yousung Jung)

- Timings in minutes (375 MHz IBM Power3)
- Basis is 6-31G*; all electrons correlated.
- 4th order algorithm wins cleanly for bigger systems.

	Auxiliary basis (N^5)	Laplace (N^4)	Error (a.u.)
C20H42	15	19	0.000000
C30H62	89	83	0.000002
C40H82	364	243	0.000003
C50H102	977	569	0.000004

ArNe dimer (CP-cc-pVQZ) (Rohini Lochan)



Modified opposite spin scaling

- Issue: At long range, same-spin and opposite spin contributions to the MP2 energy are equal.
    - But SOS scales by only 1.3, not 2.
- Solution: Define modified integrals for opposite spin correlation:

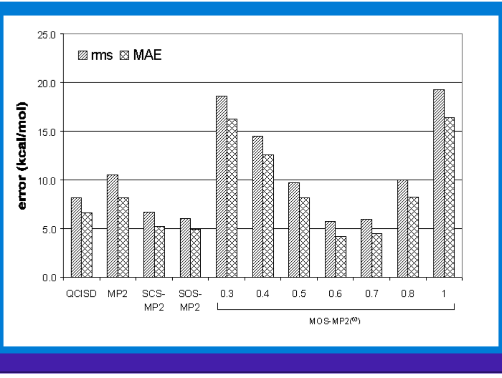
$$\left(ia\middle|jb\right)_\omega = \int d\mathbf{r}\int d\mathbf{r}'\phi_i\left(\mathbf{r}\right)\phi_a\left(\mathbf{r}\right)\left[\frac{1+K\,\mathrm{erf}\left(\omega\left|\mathbf{r}-\mathbf{r}'\right|\right)}{\left|\mathbf{r}-\mathbf{r}'\right|}\right]\phi_j\left(\mathbf{r}'\right)\phi_b\left(\mathbf{r}'\right).$$

- Choose K to get the long-range right.

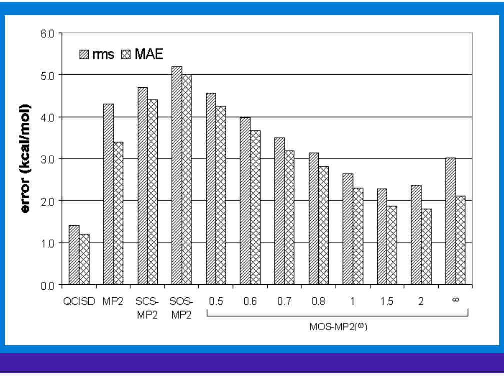
$$K=\sqrt{2}-1$$

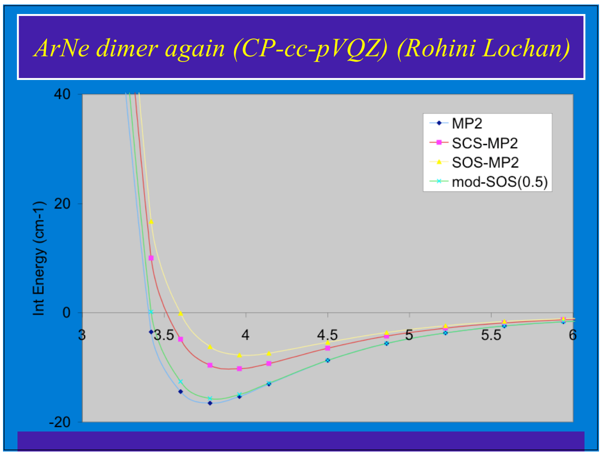
- The free parameter ω can then be adjusted.

77 atomizations as a function of ω (Rohini Lochan)

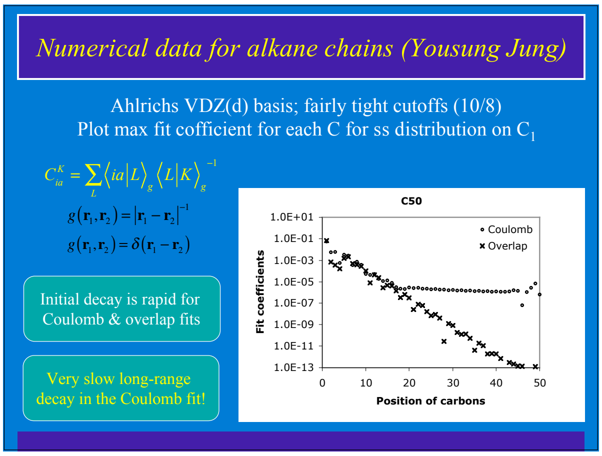


30 barrier heights as a function of ω (Rohini Lochan)





ArNe dimer again (CP-cc-pVQZ) (Rohini Lochan)



Numerical data for alkane chains (Yousung Jung)

Ahlrichs VDZ(d) basis; fairly tight cutoffs (10/8)
Plot max fit cofficient for each C for ss distribution on C_1

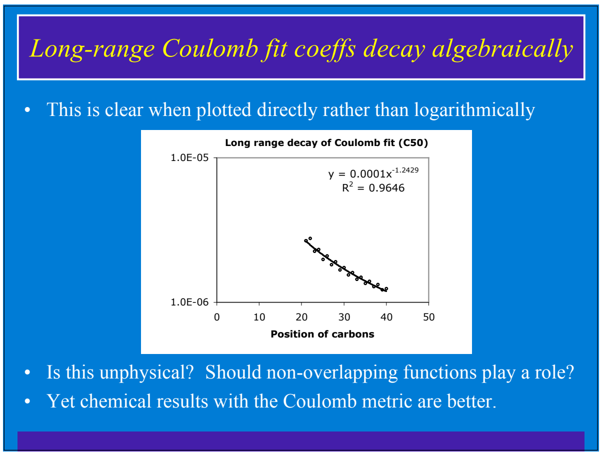
$$C_{ia}^{K} = \sum_{L} \langle ia|L\rangle_g \langle L|K\rangle_g^{-1}$$

$$g(\mathbf{r}_1,\mathbf{r}_2) = |\mathbf{r}_1-\mathbf{r}_2|^{-1}$$

$$g(\mathbf{r}_1,\mathbf{r}_2) = \delta(\mathbf{r}_1-\mathbf{r}_2)$$

Initial decay is rapid for Coulomb & overlap fits

Very slow long-range decay in the Coulomb fit!



Long-range Coulomb fit coeffs decay algebraically

- This is clear when plotted directly rather than logarithmically

- Is this unphysical? Should non-overlapping functions play a role?
- Yet chemical results with the Coulomb metric are better.

A 2-site model (Alex Sodt)

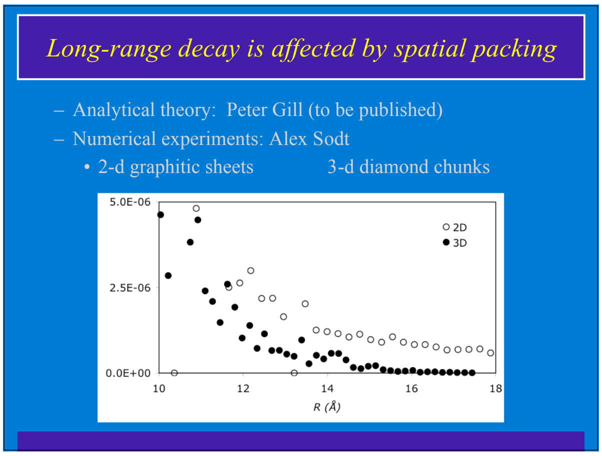
- Fit an s-type Gaussian with *q*=1 using 2 auxiliary basis functions.
  - Both have *q*=1 also, and are s functions.
  - 1st is on the same site but has wrong exponent; 2nd is on a remote site.
- The Coulomb fitting equations become:

$$\begin{bmatrix} i & r^{-1} \\ r^{-1} & i \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} j \\ r^{-1} \end{bmatrix} \quad \text{with solutions:} \quad \begin{aligned} c_1 &= (ijr^2-1)/(i^2r^2-1) \\ c_2 &= r(i-j)/(i^2r^2-1) \end{aligned}$$

- In the long-range limit (r large):

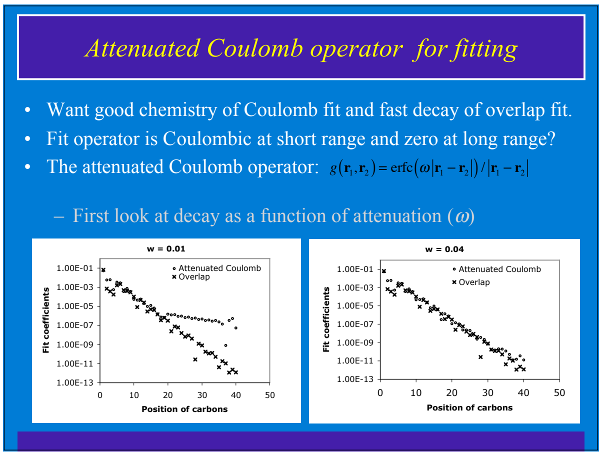
$$c_1 \to i/j \qquad c_2 \to (i-j)/(i^2 r)$$

  - On-site Gaussian does not contain correct charge
  - Off-site Gaussian partly compensates for this…
  - A *non-local* correction to partly fix a *local* deficiency



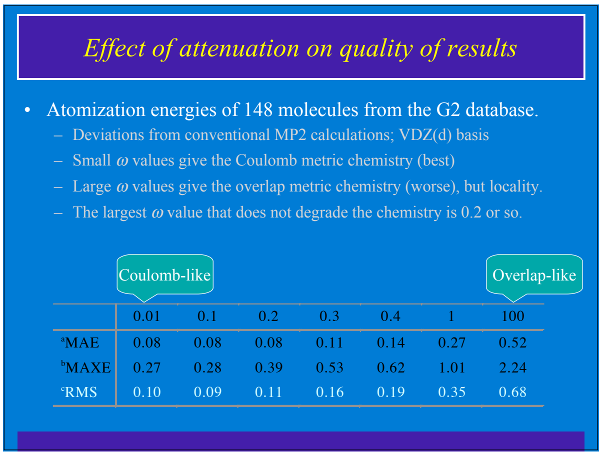
Long-range decay is affected by spatial packing

- Analytical theory: Peter Gill (to be published)
- Numerical experiments: Alex Sodt
  - 2-d graphitic sheets 3-d diamond chunks



Attenuated Coulomb operator for fitting

- Want good chemistry of Coulomb fit and fast decay of overlap fit.
- Fit operator is Coulombic at short range and zero at long range?
- The attenuated Coulomb operator: $g(\mathbf{r}_1,\mathbf{r}_2) = \operatorname{erfc}(\omega|\mathbf{r}_1-\mathbf{r}_2|)/|\mathbf{r}_1-\mathbf{r}_2|$
  - First look at decay as a function of attenuation (ω)



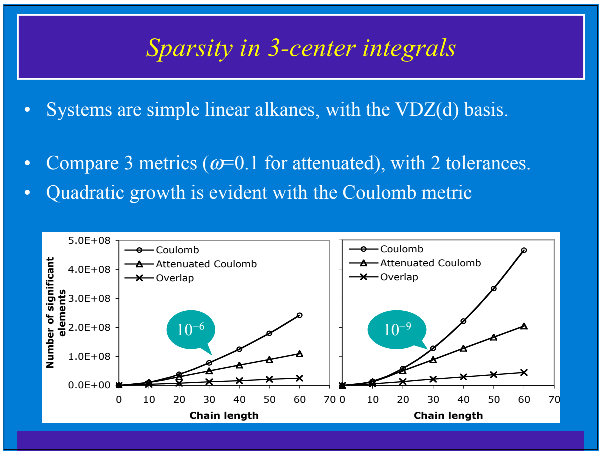
Effect of attenuation on quality of results

- Atomization energies of 148 molecules from the G2 database.
  - Deviations from conventional MP2 calculations; VDZ(d) basis
  - Small ω values give the Coulomb metric chemistry (best)
  - Large ω values give the overlap metric chemistry (worse), but locality.
  - The largest ω value that does not degrade the chemistry is 0.2 or so.

Coulomb-like

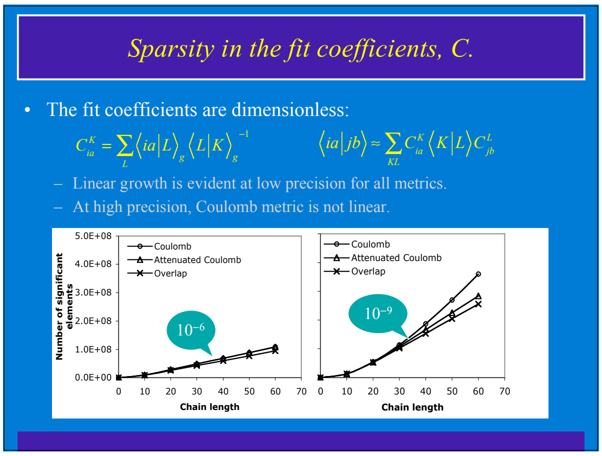
Overlap-like

	0.01	0.1	0.2	0.3	0.4	1	100
[a]MAE	0.08	0.08	0.08	0.11	0.14	0.27	0.52
[b]MAXE	0.27	0.28	0.39	0.53	0.62	1.01	2.24
[c]RMS	0.10	0.09	0.11	0.16	0.19	0.35	0.68



Sparsity in 3-center integrals

- Systems are simple linear alkanes, with the VDZ(d) basis.
- Compare 3 metrics (ω=0.1 for attenuated), with 2 tolerances.
- Quadratic growth is evident with the Coulomb metric

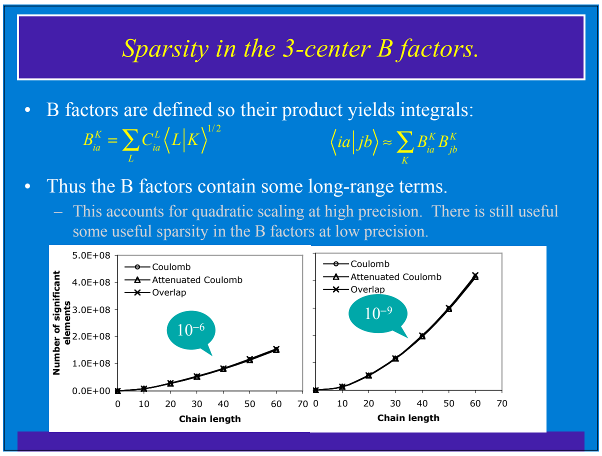


Sparsity in the fit coefficients, C.

- The fit coefficients are dimensionless:

$$C_{ia}^{K} = \sum_{L} \langle ia | L \rangle_g \langle L | K \rangle_g^{-1} \qquad \langle ia | jb \rangle \approx \sum_{KL} C_{ia}^{K} \langle K | L \rangle C_{jb}^{L}$$

  - Linear growth is evident at low precision for all metrics.
  - At high precision, Coulomb metric is not linear.

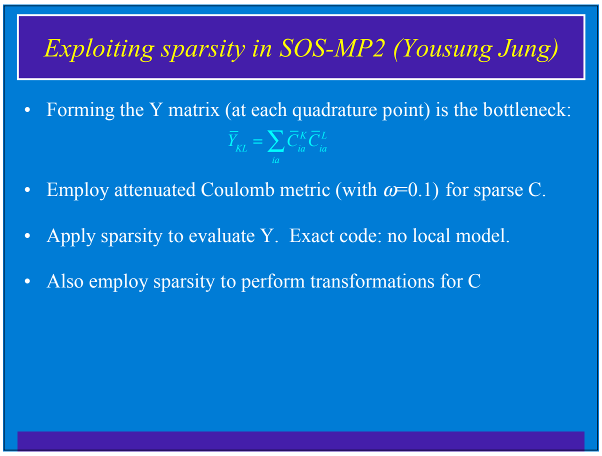


Sparsity in the 3-center B factors.

- B factors are defined so their product yields integrals:

$$B_{ia}^{K} = \sum_{L} C_{ia}^{L} \langle L | K \rangle^{1/2} \qquad \langle ia | jb \rangle \approx \sum_{K} B_{ia}^{K} B_{jb}^{K}$$

- Thus the B factors contain some long-range terms.
  - This accounts for quadratic scaling at high precision. There is still useful some useful sparsity in the B factors at low precision.

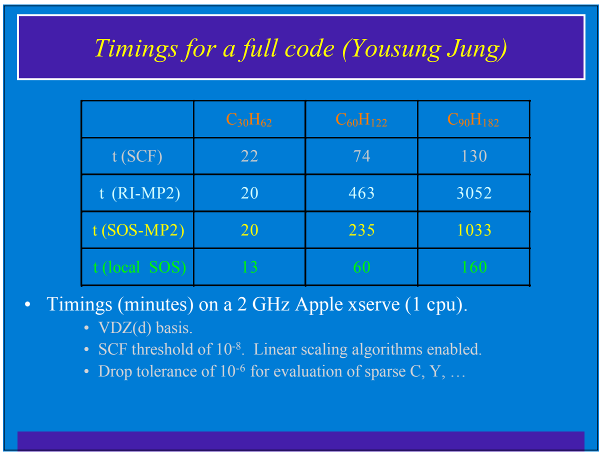


Exploiting sparsity in SOS-MP2 (Yousung Jung)

- Forming the Y matrix (at each quadrature point) is the bottleneck:

$$\bar{Y}_{KL} = \sum_{ia} \bar{C}_{ia}^{K} \bar{C}_{ia}^{L}$$

- Employ attenuated Coulomb metric (with ω=0.1) for sparse C.
- Apply sparsity to evaluate Y. Exact code: no local model.
- Also employ sparsity to perform transformations for C



Timings for a full code (Yousung Jung)

	$C_{30}H_{62}$	$C_{60}H_{122}$	$C_{90}H_{182}$
t (SCF)	22	74	130
t (RI-MP2)	20	463	3052
t (SOS-MP2)	20	235	1033
t (local SOS)	13	60	160

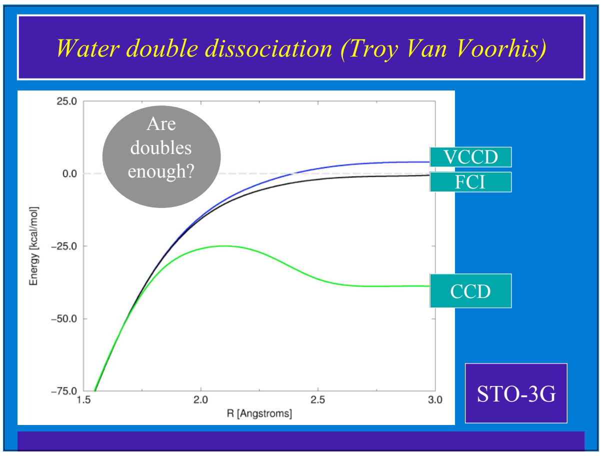
- Timings (minutes) on a 2 GHz Apple xserve (1 cpu).
  - VDZ(d) basis.
  - SCF threshold of 10^{-8}. Linear scaling algorithms enabled.
  - Drop tolerance of 10^{-6} for evaluation of sparse C, Y, …

Outline

1. Overview of standard wavefunction-based methods
2. Fast methods for dynamic correlations
3. **Fast methods for static correlations**
    - Lessons from variational coupled cluster calculations
    - Perfect and imperfect pairing
    - The world’s first indefinitely stable singlet diradical?
    - The phenalenyl dimer

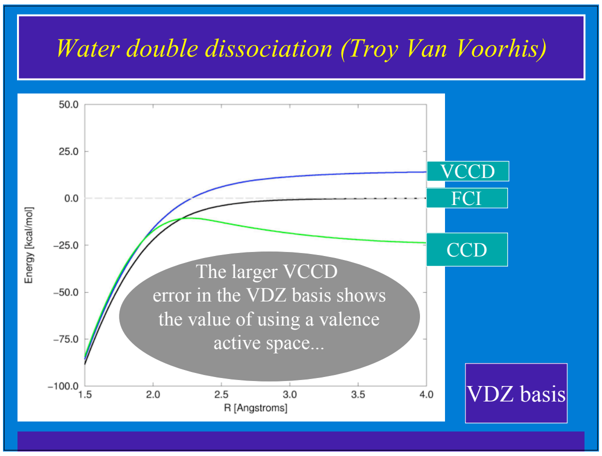
Variational coupled cluster doubles
Troy Van Voorhis

- Failures of restricted CCD and CCSD are well-known for bond-breaking problems.
    - Is the problem mainly neglect of higher excitations?
    - Is the problem nonvariational solution for the amplitudes
    - Or, perhaps more likely, are both these issues fatal?
- Performing variational coupled cluster doubles (VCCD) calculations will answer these questions.
    - VCCD energy is an expansion up to n-fold excitations.
    - Hence it is a restricted form of full CI (FCI) wavefunction.
    - Perform benchmark calculations using a special FCI code.



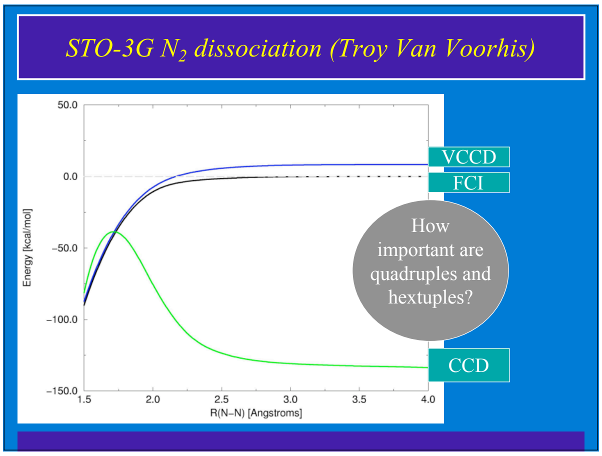
Water double dissociation (Troy Van Voorhis)

Are doubles enough?



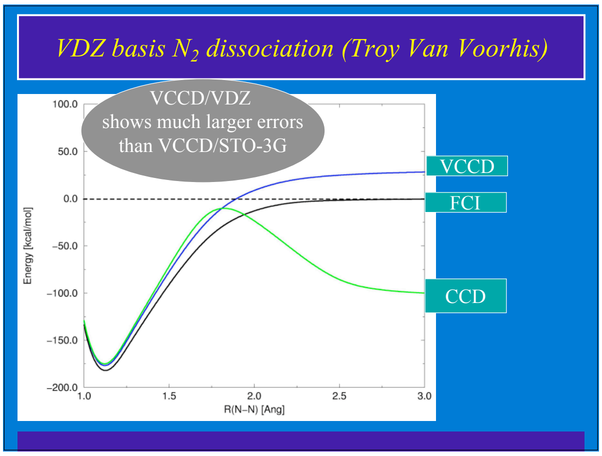
Water double dissociation (Troy Van Voorhis)

The larger VCCD error in the VDZ basis shows the value of using a valence active space...



STO-3G N_2 dissociation (Troy Van Voorhis)

How important are quadruples and hextuples?



VDZ basis N_2 dissociation (Troy Van Voorhis)

VCCD/VDZ shows much larger errors than VCCD/STO-3G

Main benchmark conclusions (Troy Van Voorhis)

(1) VCCD yields dramatically improved results relative to CCD for 4 and 6 electron bond-breaking problems.

- The main problem with restricted CCD, CCSD in bond-breaking is nonvariational failure.
- Searching for novel doubles-based coupled cluster methods for bond-breaking is potentially fruitful.

(2) VCCD performs noticeably better in the minimal basis than in the VDZ basis, relative to FCI.

- Traditional ideas about partitioning the correlation energy into two parts are going to be important.

Quadratic coupled cluster method
Troy Van Voorhis

- It is clearly desirable to improve CCD in a way which puts in more physics.
- Look for an intermediate step towards VCCD which does not greatly increase the computational cost.
- Previous efforts in this direction include:
  - extended coupled cluster (ECC) method of Arponen
  - UCC and XCC methods of Bartlett and co-workers
  - suggestions of Kutzelnigg

Quadratic coupled cluster energy functional
Troy Van Voorhis

- Usual coupled cluster energy can be written as a variational principle:

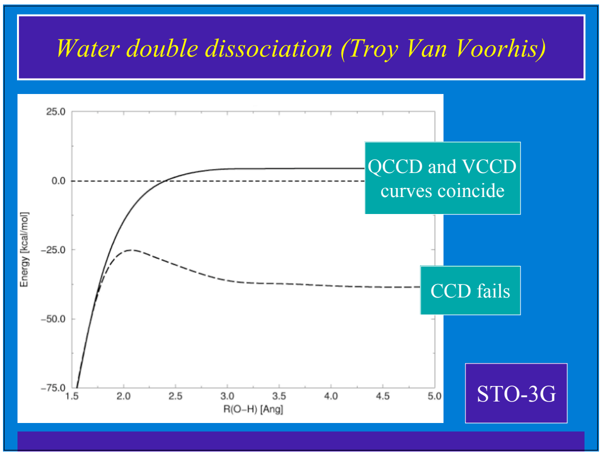
$$E_{CC} = \langle \Phi_0 | \left(1+\hat{\Lambda}\right)\hat{\bar{H}} | \Phi_0 \rangle$$

where we have defined: $\bar{H} = e^{-T} H e^{T} = \left(He^{T}\right)_c$

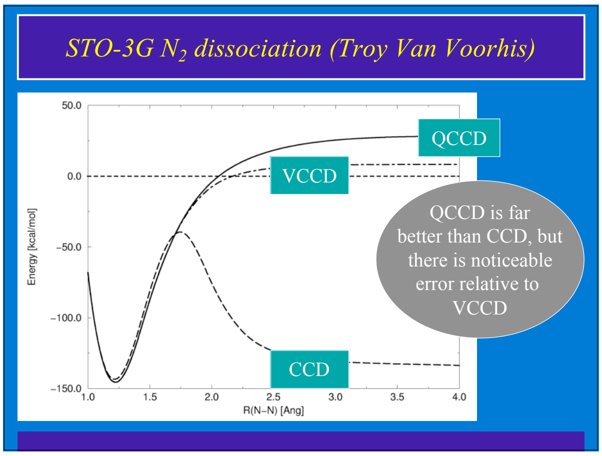
- We shall investigate a quadratic generalization:

$$E_{CC} = \langle \Phi_0 | \left(1+\hat{\Lambda}+\tfrac{1}{2}\hat{\Lambda}^2\right)\hat{\bar{H}} | \Phi_0 \rangle$$

which will be minimized with respect to T, Λ amplitudes



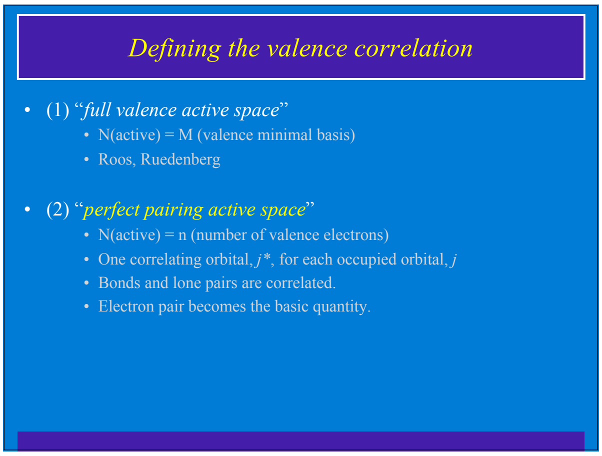
Water double dissociation (Troy Van Voorhis)



STO-3G N_2 dissociation (Troy Van Voorhis)

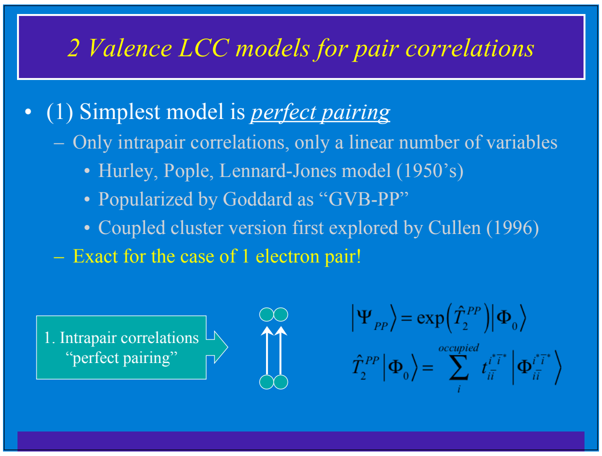
Valence space electron correlation

- Divide the correlation problem into two parts:
- "Low energy, long-wavelength" static correlations
  - Associated with near-degeneracies between orbitals (bond-breaking).
  - Important for qualitative description of molecular chemistry and potential surfaces
- "High energy, short wavelength" dynamic correlations:
  - Associated with atomic-like correlations
  - Dynamic correlation is important for quantitative prediction of reaction energies. Also dispersion forces.



Defining the valence correlation

- (1) "*full valence active space*"
  - N(active) = M (valence minimal basis)
  - Roos, Ruedenberg
- (2) "*perfect pairing active space*"
  - N(active) = n (number of valence electrons)
  - One correlating orbital, *j**, for each occupied orbital, *j*
  - Bonds and lone pairs are correlated.
  - Electron pair becomes the basic quantity.



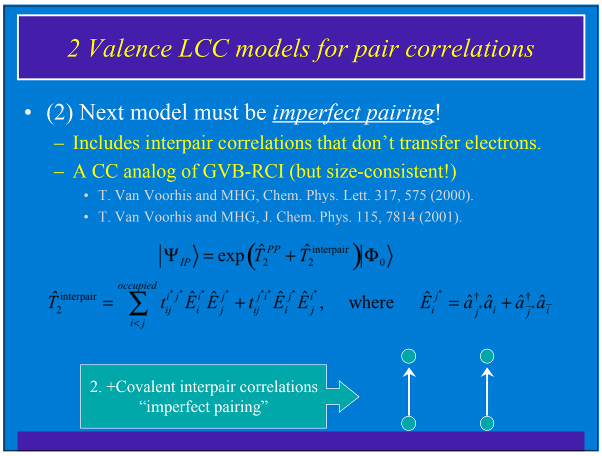
2 Valence LCC models for pair correlations

- (1) Simplest model is *perfect pairing*
  - Only intrapair correlations, only a linear number of variables
    - Hurley, Pople, Lennard-Jones model (1950's)
    - Popularized by Goddard as "GVB-PP"
    - Coupled cluster version first explored by Cullen (1996)
  - Exact for the case of 1 electron pair!

1. Intrapair correlations "perfect pairing"

$$\left|\Psi_{PP}\right\rangle = \exp\left(\hat{T}_2^{PP}\right)\left|\Phi_0\right\rangle$$

$$\hat{T}_2^{PP}\left|\Phi_0\right\rangle = \sum_{i}^{occupied} t_{i\bar{i}}^{i^*\bar{i}^*}\left|\Phi_{i\bar{i}}^{i^*\bar{i}^*}\right\rangle$$



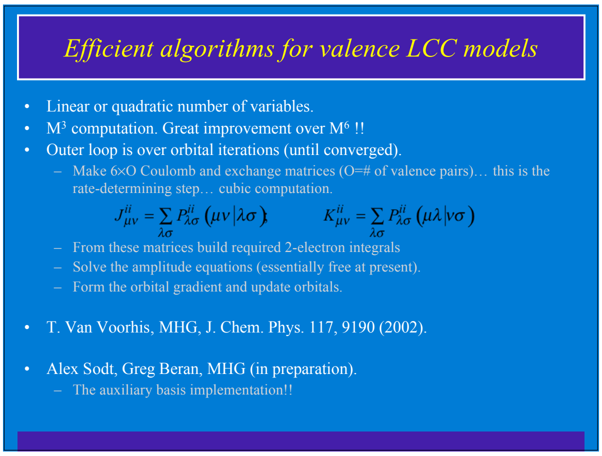
2 Valence LCC models for pair correlations

- (2) Next model must be *imperfect pairing*!
  - Includes interpair correlations that don't transfer electrons.
  - A CC analog of GVB-RCI (but size-consistent!)
    - T. Van Voorhis and MHG, Chem. Phys. Lett. 317, 575 (2000).
    - T. Van Voorhis and MHG, J. Chem. Phys. 115, 7814 (2001).

$$\left|\Psi_{IP}\right\rangle = \exp\left(\hat{T}_2^{PP} + \hat{T}_2^{\text{interpair}}\right)\left|\Phi_0\right\rangle$$

$$\hat{T}_2^{\text{interpair}} = \sum_{i<j}^{occupied} t_{ij}^{i^*j^*}\hat{E}_i^{i^*}\hat{E}_j^{j^*} + t_{ij}^{j^*i^*}\hat{E}_i^{j^*}\hat{E}_j^{i^*}, \quad \text{where} \quad \hat{E}_i^{j^*} = \hat{a}_{j^*}^{\dagger}\hat{a}_i + \hat{a}_{\bar{j}^*}^{\dagger}\hat{a}_{\bar{i}}$$

2. +Covalent interpair correlations "imperfect pairing"

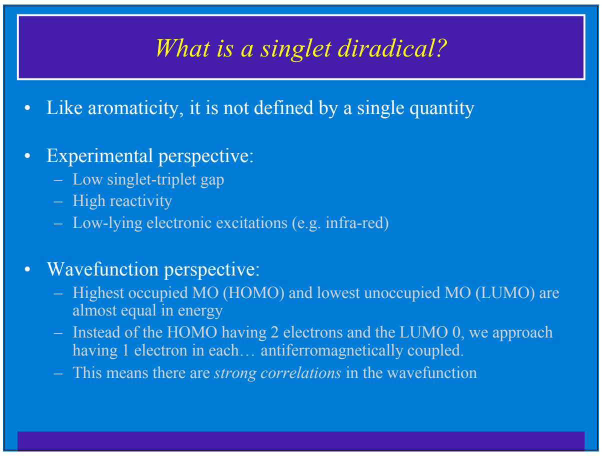


Efficient algorithms for valence LCC models

- Linear or quadratic number of variables.
- M^3 computation. Great improvement over M^6 !!
- Outer loop is over orbital iterations (until converged).
  - Make 6×O Coulomb and exchange matrices (O=# of valence pairs)… this is the rate-determining step… cubic computation.

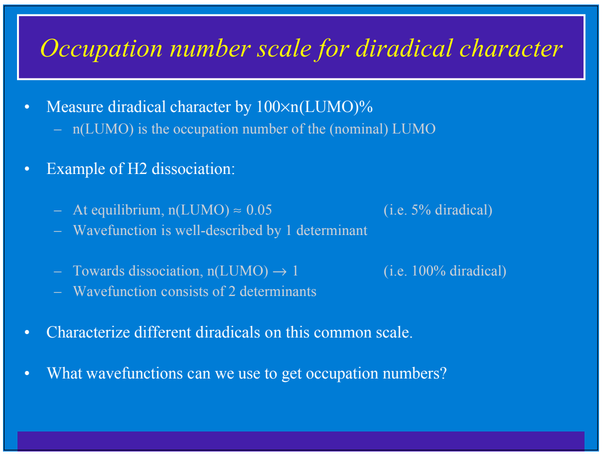
$$J_{\mu\nu}^{ii} = \sum_{\lambda\sigma} P_{\lambda\sigma}^{ii}\left(\mu\nu\middle|\lambda\sigma\right); \qquad K_{\mu\nu}^{ii} = \sum_{\lambda\sigma} P_{\lambda\sigma}^{ii}\left(\mu\lambda\middle|\nu\sigma\right)$$

  - From these matrices build required 2-electron integrals
  - Solve the amplitude equations (essentially free at present).
  - Form the orbital gradient and update orbitals.
- T. Van Voorhis, MHG, J. Chem. Phys. 117, 9190 (2002).
- Alex Sodt, Greg Beran, MHG (in preparation).
  - The auxiliary basis implementation!!



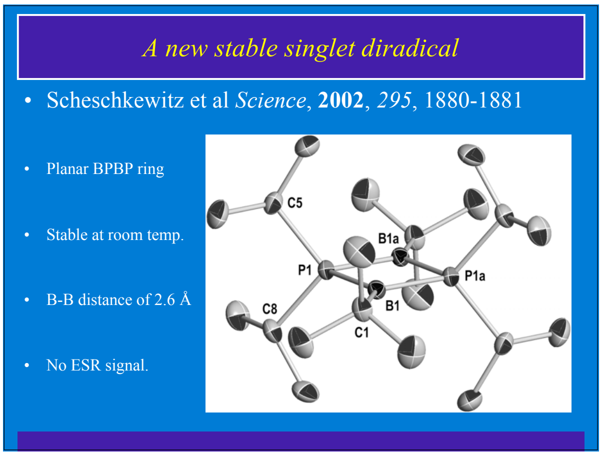
What is a singlet diradical?

- Like aromaticity, it is not defined by a single quantity
- Experimental perspective:
  - Low singlet-triplet gap
  - High reactivity
  - Low-lying electronic excitations (e.g. infra-red)
- Wavefunction perspective:
  - Highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) are almost equal in energy
  - Instead of the HOMO having 2 electrons and the LUMO 0, we approach having 1 electron in each… antiferromagnetically coupled.
  - This means there are *strong correlations* in the wavefunction



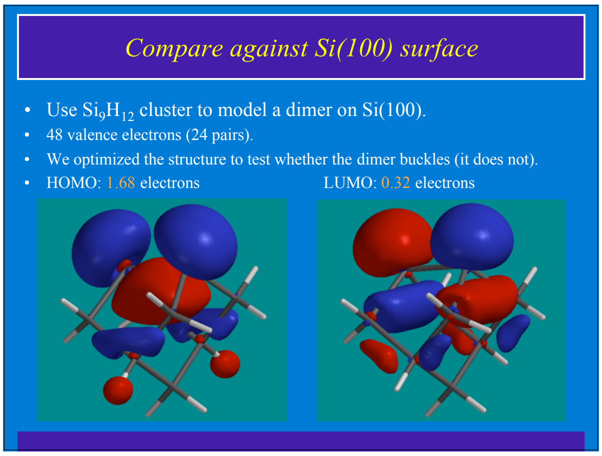
Occupation number scale for diradical character

- Measure diradical character by 100×n(LUMO)%
  - n(LUMO) is the occupation number of the (nominal) LUMO
- Example of H2 dissociation:
  - At equilibrium, n(LUMO) ≈ 0.05 (i.e. 5% diradical)
  - Wavefunction is well-described by 1 determinant
  - Towards dissociation, n(LUMO) → 1 (i.e. 100% diradical)
  - Wavefunction consists of 2 determinants
- Characterize different diradicals on this common scale.
- What wavefunctions can we use to get occupation numbers?



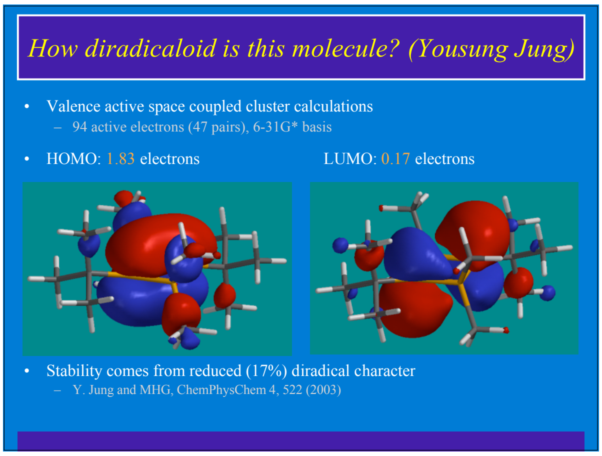
A new stable singlet diradical

- Scheschkewitz et al *Science*, **2002**, *295*, 1880-1881
- Planar BPBP ring
- Stable at room temp.
- B-B distance of 2.6 Å
- No ESR signal.



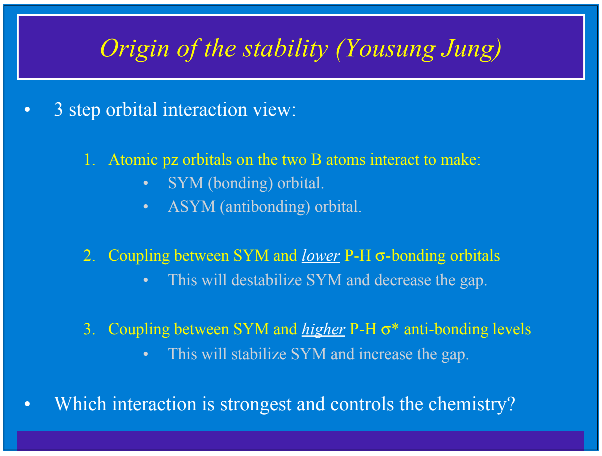
Compare against Si(100) surface

- Use Si_9H_{12} cluster to model a dimer on Si(100).
- 48 valence electrons (24 pairs).
- We optimized the structure to test whether the dimer buckles (it does not).
- HOMO: 1.68 electrons LUMO: 0.32 electrons



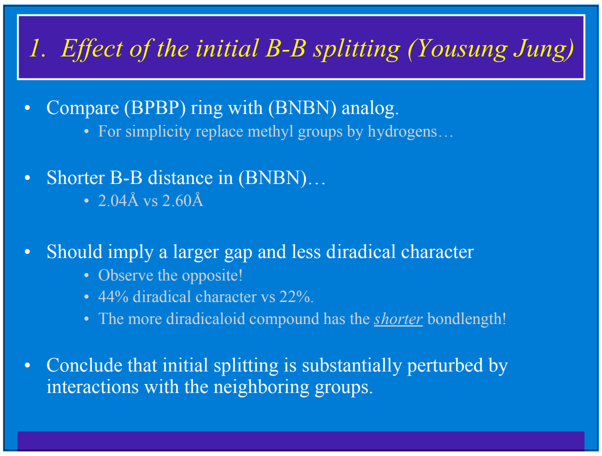
How diradicaloid is this molecule? (Yousung Jung)

- Valence active space coupled cluster calculations
  - 94 active electrons (47 pairs), 6-31G* basis
- HOMO: 1.83 electrons LUMO: 0.17 electrons
- Stability comes from reduced (17%) diradical character
  - Y. Jung and MHG, ChemPhysChem 4, 522 (2003)



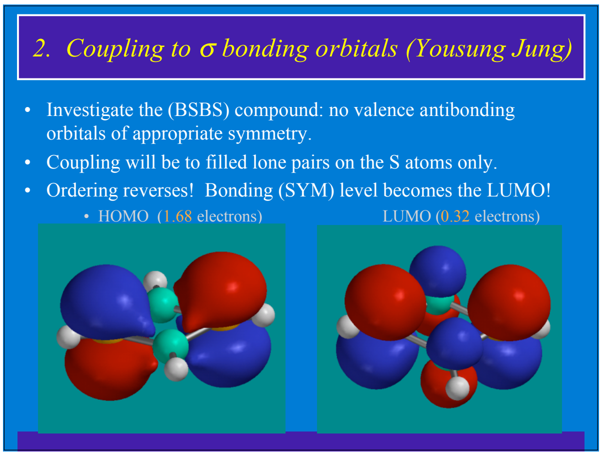
Origin of the stability (Yousung Jung)

- 3 step orbital interaction view:
  1. Atomic pz orbitals on the two B atoms interact to make:
     - SYM (bonding) orbital.
     - ASYM (antibonding) orbital.
  2. Coupling between SYM and *lower* P-H σ-bonding orbitals
     - This will destabilize SYM and decrease the gap.
  3. Coupling between SYM and *higher* P-H σ* anti-bonding levels
     - This will stabilize SYM and increase the gap.
- Which interaction is strongest and controls the chemistry?



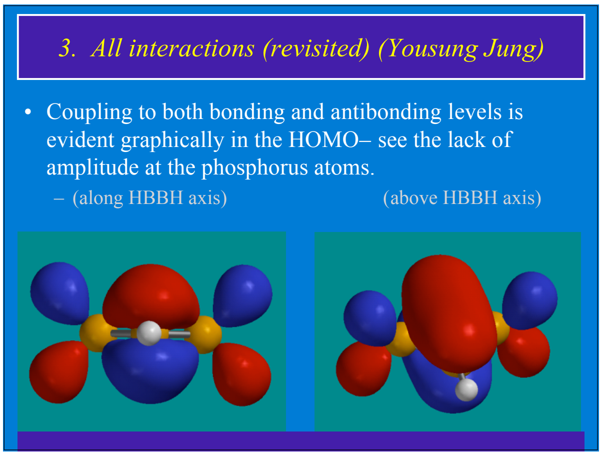
1. Effect of the initial B-B splitting (Yousung Jung)

- Compare (BPBP) ring with (BNBN) analog.
  - For simplicity replace methyl groups by hydrogens…
- Shorter B-B distance in (BNBN)…
  - 2.04Å vs 2.60Å
- Should imply a larger gap and less diradical character
  - Observe the opposite!
  - 44% diradical character vs 22%.
  - The more diradicaloid compound has the *shorter* bondlength!
- Conclude that initial splitting is substantially perturbed by interactions with the neighboring groups.



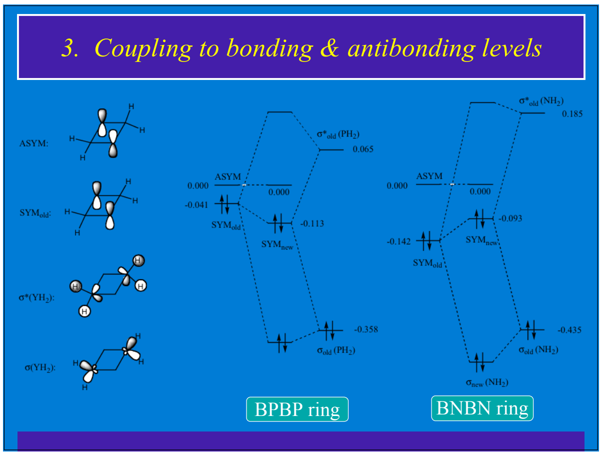
2. Coupling to σ bonding orbitals (Yousung Jung)

- Investigate the (BSBS) compound: no valence antibonding orbitals of appropriate symmetry.
- Coupling will be to filled lone pairs on the S atoms only.
- Ordering reverses! Bonding (SYM) level becomes the LUMO!
  - HOMO (1.68 electrons) LUMO (0.32 electrons)

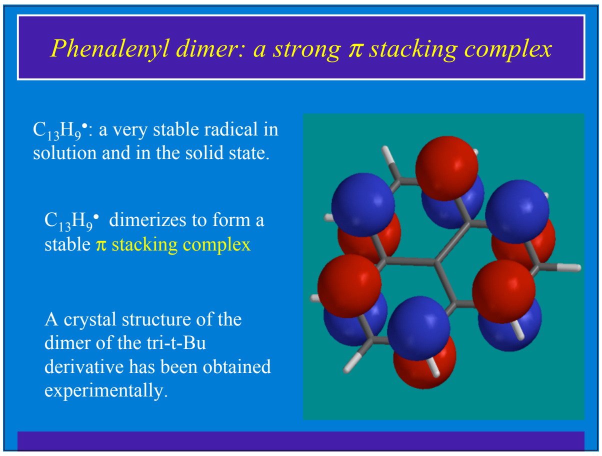


3. All interactions (revisited) (Yousung Jung)

- Coupling to both bonding and antibonding levels is evident graphically in the HOMO– see the lack of amplitude at the phosphorus atoms.
  - (along HBBH axis) (above HBBH axis)



3. Coupling to bonding & antibonding levels

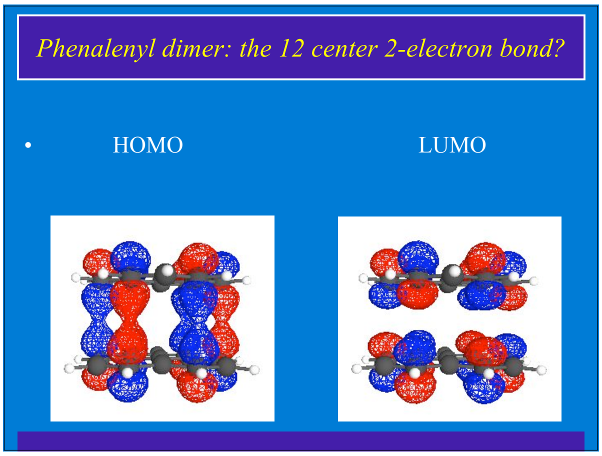


Phenalenyl dimer: a strong π stacking complex

$C_{13}H_9^\bullet$: a very stable radical in solution and in the solid state.

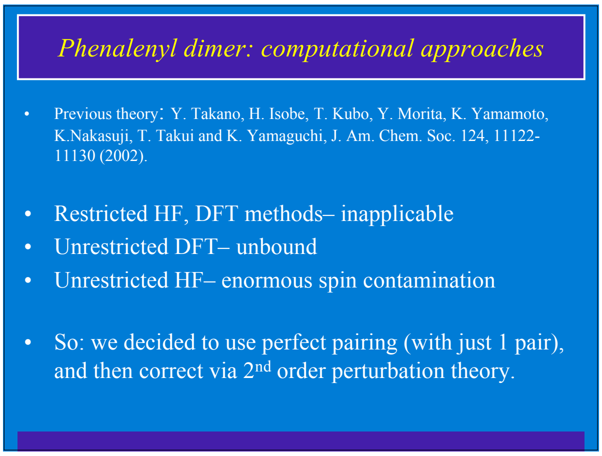
$C_{13}H_9^\bullet$ dimerizes to form a stable π stacking complex

A crystal structure of the dimer of the tri-t-Bu derivative has been obtained experimentally.



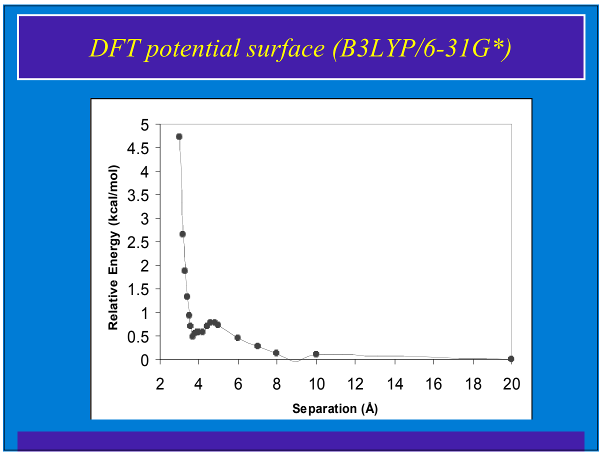
Phenalenyl dimer: the 12 center 2-electron bond?

- HOMO LUMO



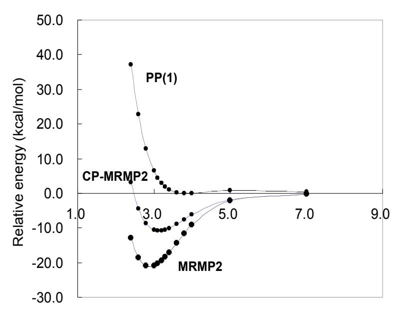
Phenalenyl dimer: computational approaches

- Previous theory: Y. Takano, H. Isobe, T. Kubo, Y. Morita, K. Yamamoto, K.Nakasuji, T. Takui and K. Yamaguchi, J. Am. Chem. Soc. 124, 11122-11130 (2002).
- Restricted HF, DFT methods– inapplicable
- Unrestricted DFT– unbound
- Unrestricted HF– enormous spin contamination
- So: we decided to use perfect pairing (with just 1 pair), and then correct via 2nd order perturbation theory.



DFT potential surface (B3LYP/6-31G*)

Phenalenyl dimer potential surface (Yousung Jung)



MRMP2 results (Yousung Jung)

- PP(1) calculations show no minimum
  - Covalency by itself is not responsible for net binding
- PP(1) + 2nd order perturbation theory– finally, a bond!!
  - Equilibrium distance (calc) 3.1 Angstroms
    (expt) 3.1 Angstroms
  - Binding energy (theory using counterpoise correction)
    (calc) -10.8 kcal/mol
    (expt) -8.8 kcal/mol
    -9.5 kcal/mol

Character of the chemical bond (Yousung Jung)

- Diradicaloid character:
  - LUMO occupation number (ON) at R=3.1A: 0.25 electrons
  - i.e. 25% diradicaloid character.

R (Å)	2.6	3.1	3.3	5.0
ON(LUMO)	0.15	0.25	0.32	0.95

- Dispersion-assisted 12-center 2-electron bond:
  - Covalency alone cannot overcome repulsions to give net binding.
  - This weak and diradicaloid chemical bond is assisted by dispersion
  - This interplay between weak covalency and dispersion makes the bond in the phenalenyl dimer distinctive relative to weaker π complexes

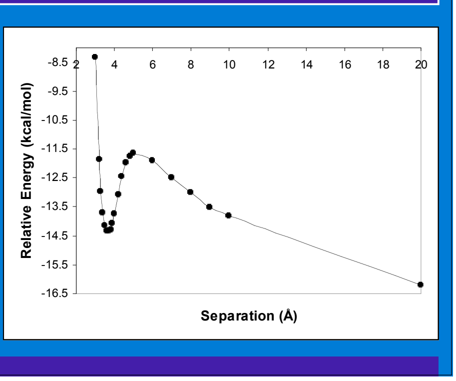
Phenalenyl dimer cation

- Compare the 12-center 2-electron bond (neutral) against the 12-center 1-electron bond (cation)
- Experimental dimer binding energies:
  - J. Kochi, unpublished (private communication).
  - Neutral: -8.8 kcal/mol (ES) –9.5 kcal/mol (ESR)
  - Cation: -5.3 kcal/mol (ES) -4.1 kcal/mol (ESR)
  - 2-electron bond roughly twice as strong as the 1-electron bond
- Theoretical methods:
  - Use ROHF based MP2 (RMP2) with counterpoise, for cation.
  - This is approximately comparable to PP(1) + MP2 for neutral.

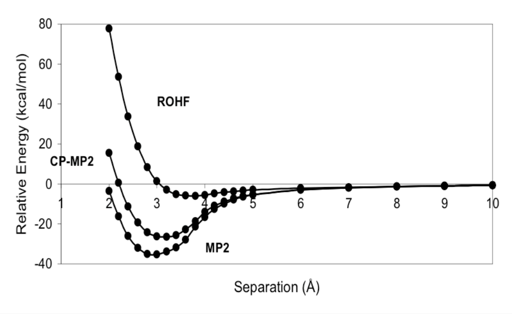
DFT surface for cation (B3LYP/6-31G)*

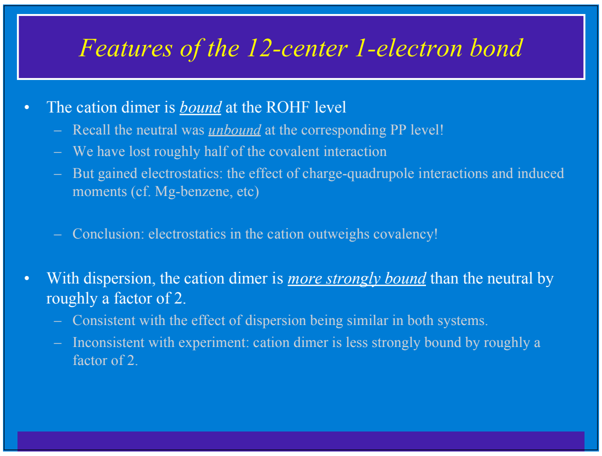
Similar to H_2^+

Self-interaction problem



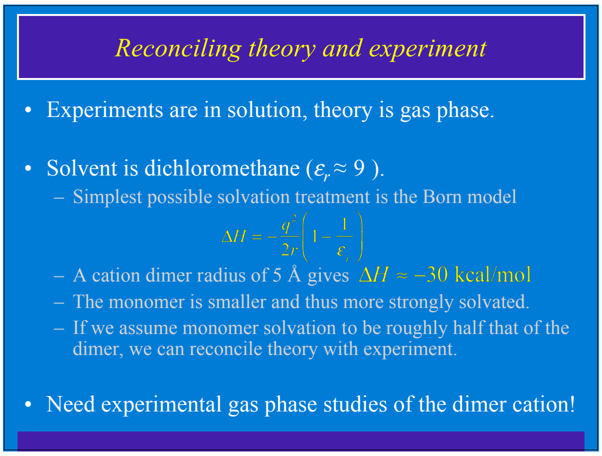
Phenalenyl dimer potential surface (David Small)





Features of the 12-center 1-electron bond

- The cation dimer is <u>*bound*</u> at the ROHF level
  - Recall the neutral was <u>*unbound*</u> at the corresponding PP level!
  - We have lost roughly half of the covalent interaction
  - But gained electrostatics: the effect of charge-quadrupole interactions and induced moments (cf. Mg-benzene, etc)
  - Conclusion: electrostatics in the cation outweighs covalency!
- With dispersion, the cation dimer is <u>*more strongly bound*</u> than the neutral by roughly a factor of 2.
  - Consistent with the effect of dispersion being similar in both systems.
  - Inconsistent with experiment: cation dimer is less strongly bound by roughly a factor of 2.

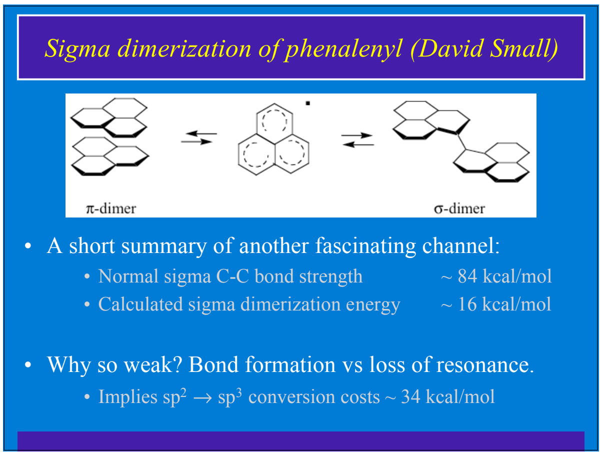


Reconciling theory and experiment

- Experiments are in solution, theory is gas phase.
- Solvent is dichloromethane ($\varepsilon_r \approx 9$).
  - Simplest possible solvation treatment is the Born model

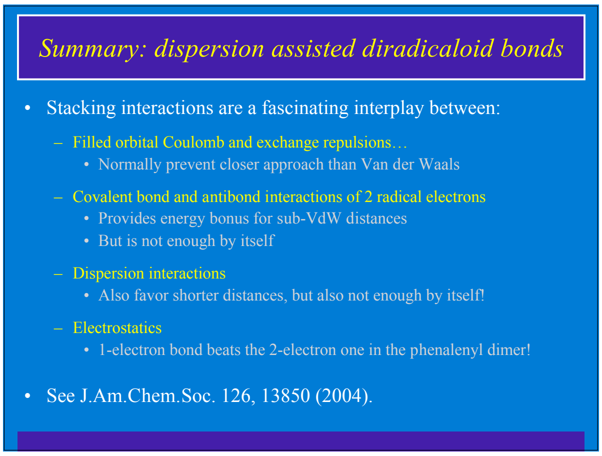
$$\Delta H = -\frac{q^2}{2r}\left(1 - \frac{1}{\varepsilon_r}\right)$$

  - A cation dimer radius of 5 Å gives $\Delta H \approx -30$ kcal/mol
  - The monomer is smaller and thus more strongly solvated.
  - If we assume monomer solvation to be roughly half that of the dimer, we can reconcile theory with experiment.
- Need experimental gas phase studies of the dimer cation!



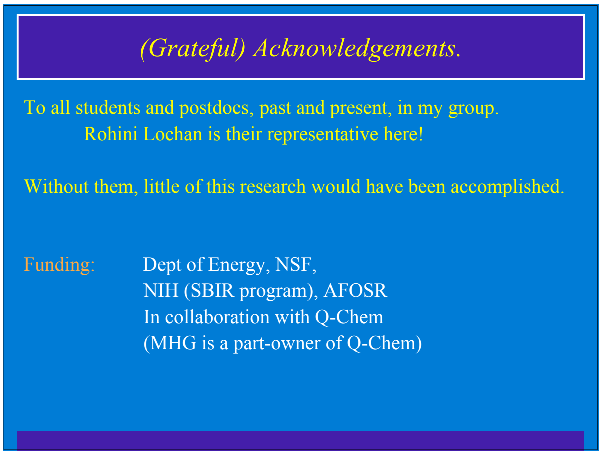
Sigma dimerization of phenalenyl (David Small)

- A short summary of another fascinating channel:
  - Normal sigma C-C bond strength ~ 84 kcal/mol
  - Calculated sigma dimerization energy ~ 16 kcal/mol
- Why so weak? Bond formation vs loss of resonance.
  - Implies $sp^2 \rightarrow sp^3$ conversion costs ~ 34 kcal/mol



Summary: dispersion assisted diradicaloid bonds

- Stacking interactions are a fascinating interplay between:
  - Filled orbital Coulomb and exchange repulsions…
    - Normally prevent closer approach than Van der Waals
  - Covalent bond and antibond interactions of 2 radical electrons
    - Provides energy bonus for sub-VdW distances
    - But is not enough by itself
  - Dispersion interactions
    - Also favor shorter distances, but also not enough by itself!
  - Electrostatics
    - 1-electron bond beats the 2-electron one in the phenalenyl dimer!
- See J.Am.Chem.Soc. 126, 13850 (2004).



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