Spin Symmetry and Size Consistency of Strongly Orthogonal Geminals

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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 are presented for both models. Numerical evaluation of EHF and EAPSG is performed for small test systems (H_4 and H_8).

$$\psi^{I+} = \sum_{\mu\nu} c_{\mu\nu}\, \varphi^+_{\mu\alpha}\, \varphi^+_{\nu\beta}, \quad c_{\mu\nu} \neq c^*_{\nu\mu}$$

$$\Psi = P^s \left(\prod_I \psi^{I+} \right) |vac\rangle$$

$$E^{EAPSG} = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \min.$$

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] and complete active space (CAS) SCF in particular, is a common choice for these systems, thanks to the favorable properties of orbital invariance within the active space, spin pure nature, and computationally manageable optimization equations.[3,4] Though recent years have seen tremendous advances 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 dynamic correlation piece 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 that is 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 the orbital occupancy in each partition.[10−12] Alternatively, optimizable parameters can be assigned to only two-electron functions (c.f., geminals) with the total wavefunction being constructed as an antisymmetric product.[13] Requiring geminals ψ_i and ψ_j and $i \neq j$ to fulfill the strong orthogonality condition

$$\int \psi_i(\mathbf{x}_1, \mathbf{x}_2)\psi_j(\mathbf{x}_1, \mathbf{x}_2)\, d\mathbf{x}_1 = 0 \tag{1}$$

the 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 that ensures polynomial scaling with system size. The well-known generalized valence bond function[15] represents a special case in which the active orbitals per geminal is restricted to two.

Strongly orthogonal geminals have been cultivated under various names in the literature. For emphasizing the fixed assignation of electrons to pairs, the 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. The singlet state of the geminals is supposed in SSG, whereas 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 the theory, it becomes important however if one wishes 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] Although DODS geminal schemes cure fragment spin upon dissociation,[27] the spin of the fragments are not properly coupled. Contamination of total spin is consequently produced, analogous to 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 1970s[32] and has recently been revitalized.[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; however, it 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 overview 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 in this small model based on numerical calculations. Size consistency violation is finally evaluated for a four-geminal model system.

In the course of the derivation, we shall make use of an extended pairing theorem, first formulated and proven 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 occupied β, and vice versa (with the value of the overlap integral being distinctly related to that of the corresponding occupied orbitals).

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 intrageminal 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, with N_g representing the number of geminals, and two orbitals 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] as discussed below.

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 of spin purification and its consequences.

Unrestricted HF (UHF). Let us start with the UHF wavefunction

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

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] then

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

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. On the basis of Arai's theorem,[14] it follows that Ψ^{UHF} is an example for a strongly orthogonal geminal wavefunction.[49,50]

Let us now invoke the alternating molecular orbital (AMO)[51] parametrization of the orbitals according to

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

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

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

with the geminal coefficient matrix

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

Above and later, 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

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

It follows that the density matrix of the total UHF wavefunction, obtained as the direct sum of geminal density matrices $\mathbf{D}_I^{UHF}$, 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]

Although the natural orbital expansion (eq 5) includes more terms than the DODS form (eq 2), it allows for the association of the singlet and triplet components of $\tilde{\psi}$ with the symmetric ($^sC^{UHF}$) and antisymmetric part of the geminal coefficient matrix. The former defines the singlet two-particle creation operator

$$\tilde{S}^+(\alpha) = \sum_{i,j=1}^{2} {}^sC_{ij}^{UHF} \varphi_{i\alpha}^+ \varphi_{j\beta}^+$$
$$= \cos^2 \alpha \, \varphi_{1\alpha}^+ \varphi_{1\beta}^+ \; - \; \sin^2 \alpha \, \varphi_{2\alpha}^+ \varphi_{2\beta}^+$$

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

$$^0\mathcal{T}^+ = \frac{1}{\sqrt{2}} (\varphi_{1\alpha}^+ \varphi_{2\beta}^+ \; - \; \varphi_{2\alpha}^+ \varphi_{1\beta}^+)$$

allowing for the UHF geminal to be written as

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

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, $\tilde{S}$ 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 this from another angle, one sees that UHF occupancies of natural orbitals φ_i (c.f., eq 6) cannot 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

$$|\Psi^{RUSSG}\rangle = \prod_I \psi_I^+|vac\rangle \qquad (8)$$

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

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

where the singlet component is expressed as

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

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), and γ independently governs the multireference character of the singlet part.[54]

The coefficient matrix behind the RUSSG geminal (eq 9) reads

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

yielding the density matrix

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

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}. The 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 as

$$\psi^+ = \cos \epsilon \; \phi_{1\alpha}^+ \chi_{1\beta}^+ + \sin \epsilon \; \phi_{2\alpha}^+ \chi_{2\beta}^+ \qquad (10)$$

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 pseudonatural 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. The relationship between pseudonatural and natural orbitals is expressed as

$$\begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = \begin{pmatrix} \cos \alpha & \sin \alpha \\ \sin \alpha & -\cos \alpha \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix} \qquad (11)$$

$$\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = \begin{pmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix} \qquad (12)$$

with $\alpha = -\arctan(\sqrt{2} \tan \delta/(\cos \gamma - \sin \gamma))/2$, and $\cos(2\epsilon) = \cos^2 \delta \cos(2\gamma)/\cos(2\alpha)$. Hence, the pure singlet belongs to $\alpha = \delta = 0$ (lack of $\alpha - \beta$ 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 because $n_2 = \sin^2 \epsilon = 0$ 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 perspective, RUSSG represents a generalization of UHF where virtual orbitals, paired to the occupied orbitals 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 approximately equilibrium geometries where restricted HF is acceptable (c.f., $\alpha \approx 0$ in UHF, whereas $\gamma \approx 0$ and $\delta \approx 0$ in RUSSG). Energy differences also disappear in the limit of breaking a single bond. As the lowest singlet and triplet solutions become degenerate in this process, an admixture of a triplet component to the ground state singlet cannot deteriorate the UHF energy. The situation is different for intermediate distances. As RUSSG involves an extra variational parameter per geminal, it may provide 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 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

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

where 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. Because of 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 of whether parameters are optimized before or after. Starting from UHF, both approaches have been studied. Spin projection after variation is comparatively easy but may lead to an 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 recently been 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 the 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" as a direct analogy to EHF. For clarity, the formal definition of the EAPSG energy is given as

$$E^{EAPSG} = \frac{\langle \Psi^{RUSSG} | \hat{P}^s \hat{H} \hat{P}^s | \Psi^{RUSSG} \rangle}{\langle \Psi^{RUSSG} | \hat{P}^s | \Psi^{RUSSG} \rangle} = \min$$

with minimization performed for natural orbitals φ_i^I and parameters δ^I, γ^I. The spin projected function $\hat{P}^s \Psi^{RUSSG}$ 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. Below, we study size consistency in Pople's sense (i.e., additivity of energy over non-interacting fragments).[62] The two spin-projected, extended geminal methods EHF and EAPSG are analyzed in parallel. This helps to reveal the points of analogies and deviations in their behavior. 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 analytic derivation of energy formulas. 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

$$|\Psi_{H_4}^{UHF}\rangle = \tilde{\psi}_1^+ \tilde{\psi}_2^+ |vac\rangle$$

with $\tilde{\psi}_1$ and $\tilde{\psi}_2$ referring to each of the H_2 units. 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. For $S = 0$, this results in

$$\hat{P}^s |\Psi_{H_4}^{UHF}\rangle = \left(\tilde{\mathcal{S}}_1^+(\alpha_1) \tilde{\mathcal{S}}_2^+(\alpha_2) + \frac{\sin(2\alpha_1) \sin(2\alpha_2)}{2\sqrt{3}} \Pi_{12}^+ \right) |vac\rangle$$

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

$$_{+1}\mathcal{T}_I^+ = \frac{1}{\sqrt{2}} \hat{S}_+ \, {}_0\mathcal{T}_I^+ = \varphi_{1\alpha}^{I+} \varphi_{2\alpha}^{I+} \tag{13}$$

$$_{-1}\mathcal{T}_I^+ = \frac{1}{\sqrt{2}} \hat{S}_- \, {}_0\mathcal{T}_I^+ = \varphi_{1\beta}^{I+} \varphi_{2\beta}^{I+} \tag{14}$$

The EHF energy is obtained from the condition

$$E_{H_4}^{EHF} = \frac{\langle \Psi_{H_4}^{UHF} | \hat{P}^s \hat{H} \hat{P}^s | \Psi_{H_4}^{UHF} \rangle}{\langle \Psi_{H_4}^{UHF} | \hat{P}^s | \Psi_{H_4}^{UHF} \rangle} = \min \tag{15}$$

Let us now assume 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

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

making use of the degeneracy of spin multiplets, and assuming the natural orbitals are 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 because calculating the H_2 molecules independently, again with $S = 0$, one obtains

$$\hat{P}^s |\Psi_{H_2}^{UHF}\rangle = \tilde{\mathcal{S}}_1^+(\alpha_1) |vac\rangle$$

yielding the following EHF energy for the H_2 unit

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

Comparison of eqs 17 and 18 clearly shows that the monomer triplet contribution to $E_{H_4}^{EHF}$ spoils the size consistency. The error disappears as $\alpha_I \rightarrow 0$ because the triplet component of geminals falls off, and the singlet component falls back to RHF. The error also vanishes at the other extreme in the dissociation limit of H_2 subunits because singlet and triplet geminal states become degenerate; therefore, spin contamination cannot 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 eq 17 necessarily lift the energy of the non-interacting dimer to over twice the energy of the monomer.

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

$$|\Psi_{H_4}^{SP\text{-}RUSSG}\rangle = \hat{P}^s \psi_1^+ \psi_2^+ |vac\rangle = \left[\cos\delta_1 \cos\delta_2 \, \mathcal{S}_1^+(\gamma_1)\mathcal{S}_2^+(\gamma_2) \right.$$
$$\left. + \frac{\sin\delta_1 \sin\delta_2}{\sqrt{3}} \Pi_{12}^+ \right] |vac\rangle \tag{19}$$

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 Π_{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

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

Condition

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

results in the EAPSG energy.

Again assuming additive separability of $\hat{H}$ according to eq 16, identical H_2 units, and localized natural orbitals, the energy expression simplifies to

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

Variational optimization of eq 24 results in $\delta = 0$; hence, twice the energy obtained for the H_2 unit based on

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

and

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

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 in 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 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 Figure 1 in STO-3G basis, together with full configuration interaction (FCI) for comparison. Energy values for EHF and EAPSG were obtained by minimizing eqs 15 and 23 with respect to parameters α, γ, and δ, following a steepest descent algorithm.
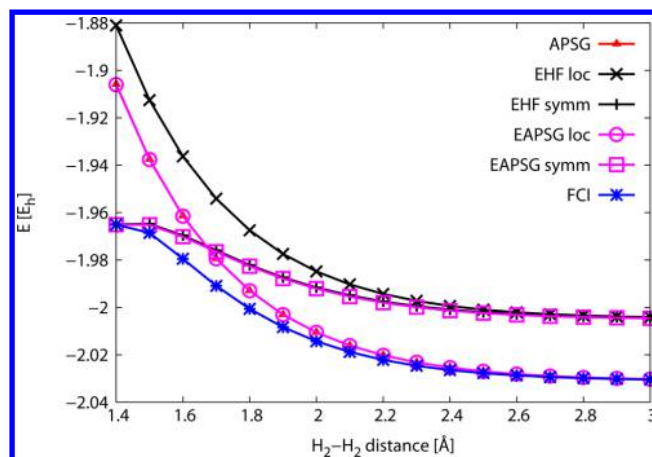

Figure 1. Total energy of two H_2 molecules oriented in parallel, in STO-3G basis, as a function of the distance between the H_2 units. Spin-projected, extended HF (EHF), singlet-coupled strongly orthogonal geminals (APSG), and a spin-projected, extended version of the latter (EAPSG) are compared. The 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.

The two sets of orbitals used for EHF and EAPSG in Figure 1 are as follows. Orbitals denoted as "symm" are symmetry adapted according to the D_{2h} (D_{4h} at square geometry) point group and set both eqs 15 and 23 as 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 eqs 15 and 23 as stationary. When using localized orbitals, geminals are localized on the H_2 molecules as well.

Examination of the EHF in Figure 1 shows that 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 ∼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 tenths of 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, whereas singlet-coupled APSG and EHF perform well only at one of the opposite extremes (antiferromagnetic coupling and weakly interacting geminals),

Table 1. Geminal Parameters, Fragment Spin, and Total Energy in STO-3G Basis Obtained by EAPSG with Symmetry Adapted Orbitals[a]

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	$2H_4$	−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	$2H_4$	−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	$2H_4$	−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	$2H_4$	−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	

[a]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 Figure 1 for the geometry of H_4. In the table, "dist" stands for the H_2–H_2 distance.

EAPSG is successful at both. This comes at the serious price of switching between fully variational solutions "EAPSG symm" and "EAPSG loc" however. Stepping from one solution to the other leads to an incorrect shape of the potential curve and produces a discontinuity in the derivative with unfavorable consequences in geometry optimization and property calculations. 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 already fails to be size consistent for the H_2 dimer. For this reason, only EAPSG is considered in this larger test case. The RUSSG wavefunction is now constructed as the product of four geminals

$$|\Psi_{(H_4)_2}^{RUSSG}\rangle = \prod_{I=1}^{4} \psi_I^+ |vac\rangle$$

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 toward EAPSG, we substitute eq 9 and perform spin projection to obtain

$$\hat{P}^s |\Psi_{(H_4)_2}^{RUSSG}\rangle = \left[\prod_{I=1}^{4} \cos(\delta_I) \mathcal{S}_I^+(\gamma_I) \right.$$
$$+ \left(\prod_{J=1}^{4} \sin(\delta_J) \right) \left(\frac{1}{3} \Pi_{12}^+ \Pi_{34}^+ + \frac{2}{3\sqrt{5}} \Omega_{1234}^+ \right)$$
$$+ \frac{1}{4} \sum_{P \in S_4} \frac{\cos(\delta_{P_1}) \cos(\delta_{P_2}) \sin(\delta_{P_3}) \sin(\delta_{P_4})}{\sqrt{3}} \mathcal{S}_{P_1}^+(\gamma_{P_1})$$
$$\left. \times \mathcal{S}_{P_2}^+(\gamma_{P_2}) \Pi_{P_3 P_4}^+ \right] |vac\rangle \tag{25}$$

where S_4 stands for the symmetric group of order four and Ω_{1234}^+ creates a singlet-coupled product of two quintet subunits according to

$$\Omega_{1234}^+ = \sqrt{\frac{1}{5}} \left({}_{+2}Q_{12}^+ {}_{-2}Q_{34}^+ - {}_{+1}Q_{12}^+ {}_{-1}Q_{34}^+ + {}_0Q_{12}^+ {}_0Q_{34}^+ \right.$$
$$\left. - {}_{-1}Q_{12}^+ {}_{+1}Q_{34}^+ + {}_{-2}Q_{12}^+ {}_{+2}Q_{34}^+ \right)$$

with

$${}_0Q_{IJ}^+ = \sqrt{\frac{1}{6}} \, {}_{+1}\mathcal{T}_I^+ \, {}_{-1}\mathcal{T}_J^+ + \sqrt{\frac{2}{3}} \, {}_0\mathcal{T}_I^+ \, {}_0\mathcal{T}_J^+ + \sqrt{\frac{1}{6}} \, {}_{-1}\mathcal{T}_I^+ \, {}_{+1}\mathcal{T}_J^+$$

Similarly to eqs 13 and 14, the $M_S \neq 0$ quintet operators (${}^mQ^+$, $m = \pm 1, \pm 2$) are generated with operators $\hat{S}_+$ and $\hat{S}_-$, starting from ${}_0Q_{IJ}^+$.

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^+. Let us assume for simplicity that the two H_4 systems are identical, which is reflected in the parameters as

$$\delta_1 = \delta_3, \quad \delta_2 = \delta_4, \quad \gamma_1 = \gamma_3, \quad \text{and} \quad \gamma_2 = \gamma_4.$$

Using the above eqs, and assuming degeneracy of spin multiplets, the Rayleigh quotient can be expressed as

$$E_{(H_4)_2}^{EAPSG} = \frac{2}{\langle \Psi_{(H_4)_2}^{EAPSG} | \Psi_{(H_4)_2}^{EAPSG} \rangle} \left[E_{H_4}^{EAPSG} + \frac{4}{5} \sin^4 \delta \langle {}_0Q_{12} | \hat{H}_{12} | {}_0Q_{12} \rangle \right.$$
$$+ \cos^2 \delta \left(\sin^2 \delta + \frac{\cos^2 \delta \tan^4 \delta_2}{3} \right) \langle {}_0\mathcal{T}_2 \, \mathcal{S}_1(\gamma_1) | \hat{H}_{12} | \mathcal{S}_1(\gamma_1) \, {}_0\mathcal{T}_2 \rangle$$
$$+ \sin^2 \delta (\cos^2 \delta + 3 \sin^2 \delta \, ctg^4 \delta_2) \langle {}_0\mathcal{T}_1 \, \mathcal{S}_2(\gamma_2) | \hat{H}_{12} | \mathcal{S}_2(\gamma_2) \, {}_0\mathcal{T}_1 \rangle$$
$$+ \sin(2\delta) \left(\sqrt{3} \sin^2 \delta \, ctg^2 \delta_2 + \frac{\cos^2 \delta \tan^2 \delta_2}{\sqrt{3}} \right)$$
$$\left. \times \langle {}_0\mathcal{T}_2 \, \mathcal{S}_1(\gamma_1) | \hat{H}_{12} | \mathcal{S}_2(\gamma_2) \, {}_0\mathcal{T}_1 \rangle \right] \tag{26}$$

Minimization of the expression listed above with respect to parameters δ, δ_2, γ_1, γ_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 shown in eq 26, the EAPSG energy is composed of the energies of the monomers, $2\,E_{H_4}^{EAPSG}$, plus the remaining terms in the square bracket, inducing size inconsistency. Size consistency violation of EAPSG is analogous to EHF in many respects (e.g., size inconsistency stems from nonsinglet 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 the 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; the consistency violating terms consequently disappear from the square bracket of eq 26, and the norm $\langle \Psi_{(H_4)_2}^{EAPSG} | \Psi_{(H_4)_2}^{EAPSG} \rangle$ becomes unity. Such a situation is produced, for example, if breaking down the H_4 subunits further 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 Figure 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 approximately half the δ of the monomer in absolute value. Weight of triplet geminal components is accordingly reduced in the dimer. Changes to γ_1 and γ_2 are 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 reflected in the last column of Table 1, size inconsistency is substantial, amounting to a couple percent of the total energy. Comparison with Figure 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 Table 1. 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 ~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, and both belong to the strongly orthogonal geminal wavefunction category. Whereas 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 intergeminal correlation that is described by RUSSG at the price of spoiling total spin, analogous 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. Whereas 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. Whereas 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 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 this 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 are 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, for example, by lifting strong orthogonality[64−67] or breaking further symmetries,[68] may alleviate the problems presented here. On the basis of 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.

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Notes
The authors declare no competing financial interest.

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