Spin symmetry and size consistency of strongly orthogonal geminals

Péter Jeszenszki, Péter R. Surján, and Ágnes Szabados*

Laboratory of Theoretical Chemistry, Institute of Chemistry, Loránd Eötvös University,
1518 Budapest, POB 32, Hungary

E-mail: szabados@chem.elte.hu

Abstract

An overview of geminal based wavefunctions is given, allowing for singlet-triplet mixing within the two-electron units. Spin contamination of the total wavefunction (obtained as an antisymmetrized product) is restored by spin projection. Full variation after projection is examined for two models. One is the long known spin projected Extended Hartree-Fock (EHF). The other is a yet unexplored function, termed spin projected Extended Antisymmetrized Product of Strongly orthogonal Geminals (EAPSG). Studies on size consistency is presented for both models. Numerical evaluation of EHF and EAPSG is performed for small test systems (H_4 and H_8).

---

*To whom correspondence should be addressed

Introduction

Proper description of static correlation is crucial in many systems of chemical interest, e.g. covalent bond dissociation processes or organometallic compounds of open-shell character. Multiconfigurational Self-Consistent Field (MC-SCF),[1,2] in particular Complete Active Space SCF (CAS) is a common choice for these systems, thanks to the favourable properties of orbital invariance within the active space, spin pure nature and computationally manageable optimization equations.[3,4] Though recent years have seen tremendous advance in the applicability of CAS for large systems,[5–8] the formal exponential scaling with the number of active orbitals remains. A CAS wavefunction characteristically includes a part of dynamic correlation along with static, with antagonistic consequences in a multireference correlation treatment.[9] Conceptual as well as computational considerations appear to point to the need for a model, more economic than CAS in the configuration interaction (CI) space.

One way to decrease scaling of the CAS Ansatz is to partition the active space and restrict orbital occupancy in each partition.[10–12] Alternatively, optimizable parameters can be assigned only to two-electron functions (c.f. geminals), the total wavefunction being constructed as an antisymmetric product.[13] Requiring geminals ψ_i and ψ_j, $i \neq j$ to fulfill the strong orthogonality condition

$$\int \psi_i \left(\mathbf{x_1}, \mathbf{x_2}\right) \psi_j \left(\mathbf{x_1}, \mathbf{x_2}\right) \mathrm{d}\mathbf{x_1} = 0 \ , \tag{1}$$

geminals are found to be expanded in mutually orthogonal molecular orbital (MO) subspaces, based on Arai's theorem.[14] This allows one to identify the strongly orthogonal geminal Ansatz as a direct product of CAS functions, each furnished with two active electrons. It is the direct product nature, which ensures polynomial scaling with system size. The well-known generalized valence bond function[15] represents a special case, where active orbitals per geminal is restricted to two.

Strongly orthogonal geminals have been cultivated under various names in the literature.

To emphasize the fixed assignation of electrons to pairs, terminology 'Perfect Pairing' was introduced (GVB-PP).[15,16] Singlet type Strongly orthogonal Geminals (SSG),[17] and Antisymmetric Product of Strongly Orthogonal Geminals (APSG)[13,18,19] represent extensions to GVB-PP, allowing for more than two orbitals per geminal. In the SSG model of Rassolov,[17] the number of orbitals per geminal is also subject to variation. Singlet state of the geminals is supposed in SSG, while it is abandoned by adopting a different orbitals for different spin (DODS) framework in Unrestricted SSG (USSG)[17] and Unrestricted Perfect Pairing (UPP).[20] In both USSG and UPP strong orthogonality implies integration over spatial as well as spin variables of electron 1 in Eq.(1). As a consequence, spatial parts of the α and β orbitals of different subspaces have nonzero overlap in general. Requiring Eq.(1) to hold when integrating solely for the spatial variables of electron 1 restricts the expansion of the spatial part of α and β MOs to the corresponding geminal subspace. Such a restricted but still DODS approach was found desirable for spin symmetry and qualitatively correct definition of geminal subspaces.[21,22] The related models are termed Restricted USSG (RUSSG)[21] and Unrestriction in Active Pairs (UAP).[22] Note, that the UPP and UAP schemes resort to two orbitals per geminal.

Allowing for triplet geminals complicates theory, it however becomes important if wishing to describe elongation of interacting (e.g. multiple) covalent bonds[23–25] or molecules that require multiple Lewis structures for a qualitative description.[26,27] In particular, breaking multiple bonds with singlet coupled geminals produces erroneous spin states of the fragments in the dissociation limit.[27,28] While DODS geminal schemes cure fragment spin upon dissociation,[27] the spin of the fragments are not coupled properly. A contamination of total spin is produced consequently, in analogy with the Unrestricted Hartree-Fock (UHF) method.

In fact, breaking spin symmetry in the HF framework to account for static correlation has been exploited in several instances.[29,30] Restoration of spin symmetry in the unrestricted HF theory, advocated by Löwdin,[31] was extensively studied in the 1970's[32] and has been revitalized recently.[33] Spin purification of the DODS geminal model has been investigated for the UAP function in an approximate manner,[34] based on Yamaguchi's idea.[35] For the RUSSG function, rigorous spin projection has been developed and evaluated in numerical terms.[26]

A caveat concerning spin projection is that potential curves may be ill-behaved, if subsequent optimization of wavefunction parameters is omitted. Full variation of the spin purified UHF function – termed spin projected Extended Hartree Fock (EHF) – leads to continuous potential curves, it however violates size consistency as well as size extensivity.[33,36–38]

In this study, the yet unexplored (restricted) DODS based geminal Ansatz, subjected to variation after spin projection is examined. The presentation starts with a comparative overwiev of DODS geminal Ansätze UHF and RUSSG. This is followed by a formal analysis of size consistency on a two-geminal model system. Properties of DODS geminal based models are also compared on this small model, based on numerical calculation. Size consistency violation is finally evaluated for a four-geminal model system.

In course of the derivation we shall make use of an extended pairing theorem, formulated and proven first by Karadakov.[39] As an extension of the original pairing theorem, relating the occupied UHF orbitals,[40–42] Karadakov proved that virtuals can be paired in such a manner, that the overlap of each α virtual orbital is nonzero for at most one β occupied, and vice versa (with the value of the overlap integral being distinctly related to that of the corresponding occupied orbitals).

Closing the introduction, let us note that triplet geminals can be incorporated in a spin-pure manner by multireference coupled cluster[43–45] or perturbation[46,47] corrections based on the singlet-coupled geminal wavefunction. The Coupled Cluster Valence Bond (CCVB) approach of Small et al.[45] is particularly relevant in the present context as it resorts solely to pairs of intra-geminal triplet states, bringing in essentially the same effect as EAPSG. There are $N_g(N_g-1)/2$ extra parameters considered in CCVB in addition to those in APSG, N_g standing for the number of geminals, and two orbitals being assigned to each geminal. This facilitates an overall polynomial scaling of the resulting method.[45] In comparison, EAPSG studied below is more economic, bringing N_g extra variational parameters in addition to APSG. The potentially exponential scaling of the spin treatment can be avoided due to the simplicity of the spin projection procedure,[26] vide infra.

DODS geminal Ansätze

A brief, transparent recapitulation of two DODS Ansätze based on strongly orthogonal geminals is given below. We start with the well known UHF wavefunction, then present the extension, known as RUSSG or UAP. Comparison of the main features of the two wavefunctions is followed by a discussion on spin purification and its consequences.

Unrestricted HF (UHF)

Let us start with the UHF wavefunction

$$|\Psi^{\text{ UHF}}\rangle = \prod_I \phi_\alpha^{I+}\ \chi_\beta^{I+}|\text{vac}\rangle \ ,$$

which is apparently an antisymmetrized product of geminals $\tilde{\psi}_I$, written as

$$\tilde{\psi}_I^+ \ = \ \phi_\alpha^{I+}\ \chi_\beta^{I+} \ . \tag{2}$$

Assuming that α and β orbitals are paired in Löwdin's sense,[40,41,48]

$$\langle \phi^I | \chi^J \rangle \ = \ \lambda_I \delta_{IJ} \tag{3}$$

we can further state that geminals $\tilde{\psi}_I$ and $\tilde{\psi}_J$, $I \neq J$ are expanded in mutually orthogonal spaces, spanned by $\{\phi^I, \chi^I\}$ and $\{\phi^J, \chi^J\}$, respectively. Based on Arai's theorem,[14] it follows that Ψ^{UHF} is a specimen of strongly orthogonal geminal wavefunction.[49,50]

Let us now invoke the Alternating Molecular Orbital (AMO)[51] parametrization of the orbitals, according to

$$\begin{aligned} \phi^I &= \cos\alpha_I\,\varphi_1^I \;+\; \sin\alpha_I\,\varphi_2^I \\ \chi^I &= \cos\alpha_I\,\varphi_1^I \;-\; \sin\alpha_I\,\varphi_2^I\ , \end{aligned} \tag{4}$$

with $\langle\varphi_i^I|\varphi_j^J\rangle = \delta_{IJ}\delta_{ij}$. Variational optimization MOs φ_1^I, φ_2^I for all I (c.f. paired orbital method[52]) yields the UHF wavefunction.[32] (With this parametrization, the overlap of Eq.(3) is easily found to be $\lambda_I = \cos(2\alpha_I)$.)

Substituting expansion (4) into Eq.(2) an equivalent expression of geminal $\tilde{\psi}$ is obtained as

$$\tilde{\psi}^+ \;=\; \sum_{i,j=1}^{2} C_{ij}^{\text{UHF}}\,\varphi_{i\alpha}^+\varphi_{j\beta}^+\ , \tag{5}$$

with the geminal coefficient matrix

$$\mathbf{C}^{\text{UHF}} \;=\; \begin{pmatrix} \cos^2\alpha & -\sin(2\alpha)/2 \\ \sin(2\alpha)/2 & -\sin^2\alpha \end{pmatrix} .$$

In the above, and further on, index I of the geminal is omitted for clarity, whenever possible. The (spatial) density matrix of geminal $\tilde{\psi}$ is readily found to be diagonal on the basis of orbitals φ_i

$$\mathbf{D}^{\text{UHF}} \;=\; 2\begin{pmatrix} \cos^2\alpha & 0 \\ 0 & \sin^2\alpha \end{pmatrix} . \tag{6}$$

It follows, that the density matrix of the total UHF wavefunction – obtained as the direct sum of geminal density matrices $\mathbf{D}_I^{\text{UHF}}$ – is also diagonal. Orbitals φ_i^I are hence identified as natural orbitals of Ψ^{UHF} and Eq.(6) reflects the well known paired nature of UHF natural occupation numbers[53] utilized effectively in finding the appropriate active orbitals in multireference cases.[29]

While the natural orbital expansion (5) includes more terms than the DODS form Eq.(2), it allows to associate the singlet and triplet components of $\tilde{\psi}$, with the symmetric (${}^{s}C^{\text{UHF}}$) and antisymmetric part of the geminal coefficient matrix. The former defines a singlet two-particle creation operator

$$\tilde{\mathcal{S}}^{+}(\alpha) \;=\; \sum_{i,j=1}^{2} {}^{s}C^{\text{UHF}}_{ij}\, \varphi^{+}_{i\alpha}\varphi^{+}_{j\beta} \;=\; \cos^2\alpha\; \varphi^{+}_{1\alpha}\; \varphi^{+}_{1\beta} \;-\; \sin^2\alpha\; \varphi^{+}_{2\alpha}\; \varphi^{+}_{2\beta}\;,$$

the latter is related to a triplet two-particle operator, with $M_S = 0$

$${}^{0}\mathcal{T}^{+} \;=\; \frac{1}{\sqrt{2}}\left(\varphi^{+}_{1\alpha}\; \varphi^{+}_{2\beta} \;-\; \varphi^{+}_{2\alpha}\varphi^{+}_{1\beta}\right)\;,$$

allowing to write the UHF geminal as

$$\tilde{\psi}^{+} \;=\; \tilde{\mathcal{S}}^{+}(\alpha) + \frac{\sin(2\alpha)}{\sqrt{2}}\;{}^{0}\mathcal{T}^{+}\;. \tag{7}$$

Note, that $\tilde{\psi}$ is normalized, but the norm of its singlet and triplet components are in general smaller than unity. The UHF geminal of Eq.(7) becomes spin pure at $\alpha = 0$ (as $\sin\alpha = 0$). The singlet part, $\tilde{\mathcal{S}}$ falls back to restricted HF in such case. Accordingly, it is not possible to obtain a multireference description with proper spin in UHF parametrization, even for two-electrons. Approaching from another angle, one sees that UHF occupancies of natural orbitals φ_i (c.f. Eq.(6)) can not be changed independently from the relative weight of singlet and triplet components (c.f. Eq.(7)).

Restricted Unrestricted SSG (RUSSG)

The RUSSG[21] wavefunction exhibits an antisymmetrized geminal product form, similar to UHF

$$|\Psi^{\text{RUSSG}}\rangle = \prod_{I} \psi_I^+ |\text{vac}\rangle \ . \tag{8}$$

The geminal in Ψ^{RUSSG} is however different from UHF, reading as

$$\psi^+ \ = \ \cos\delta \ \mathcal{S}^+(\gamma) + \sin\delta \ {}^0\mathcal{T}^+ \ , \tag{9}$$

where the singlet component is expressed as

$$\mathcal{S}^+(\gamma) \ = \ \cos\gamma \ \varphi_{1\alpha}^+ \ \varphi_{1\beta}^+ \ - \ \sin\gamma \ \varphi_{2\alpha}^+ \ \varphi_{2\beta}^+ \ ,$$

for normalization. Comparison of Eqs.(7) and (9) shows that the UHF concept is generalized by including one additional parameter per geminal. Angle δ in Eq.(9) controls singlet-triplet mixing (c.f spin purity) while γ independently governs the multireference character of the singlet part.[54]

The coefficient matrix behind the RUSSG geminal (9) reads

$$\mathbf{C}^{\text{RUSSG}} \ = \ \begin{pmatrix} \cos\delta \ \cos\gamma & \sin\delta/\sqrt{2} \\ -\sin\delta/\sqrt{2} & -\cos\delta \ \sin\gamma \end{pmatrix} \ ,$$

yielding the density matrix

$$\mathbf{D}^{\text{RUSSG}} \ = \ \begin{pmatrix} 2\cos^2\delta \ \cos^2\gamma \ + \ \sin^2\delta & 0 \\ 0 & 2\cos^2\delta \ \sin^2\gamma \ + \ \sin^2\delta \end{pmatrix} \ .$$

Assuming orthogonality of geminal subspaces, according to $\langle\varphi_i^I|\varphi_j^J\rangle = \delta_{IJ}\delta_{ij}$, it again follows that orbitals φ_i^I represent natural orbitals of Ψ^{RUSSG}. Paired nature of natural orbitals still holds, as a direct consequence of the strongly orthogonal geminal character.

It is common to write a DODS expansion[22] for the RUSSG geminal ψ

$$\psi^+ \ = \ \cos\epsilon\ \phi_{1\alpha}^+\chi_{1\beta}^+ \ + \ \sin\epsilon\ \phi_{2\alpha}^+\chi_{2\beta}^+ \ , \tag{10}$$

as an extension of the UHF geminal, Eq.(2). Orbitals ϕ_i and χ_i above are eigenvectors of the α and β density matrix (so-called pseudo-natural orbitals). The associated occupation numbers, $n_1 = \cos^2\epsilon$ and $n_2 = \sin^2\epsilon$, are the same for the α and β set. Relation between pseudo-natural and natural orbitals is expressed as

$$\begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = \begin{pmatrix} \cos\alpha & \sin\alpha \\ \sin\alpha & -\cos\alpha \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix} , \tag{11}$$

$$\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = \begin{pmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix} , \tag{12}$$

with $\alpha \ = \ -\arctan\left(\sqrt{2}\tan\delta/(\cos\gamma - \sin\gamma)\right)/2\,$, and $\cos(2\epsilon) \ = \ \cos^2\delta\cos(2\gamma)/\cos(2\alpha)\,$. Pure singlet hence belongs to $\alpha = \delta = 0$ (lack of α-β splitting) and occupation numbers can be deduced from $\epsilon = \gamma$. Pure triplet, $\delta = \pi/2$ generates $\alpha = \pi/4$ and $\epsilon = 3\pi/4$.

Characteristics of UHF and RUSSG

Comparing the DODS expansion of UHF and RUSSG, one can see that the UHF parametrization, Eq.(4), works only with ϕ_1 and χ_1 of the RUSSG unitary transformation pair of Eqs.(11) and (12), since $n_2 = \sin^2\epsilon = 0$ for UHF. Orbitals ϕ_2 and χ_2 are virtuals in the UHF framework, fulfilling $\langle\phi_1|\chi_2\rangle = \langle\phi_2|\chi_1\rangle = \sin(2\alpha)$, c.f. Karadakov's extended pairing theorem.[39,42,48,55] From this point of view, RUSSG represents a generalization of UHF where virtual orbitals – paired to the occupieds according to Karadakov – can become partially occupied. This aspect was emphasized by Head-Gordon et al., when deriving the UAP formalism.[22]

The UHF and RUSSG energies – obtained upon variational optimization of all parameters – are usually close to each other at around equilibrium geometries where restricted HF is acceptable (c.f. $\alpha \approx 0$ in UHF, while $\gamma \approx 0$ and $\delta \approx 0$ in RUSSG). Energy difference also disappears in the limit of breaking a single bond. As the lowest singlet and triplet solutions become degenerate in this process, admixture of a triplet component to the ground state singlet can not deteriorate the UHF energy. The situation is different for intermediate distances. As RUSSG involves an extra variational parameter per geminal, it may provide a better energy than UHF.

The unrestricted HF solution appears at a well defined point on the potential surface, named after Coulson and Fischer.[56,57] There is a similar point on the SSG surface, connected to the appearance of the RUSSG solution.[22] When a RUSSG solution appears below restricted SSG in energy, an improved description of inter geminal correlation is obtained at the price of mixing singlet and triplet components at the two-electron level. As a consequence, spin symmetry is lost in general for RUSSG beyond one geminal.

Ensuring spin symmetry

Spin symmetry of Ψ^{RUSSG} can be achieved on one hand by restricting geminal spins as singlet. This, so-called singlet coupling operates with a single parameter per geminal, c.f. Eq.(9) with $\delta = 0$ or Eq.(10) with $\alpha = 0$. Spin symmetry, however, can also be restored without imposing a constraint on geminals. This necessitates coupling geminal spins following Serber's scheme,[58,59] or alternatively, spin purification of the total wavefunction as

$$|\Psi^{\text{SP-RUSSG}}\rangle \;\; = \;\; \hat{P}^{s}|\Psi^{\text{RUSSG}}\rangle \; ,$$

where $\hat{P}^s$ stands for Löwdin's spin projector, picking the component corresponding to the desired spin quantum number.[59,60] The approach of Rassolov[26] to spin-purification of RUSSG represents a third option whereby the lowest singlet root of the squared spin operator is determined iteratively. Due to the special structure of RUSSG, the procedure necessitates tackling a considerably small subspace of the CI space, the dimension scaling with N_g^2 for $S_z = 0$ systems.

Spin projection is always accompanied by the question whether parameters are optimized before or after. Starting from UHF, both approaches have been studied. Spin projection after variation is comparatively easy, but it may lead to ill-shaped potential energy curve near the Coulson-Fischer point.[61] Potential curves obtained by the more complicated 'variation after projection' (EHF)[32] are free from the Coulson-Fischer point, hence they are continuously differentiable. An alternative to Löwdin's spin projection operator has been recently shown to simplify the implementation of EHF.[33] Spin projection of the RUSSG wavefunction[26] is still relatively easy, compared to the general case, thanks to the orthogonality of the spatial parts of the MOs corresponding to different geminals.

We use acronym SP-RUSSG to refer to the 'projection after variation' method based on the RUSSG model. Rassolov also considered partial variation after projection.[26,27] The purpose of the present study is the analysis of 'full variation after spin projection' of the RUSSG Ansatz. We term this approach 'EAPSG', in direct analogy with EHF. For clarity, the formal definition of the EAPSG energy is given as

$$E^{\text{EAPSG}} \;=\; \frac{\left\langle \Psi^{\text{RUSSG}} \middle| \hat{P}^s \hat{H} \hat{P}^s \middle| \Psi^{\text{RUSSG}} \right\rangle}{\left\langle \Psi^{\text{RUSSG}} \middle| \hat{P}^s \middle| \Psi^{\text{RUSSG}} \right\rangle} \;=\; \text{min.}\ ,$$

with minimization performed for natural orbitals φ_i^I and parameters δ^I, γ^I. The spin projected function $\hat{P}^s \Psi^{\text{RUSSG}}$ at the optimal parameter set is termed the EAPSG wavefunction.

Loss of size consistency as a byproduct of spin projection has been reported in connection with EHF in several studies.[33,36,37] Violation of size consistency is of primary concern, as it may have far reaching consequences on energy differences and the shape of potential curves. We study below size consistency in Pople's sense,[62] i.e. additivity of energy over non-interacting fragments. The two spin projected, extended geminal methods, EHF and EAPSG are analysed in parallel. This helps to reveal the points of analogies and deviations in their behaviour. We note here, that both parent methods, UHF and RUSSG can fulfill size consistency, provided that a geminal structure, with the appropriate number of electrons kept unpaired, is imposed on the monomer units.

The case of two geminals

This section is devoted to an analysis of the size consistency properties of EHF and EAPSG for a system composed of two geminals. First we treat the fully separated (non interacting) cases, giving analytical derivation of energy formulae. Then, for the interacting case, numerically obtained potential curves are shown for the various solutions.

A system of two geminals can be thought of as H_4 composed of two H_2 subunits. Let us assume that geminals have a considerable multireference character (elongated H−H bonds), to incorporate the general (potentially singlet-triplet mixed) case.

Non-interacting geminals

EHF

The UHF wavefunction of the supersystem is written as

$$|\Psi^{\text{UHF}}_{H_4}\rangle = \tilde{\psi}^+_1 \tilde{\psi}^+_2 |\text{vac}\rangle \ ,$$

with $\tilde{\psi}_1$ and $\tilde{\psi}_2$ referring to one and the other H_2 unit. The effect of spin projection, $\hat{P}^s$ is evaluated by relying on the natural orbital expansion of geminals and constructing spin pure functions via coupling geminal spins with the appropriate Clebsch-Gordan coefficients. This results, for $S = 0$

$$\hat{P}^s |\Psi^{\mathrm{UHF}}_{H_4}\rangle \;=\; \left(\tilde{\mathcal{S}}^+_1(\alpha_1) \tilde{\mathcal{S}}^+_2(\alpha_2) \;+\; \frac{\sin(2\alpha_1)\sin(2\alpha_2)}{2\sqrt{3}}\, \mathit{\Pi}^+_{12} \right) |\mathrm{vac}\rangle \;,$$

where a four-electron singlet state is associated with

$$\Pi^+_{12} = \sqrt{\frac{1}{3}} \left({}_{+1}\mathcal{T}^+_1 \; {}_{-1}\mathcal{T}^+_2 \;+\; {}_{-1}\mathcal{T}^+_1 \; {}_{+1}\mathcal{T}^+_2 \;-\; {}_{0}\mathcal{T}^+_1 \; {}_{0}\mathcal{T}^+_2 \right) \;.$$

States ${}_{\pm 1}\mathcal{T}_I$ are $M_S = \pm 1$ triplet geminal states, obtained by applying the spin raising (lowering) operator on the $M_S = 0$ geminal, as

$$ {}_{+1}\mathcal{T}^+_I \;=\; \frac{1}{\sqrt{2}}\, \hat{S}_+ \; {}_{0}\mathcal{T}^+_I \;=\; \varphi^{I+}_{1\alpha}\, \varphi^{I+}_{2\alpha} \;, \tag{13}$$

$$ {}_{-1}\mathcal{T}^+_I \;=\; \frac{1}{\sqrt{2}}\, \hat{S}_- \; {}_{0}\mathcal{T}^+_I \;=\; \varphi^{I+}_{1\beta}\, \varphi^{I+}_{2\beta} \;. \tag{14}$$

The EHF energy is obtained from the condition

$$E^{\mathrm{EHF}}_{H_4} \;=\; \frac{\langle \Psi^{\mathrm{UHF}}_{H_4} | \hat{P}^s \hat{H} \hat{P}^s | \Psi^{\mathrm{UHF}}_{H_4} \rangle}{\langle \Psi^{\mathrm{UHF}}_{H_4} | \hat{P}^s | \Psi^{\mathrm{UHF}}_{H_4} \rangle} \;=\; \mathrm{min.} \tag{15}$$

Let us assume now additive separability of the Hamiltonian as

$$\hat{H} \;=\; \hat{H}_1 \;+\; \hat{H}_2 \,. \tag{16}$$

For identical H_2 units, the energy expression is specified as

$$E^{\mathrm{EHF}}_{H_4} \;=\; 2\; \frac{(\cos^4\alpha_1 + \sin^4\alpha_1) \langle \tilde{\mathcal{S}}_1(\alpha_1) | \hat{H}_1 | \tilde{\mathcal{S}}_1(\alpha_1) \rangle \;+\; \frac{\sin^4(2\alpha_1)}{12} \langle {}_0\mathcal{T}_1 | \hat{H}_1 | {}_0\mathcal{T}_1 \rangle}{(\cos^4\alpha_1 + \sin^4\alpha_1)^2 + \frac{\sin^4(2\alpha_1)}{12}} \;, \tag{17}$$

making use of the degeneracy of spin multiplets and assuming natural orbitals localized on one or the other H_2. Note, that the triplet state of H_2 units figure in the dimer energy for nonzero α_I. As $\alpha_I = 0$ belongs to the RHF solution, triplet geminals contribute to the variationally optimized energy of the dimer in the general case. This is obviously a problem, since calculating the H_2 molecules independently, one obtains, again for $S = 0$

$$\hat{P}^s|\Psi^{\text{UHF}}_{H_2}\rangle \;=\; \tilde{\mathcal{S}}^+_1(\alpha_1)|\text{vac}\rangle \;,$$

yielding the following EHF energy for the H_2 unit

$$E^{\text{EHF}}_{H_2} \;=\; \frac{1}{\cos^4\alpha_1 + \sin^4\alpha_1}\langle\text{vac}|\tilde{\mathcal{S}}^-_1(\alpha_1)\,\hat{H}\,\tilde{\mathcal{S}}^+_1(\alpha_1)|\text{vac}\rangle \;=\; \text{min.} \tag{18}$$

Comparison of Eqs.(17) and (18) clearly shows, that the monomer triplet contribution to $E^{\text{EHF}}_{H_4}$ spoils size consistency. The error disappears as $\alpha_I \rightarrow 0$, since the triplet component of geminals falls off and the singlet component falls back to RHF. The error vanishes also in the other extreme, in the dissociation limit of H_2 subunits, since singlet and triplet geminal states become degenerate, therefore spin contamination can not influence the energy. In all other cases the monomer triplet component has a nonzero contribution to Eq.(17). As EHF provides the FCI solution with two orbitals for H_2, size consistency violating terms of Eqs.(17) necessarily lift the energy of the non-interacting dimer above twice the energy of the monomer.

EAPSG

Starting from the spin projection of Ψ^{RUSSG}, written as

$$|\Psi^{\text{SP-RUSSG}}_{H_4}\rangle = \hat{P}^s\psi^+_1\psi^+_2|\text{vac}\rangle = \left[\cos\delta_1\,\cos\delta_2\,\mathcal{S}^+_1(\gamma_1)\mathcal{S}^+_2(\gamma_2) + \frac{\sin\delta_1\,\sin\delta_2}{\sqrt{3}}\mathit{\Pi}^+_{12}\right]|\text{vac}\rangle \;, \tag{19}$$

it is apparent, that the role of parameters δ_1 and δ_2 is merely to control the relative weight of $\mathcal{S}_1^+(\gamma_1)\mathcal{S}_2^+(\gamma_2)$ and $\mathit{\Pi}_{12}^+$. Introducing the following, equivalent definitions

$$\cos\delta \;=\; \frac{\cos\delta_1\cos\delta_2}{\sqrt{\cos^2\delta_1\cos^2\delta_2+(\sin^2\delta_1\sin^2\delta_2)/3}}\;, \tag{20}$$

$$\sin\delta \;=\; \frac{\sin\delta_1\sin\delta_2}{\sqrt{\cos^2\delta_1\cos^2\delta_2+(\sin^2\delta_1\sin^2\delta_2)/3}}\;, \tag{21}$$

Eq.(19) can be recast without lack of generality as

$$|\Psi_{H_4}^{\text{SP-RUSSG}}\rangle \;=\; \big(\cos\delta\,\mathcal{S}_1^+(\gamma_1)\,\mathcal{S}_2^+(\gamma_2)\;+\;\sin\delta\,\mathit{\Pi}_{12}^+\big)\,|\text{vac}\rangle\;. \tag{22}$$

Condition

$$E_{H_4}^{\text{EAPSG}} \;=\; \frac{\langle\Psi_{H_4}^{\text{SP-RUSSG}}|\hat{H}|\Psi_{H_4}^{\text{SP-RUSSG}}\rangle}{\langle\Psi_{H_4}^{\text{SP-RUSSG}}|\Psi_{H_4}^{\text{SP-RUSSG}}\rangle}\;=\;\text{min.} \tag{23}$$

results the EAPSG energy.

Assuming again additive separability of $\hat{H}$ according to Eq.(16), identical H_2 units and localized natural orbitals, the energy expression simplifies to

$$E_{H_4}^{\text{EAPSG}} \;=\; 2\left(\cos^2\delta\,\langle\text{vac}|\mathcal{S}_1^-(\gamma_1)\,\hat{H}_1\,\mathcal{S}_1^+(\gamma_1)|\text{vac}\rangle\;+\;\sin^2\delta\langle\text{vac}|{}_0\mathcal{T}_1^-\,\hat{H}_1\,{}_0\mathcal{T}_1^+|\text{vac}\rangle\right)\;. \tag{24}$$

Variational optimization of Eq.(24) results $\delta = 0$, hence twice the energy obtained for the H_2 unit based on

$$|\Psi_{H_2}^{\text{SP-RUSSG}}\rangle \;=\; \hat{P}^s\psi_1^+|\text{vac}\rangle = \mathcal{S}_1^+(\gamma_1)|\text{vac}\rangle\;,$$

and

$$E_{H_2}^{\text{EAPSG}} \;=\; \langle\text{vac}|\mathcal{S}_1^-(\gamma_1)\,\hat{H}\,\mathcal{S}_1^+(\gamma_1)|\text{vac}\rangle\;\;=\;\text{min.}$$

Accordingly, EAPSG is size consistent for a system composed of two geminals. Note, that in this simple case, size consistency is achieved by eliminating the triplet component of Eq.(24) upon variation of the EAPSG energy for the dimer. This is not always the case: dissociating a double bond (two geminals), e.g. ethylene, the triplet component would survive purely.

Interacting geminals

Numerical assessment of EHF and EAPSG is presented on the example of H_4, by monitoring a square to rectangle distortion. Near to square geometry, the same system was examined by a geminal coefficient optimized version of SP-RUSSG.[26] Here, the dissociation of H_4 to two H_2 units is considered.

Bond lengths of two H_2 molecules, aligned parallel, are fixed to 1.4 Å , roughly twice the equilibrium distance, to generate a considerable multireference character of the wavefunction. Starting from the square geometry, the H_2 units are gradually drawn apart. Energies of various geminal based methods are shown in Fig. 1 in STO-3G basis, together with Full Configuration Interaction (FCI), for comparison. Energy values for EHF and EAPSG were obtained by minimizing Eq.(15) and Eq.(23), with respect to parameters α, γ and δ, following a steepest descent algorithm.

The two sets of orbitals used for EHF and EAPSG in Fig. 1 are as follow. Orbitals denoted as 'symm' are symmetry adapted according to the D_{2h} (D_{4h} at square geometry) point group, and set both Eq.(15) and Eq.(23) stationary. Orbitals a_g and b_{1g} are assigned to one geminal, and b_{2u} and b_{3u} constitute the other geminal in D_{2h}. As checked by numerical means, bonding and antibonding orbitals of the two H_2 molecules, denoted as 'loc' also set both Eq.(15) and Eq.(23) stationary. When using localized orbitals, geminals are localized on the H_2 molecules as well.

Examining EHF in Fig. 1, the solution with symmetric orbitals remains below (or equal to) the curve with localized geminals, all along the potential curve. The two curves tend to the same value with increasing distance. Size inconsistency of EHF is already obvious at 3

Å . As EHF matches FCI for minimal basis H_2, the cca. 25 mE_h difference from FCI can be readily identified as size consistency error. It is interesting to observe, that the energy of the fully variational solution, 'EHF symm' improves with decreasing distance (the energy difference from FCI is only 0.100 mE_h at the square geometry). This is in accordance with the observation that EHF is the appropriate model of antiferromagnetic spin coupling.[49,63] The present 'EHF symm' solution at square geometry matches the EHF solution obtained for cyclobutadiene within a π-electron model.[36] This orbital set was reportedly reached by Mayer and Kertész starting from a UHF guess.

The energy curves of EAPSG show somewhat different characteristics. Whereas the delocalized solution runs only a few 0.1 mE_h below 'EHF symm' (at square geometry 'EAPSG symm' equals FCI), the curve with localized geminals drops below 'EAPSG sym' at large distances. The curve 'EAPSG loc' practically overlaps singlet coupled APSG and both tend to FCI in the large distance limit, reflecting size consistency.

Remarkably, while singlet coupled APSG and EHF perform well for only at one of the opposite extremes (antiferromagnetic coupling and weakly interacting geminals), EAPSG is successful for both. This however comes at the serious price of switching between fully variational solutions 'EAPSG symm' and 'EAPSG loc'. Stepping from one solution to the other leads to an incorrect shape of the potential curve and produces a discontinuity in the derivative, with unfavourable consequences in geometry optimization or property calculation. It remains to be checked whether there exists a further set of orbitals providing a solution that would interpolate smoothly between the strongly and weakly correlated regimes.

The case of four geminals

Finally, we investigate additivity over non-interacting two-geminal units in the example of the H_4 dimer. According to the previous section, EHF fails to be size consistent already for the H_2 dimer. For this reason only EAPSG is considered in this larger test case. The

RUSSG wave function is now constructed as the product of four geminals

$$|\Psi^{\mathrm{RUSSG}}_{(H_4)_2}\rangle \;=\; \prod_{I=1}^{4}\psi^{+}_{I}|\mathrm{vac}\rangle\ ,$$

where $I \in \{1,2\}$ ($I \in \{3,4\}$) constitute one (and the other) subsystem, each composed of two interacting geminals. Size consistency of the RUSSG method readily follows from the product separability of the above wavefunction. Stepping towards EAPSG, let us substitute Eq.(9) and perform spin projection, to obtain

$$\begin{aligned}\hat{P}^{s}|\Psi^{\mathrm{RUSSG}}_{(H_4)_2}\rangle = \Bigg[&\prod_{I=1}^{4}\cos(\delta_I)\mathcal{S}^{+}_{I}(\gamma_I)\ + \\ &+\left(\prod_{J=1}^{4}\sin(\delta_J)\right)\left(\frac{1}{3}\mathit{\Pi}^{+}_{12}\mathit{\Pi}^{+}_{34}+\frac{2}{3\sqrt{5}}\mathit{\Omega}^{+}_{1234}\right)\ + \\ &+\frac{1}{4}\sum_{P\in S_4}\frac{\cos(\delta_{P_1})\cos(\delta_{P_2})\sin(\delta_{P_3})\sin(\delta_{P_4})}{\sqrt{3}}\mathcal{S}^{+}_{P_1}(\gamma_{P_1})\,\mathcal{S}^{+}_{P_2}(\gamma_{P_2})\,\mathit{\Pi}^{+}_{P_3P_4}\Bigg]|\mathrm{vac}\rangle,\end{aligned} \tag{25}$$

where S_4 stands for the symmetric group of order four and $\mathit{\Omega}^{+}_{1234}$ creates a singlet coupled product of two quintet subunits according to

$$\begin{aligned}\mathit{\Omega}^{+}_{1234} \;=\; \sqrt{\frac{1}{5}}\Bigg(&{}_{+2}\mathcal{Q}^{+}_{12}\ {}_{-2}\mathcal{Q}^{+}_{34}\ -\ {}_{+1}\mathcal{Q}^{+}_{12}\ {}_{-1}\mathcal{Q}^{+}_{34}\ +\ {}_{0}\mathcal{Q}^{+}_{12}\ {}_{0}\mathcal{Q}^{+}_{34}\ - \\ &-\ {}_{-1}\mathcal{Q}^{+}_{12}\ {}_{+1}\mathcal{Q}^{+}_{34}\ +\ {}_{-2}\mathcal{Q}^{+}_{12}\ {}_{+2}\mathcal{Q}^{+}_{34}\Bigg)\ ,\end{aligned}$$

with

$${}_{0}\mathcal{Q}^{+}_{IJ} \;=\; \sqrt{\frac{1}{6}}\ {}_{+1}\mathcal{T}^{+}_{I}\ {}_{-1}\mathcal{T}^{+}_{J}\ +\ \sqrt{\frac{2}{3}}\ {}_{0}\mathcal{T}^{+}_{I}\ {}_{0}\mathcal{T}^{+}_{J}\ +\ \sqrt{\frac{1}{6}}\ {}_{-1}\mathcal{T}^{+}_{I}\ {}_{+1}\mathcal{T}^{+}_{J}.$$

Similarly to Eqs.(13) and (14), the $M_S \neq 0$ quintet operators (${}^{m}\mathcal{Q}^{+}$, $m = \pm1, \pm2$) are generated with operators $\hat{S}_{+}$ and $\hat{S}_{-}$, starting from ${}_{0}\mathcal{Q}^{+}_{IJ}$.

The Hamiltonian is additively separable as

$$\hat{H} \;=\; \hat{H}_{12} \,+\, \hat{H}_{34}\ ,$$

reflecting the non-interacting situation of two H_4 units, composed of ψ_1^+, ψ_2^+ and ψ_3^+, ψ_4^+, respectively. Let us assume for simplicity that the two H_4 systems are identical, which is reflected in the parameters as

$$\begin{aligned}\delta_1 &= \delta_3\ ,\\ \delta_2 &= \delta_4\ ,\\ \gamma_1 &= \gamma_3\ ,\\ \gamma_2 &= \gamma_4\ .\end{aligned}$$

By using the above, and assuming degeneracy of spin multiplets, the Rayleigh quotient can be expressed as

$$\begin{aligned} E^{\mathrm{EAPSG}}_{(H_4)_2} = & \frac{2}{\langle \Psi^{\mathrm{EAPSG}}_{(H_4)_2} | \Psi^{\mathrm{EAPSG}}_{(H_4)_2} \rangle} \Bigg[E^{\mathrm{EAPSG}}_{H_4} \;+\; \frac{4}{5} \sin^4\delta \langle {}_0Q_{12} | \hat{H}_{12} | {}_0Q_{12} \rangle \;+ \\ & +\; \cos^2\delta \left(\sin^2\delta + \frac{\cos^2\delta \tan^4\delta_2}{3} \right) \langle {}_0\mathcal{T}_2\, \mathcal{S}_1(\gamma_1) | \hat{H}_{12} | \mathcal{S}_1(\gamma_1)\, {}_0\mathcal{T}_2 \rangle \;+ \\ & + \sin^2\delta \left(\cos^2\delta + 3\sin^2\delta\, \mathrm{ctg}^4\,\delta_2 \right) \langle {}_0\mathcal{T}_1\, \mathcal{S}_2(\gamma_2) | \hat{H}_{12} | \mathcal{S}_2(\gamma_2)\, {}_0\mathcal{T}_1 \rangle \;+ \\ & +\; \sin(2\delta) \left(\sqrt{3} \sin^2\delta\, \mathrm{ctg}^2\,\delta_2 + \frac{\cos^2\delta \tan^2\delta_2}{\sqrt{3}} \right) \langle {}_0\mathcal{T}_2\, \mathcal{S}_1(\gamma_1) | \hat{H}_{12} | \mathcal{S}_2(\gamma_2)\, {}_0\mathcal{T}_1 \rangle \Bigg]\ . \end{aligned} \tag{26}$$

Minimization of the expression above with respect to parameters $\delta, \delta_2, \gamma_1, \gamma_2$ yields the EAPSG energy. Note, that δ_1 is eliminated by introducing δ via Eqs.(20) and (21), to facilitate comparison with H_4. As Eq.(26) shows, the EAPSG energy is composed of the energies of the monomers, $2\,E^{\mathrm{EAPSG}}_{H_4}$ plus the remaining terms in square bracket, inducing size inconsistency. Size consistency violation of EAPSG is analogous to EHF in many respects, e.g. size inconsistency stems from non-singlet components of the monomer wavefunction.

(Note, that $(H_4)_2$ is spin pure but the individual H_4 units are not.) The energy of the dimer is expected to be higher than that of two monomers, in cases where EAPSG is a reasonable approximation to the monomer ground state. This follows from the fact, that consistency violating terms are contributions from exact states, high above the ground state. In general, size consistency violation of EAPSG is nonzero. Size consistency is recovered for $\sin\delta_1 = \sin\delta_2 = 0$ (consequently $\sin\delta = 0$). Geminals lack any triplet contribution (c.f. Eqs.(9) and (22)) in this case, consistency violating term consequently disappear from the square bracket of Eq.(26) and the norm $\langle\Psi^{\mathrm{EAPSG}}_{(H_4)_2}|\Psi^{\mathrm{EAPSG}}_{(H_4)_2}\rangle$ becomes unity. Such a situation is produced e.g. if breaking further down the H_4 subunits to non-interacting H_2 systems.

Numerical evaluation of size inconsistency is performed with the same monomer geometry as described in the previous section. According to Fig. 1, the EAPSG solution labeled 'EAPSG loc' essentially agrees with singlet-coupled APSG, indicating a marginal role of the triplet component of geminals. Size inconsistency is correspondingly surely negligible for 'EAPSG loc', it occurs only with 'EAPSG symm'. For this reason the numerical evaluation focuses on the $[1.4, 1.7]$ Å $H_2{-}H_2$ distance interval.

Geminal parameters optimized for the monomer (c.f. Eq.(23)) and the dimer (c.f. Eq.(26)) are collected in Table 1. The latter parameter set was obtained by minimization over a numerical grid. Inspecting parameter δ, one finds that δ of the dimer is about half of the δ of the monomer, in absolute value. Weight of triplet geminal components is accordingly reduced in the dimer. Change in γ_1 and γ_2 is less significant. Parameter δ getting closer to zero in the dimer has a direct size inconsistency reducing effect (c.f. Eq.(26)). However, neither δ nor δ_2 become exactly zero upon optimization, yielding a nonzero size consistency error. As the last column of Table 1 reflects, size inconsistency is substantial, amounting to a couple of percents of the total energy. Comparison with Fig. 1 reveals, that size inconsistency swaps the order of 'EAPSG loc' and 'EAPSG symm' in the $[1.4, 1.7]$ Å $H_2{-}H_2$ distance interval for the dimer. The energy of $(H_4)_2$ with symmetry adapted orbitals is higher than twice the 'EAPSG loc' energy of H_4. An artifactual consequence is, that the ground state EAPSG solution differs qualitatively for H_4 and the non-interacting dimer.

Apart from energies, monomer spin is also reported in the Table. As expected, size inconsistency is accompanied by a nonzero spin quantum number of the H_4 subunits in the dimer calculation. Interestingly, the slight shoulder discernible on the dimer energy curve at around 1.5 Å is missing from the monomer spin values.

Conclusions

A comparative presentation of UHF and (two orbital per geminal) RUSSG reveals that the latter is an extension of the former, both belonging to the strongly orthogonal geminal wavefunction category. While UHF describes the correlation of two electrons at the price of spoiling spin, RUSSG is flexible enough to incorporate correlation in a spin pure manner for two electrons. Spin contamination appears at a higher level of complexity in RUSSG. It is inter-geminal correlation that is described by RUSSG at the price of spoiling total spin, analogously to UHF. In general both UHF and RUSSG exhibit critical points of the Coulson-Fischer type on the potential surface, where the spin contaminated solution deviates from the corresponding restricted curve.

Spin projection followed by variation removes critical points of UHF, but induces size inconsistency. The same holds for the spin projected, extended version of singlet coupled strongly orthogonal geminals, termed EAPSG. Here again, the problem appears at a higher level of complexity. While EHF is not size consistent for a four-electron system, EAPSG is yet size consistent. Size inconsistency of EAPSG is shown to appear in a four-geminal (eight-electron) test case. Numerical assessment reveals a substantial consistency error of EAPSG, on the order of a couple of percent of the total energy. For both EHF and EAPSG, size inconsistency stems from higher than singlet components of the non-interacting fragments. While these components can play an important role in the interacting region, they correspond to highly excited exact solutions in the non-interacting limit. Parametrization of EHF and

EAPSG is however is not flexible enough to allow for the gradual decrease of these terms when decomposing the total system into two independent subsystems. We note, without detailed derivation that EAPSG still fulfills size consistency on a three geminal system. The reason behind is that the spin coupling pattern of triplet geminals to overall singlet are similar to the two-geminal case (triplets coupled to quadruples have no contribution).

A remarkable feature of EAPSG is its ability to interpolate between strongly correlated (antiferromagnetic) and weakly correlated geminal regimes of a two-geminal model system. The character of EAPSG orbitals reported here changes sharply in the switching region. Natural orbitals are found delocalized for the antiferromagnet but localized on the geminals as the interaction becomes weaker. Both orbital sets represent a solution to the EAPSG equations all along the process. Unless a further set of orbitals corresponding to a lower lying minimum exists, EAPSG implies a switch from one solution to the other. In the latter case averaging the two solutions[29] may be a simple to way to avoid discontinuous derivatives or ill-behaving energy correction schemes.

Extension of the flexibility of the geminal Ansatz, e.g. by lifting strong orthogonality[64–67] or breaking further symmetries[68] may alleviate the problems presented here. Based on the current study, EAPSG appropriately describes breaking or rearrangement of two geminals. It is definitely not recommended for four or more strongly interacting bonds, if size consistency is of interest.

Acknowledgement

The authors are indebted to István Mayer (Budapest, Hungary) for numerous instructive interaction on the subject of EHF. The FCI results were computed with a code implemented by Zoltán Rolik (Budapest).

Notes and References

(1) Werner, H.-J. *Matrix-Formulated Direct Multiconfiguration Self-Consistent Field and Multiconfiguration Reference Configuration-Interaction Methods*; Advances in Chemical Physics; John Wiley & Sons: New York, 1987; Vol. 69; pp 1–62.

(2) Szalay, P. G.; Müller, T.; Gidofalvi, G.; Lischka, H.; Shepard, R. *Chem. Rev.* **2012**, *112*, 108–181.

(3) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157 – 173.

(4) Roos, B. O. *The Complete Active Space Self-Consistent Field Method and its Applications in Electronic Structure Calculations*; Advances in Chemical Physics; John Wiley & Sons: New York, 1987; Vol. 69; pp 399–445.

(5) Kurashige, Y.; Chan, G. K.-L.; Yanai, T. *Nat. Chem.* **2013**, *5*, 660–666.

(6) Sharma, S.; Sivalingam, K.; Neese, F.; Chan, G. K.-L. *Nat. Chem.* **2014**, *6*, 927–933.

(7) Thomas, R. E.; Booth, G. H.; Alavi, A. *Phys. Rev. Lett.* **2015**, *114*, 033001.

(8) Klahm, S.; Lüchow, A. *Chem. Phys. Lett.* **2014**, *600*, 7 – 9.

(9) Pulay, P. *Int. J. Quantum Chem.* **2011**, *111*, 3273–3279.

(10) Walch, S. P.; Jr., C. W. B.; Roos, B. O.; Nelin, C. J. *Chem. Phys. Lett.* **1983**, *103*, 175 – 179.

(11) Olsen, J.; Roos, B. O.; Jørgensen, P.; Jensen, H. J. A. *J. Chem. Phys.* **1988**, *89*, 2185–2192.

(12) Ma, D.; Li Manni, G.; Gagliardi, L. *J. Chem. Phys.* **2011**, *135*, 044128.

(13) Surján, P. R. *Top. Curr. Chem.* **1999**, *203*, 63–88.

(14) Arai, T. *J. Chem. Phys.* **1960**, *33*, 95.

(15) Bobrowicz, F. W.; Goddard-III, W. A. In *Methods of Electronic Structure Theory*; Schaefer-III, H. F., Ed.; Plenum: New York, 1977; p 79.

(16) Voorhis, T. V.; Head-Gordon, M. *J. Chem. Phys.* **2001**, *115*, 7814–7821.

(17) Rassolov, V. A. *J. Chem. Phys.* **2002**, *117*, 5978.

(18) Hurley, A. C.; Lennard-Jones, J.; Pople, J. A. *Proc. Roy. Soc. (London)* **1953**, *220*, 446.

(19) Parks, J. M.; Parr, R. G. *J. Chem. Phys.* **1957**, *28*, 335.

(20) Beran, G. J. O.; Austin, B.; Sodt, A.; Head-Gordon, M. *J. Phys. Chem. A* **2005**, *109*, 9183–9192.

(21) Rassolov, V. A.; Xu, F. *J. Chem. Phys.* **2007**, *126*, 234112.

(22) Lawler, K. V.; Small, D. W.; Head-Gordon, M. *J. Phys. Chem. A* **2010**, *114*, 2930–2938.

(23) Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1993**, *115*, 10938–10942.

(24) Li, S.; Ma, J.; Jiang, Y. *J. Chem. Phys.* **2003**, *118*, 5736–5745.

(25) Xu, E.; Li, S. *J. Chem. Phys.* **2013**, *139*, 174111.

(26) Rassolov, V. A.; Xu, F. *J. Chem. Phys.* **2007**, *127*, 044104.

(27) Jeszenszki, P.; Rassolov, V.; Surján, P. R.; Szabados, Á. *Mol. Phys.* **2015**, *113*, 249–259.

(28) Ramos-Cordoba, E.; Salvador, P.; Piris, M.; Matito, E. *J. Chem. Phys.* **2014**, *141*, 234101.

(29) Pulay, P.; Hamilton, T. P. *J. Chem. Phys.* **1988**, *88*, 4926–4933.

(30) Yamaguchi, K.; Ohta, K.; Yabushita, S.; Fueno, T. *Chem. Phys. Lett.* **1977**, *49*, 555 – 559.

(31) Löwdin, P.-O. *Phys. Rev.* **1955**, *97*, 1509–1520.

(32) Mayer, I. In *The Spin-Projected Extended Hartree-Fock Method*; Löwdin, P.-O., Ed.; Advances in Quantum Chemistry; Academic Press, 1980; Vol. 12; pp 189 – 262.

(33) Jiménez-Hoyos, C. A.; Henderson, T. M.; Tsuchimochi, T.; Scuseria, G. E. *J. Chem. Phys.* **2012**, *136*, 164109.

(34) Mak, A. M.; Lawler, K. V.; Head-Gordon, M. *Chem. Phys. Lett.* **2011**, *515*, 173 – 178.

(35) Kitagawa, Y.; Saito, T.; Ito, M.; Shoji, M.; Koizumi, K.; Yamanaka, S.; Kawakami, T.; Okumura, M.; Yamaguchi, K. *Chem. Phys. Lett.* **2007**, *442*, 445 – 450.

(36) Mayer, I.; Kertész, M. *Int. J. Quantum Chem.* **1976**, *10*, 961–966.

(37) Castano, O.; Karadakov, P. *Chem. Phys. Lett.* **1986**, *130*, 123 – 126.

(38) Henderson, T. M.; Scuseria, G. E. *J. Chem. Phys.* **2013**, *139*, 234113.

(39) Karadakov, P. *Int. J. Quantum Chem.* **1985**, *27*, 699–707.

(40) Löwdin, P.-O. *J. Appl. Phys.* **1962**, *33*, 251–280

(41) Amos, A. T.; Hall, G. G. *Proc. Roy. Soc. (London)* **1961**, *263*, 483.

(42) Mayer, I. *Mol. Phys.* **2010**, *108*, 3273–3278.

(43) Small, D. W.; Head-Gordon, M. *J. Chem. Phys.* **2009**, *130*, 084103.

(44) Small, D. W.; Head-Gordon, M. *J. Chem. Phys.* **2012**, *137*, 114103.

(45) Small, D. W.; Lawler, K. V.; Head-Gordon, M. *J. Chem. Theory Comput.* **2014**, *10*, 2027.

(46) Zoboki, T.; Szabados, Á.; Surján, P. R. *J. Chem. Theory Comput.* **2013**, *9*, 2602.

(47) Surján, P. R.; Jeszenszki, P.; Szabados, Á. *submitted to Mol. Phys.* **2015**

(48) Mayer, I. *Simple Theorems, Proofs, and Derivations in Quantum Chemistry*; Kluwer Academic/Plenum Publisher, 2003.

(49) Ellis, J. K.; Martin, R. L.; Scuseria, G. E. *J. Chem. Theory Comput.* **2013**, *9*, 2857–2869.

(50) Small, D. W.; Sundstrom, E. J.; Head-Gordon, M. *J. Chem. Phys.* **2015**, *142*, 024104.

(51) Pauncz, R. In *Fundamental World of Quantum Chemistry*; Brändas, E., Kryachko, E. K., Eds.; Kluwer Academic Publisher, 2003; Vol. 1; Chapter Different Orbitals for Different Spins, Löwdin's Idea, pp 155–182.

(52) Pauncz, R. *Int. J. Quantum Chem.* **1992**, *44*, 161–169.

(53) Harriman, J. E. *J. Chem. Phys.* **1964**, *40*, 2827–2839.

(54) To be precise, the RUSSG geminal is more general than Eq.(9), by allowing for any number of orbitals per geminal. The two orbitals per geminal version of RUSSG is equivalent to UAP. As the number of orbitals per geminal is restricted to two in this study, we refer to the two orbitals per geminal variant of RUSSG shortly as RUSSG.

(55) Mayer, I. *Int. J. Quantum Chem.* **1986**, *29*, 31–34.

(56) Coulson, P. C.; Fischer, M. I. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1949**, *40*, 386–393.

(57) Mayer, I. *Acta Phys. Hung.* **1983**, *54*, 249.

(58) Serber, R. *J. Chem. Phys.* **1934**, *2*, 697–710.

(59) Pauncz, R. *Spin Eigenfunctions*; Plenum Press: New York, 1979.

(60) Löwdin, P. O. *Phys. Rev.* **1955**, *97*, 1509.

(61) Mayer, I. *Int. J. Quantum Chem.* **1978**, *14*, 29–38.

(62) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *10*, 1–19.

(63) Angelov, S.; Mayer, I. *Acta Phys. Hung.* **1985**, *58*, 161–167.

(64) Cassam-Chenai, P.; Rassolov, V. *Chem. Phys. Lett.* **2010**, *487*, 147 – 152.

(65) Johnson, P. A.; Ayers, P. W.; Limacher, P. A.; Baerdemacker, S. D.; Neck, D. V.; Bultinck, P. *Comput. Theor. Chem.* **2013**, *1003*, 101 – 113.

(66) Limacher, P. A.; Ayers, P. W.; Johnson, P. A.; De Baerdemacker, S.; Van Neck, D.; Bultinck, P. *J. Chem. Phys.* **2013**, *9*, 1394–1401.

(67) Cagg, B. A.; Rassolov, V. A. *J. Chem. Phys.* **2014**, *141*, 164112.

(68) Scuseria, G. E.; Jiménez-Hoyos, C. A.; Henderson, T. M.; Samanta, K.; Ellis, J. K. *J. Chem. Phys.* **2011**, *135*, 124108.

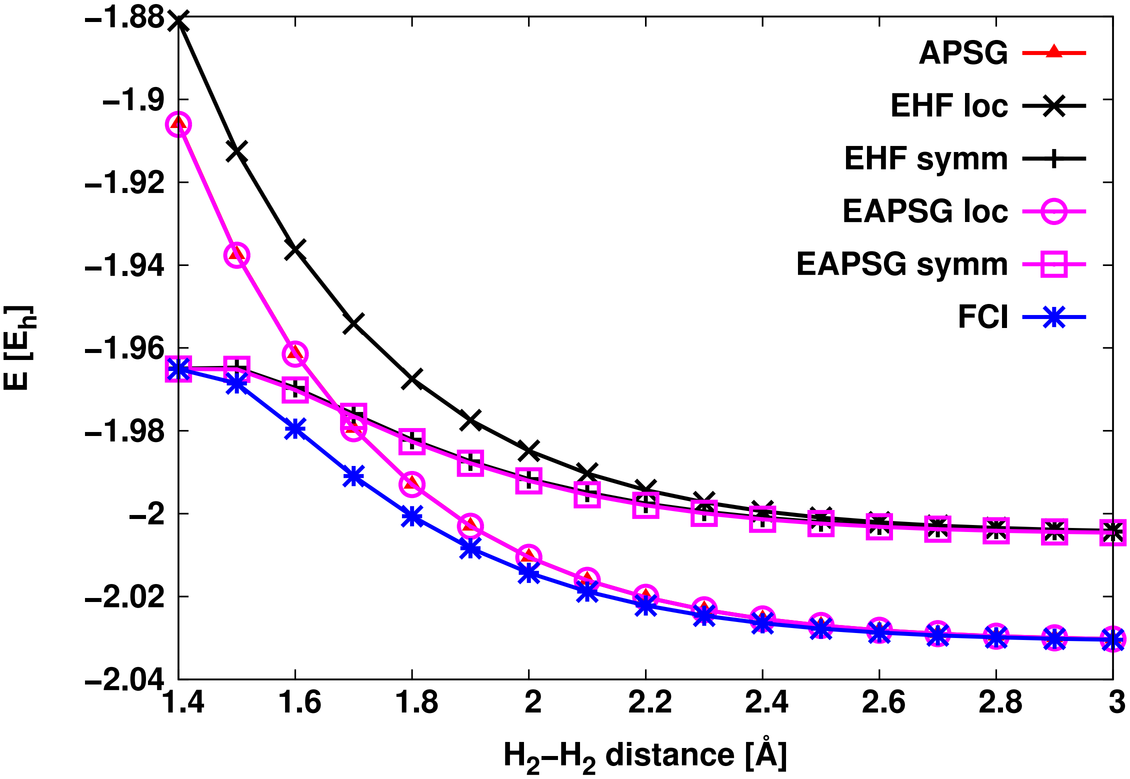

Figure 1: Total energy of two H_2 molecules oriented in parallel, in STO-3G basis, as a function of the distance between the H_2 units. Spin projected, extended HF (EHF), singlet coupled strongly orthogonal geminals (APSG) and spin projected, extended version of the latter (EAPSG) are compared. The H−H bond length is fixed at 1.4 Å . Key legend 'symm' refers to orbitals, symmetry adapted according to the D_{2h} (D_{4h} at 1.4 Å) point group. See text for assignation of orbitals to geminals. Legend 'loc' stands for orbitals localized on the H_2 molecules.

Table 1: Geminal parameters, fragment spin and total energy in STO-3G basis obtained by EAPSG with symmetry adapted orbitals. Independent H_4 calculation is compared to $(H_4)_2$, composed of non-interacting H_4 fragments. Size consistency error is tabulated in the last column. See Fig. 1 for the geometry of H_4. In the Table, 'dist' stands for the H_2-H_2 distance.

dist		δ	δ_2	γ_1	γ_2	$\langle\hat{S}^2\rangle_{H_4}$	E_{EAPSG} / E_h	$(E_{(H_4)_2} - 2E_{H_4})$ / mE_h
1.4	2 H_4	-0.3182	–	0.1535	0.7813	0	-3.930152	148.00
	$(H_4)_2$	-0.1282	0.5199	0.1011	0.7813	0.1394	-3.782148	
1.5	2 H_4	-0.3256	–	0.1665	0.9257	0	-3.930332	150.94
	$(H_4)_2$	-0.1292	0.5132	0.1093	0.9813	0.1379	-3.779397	
1.6	2 H_4	-0.3251	–	0.1765	1.0258	0	-3.940264	147.15
	$(H_4)_2$	-0.1252	0.4960	0.1162	1.1101	0.1264	-3.793110	
1.7	2 H_4	-0.3217	–	0.1850	1.0964	0	-3.952988	130.02
	$(H_4)_2$	-0.1202	0.4778	0.1222	1.1910	0.1145	-3.822974	