Geminal product wave function ansatz for the description of correlated systems

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Introduction

- Exploration of the possibility to get rid of the single-electron orbital-based picture of electronic structure, in favour of a picture based on electron pairs (or geminals).
- A geminal-based picture seems to have quantum chemists (the ones that I know) salivating as it corresponds to their fondest conceptions of chemical bonds forming and breaking.
- Personally, I wouldn't know. For me, it's an interesting wave function ansatz.
- In order to dampen expectations: it's all a bit premature, as we have just explored (and got numerical results) for a tiny bit of all feasible geminal product wave functions. The rest is speculative and awaits further scrutiny.
- More details can be found in Journal of Chemical Theory and Computation 9, 1394 (2013) and Computational and Theoretical Chemistry 1003, 101 (2013). This inludes ample references to previous work along similar lines.

Antisymmetrized product of single electron states

- Independent electron wave function or Slater determinant:

$$|\Phi\rangle = \prod_{h=1}^{N} c_h^\dagger |0\rangle$$

- N occupied s.p. states

$$c_h^\dagger = \sum_{i=1}^{M} x_{h;i} a_i^\dagger$$

- Spin orbitals $\psi_i(x)$, with $x \equiv \boldsymbol{r}\sigma$
- $|\Phi\rangle$ = Antisymmetrized product of single-electron states
- Next: build single, double, triple,.., excitations on top of reference state $|\Phi\rangle$

Antisymmetrized product of two-electron states

- Alternative reference state ? Most obvious generalization: consider Antisymmetrized product of two-electron states
- Two-electron states, or pair states, or geminals:

$$b_p^\dagger = \sum_{i,j=1}^{M} x_{p;i,j}\, a_i^\dagger a_j^\dagger$$

  where $x_{p;i,j} = -x_{p;j,i}$.
- General APG state: $|\Psi_{APG}\rangle = \prod_{p=1}^{P} b_p^\dagger |0\rangle$, where $N = 2P$.
- Computationally intractable...

Strongly orthogonal geminals

- Commutation relations:

$$[b_{p'}, b_p^\dagger] = \delta_{p,p'} - 4 \sum_{i,j,j'} x^*_{p';i,j'} x_{p;i,j} a_j^\dagger a_{j'}$$

- Last term reflects the fact that the $b_p^\dagger$'s are composite bosons, and is present for $p \neq p'$ even when the pair states are orthogonal,

$$\langle 0 | b_{p'} b_p^\dagger | 0 \rangle = 2 \sum_{i,j} x^*_{p';i,j} x_{p;i,j} = \delta_{p,p'}$$

- Possible way out: partition s.p. space into P orthogonal subspaces, one for each geminal. So each geminal is buit with s.p. states that lie exclusively in one subspace. The geminals are strongly orthogonal in the sense that $x^*_{p';i,j'} x_{p;i,j} = 0$ unless $p = p'$.

Strongly orthogonal geminals

- Antisymmetrized product of strongly orthogonal geminals

$$|\Psi_{APSG}\rangle = \prod_{p=1}^{P} b_p^\dagger |0\rangle$$

is now very manageable because $[b_{p'}, b_p^\dagger] \sim \delta_{p,p'}$, e.g.,

$$b_{p'}|\Psi_{APSG}\rangle = \left(\prod_{p(\neq p')=1}^{P} b_p^\dagger\right) b_{p'} b_{p'}^\dagger |0\rangle = \left(\prod_{p(\neq p')=1}^{P} b_p^\dagger\right) |0\rangle$$

Strongly orthogonal geminals

- More compact notation: any fermion pair wave function can be written, after a unitary transformation on s.p. space, in its canonical form

$$b_p^\dagger = \sum_{k=1}^{M/2} x_{p;k}\, a_{p;k}^\dagger a_{p;\bar{k}}^\dagger$$

  i.e. the s.p. states are paired off in pairs $(k, \bar{k})$.

- The pairing scheme is in general different for each geminal, but in the case of strongly orthogonal geminals the pairing takes place in different subspaces. So there is one global set of $(k, \bar{k})$ pairs, and the general APSG wave function can be written as $|\Psi_{APSG}\rangle = \prod_{p=1}^{P} b_p^\dagger |0\rangle$ with $b_p^\dagger = \sum_{k=1}^{M/2} x_{p;k}\, a_k^\dagger a_{\bar{k}}^\dagger$

Antisymmetrized product of interacting geminals

- In APSG the pairs live in different subspaces and are totally noninteracting, which is a rather severe assumption. We can restore correlation between the pairs by lifting the strong orthogonality constraint.
- We do keep the same pairing scheme for all geminals and end up with "antisymmetrized products of interacting geminals":

$$|\Psi_{APIG}\rangle = \prod_{p=1}^{P} b_p^\dagger |0\rangle = \prod_{p=1}^{P} \left(\sum_{k=1}^{M/2} x_{p;k}\, a_k^\dagger a_{\bar{k}}^\dagger \right) |0\rangle$$

- So formally the same expression as APSG, but without partitioning s.p. space (so general $x_{p;k}$ amplitudes).

Antisymmetrized product of interacting geminals

- Can we handle APIG ? Not in general but, as it turns out, in a lot more cases than just APSG.
- APIG wave functions lie in DOCI space, i.e. the Hilbert space spanned by the Slater determinants built with doubly occupied $(k, \bar{k})$ pairs:

$$|\Psi_{DOCI}\rangle = \sum_{k_1..k_P} C_{k_1..k_P} (a^\dagger_{k_1} a^\dagger_{\bar{k}_1})..(a^\dagger_{k_P} a^\dagger_{\bar{k}_P})|0\rangle$$

- Combined with orbital optimization, DOCI is quite good at describing static correlations in strongly correlated systems. But, of course, dimension goes exponentially with increasing system size...
- DOCI is our benchmark for evaluating performance of various APIG ansatzes.

Permanents

- APIG wave function

$$|\Psi_{APIG}\rangle = \prod_{p=1}^{P} \left(\sum_{k=1}^{M/2} x_{p;k}\, a_k^\dagger a_{\bar{k}}^\dagger \right) |0\rangle$$

  is determined by the $(P \times M/2)$ coefficient matrix $x_{p;k}$. Rows= geminals. Columns=DO pairs.
- At least, APIG has a "simple" expression for its DO Slater components:

$$\langle 0|(a_{\bar{k}_P} a_{k_P})..(a_{\bar{k}_1} a_{k_1})|\Psi_{APIG}\rangle = \mathrm{Per}\left(x_{p;k}\right)_{k=k_1..k_P}^{p=1..P}$$

- This is in terms of permanents:

$$\mathrm{Per}\left(x_{p;k}\right)_{k=k_1..k_P}^{p=1..P} = \sum_{\pi \in S_P} x_{1;k_{\pi(1)}}..x_{P;k_{\pi(P)}}$$

Feasible classes of geminals

- Bad news: permanents, in contrast to determinants, have no link with linear algebra. Evaluation of a permanent scales exponentially with its dimension.
- Only certain classes of $x_{p;k}$ are feasible (giving rise to easy permanents). We identified two main types:
  1. "Limited reference-orbital" geminals.
  2. Inverse rank-2 geminals (Cauchy form). Important subclass: solutions of exactly solvable Richardson-Gaudin hamiltonians.
- Combinations are also possible...

Variational calculation versus projected Schrödinger equation

- Even if individual APIG wave-function components are easy to calculate, a fully fledged variational calculation by minimizing $\langle \Psi_{APIG}|H|\Psi_{APIG}\rangle$ is (except in the Richardson-Gaudin case) not feasible, since a factorial number of permanents come into play.
- This can be avoided by the (coupled cluster inspired) idea of a projected Schrödinger equation to determine the parameters of the geminals:

$$\langle \Phi_{test}|H|\Psi_{APIG}\rangle = E\langle \Phi_{test}|\Psi_{APIG}\rangle$$

- For $|\Phi_{test}\rangle$ one can take e.g. a doubly-occupied Slater determinant $|\Phi_0\rangle = \prod_{i=1}^{P}(a_i^\dagger a_{\bar{i}}^\dagger)|0\rangle$ and its single-pair excitations $|\Phi_{i\bar{i}}^{a\bar{a}}\rangle = (a_a^\dagger a_{\bar{a}}^\dagger)(a_{\bar{i}}a_i)|\Phi_0\rangle$. Other choices are possible.

This gives a system of coupled-cluster-like nonlinear equations.

$$E = \left\langle \Phi_0 \middle| \hat{H} \middle| \Psi_{\text{APIG}} \right\rangle$$

$$0 = \left\langle \Phi_{i\bar{i}}^{a\bar{a}} \middle| \hat{H} \middle| \Psi_{\text{APIG}} \right\rangle - E \left\langle \Phi_{i\bar{i}}^{a\bar{a}} \middle| \Psi_{\text{APIG}} \right\rangle$$

$$0 = \left(\left(h_{aa} - h_{ii} \right) + \left(K'_{aa} - K'_{ii} \right) + \sum_{\substack{j=1 \\ j \neq i}}^{P} \left(\left(J_{ja} - J_{ij} \right) - \left(K_{ja} - K_{ij} \right) \right) \right) p_i^a$$

$$+ K'_{ia} \left(1 - \left(p_i^a \right)^2 \right) + \sum_{\substack{b=P+1 \\ b \neq a}}^{K} \left(K'_{ab} - K'_{ib} p_i^a \right) p_i^b + \sum_{\substack{j=1 \\ j \neq i}}^{P} \left(K'_{ij} - K'_{ja} p_i^a \right) p_j^a$$

$$+ \sum_{\substack{j=1 \\ j \neq i}}^{P} \sum_{\substack{b=P+1 \\ b \neq a}}^{K} K'_{jb} \left(p_{ij}^{ab} - p_i^a p_j^b \right)$$

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Variational calculation versus projected Schrödinger equation

- For $H = \sum_{i,j} t_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{i,j,k,l} V_{ijkl} a_i^\dagger a_j^\dagger a_l a_k$:

$$
\begin{aligned}
h_{mn} &= t_{mn} + t_{\bar{m}\bar{n}} \\
J_{mn} &= V_{mnmn} + V_{m\bar{n}m\bar{n}} + V_{\bar{m}n\bar{m}n} + V_{\bar{m}\bar{n}\bar{m}\bar{n}} \\
K_{mn} &= V_{mnnm} + V_{m\bar{n}\bar{n}m} + V_{\bar{m}nn\bar{m}} + V_{\bar{m}\bar{n}\bar{n}\bar{m}} \\
K'_{mn} &= V_{m\bar{m}n\bar{n}} - V_{m\bar{m}n\bar{n}}
\end{aligned}
$$

  (last one is recognized as a pairing matrix element)

- Limited number of permanents:
  p_i^a = wave function coefficient of $|\Phi_{i\bar{i}}^{a\bar{a}}\rangle$ = permanent of $x_{p;k}$ with $p = 1..P$ and $k = 1..P$ but column i replaced with column a.
  p_{ij}^{ab} = wave function coefficient of double pair excitation = etc.

1-reference-orbital geminals

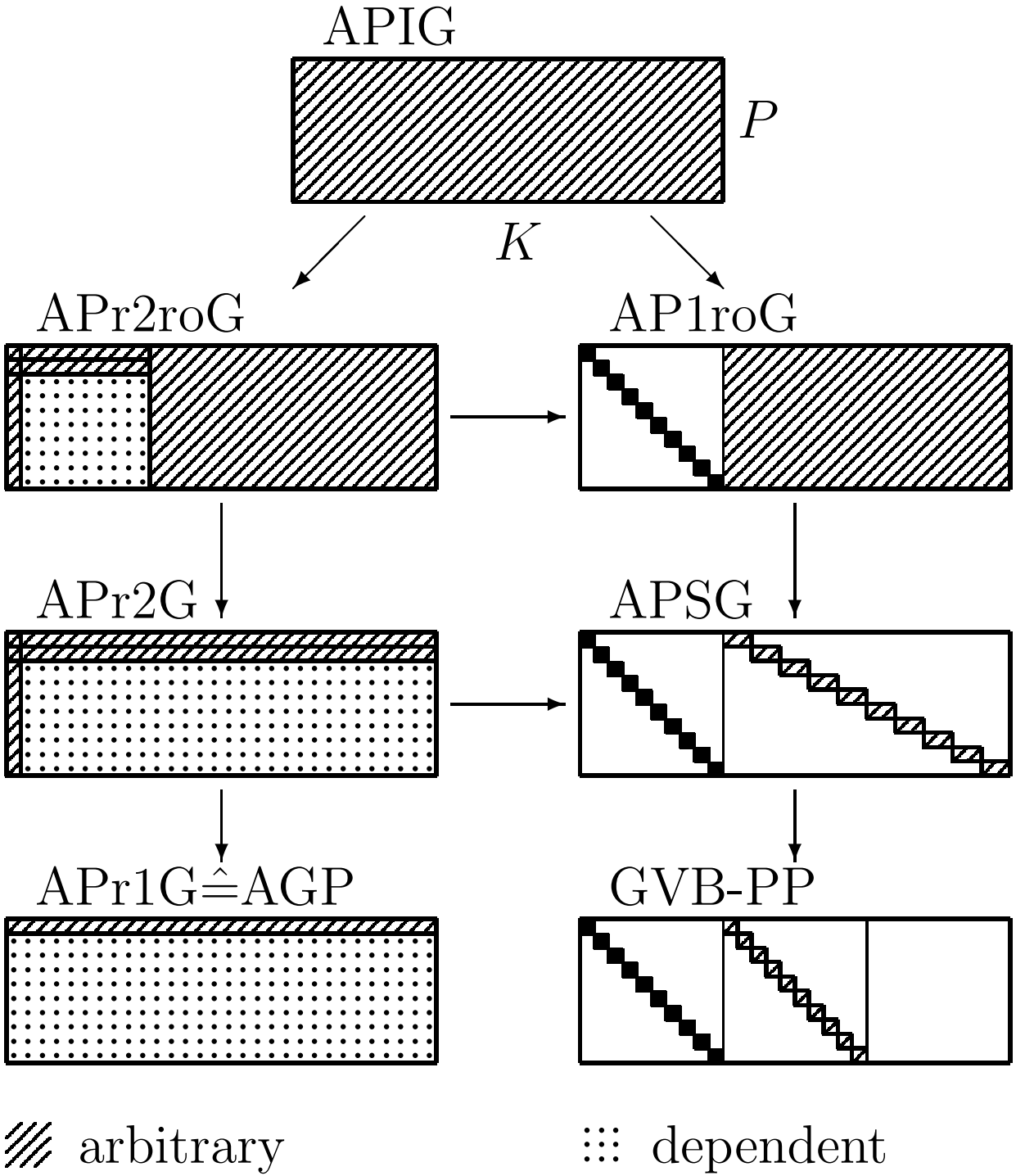
- In the class of limited reference-orbital geminals, APJroG, each geminal can contain at most a small number J of orbital pairs from a reference Slater determinant $|\Phi_0\rangle$ (at present always taken as the lowest energy SD).
- The most basic of this type is for $J = 1$, the AP1roG geminal class:

$$|\Psi_{AP1roG}\rangle = \prod_{i=1}^{P} \left(a_i^\dagger a_{\bar{i}}^\dagger + \sum_{a=P+1}^{M/2} x_{p;a} a_a^\dagger a_{\bar{a}}^\dagger \right) |0\rangle$$

- This is actually an exponential-type wave function, as one can show that

$$|\Psi_{AP1roG}\rangle = \exp \left(\sum_{i=1}^{P} \sum_{a=P+1}^{M/2} x_{i;a} a_a^\dagger a_{\bar{a}}^\dagger a_{\bar{i}} a_i \right) |\Phi_0\rangle$$

- For $J > 1$, APJroG wave functions are not (obviously) expressible in exponential form.


APIG
P
K
APr2roG
AP1roG
APr2G
APSG
APr1G≙AGP
GVB-PP
arbitrary
dependent

Results for AP1roG wave functions

- Combined with the projected Schrödinger equation (up to single -pair excitations), the resulting equations are equivalent with CC-D(DO). These are non-spin symmetry breaking pairing schemes, i.e. pairing is spin-up/down for each spatial orbital.
- Amazingly, we find for various small Coulomb systems, even at this simplest level, a very accurate reproduction of DOCI results.
- Energies of 2-, 4-, and 10-electron systems agree to within 10^{-5} a.u.. Caveat: orbital optimization is very important here (see later). For all 2-electron systems, this is no surprise: should be exact in any geminal theory with optimized orbitals. For the 4-electron systems, the stretched He dimer result shows the size-extensivity, provided the orbital optimization is taken into account, which provides a continuous accomodation between ”delocalized” molecular orbitals and localized atomic orbitals.

Preliminary Results for AP1roG: Energies in multiples

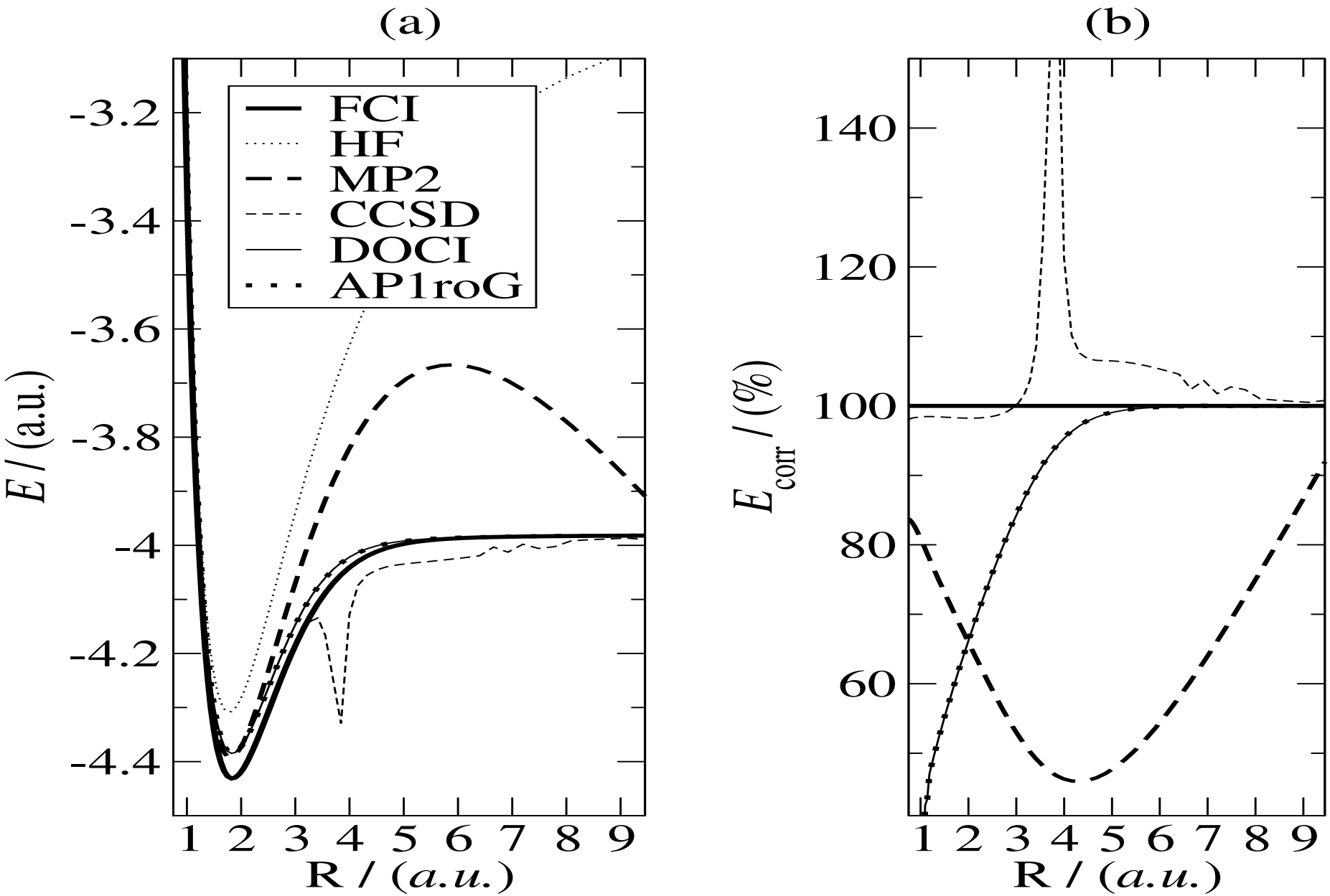
System	Basis	R^a	Δ_{DOCI}	$\Delta^{\mathrm{opt}}_{\mathrm{DOCI}}$	$\Delta^{\mathrm{opt}}_{\mathrm{AP1roG}}$	$\%E_c$
2-electron systems						
H_2	STO-6G	2.0	-39.641	-39.641	-39.641	100.0%
H_2	6-31G**	2.0	-27.663	-38.860	-38.860	100.0%
He	6-31G**	–	-32.194	-32.205	-32.205	100.0%
HeH^+	6-31G**	2.0	-20.610	-36.596	-36.596	100.0%
4-electron systems						
Be	6-31G	–	-33.321	-46.264	-46.261	98.9%
He_2	6-31G**	4.0	-26.047	-64.147	-64.147	99.5%
He_2	6-31G**	200.0	-23.669	-64.409	-64.409	100.0%
10-electron systems						
Ne	6-31G	–	-36.151	-43.382	-43.384	37.4%
Ne	6-311G*	–	-70.388	-84.528	-84.524	36.3%
CH_4	STO-6G	2.05311	-25.004	-62.653	-62.646	78.2%
CH_4	6-31G	2.05311	-21.072	-75.953	-75.946	63.0%
$(H_2)_5$	STO-6G	2.0/2.5	-26.004	-162.208	-162.273	86.7%
$(H_2)_5$	STO-6G	2.0/3.0	-22.881	-182.020	-182.083	94.4%
$(H_2)_5$	STO-6G	2.0/4.0	-20.568	-195.507	-195.535	98.9%

Results for AP1roG wave functions

- Here and in the following, we took the optimized orbitals from DOCI.
- 10-electron systems: close reproduction of DOCI remains, but only a limited fraction of the total correlation energy is reproduced, when dynamical correlations are more important (Ne, CH_4). Dynamical correlations should be added (methods to do this are available).
- But looking at the stretching of a linear chain of H_2 molecules, AP1roG performs well, along with DOCI.

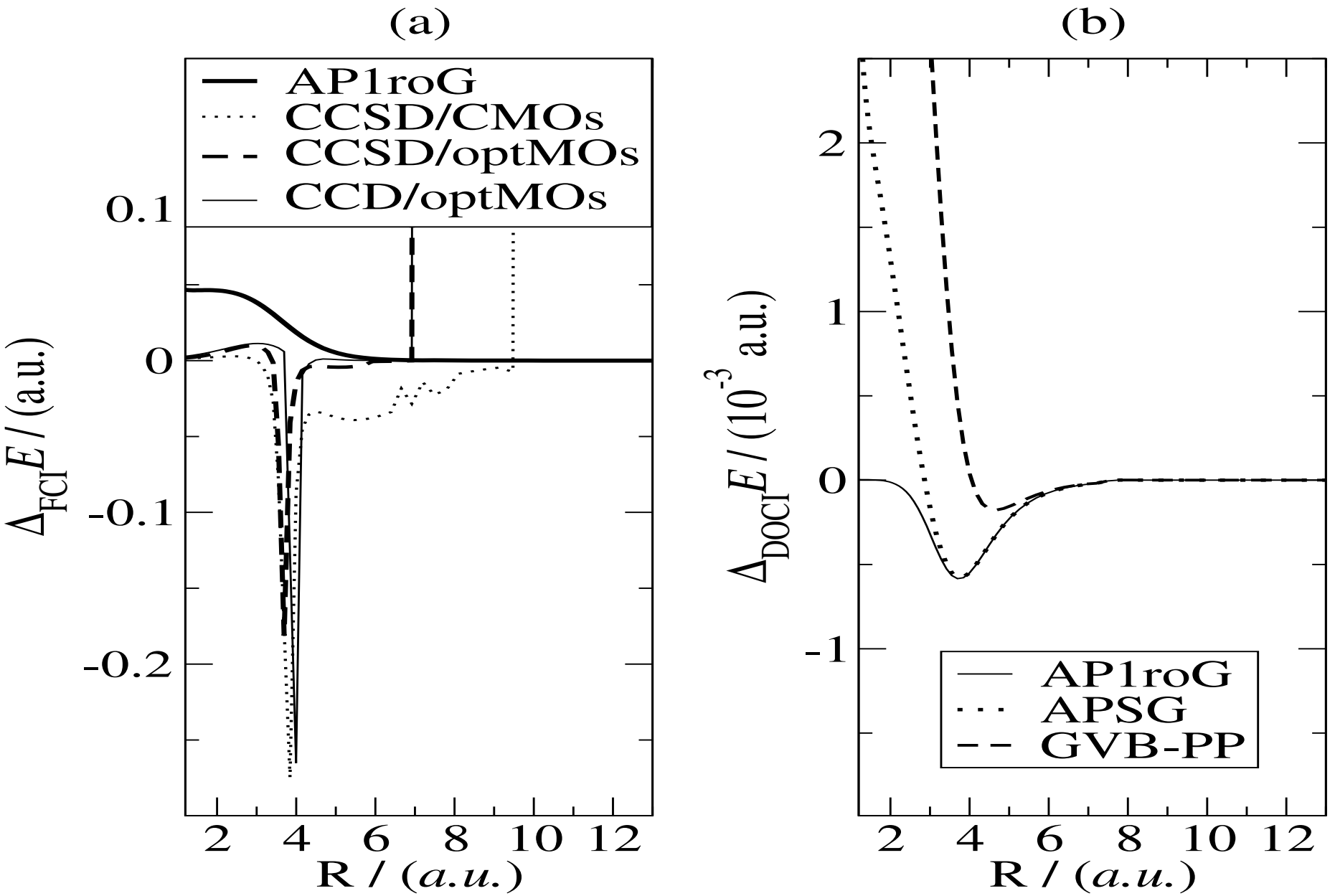
Results for AP1roG wave functions

- Let's try a typical "strong electron correlation" example: an equidistant linear chain of n H-atoms. At small distance, delocalized orbitals (metallic regime). When stretched, a massively degenerate ground state (2^n) is the correct picture.
- Next figure: H_8 chain, ANO-2s basis set.
- (a) Energy versus distance between H-atoms. DOCI=AP1roG. Qualitatively same behaviour as FCI ("fat" curve, somewhat deeper). Dangerous region at about 4 a.u. (transition from metallic to insulating regime). HF is, of course, disastrous. MP2 and CCSD (with HF as reference) also fail here. (For CC, it would require 8p-h excitations to get it right?)
- (b) fraction of FCI correlation energy. Upper panel: CCSD, showing serious spike at transition distance. Lower panel: AP1roG faithfully follows DOCI.


(a)
(b)
FCI
HF
MP2
CCSD
DOCI
AP1roG
E / (a.u.)
E_corr / (%)
R / (a.u.)
R / (a.u.)
-3.2
-3.4
-3.6
-3.8
-4
-4.2
-4.4
140
120
100
80
60
1 2 3 4 5 6 7 8 9
1 2 3 4 5 6 7 8 9

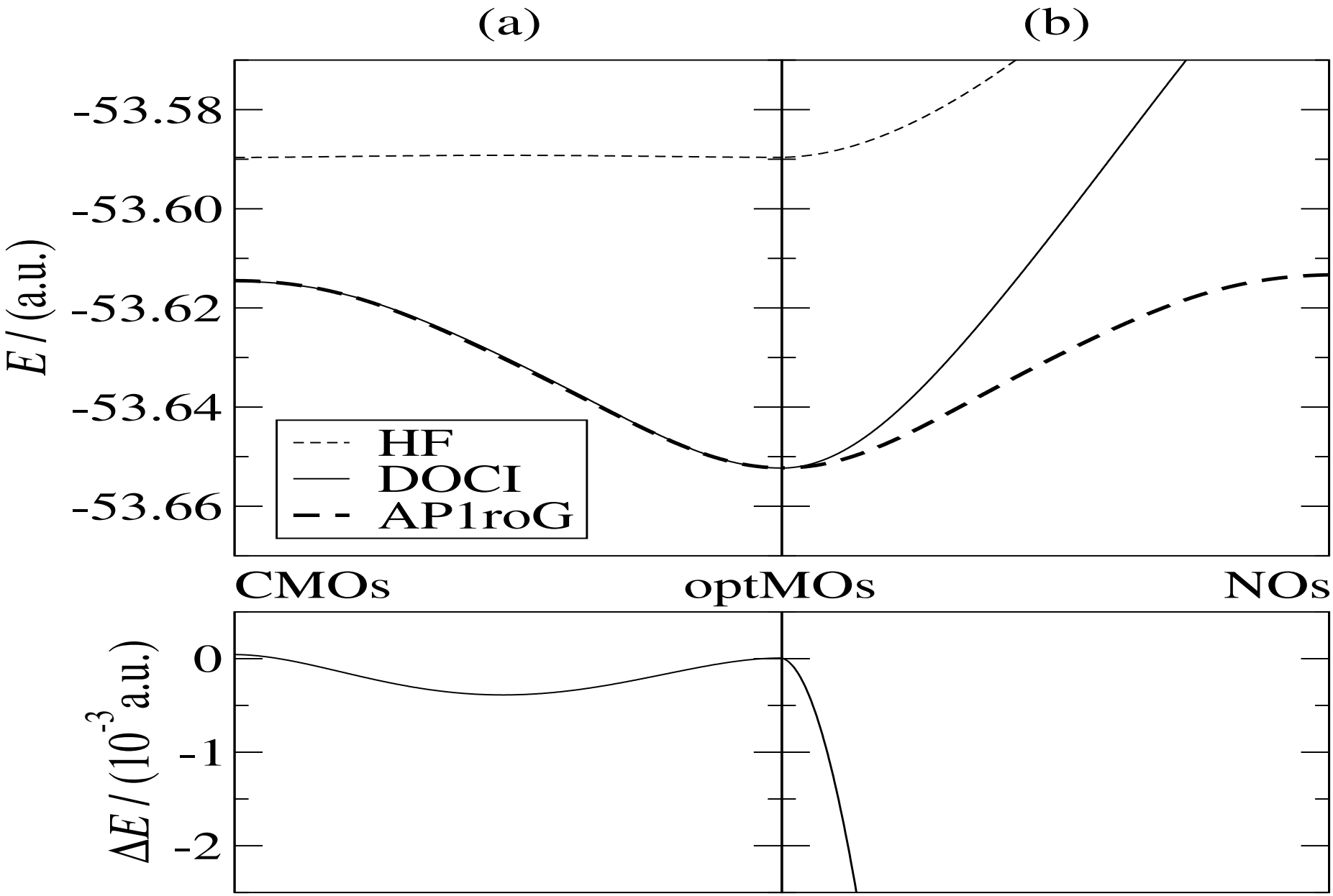
Results for AP1roG wave functions

- The same H_8 chain. What with CCSD and CCD results with the DOCI optimized orbitals? Still serious trouble at 4 a.u..
- (a) Deviation with FCI: dotted line is CCSD with HF orbitals. Other lines are CCSD and CCD with the DOCI optimized orbitals.
- (b) Comparison between DOCI and, AP1roG/APSG/GVB-PP: AP1roG faithfully reproduces DOCI over all distances. APSG and GVB-PP start getting wrong at distances about 3 a.u. and 5 a.u., respectively.


(a)
AP1roG
CCSD/CMOs
CCSD/optMOs
CCD/optMOs
0.1
0
-0.1
-0.2
$\Delta_{FCI}E$ / (a.u.)
2
4
6
8
10
12
R / (a.u.)
(b)
2
1
0
-1
$\Delta_{DOCI}E$ / (10^{-3} a.u.)
AP1roG
APSG
GVB-PP
2
4
6
8
10
12
R / (a.u.)

Role of orbital optimization

- DOCI and related geminal-based methods are strongly orbital dependent. As an example: for the CH_4 calculation we plot the gradual change in energy from canonical HF orbitals to the DOCI optimized orbitals; and from the FCI natural orbitals to the DOCI optimized orbitals. Full: DOCI energy. Dashed: AP1roG energy with the same orbitals.
- Conlusion: AP1roG is almost equivalent to DOCI provided that the optimized orbitals are used. AP1roG is less sensitive to orbital changes than the DOCI result.
- Lower panel: energy difference between Ap1roG and DOCI.


(a)
(b)
-53.58
-53.60
-53.62
-53.64
-53.66
E / (a.u.)
HF
DOCI
AP1roG
CMOs
optMOs
NOs
0
-1
-2
ΔE / (10^-3 a.u.)

Cauchy and Richardson-Gaudin classes

- Another class of easy permanents: Inverse rank-2 matrices:

$$x_{p;k} = \frac{1}{\lambda_p - \epsilon_k}$$

Borchardt's theorem (1855) states that

$$\mathrm{Per}(x_{p;k})_{k=1..P}^{p=1..P} = \frac{\mathrm{Det}(x_{p;k}^2)_{k=1..P}^{p=1..P}}{\mathrm{Det}(x_{p;k})_{k=1..P}^{p=1..P}}$$

- Expressible in terms of determinants, which are cheap to evaluate.
- Wave function:

$$|\Psi_{Cauchy}\rangle = \prod_{p=1}^{P} \left(\sum_{k=1}^{M/2} \frac{1}{\lambda_p - \epsilon_k} a_k^\dagger a_{\bar{k}}^\dagger \right) |0\rangle$$

Cauchy and Richardson-Gaudin classes

- This class contains the AGP wave function as a special case (take λ_p constant).
- It is precisely the form of exact solutions to the reduced BCS hamiltonian (or more generally, Richardson-Gaudin type hamiltonians.
- In this case, the λ_p should obey a set of nonlinear equations. Then also the 2-DM is known as a cheap expression in terms of the parameters.
- No complete calculations yet.

Example: The Richardson-Gaudin (RG) Hamiltonians describes competition between electron-pairing and independent electrons. Used to describe superconducting nanograins. The RG Hamiltonians do not describe open shells. [R. W. Richardson, Phys. Lett. A v3, 277 (1963).]

$$\hat{H} = \sum_i \varepsilon_i \left(a^+_{i\alpha} a_{i\alpha} + a^+_{i\beta} a_{i\beta} \right) + g \sum_{ij} a^+_{j\alpha} a^+_{j\beta} a_{i\beta} a_{i\alpha} \qquad \text{"pairing" model}$$

Solve with Bethe ansatz:

$$\Psi_{\text{model}} = \left(\prod_{p=1}^{P} B^+_p \right) \Big| N - 2P \text{ electron Slater determinant} \Big\rangle$$

$$B^+_p = \sum_i \left(\frac{1}{2\varepsilon_i - \lambda_p} \right) a^+_{i\beta} a^+_{i\alpha}$$

$$0 = 1 + g \sum_i \frac{1}{2\varepsilon_i - \lambda_p} + 2g \sum_{q \neq p} \frac{1}{\lambda_p - \lambda_q}$$

ε_i = parameters defining the Hamiltonian

λ_p = pairing energies; "quasimomenta"

Summary and conclusions

- Exploration of the feasible geminal-based descriptions of electronic structure.
- Promising initial results for AP1roG, but a lot has still to be done...
- AP2roG and AP3roG are worked out theoretically and in the pipeline.
- Inclusion of dynamical correlations?
- Cauchy form of geminals needs more scrutiny, in conjunction with Bethe ansatz for exactly solvable models.