

Geminals as wavefunction building blocks: new level of model chemistries

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Guiding principles

1. All known size consistent model chemistries are based on single determinant wavefunction
 - Size-consistent: Energy is a rigorously extensive property
 - Model chemistry: Widely applicable theoretical model free from specific adjustable parameters
2. Problems:
 - Non-dynamic correlation: Single determinant is sometimes qualitatively deficient
 - Dynamic correlation: Slow convergence of correlation expansion
 - “Deadwood” configurations of FCI
 - Search for optimal single determinant (i.e. Brueckner orbitals)
3. Electron pair (or “geminal”) is a natural building block in chemistry
 - Physically better reference wavefunction
 - Better analysis of perturbative corrections

Brief (and biased!) summary of dynamic correlation

We have applied spin-restricted (RSSG) and spin-unrestricted (USSG) geminals to the whole bunch of molecules. Then we used Epstein-Nesbet perturbation theory to improve the wavefunction. We check which type of excitations is more important by monitoring perturbative amplitudes. Next slide shows data for TM hydrides, but the conclusions, AFAWK, are universal.

- Spin treatment is important
- **All** non-dynamic correlation is described by strongly orthogonal geminals
- Strong orthogonality is not a severe approximation

Overall conclusion: geminals are useful in breaking down a (exponentially scaling) dynamic correlation problem into smaller components.

Magnitudes of leading perturbative corrections and their types for geminal and coupled cluster wavefunctions. The leading CC perturbative corrections are **green** for single, or **red** double excitations. The geminal corrections are **green** for two intra-geminal excitations, or dispersion interactions, and **red** for one inter- and one intra-geminal excitation, or mixed. Pure charge transfer excitations have smaller amplitudes than either dispersion or mixed types for all wavefunctions in the Table. All calculations are done with 6-31G* basis set at experimental equilibrium geometries.

molecule	USSG(EN2)	RUSSG(EN2)	RSSG(EN2)	UCCSD	RCCSD
TiH($^4\Phi$)	.041	.036	.040	.090	.074
CrH($^6\Sigma^+$)	.022	.032	.032	.266	.242
MnH($^7\Sigma^+$)	.018	.042	.042	.065	.076
FeH($^4\Delta$)	.028	.042	.297	.642	.792
CoH($^3\Phi$)	.050	.051	.369	.830	.494
NiH($^2\Delta$)	.051	.052	.669	.533	.419
ZnH($^2\Sigma^+$)	.049	.064	.066	.079	.117

Today: Spin treatment of reference functions

A conjecture: most important MR effects are due to spins

A statement: Currently there is no practical model (i.e. polynomial scaling) that treats electron spins **even qualitatively** correct

A classic example 1: H₂ molecule

Minimal basis set, χ_1 and χ_2

In delocalized representation $\phi_g = \chi_1 + \chi_2$

In localized representation

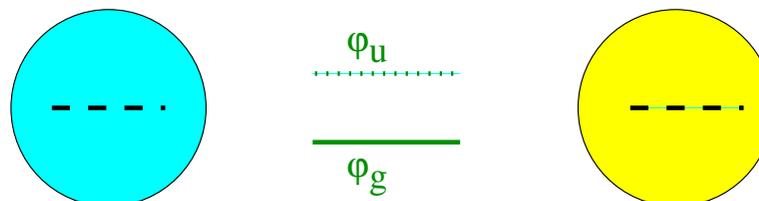
$\phi_1 = \text{lots of } \chi_1 + \text{a little } \chi_2$,

$\phi_2 = \text{a little } \chi_1 + \text{lots of } \chi_2$

$$\Psi = D_g |\phi_g \bar{\phi}_g| + D_u |\phi_u \bar{\phi}_u| = |\phi_1 \bar{\phi}_2| + |\phi_2 \bar{\phi}_1|$$

For fully dissociated H₂ this wavefunction is an overall singlet, and a doublet in the subspace of each atom.

SCF models keeps only one configuration. RHF chooses $|\phi_g \bar{\phi}_g|$, UHF keeps $|\phi_1 \bar{\phi}_2|$.



Both UHF and RHF give describe spins incorrectly: for fully dissociated H₂ UHF gives the overall wavefunction as a mixture of singlet and a triplet, while RHF gives a singlet in the half space.

Energetically, UHF is much better. For complete basis set it is lower than RHF by **179 kcal/mol** ($E(\text{H}^-)$ vs. $E(\text{H})$). However, it is very hard to correct it perturbatively.

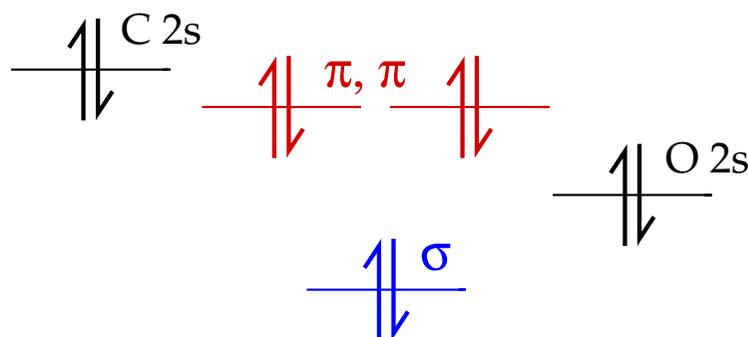
GVB, or geminals, help, but do not solve a problem.

An example 2: CO molecule

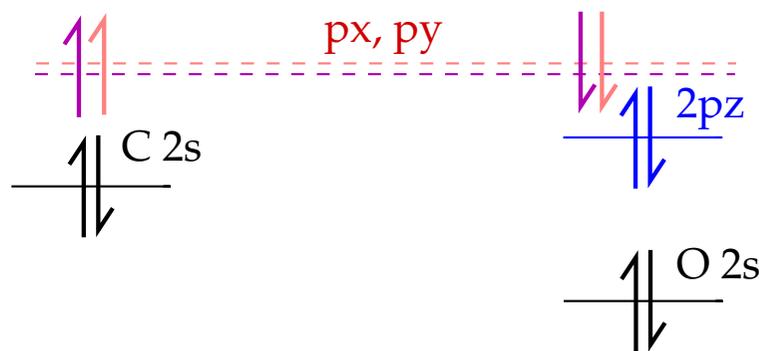
The overall wavefunction is a singlet. For fully dissociated molecule it is a triplet in the subspace of each atom.

Spin restricted geminals force singlet coupling of unpaired electrons: error of approx. **75 kcal/mol**. We use spin-unrestricted geminals, but observe slow perturbative convergence in model systems

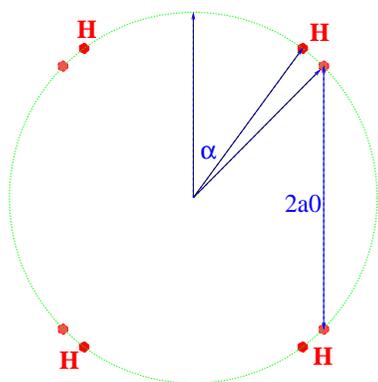
CO molecule



C, O atoms

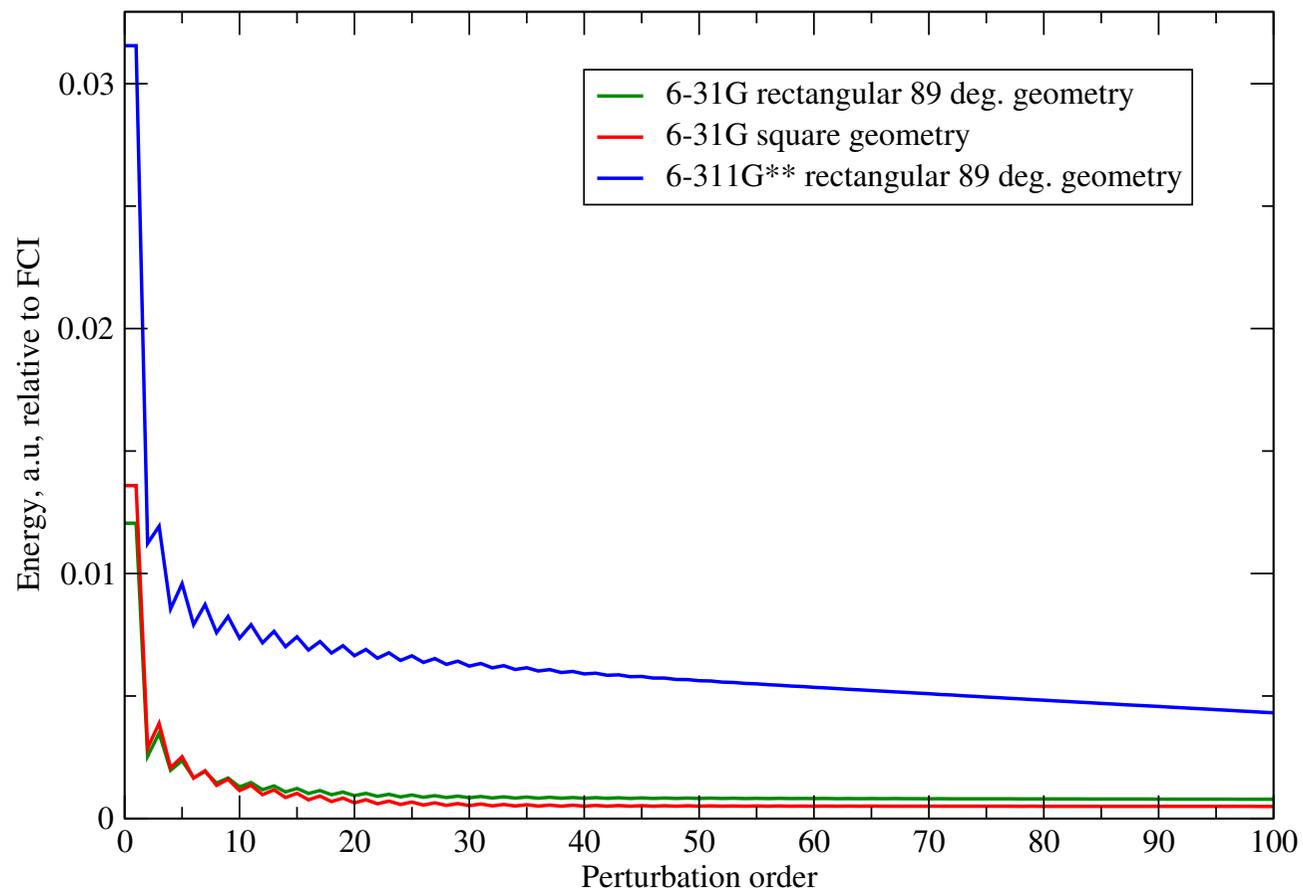


Energy cusp in H_4 system

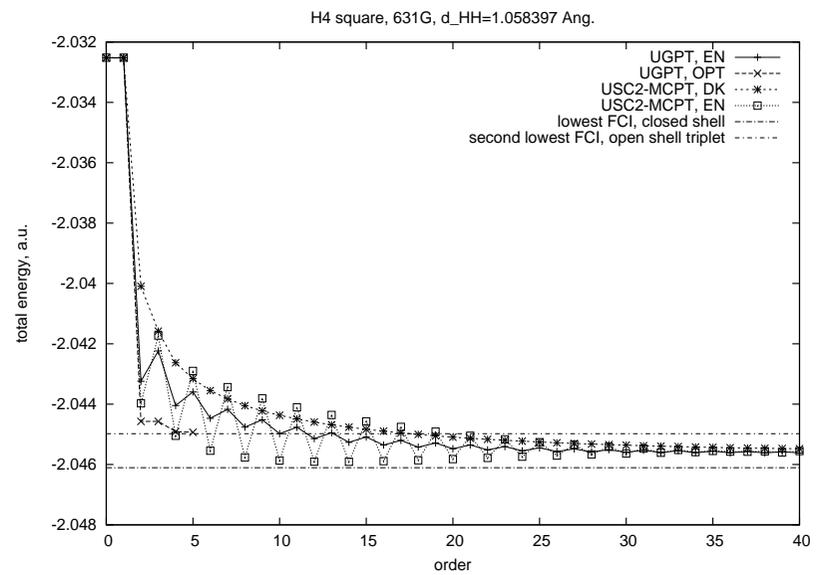
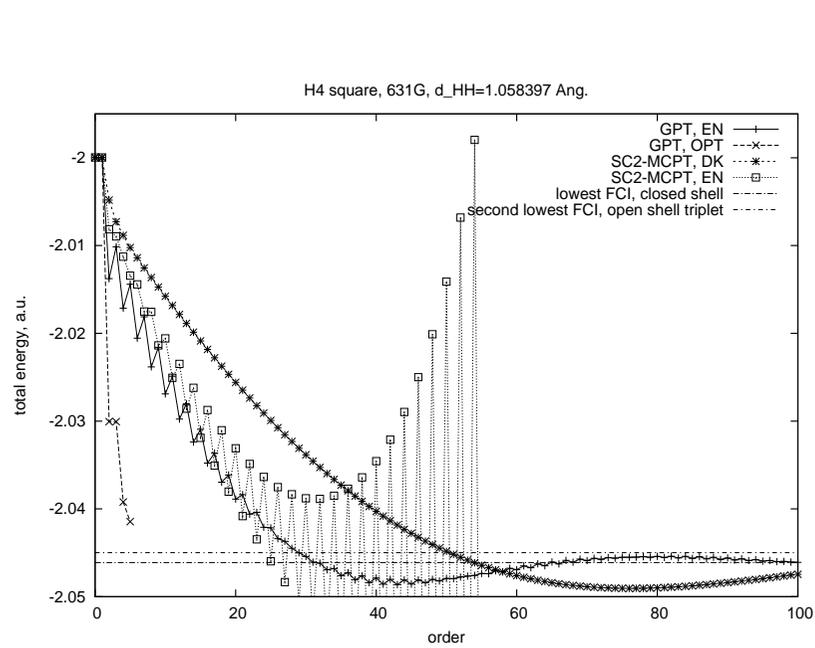


H_4 , $2a_0$ rectangle

USSG reference, Epstein-Nesbet PT



Other forms of PT are as bad



- Problem again: Model that describes $\langle S^2 \rangle$ qualitatively correct (i.e. both for the overall wavefunction and for its parts).
- Formal solution: Full CI in the spin space (so-called spin coupled theories, particularly for SCF reference)
- Challenge: exponential scaling

Can (strongly orthogonal) geminals reduce scaling from exponential to polynomial?

The answer is **yes**, but it requires two steps.

1. Partial spin restriction
2. Variational minimization in the minimal spin space

Partial spin restriction

The logic:

- spin contaminated wavefunctions are difficult to improve perturbatively
- Geminal framework treats intra- and inter- geminal perturbation differently
- Couldn't spin contamination be different for intra- and inter- geminal interactions?

End result:

- Force Arai subspaces of each geminal to be orthogonal (i.e. all α orbitals of geminal A orthogonal to all β orbitals of geminal B)
- α and β orbitals of the same geminal may be non-orthogonal

Mathematical formalism is elegant

- In fully spin restricted formulation this means that geminal expansions are no longer diagonal

$$\psi_A(\mathbf{r}_1, \mathbf{r}_2) = \sum_{j,k \in A} D_{j,k}^A |\phi_j(\mathbf{r}_1)\bar{\phi}_k(\mathbf{r}_2)|$$

- Wavefunction optimization is done in atomic orbital (AO) basis, and the procedure doesn't care if molecular orbital (MO) representation is diagonal or not
- For perturbative corrections, one can switch back to diagonal, but spin-unrestricted, MO representation

Application of RUSSG

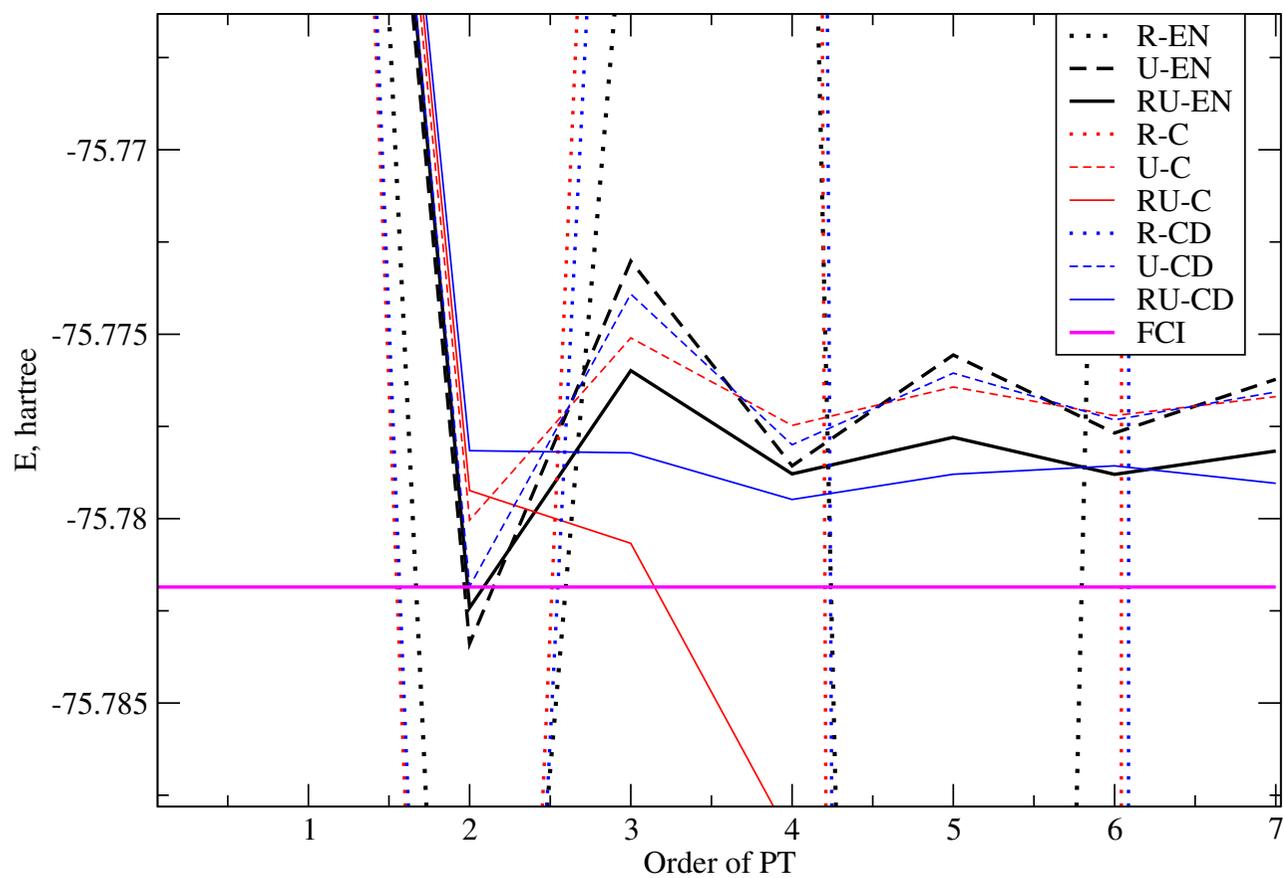
Comparison of bond lengths of non-singlet first transition row hydrides using G3MP2Large basis. All geminal calculations are performed on the second-order Epstein-Nesbet Perturbation Theory SSG(EN2) level. The second column gives experimental equilibrium bond distances. All subsequent columns show optimized bond lengths with two types of spin coupling (**U** for fully spin unrestricted, and **RU** for partial spin restriction). The comparison is made with spin-unrestricted B3LYP, MP2, and CCSD(T) models, with all electrons correlated. The bottom line gives root-mean-square deviations from experiment. All values are in angstroms.

molecule	$R_e(\text{exp})$	USSG(EN2)	RUSSG(EN2)	UB3LYP	UMP2	UCCSD(T)
TiH($^4\Phi$)	1.761	1.809	1.802	1.768	1.778	1.784
VH($^5\Delta$)		1.727	1.721	1.721	1.725	1.719
CrH($^6\Sigma^+$)	1.6554	1.623	1.617	1.667	1.506	1.645
MnH($^7\Sigma^+$)	1.731	1.746	1.763	1.739	1.722	1.738
FeH($^4\Delta$)	1.610	1.659	1.590	1.576	1.626	1.585
CoH($^3\Phi$)	1.532	1.642	1.532	1.529	1.559	1.512
NiH($^2\Delta$)	1.475	1.555	1.468	1.479	1.486	1.422
ZnH($^2\Sigma^+$)	1.595	1.625	1.619	1.614	1.570	1.603
RMS		.060	.027	.016	.059	0.026

Convergence of perturbative expansion is slightly improved

Symmtric stretch of H2O

R=2.5Re, mixed basis



Conclusion on partial spin restriction: It is the proper way to do formulate strongly orthogonal geminals (GVB included)

How can we fix remaining spin contamination?

Variational minimization in the minimal spin space

Let us use oxygen atom wavefunction as an example. Its RUSG geminal wavefunction consists of antisymmetrized product of three geminals and two open shell orbitals.

We graphically represent each spin contaminated geminal as a mixture of singlet and triplet $S_z = 0$ components



What does the S^2 operator do to a RUSG wavefunction?

$$\begin{aligned}
S^2[\uparrow\uparrow\uparrow\uparrow] = & 2[\uparrow\uparrow\uparrow\uparrow] + 2[\uparrow\uparrow\uparrow\uparrow] + 2[\uparrow\uparrow\uparrow\uparrow] + \\
& 4[\uparrow\uparrow\uparrow\uparrow] + 4[\uparrow\uparrow\uparrow\uparrow] + 4[\uparrow\uparrow\uparrow\uparrow] + \\
& 4[\uparrow\uparrow\uparrow\uparrow] + 4[\uparrow\uparrow\uparrow\uparrow] + 4[\uparrow\uparrow\uparrow\uparrow] + \\
& 2[\uparrow\uparrow\uparrow\uparrow] + 2[\uparrow\uparrow\uparrow\uparrow] + 2[\uparrow\uparrow\uparrow\uparrow] + \\
& 2[\uparrow\uparrow\uparrow\uparrow] + 2[\uparrow\uparrow\uparrow\uparrow] + 2[\uparrow\uparrow\uparrow\uparrow]
\end{aligned}$$

: Unrestricted Geminal (g_i)
: Triplet Geminal (t_i^0), $s_z=0$
: Triplet Geminal (t_i^+), $s_z=+1$
: Triplet Geminal (t_i^-), $s_z=-1$
: Alpha electron : Beta electron

The exponentially large space of all possible spin flips can be reduced to much smaller space of multireference wavefunctions

$$B(1,0,0) = \text{[orbital diagram 1]} + \text{[orbital diagram 2]} + \text{[orbital diagram 3]}$$

We define $B(i, j, k)$ as sum of all possible geminal functions, each with precisely i triplet $S_z = 0$ geminals, j triplet $S_z = 1$ geminals, and k open shell β orbitals. Note that reference wavefunction is $B(0, 0, 0)$. We have

$$\hat{S}^2 B(0, 0, 0) = 2B(1, 0, 0) + 4B(0, 1, 0) + 2B(0, 1, 1)$$

Properties of the $\{B\}$ set

- There is only roughly $O(n_\beta^2 n_{os})$ of B functions
- They define an invariant subspace of S^2
- The functions are neither normalized nor orthogonal, but in general are linearly independent
- Each B function contain exponential number of terms

but

- there are simple equations for the matrix elements in $\{B\}$

To illustrate the last item, let's consider the overlap integral

$$S(k) \equiv \langle B(0, 0, 0) | B(k, 0, 0) \rangle$$

All other required matrix elements can be reduced to it.

Because partial spin restriction forces all α orbitals of any geminal to orthogonal to all (α and β) orbitals of other geminals, the orthogonality between geminals is preserved even when spins are flipped.

That means that each $S_z = 1$ geminal in $\langle \Psi |$ must match with $S_z = 1$ geminal in $|\Psi\rangle$, and triplet $S_z = 0$ geminal may match with either triplet $S_z = 0$ or a mixed geminal. Therefore, the following is true

$$S(k) = \sum_{i=0}^k \langle B(0, 0, 0) | B(i, 0, 0) \rangle_A \langle B(0, 0, 0) | B(k - i, 0, 0) \rangle_{1-A}$$

where $\langle | \rangle_A$ notation means overlap on the subspace A , for **arbitrary** division of geminal product into A and $1 - A$ subspaces.

- All $S(k)$ are computed recursively **very quickly** ($O(n_\beta^2)$ flops)
- Matrix elements over all B functions are expressible through $S(k)$ as

$$\langle B(n_1, k_1, m_1) | B(n_2, k_2, m_2) \rangle = \delta_{k_1, k_2} \delta_{m_1, m_2} \times \sum_{i=\max(n_1, n_2)}^{n_1+n_2} [S(i + k_1 + km) \frac{(i + k_1 + km)!}{(i - n_1)!(i - n_2)!(n_1 + n_2 - i)!} \frac{(m_\alpha + m_\beta)!}{m_\alpha!m_\beta!}],$$

where δ is a Kronecker delta function, km is a number of $S_z = -1$ geminals, $km = k_1 + m_1$, $m_\alpha = m_1$, $m_\beta = n_{os} - m_1$.

- Hamiltonian matrix elements also need $S^A(k)$, which is just like $S(k)$ except geminal A is removed from the system; and $S^{A,B}(k)$

The $\{B\}$ set is great (small enough and easy to work with), but it does not treat geminal and open shell electrons with equal flexibility. Therefore, it is reduced to a new set $\{\tilde{B}\}$ by repeated action of \hat{S}^2 . The set $\{\tilde{B}\}$ defines a **minimal invariant subspace of \hat{S}^2 that contain a reference function $\Psi_{RUSSG} \equiv B(0, 0, 0)$.**

Variational minimization of energy in $\{\tilde{B}\}$ yields pure spin functions.

We have also proven that the procedure is rigorously size consistent, but I'll not bore you with a proof.

Ta-ta!

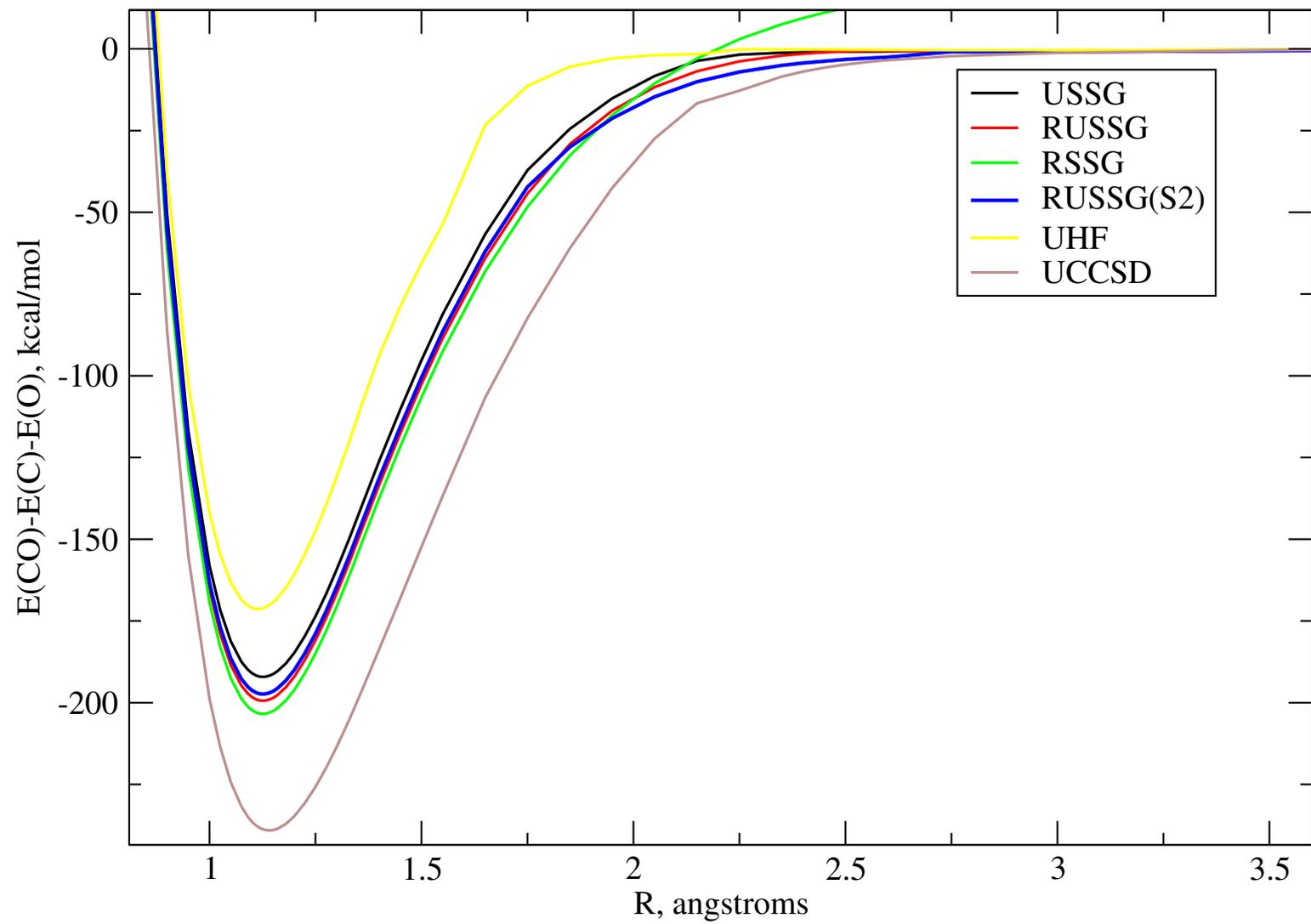
Some results: broken bond

Energies (in hartrees) and expectation values of \hat{S}^2 of the dissociated CO molecule, and of individual atoms, all with 6-31G* basis. The last column shows the difference between the molecular and the atomic energies.

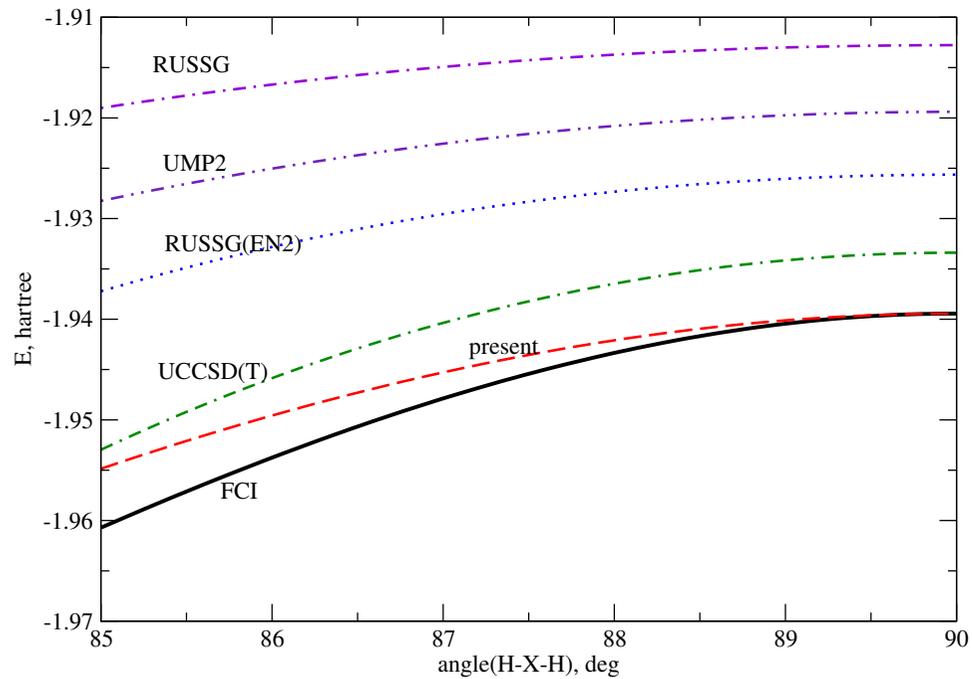
method	E(C)	$S^2(C)$	E(O)	$S^2(O)$	E(CO)	$S^2(CO)$	Δ (E)
RSSG	-37.7027765	2.0000	-74.8034603	2.0000	-112.4706374	0.0000	3.56e-2
USSG	-37.7083079	2.0038	-74.8159651	2.0060	-112.5242732	2.0098	2.03e-7
RUSSG	-37.7062691	2.0041	-74.8064817	2.0046	-112.5127512	2.0087	1.59e-7
present	-37.7078714	2.0000	-74.8081185	2.0000	-112.5159880	0.0000	1.82e-6

CO PES

6-31G* basis



Some results: H₄ revisited



Astonishingly (at least for me), the new spin purification method can describe H₄ in square configuration exactly! It does require a re-optimization of geminals, though.

Outstanding issues

- The spin purification procedure needs to be combined with geminal re-optimization
- Perturbative corrections are needed
- Extend to Hartree-Fock? *it's doable, just cumbersome. Can one make it simple?*

Conclusions

- Geminals offer a **very** promising way to take electronic structure models to a new level
 - They can offer nearly the quality of spin-coupled or CASSCF wavefunctions at polynomial scaling
 - They may speed up perturbative convergence
- We still don't know what effects/systems can be described by geminals
 - *Geminals can't describe N_2 bond breaking (2001)*
 - *Geminals will produce a cusp in H_4 , but they may have other areas of application (2003)*
 - I think they are bad for transport properties, but who knows?
- Math is still cumbersome
 - Perturbative corrections area nightmare