

A stationary property of the APSG wave function

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Abstract The method of antisymmetrized product of strongly orthogonal geminals (APSG) emerges by optimizing the one-electron functions used to construct two-electron functions (geminals), the latter being expanded (with coefficients selected variationally) in mutually exclusive subspaces of the former ones. Accordingly, E_{APSG} is stationary with respect to the expansion coefficients and to unitary transformations of the one-electron orbitals. We show that the APSG energy is also stationary to the unitary transformation of identical geminals. For non-identical geminals, this statement holds only approximately.

Keywords Geminal · APSG wave function · Stationarity · Unitary transformation

1 Introduction

It is well accepted that two-electron functions (geminals) offer a natural generalization of one-electron molecular orbitals, and represent a natural basis to describe classical, two-electron chemical bonds [1,2]. The most often applied geminal-type wave function is the APSG wave function [3–8] or its special case: the GVB wave function [9,10]. Although they, mainly due to the perfect pairing approximation [11], do not contain a sufficient amount of electron correlation, their advantageous properties make them suitable as reference functions for further refinement [12–15] or as a basis of extended geminal models [16–20].

The variational APSG energy is known to be stationary with respect to orbital variations and variations of geminal expansion coefficients. In this paper we call the

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attention to its stationary property with respect to unitary transformation of geminals as well.

1.1 The invariance of the HF determinant

The well-known Hartree-Fock (one-determinantal) wave function

$$\Psi_{\text{HF}} = \psi_1^+ \psi_2^+ \dots \psi_i^+ \dots \psi_j^+ \dots \psi_N^+ |\text{vac}\rangle$$

is invariant to any arbitrary unitary transformation of the occupied molecular orbitals, as a consequence of the properties of determinants. Since any unitary transformation can be represented by successive 2 by 2 rotations, it is sufficient to see this by considering the unitary transformation of two orbitals:

$$\begin{aligned}\psi'_i &= \cos \alpha \psi_i^+ - \sin \alpha \psi_j^+ \\ \psi'_j &= \sin \alpha \psi_i^+ + \cos \alpha \psi_j^+, \end{aligned}$$

by which the transformed determinant is written as

$$\begin{aligned}\Psi' &= \psi_1^+ \psi_2^+ \dots \psi_i^+ \dots \psi_j^+ \dots \psi_N^+ |\text{vac}\rangle \\ &= \left(\cos^2 \alpha \psi_1^+ \psi_2^+ \dots \psi_i^+ \dots \psi_j^+ \dots \psi_N^+ \right. \\ &\quad \left. - \sin^2 \alpha \psi_1^+ \psi_2^+ \dots \psi_j^+ \dots \psi_i^+ \dots \psi_N^+ \right) |\text{vac}\rangle \\ &= \left(\cos^2 \alpha + \sin^2 \alpha \right) \psi_1^+ \psi_2^+ \dots \psi_i^+ \dots \psi_j^+ \dots \psi_N^+ |\text{vac}\rangle = \Psi_{\text{HF}}. \quad (1)\end{aligned}$$

Here the terms containing the same fermion creation operators twice, like $\psi_i^+ \psi_i^+$, were dropped, and we applied a sign change reverting the order of ψ_j^+ and ψ_i^+ . Both are required by the anticommutative fermion relation

$$\left[\psi_i^+, \psi_j^+ \right]_+ = 0.$$

1.2 The non-invariance of the APSG wave function

This situation is completely different for the APSG wave function, which, for closed shells, reads

$$\begin{aligned}\Psi(1, 2, \dots, N-1, N) &= \hat{A} \left[\Phi_1(1, 2) \dots \Phi_{\frac{N}{2}}(N-1, N) \right] \\ &= \Phi_1^+ \Phi_2^+ \dots \Phi_{\frac{N}{2}}^+ |\text{vac}\rangle,\end{aligned}$$

where composite-particle creators Φ_i^+ obey the Bose-like commutation rules

$$[\Phi_i^+, \Phi_k^+]_- = 0.$$

This makes that

- (a) $\Phi_i^+ \Phi_i^+ \neq 0$ in general, and
- (b) transposition of Φ_i^+ and Φ_k^+ does not generate sign change.

Accordingly, the conditions leading to invariance at Eq. (1) do not hold here, and we conclude that the APSG wave function is not invariant with respect to unitary transformation of geminals.

1.3 Strongly orthogonal geminals

For further use, we collect some basic facts of APSG theory.

The geminals are expanded over one-electron functions χ_m as

$$\begin{aligned} \Phi_i(1, 2) &= \sum_{m,n} C_{mn}^i \hat{A} [\chi_{m\alpha}(1)\chi_{n\beta}(2)] \\ &= \sum_{m,n} C_{mn}^i \chi_{m\alpha}^+ \chi_{n\beta}^+ |\text{vac}\rangle. \end{aligned}$$

The natural representation of singlet geminals can be formed by diagonalizing the symmetric coefficient matrix \mathbf{C} :

$$\begin{aligned} \Phi_i(1, 2) &= \sum_m C_m^i \hat{A}[\varphi_{m\alpha}(1)\varphi_{m\beta}(2)] \\ &= \sum_m C_m^i \varphi_{m\alpha}^+ \varphi_{m\beta}^+ |\text{vac}\rangle. \end{aligned} \quad (2)$$

The condition of strong orthogonality for geminals

$$\int \Phi_i(1, 2)\Phi_k(1, 2)d\tau_1 = 0$$

is manifested in the condition for the coefficients:

$$\sum_n C_{mn}^i C_{ln}^k = 0 \quad \forall m, l,$$

which, for the natural case is reduced as

$$C_m^i C_m^k = 0 \quad \forall m, \text{ if } i \neq k.$$

This latter condition implies that strongly orthogonal geminals are necessarily expanded in mutually exclusive subspaces of natural orbitals.

Geminal optimization consists of two parts: optimizing the form of natural orbitals and the minimization of the energy within each subspace via the optimization of geminal expansion coefficients C_m^i . In classical geminal theories the dimensions of the subspaces are arbitrary and usually selected by chemical intuition. In GVB theory the subsets are always two-dimensional. An important achievement is by Rassolov who optimized also the subspace dimensions variationally [21].

2 Unitary transformation of two geminals

Since the APSG wave function is not invariant to the unitary transformation of the constituting geminals, one may ask whether a geminal energy can be further lowered by applying such a transformation. In this paper we point out that this is not the case. On the contrary, the APSG energy is stationary with respect to such a transformation, and the stationary point is a minimum. This statement holds strictly for identical (i.e., symmetry-equivalent) geminals, and approximately in the general case.

For the sake of simplicity, let's consider only two geminals, Φ_1 and Φ_2 . Their unitary transformation

$$\begin{bmatrix} \tilde{\Phi}_1 \\ \tilde{\Phi}_2 \end{bmatrix} = \begin{bmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{bmatrix} \begin{bmatrix} \Phi_1 \\ \Phi_2 \end{bmatrix}$$

or compactly

$$\tilde{\Phi} = \mathbf{U}\Phi \quad (3)$$

leads to the following wave function:

$$|\Psi\rangle = \tilde{\Phi}_2^+ \tilde{\Phi}_1^+ |\text{vac}\rangle. \quad (4)$$

It is important to mention that transformation (3) does not preserve the strong orthogonality of the geminals. Dealing with the transformed geminals is therefore the most simple by substituting transformation (3) into the expression studied, thereby reducing the problem to an expression constructed from the original geminals. Let us see this technique in studying the norm of the wave function (4). We see that the norm is not invariant:

$$\begin{aligned} \mathcal{N}^2 = \langle \Psi | \Psi \rangle &= \sum_{i,j,k,l=1}^2 U_{1i} U_{2j} U_{2k} U_{1l} \langle \text{vac} | \Phi_i^- \Phi_j^- \Phi_k^+ \Phi_l^+ | \text{vac} \rangle \\ &= \sum_{i,j=1}^2 U_{1i} U_{2j} (U_{1i} U_{2j} + U_{2i} U_{1j}) - 2 \sum_{i=1}^2 U_{1i}^2 U_{2i}^2 \sum_{m \in i} (C_m^i)^4, \end{aligned}$$

where we substituted the natural expansion (2) of the original geminals. This expression obviously depends on \mathbf{U} so the wave function will not be normalized to unity in general.

The transformed energy expression is thus the general Rayleigh quotient:

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \text{vac} | \tilde{\Phi}_1^- \tilde{\Phi}_2^- \hat{H} \tilde{\Phi}_2^+ \tilde{\Phi}_1^+ | \text{vac} \rangle}{\mathcal{N}^2} = \frac{1}{\mathcal{N}^2} \left[\sum_{i,j,k,l=1}^2 U_{ijkl} \langle \text{vac} | \Phi_i^- \Phi_j^- \hat{H} \Phi_k^+ \Phi_l^+ | \text{vac} \rangle \right],$$

where we used the shorthand $U_{ijkl} = U_{1i}U_{2j}U_{2k}U_{1l}$. Writing the Hamiltonian in spatial indices we arrive at the following expression for the transformed energy:

$$E = \frac{1}{\mathcal{N}^2} \sum_{i,j,k,l=1}^2 U_{ijkl} \left[\sum_{m,n} h_{mn} \sum_{\sigma} \langle \text{vac} | \Phi_i^- \Phi_j^- m_{\sigma}^+ n_{\sigma}^- \Phi_k^+ \Phi_l^+ | \text{vac} \rangle + \frac{1}{2} \sum_{m,n,l,s} \sum_{\sigma,\sigma'} [mn|ls] \langle \text{vac} | \Phi_i^- \Phi_j^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma'}^- l_{\sigma}^- \Phi_k^+ \Phi_l^+ | \text{vac} \rangle \right]$$

Using the natural expansion (2) of the geminals and evaluating the matrix elements results in a lengthy energy expression which we find unnecessary to detail here. We only note that during the evaluation procedure some matrix elements showed up which are unusual in standard geminal theory. These are the following ones:

$$\begin{aligned} \langle \text{vac} | \Phi_i^- \Phi_i^- m_{\sigma}^+ n_{\sigma}^- \Phi_i^+ \Phi_i^+ | \text{vac} \rangle & \quad (m, n \in i) \\ \langle \text{vac} | \Phi_i^- \Phi_i^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma'}^- l_{\sigma}^- \Phi_i^+ \Phi_i^+ | \text{vac} \rangle & \quad (m, n, l, s \in i) \\ \langle \text{vac} | \Phi_i^- \Phi_i^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma'}^- l_{\sigma}^- \Phi_k^+ \Phi_i^+ | \text{vac} \rangle & \quad (l, s \in k; m, n \in i) \\ \langle \text{vac} | \Phi_i^- \Phi_k^- m_{\sigma}^+ n_{\sigma'}^+ s_{\sigma'}^- l_{\sigma}^- \Phi_i^+ \Phi_i^+ | \text{vac} \rangle & \quad (l, s \in i; m, n \in k) \end{aligned}$$

The common feature in these novel matrix elements is that the four-electron quantity, $\Phi_i^+ \Phi_i^+$ appears in each. While absent in common APSG theory, these are nonzero due to the quasi-bosonic behavior of geminal creation operators [2].

2.1 Stationary property to infinitesimal rotations

In this section we are going to prove that we cannot lower the energy with the introduction of this extra variational parameter, the energy is stationary to the rotation of geminals and the stationary point is at the standard APSG energy. We also show that the stationary point is a minimum for the ground state. The proof is rigorously carried out for the special case of two identical geminals, while qualitative arguments and numerical illustration will show that it holds approximately in the general case.

Consider an infinitesimal transformation for which the 2 by 2 rotation matrix takes the form

$$U = \begin{bmatrix} 1 & -\alpha \\ \alpha & 1 \end{bmatrix}$$

The norm of the wave function remains one up to the first order of α :

$$\begin{aligned} \mathcal{N}^2 &= \langle \Psi | \Psi \rangle = \langle (\Phi_1^- - \alpha \Phi_2^-)(\alpha \Phi_1^- + \Phi_2^-)(\alpha \Phi_1^+ + \Phi_2^+)(\Phi_1^+ - \alpha \Phi_2^+) \rangle \\ &= \langle \Phi_1^- \Phi_2^- \Phi_2^+ \Phi_1^+ \rangle + 2\alpha \left[\langle \Phi_1^- \Phi_1^- \Phi_2^+ \Phi_1^+ \rangle - \langle \Phi_2^- \Phi_2^- \Phi_2^+ \Phi_1^+ \rangle \right] + \mathcal{O}(\alpha^2) \\ &= 1 + \mathcal{O}(\alpha^2). \end{aligned}$$

In the above expression, the terms linear in α (the two expectation values in the brackets) are zero separately, because there are two geminal annihilation operators in both of them, while there is only one which creates the geminal that is annihilated. The energy expression, up to the second order is

$$\begin{aligned} E &= \langle \Psi | \hat{H} | \Psi \rangle \\ &= E_{\text{APSG}} + 2\alpha \left[\langle \Phi_1^- \Phi_1^- \hat{H} \Phi_2^+ \Phi_1^+ \rangle - \langle \Phi_2^- \Phi_2^- \hat{H} \Phi_2^+ \Phi_1^+ \rangle \right] \\ &\quad + \alpha^2 \left[\langle \Phi_2^- \Phi_2^- \hat{H} \Phi_2^+ \Phi_2^+ \rangle + \langle \Phi_1^- \Phi_1^- \hat{H} \Phi_1^+ \Phi_1^+ \rangle - 2 \underbrace{\langle \Phi_1^- \Phi_1^- \hat{H} \Phi_2^+ \Phi_2^+ \rangle}_0 - 2E_{\text{APSG}} \right]. \end{aligned}$$

In the last bracket, the under-braced term is zero, since a two-electron Hamiltonian cannot lift four electrons from geminal 2 to 1. Since α is infinitesimal, the condition of stationarity

$$\left. \frac{\partial E}{\partial \alpha} \right|_{\alpha=0} = 2 \left[\langle \Phi_1^- \Phi_1^- \hat{H} \Phi_2^+ \Phi_1^+ \rangle - \langle \Phi_2^- \Phi_2^- \hat{H} \Phi_2^+ \Phi_1^+ \rangle \right] = 0$$

holds exactly if the two geminals are interchangeable. The second derivative is

$$\left. \frac{\partial^2 E}{\partial \alpha^2} \right|_{\alpha=0} = 2 \left[\langle \Phi_2^- \Phi_2^- \hat{H} \Phi_2^+ \Phi_2^+ \rangle + \langle \Phi_1^- \Phi_1^- \hat{H} \Phi_1^+ \Phi_1^+ \rangle - 2E_{\text{APSG}} \right].$$

The term in the bracket containing four-electron functions like $\Phi_1^+ \Phi_1^+ |_{\text{vac}}$ correspond to doubly ionized (charge transfer) states which, for ground state wave function, are of much higher energy than E_{APSG} . This makes the second derivative positive indicating that the stationary point at $\alpha = 0$ is a minimum. For inequivalent geminals the above proof is not rigorous, but if their internal structure is not very different, we do not expect large changes in the qualitative features of the energetics. An example reported in the next section will show that this is indeed the case.

We should also mention that in the case of in situ rotating the geminals during the orbital optimization, we could not lower the energy as well, which is in accordance with the variational character of the APSG wave function.

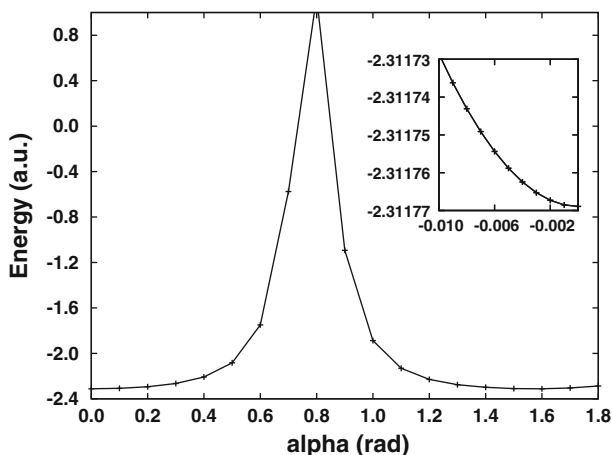


Fig. 1 Energy of two hydrogen molecules as a function of the geminal mixing parameter α (see Eq. (3)). The inset is a zoom into the $\alpha = 0$ region indicating that the APSG energy is a minimum indeed

3 Numerical illustrations

3.1 Geminal rotation for two hydrogen molecules

As a sample calculation we performed the unitary transformation of the geminals of two hydrogen molecules treated in 6-311G** basis set. The four hydrogen atoms were collinear, the distance between the hydrogen atoms in the H_2 molecules is 0.74 \AA and the distance between the molecules is 1.26 \AA .

In the previous section we could see that there should be a minimum at the APSG energy. This is illustrated by Fig. 1 showing an exact minimum at $\alpha = 0$. The location of the extremal points is easy to understand: the energy formula contains trigonometric expressions having minima at angles $\{\frac{k\pi}{2} | k \in \mathbb{Z}\}$ and maxima at angles $\{\frac{\pi}{4} + \frac{k\pi}{2} | k \in \mathbb{Z}\}$. The angle $\alpha = 0$ refers to the identity transformation of geminals and $\alpha = \frac{\pi}{2}$ is simply the interchange of the two geminals.

3.2 Geminal rotation for a hydrogen molecule and a helium atom

To study the example of two non-equivalent geminals, calculations were done for a hydrogen molecule and a helium atom in the 6-311G** basis set. The three atoms were kept collinear with the R_{HH} distance of 0.74 \AA and choosing 1.26 \AA between the helium and the closer hydrogen.

The results shown in Fig. 2. give the impression that the APSG energy is a minimum also here. However, a zoom into the neighborhood of the minimum shows that—in accord with the discussion in the theoretical section—at $\alpha = 0$ there is a small gradient of the energy, generating a slight shift of the minimum to $\alpha \approx -0.004$ in this case. The associated energy gain is very small, merely a few microhartrees (the total

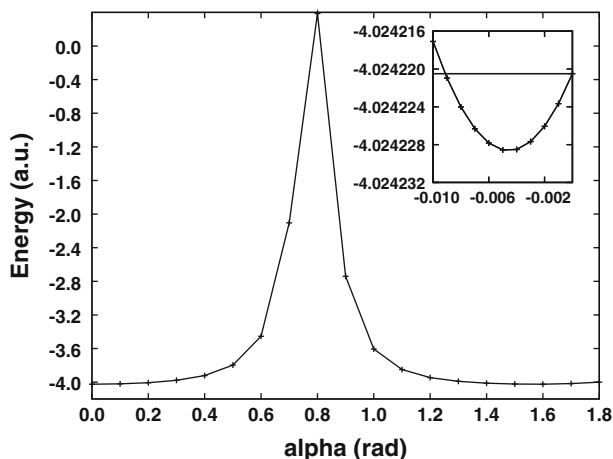


Fig. 2 Energy of a hydrogen molecule and a helium atom as a function of the geminal mixing parameter α , see Eq. (3). The inset is a zoom into the $\alpha = 0$ region with the horizontal line indicating the APSG-energy

energy comes out as -4.024228 a.u., to be compared with the standard APSG energy of -4.024220 a.u.).

4 Conclusions

The stationarity property of the APSG wave function with respect to unitary transformation of geminals was discussed. An energy expression was derived which depends on the rotation matrix. By considering infinitesimal rotations, we could prove analytically that for two equivalent geminals, the APSG-energy is a stationary point on this energy surface and, for the ground electronic state, it is necessarily a minimum. This was illustrated by sample calculations for two hydrogen molecules. For two different geminals we pointed out that the theorem does not hold exactly, although the $\left. \frac{\partial E}{\partial \alpha} \right|_{\alpha=0}$ gradient is expected to be small.

One more remark should be added to this stationary property, exact or approximate. Since the Hartree-Fock energy is invariant to the unitary transformation of orbitals, forming localized orbitals from the canonical ones does not affect the energy of the system. In case of APSG theory, as we have seen, this is not the case, the energy expression obtained is not invariant to the transformation of geminals.

In other words, energy-optimized orbitals are unique in APSG, unlike in HF. Since the optimal APSG orbitals are—according to the numerical practice—usually localized in space, the APSG theory offers a natural mathematical representation of local two-electronic chemical bonds. Should the stationarity of APSG discussed in this paper not be hold, or were it drastically violated, mixing of localized geminals would destroy this interpretation. The fact that the APSG energy is an exact (or approximate) minimum with respect to geminal mixing underlines the inherently localized nature of this wave-function, offering a mathematical representation of the two-electron chemical bond in molecules.

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